High Performance Pigments. Edited by Hugh M. Smith

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Original artwork by Maria da Rocha, formerly manager of Analytical Services with the Colors Group of Sun Chemical, and chair person of CPMA's Analytical Committee. The work represents the expansive palette of colors now possible with today's organic and inorganic high performance pigments.

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Preface

In releasing another volume of pigments technology to readers around the world, it is appropriate first to answer the question as to why such a work is needed, in light of the monumental works already written on Organic Pigments by Willi Herbst and Klaus Hunger, and Inorganic Pigments, edited by Gunter Buxbaum, together with the earlier Pigment Handbook edited by my colleague, Peter Lewis.

Perhaps the following sixfold explanation will suffice:

1. In the light of several recent international conferences, in Chicago, Miami Beach and Barcelona, each dealing with High Performance Pigments, there seems to be a resurgence of interest in this topic, coupled with some confusion as to what the word “high performance pigment”, (often abbreviated to “HPP”) really means.
   Compilation of what is essentially the first book devoted to this topic thus appears overdue.
2. Once the concept of “high performance” is understood, it appears quite appropriate to assemble a collection of Chapters dealing with both organic as well as inorganic pigment topics, each written by experts in their respective fields of science and technology.
3. So as to gain an understanding of the changing role of high performance pigments in today’s global marketplace, it is also helpful to view the field from the viewpoint of a businessman who also understands the language of pigment technology, and this we have done with Fritz Brenzikofer’s Chapter.
4. With a seemingly never-ending change in the regulatory “drivers” for successful manufacture, importation and marketing of high performance pigments around the world, we have included two Chapters dealing with this topic, drawn from the somewhat different perspectives of Europe and the United States. No longer can we conclude that “mere” technical supremacy, coupled with apparently good profitability, is sufficient to launch or maintain a particular high performance pigment, when new regulatory requirements, focusing on some impurity inadvertently produced in minute quantities during the course of the production process or released from trace breakdown of the pigment in some demanding application, transform the investment needed to a much higher level than was originally considered, and may change a pre-

viously good level of profitability into a questionable one. Gaining expertise in this area is thus essential to the pursuit of business in today's marketplace.

5. In recent years, production of what is called by some "classical" and by others "commodity" pigments has begun to migrate out of Europe, the United States and Canada into Third World Countries, where labor wages are much lower but adequate production facilities, together with some technical "know how", are available. In the light of this paradigm shift, the largest colored pigment manufacturers have refocused their attention on High Performance Pigments because of the greater return still possible with such products.
6. Since the publication of Hunger and Buxbaum's excellent monographs on Organic and Inorganic Pigments, a number of technical developments have surfaced, which are of significance to an understanding of high performance pigments. Consequently, we have introduced for the first time in one volume, for example, chapters on the technology of cerium pigments, crystal engineering, the growing family of special effect pigments, and the new "quinox" family of azo pigments, to extend our knowledge of the frontiers of successful HPP research.

Unlike the original "Pigment Handbook", which presented a uniform pattern of information on each pigment class identified, each author in this volume has been encouraged to produce a manuscript truly reflective of their own personality, motivation and insight. For example, the Chapter written by Paul Dunning of Johnson Matthey on the old and well established cadmium pigment family includes useful historical data, together with much process information, and ends with a plea for objective assessment of this pigment, still considered suspect by some countries but now reassessed in the EU as without significant risk to human health or the environment.

Conversely, Jean-Noel Berte of Rhodia, writing on the commercial launch of the family of cerium pigments, provides a host of technical information, establishing this new class as High Performance Pigments in their own right and not "merely" as substitutes for cadmiums.

Again, Masao Tanaka of Dainippon, author of a past Japanese booklet on the chemistry of the phthalocyanine family, in dealing with this class of colorants, has chosen to explore the universe of functional derivatives of phthalocyanines and leave the traditional pigment technology of phthalocyanines to the excellent text of Herbst/ Hunger.

Throughout each chapter, pigments are identified according to the system set forth by the Colour Index International, which is produced by the Society of Dyers and Colourists in Bradford, England. For accuracy of terminology, while it is understood that the full and correct name for a pigment might be, for example, C.I. Pigment Red xyz, etc., most authors will eliminate the "C.I." prefix, and some abbreviate the "Pigment Red" to P.R. xyz etc.

At this point, some comment on definition is overdue. Entry of the phrase "high performance" into the pigment literature appears to date from the mid 1960s, when it was applied to certain high value vat pigments possessing excellence of fastness as well as good tinctorial properties. But an actual definition was never proposed. Later, the author, at an Intertech Conference in 1998, suggested adoption of the following phrase: "A high performance pigment is a colored, black, white, pearlescent, luminescent or fluorescent particulate organic or inorganic pigment that demonstrates high performance properties in its end use application".

Since that time, realizing that the above definition was proposed from a strictly technical basis, Fritz Brenzikofer of Clariant, has offered the following definition from a "business" perspective: "A high performance pigment is the right pigment selected for a specific use, with well defined quality criteria, at an optimized pigment cost".

Regardless of which definition is favored, another issue has to be considered, in that the high performance pigment of yesteryear may eventually become the "classical" or "commodity" pigment of tomorrow because of shift in acceptable standards of performance. A masterly presentation on this topic was given by Klaus Hunger in Berlin during Intertech's High Performance Pigments 2000 Conference.

In realizing that no definition of high performance pigments will ever be a static one or fully agreed to by all, I would further propose that the four essential elements of such products should include:

- Excellence of performance
- Applicational permanence
- Compatibility with health, safety and environmental issues
- Good profitability in value-in-use to the consumer and return of investment to the producer

In presenting the many work products in this volume, it was thought appropriate to divide up the contents into four separate sections, dealing successively with

1. inorganic HPPs in Chapters 1 through 6,
2. topics that include both organic and inorganic products, such as crystal engineering and special effect pigments in Chapters 7 and 8,
3. organic HPPs in Chapters 9 through 20, and
4. analytical chemistry of HPPs and regulatory, legislative and product safety issues impacting high performance pigments in Chapters 21 through 24. We are particularly grateful to all authors for their hard work and insight, and congratulate them on a job well done.

In this field of rapid technological and/or environmental change, it is inevitable that some of the information provided in this volume may soon become less significant in the light of future discoveries. For example, the application of molecular recognition in design chemistry to providing additives capable of quantum enhancement of pigmentation in thermoplastic resins is an exciting new chemistry pioneered by Clariant Corporation, and should open new doors to progress in high performance pigments. It would therefore appear that any future publication in this field should not only deal with high performance pigments per se, but also with the various additives, synergists, and functional derivatives that enable pigments to do their work better. Again, the inevitable search for the regulatory "needles in haystacks" may render some pigments less desirable because of the continued fostering of chemophobia on the part of some NGO organizations, producing a misperception that some trace impurity (at present unknown), measured at parts per billion or trillion, contained in the pigment, may be prejudicial to the pigment consuming public, thus triggering an urgent search by the pigment producers to come up with a replacement product.

In conclusion, I know I would be remiss if I did not thank four special ladies, without whom this work could not have been accomplished: Firstly, my remarkable and never complaining secretary, Kelley Vonderheide, for her untiring labors at the keyboard. Secondly, my creative and respected colleague, Maria da Rocha, whose art work on the cover matched her skills as an analytical expert in the field of pigments. Thirdly, Karin Sora, Publishing Editor of Wiley-VCH, whose patience, insight and counseling skills were much used in bringing this volume finally to light. And lastly, my wife Riona, without whom I would never have finished the task! Thank you, with our multinational authors, for making this volume possible.

Gray Fox Trail, November 2001 Hugh M. Smith
Milford, Ohio, USA

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Part I

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1
Introduction to Inorganic High Performance Pigments

Gunter Buxbaum

1.1
Introduction

In 1998, the world production of inorganic pigments was approximately 5.3 million tonnes, representing a value of about $15 billions. BCMA (the British Colour Makers' Association) estimates the economic value of downstream colored industrial products using inorganic pigments as approaching $500 billions per annum.

In writing an introductory chapter to colored Inorganic High Performance Pigments, one is faced with a definitional dilemma, as the term "high performance pigment" is more usually met with in organic rather than inorganic literature. Cost alone is not the determining factor, otherwise the natural semi-precious stone lapis lazuli would have to be included, with its deep blue characteristics. One of the problems with high performance inorganic pigments is the limitation in available chemistry, so that very few really new compounds have been developed in recent decades.

Most inorganic pigment applications have thus been achieved by the well known "workhorses" of conventional pigments, but the economic pressures of the last decade have dictated two main directions for product development: on the one hand an economization of existing pigment manufacture, in line with world price competition, and on the other hand, discovery and development of "new" and "improved" inorganic pigments with higher performing characteristics. Even in the more "commodity" or conventional inorganics such as chrome yellow, titanium dioxide, iron oxide and carbon black, incrementally improved performance is required, e.g. in dust free preparations for the construction industry.

A third development started earlier. Driven by national laws and regulations in the ecological and toxicological area, "sustainable development" and substitution pressures have resulted in the replacement of formerly well known, and highly recommended inorganic pigments, such as red lead, lead molybdate, and chrome orange, by more "environmentally friendly" or less toxic substances, which can surely be considered as "high performance" pigments.

Finally, in the field of "functional pigments" such as corrosion inhibiting or optically variable types, the development of "high performance" types has been necessary.

1.2
Survey of Inorganic Pigments

When we consider a short survey of today's major Inorganic Pigments, we are faced with the realization that the three major pigment families: titanium dioxide, carbon black and iron oxides, accounting for more than 90 % of the world wide tonnage, as shown in Table 1–1, are all outside of our subject matter. They are well known to everyone, and have already been discussed in depth in recent handbooks[1, 2].

Further inspection of Table 1–1, however, reveals a selection of "high performance" pigments classified according to their chemical composition. In particular, the families of complex (or mixed) metal oxides, and functional pigments show a wide variety in their chemical composition.

Table 1–1: Inorganic pigments, classified by composition.

Class	*Pigment*	*High performance*
Elements		
	Carbon black	+
	Al-flakes	+
	Zn-Dust	
	Nanoscale silicon	#
Oxides/hydroxides		+
	TiO_2	
	Fe_2O_3	
	FeOOH	
	Fe_3O_4	
	Cr_3O_3	
	Pb_3O_4	
Mixed metal oxides		+
	$ZnFe_2O_4$	
	$CoAl_2O_4$	
	$(Co,Ni,Zn)_2TiO_4$	+
	$Ti(Ni,Nb)O_2$	+
	$Ti(Cr,Nb)O_2$	+
Sulfides		
	ZnS	
	$ZnS/BaSO_4$ (lithopone)	
	CdS,	+
	(Cd/Hg)(S,Se)	
	CeS_2	+
Oxide/nitride		
	$(Ca,La)Ta(O,N)_3$	#
Chromates		
	$Pb(Cr,S)O_4$	
	$Pb(Cr,Mo,S)O_4$	

Class	***Pigment***	***High performance***
Vanadates		
	$BiVO_3$	+
Silicates		
	$Na_3Al_6Si_6\,O_{24}S_3$ (ultramarine)	
	Mica based effect pigments	+
Cyanides		
	$KFe[Fe(CN)_6]$	

Note: # not yet in industrial scale

In every pigment class illustrated, one will find at least one grade with a high performance characteristic, which may be the determining factor, or driver, for the end user to purchase this pigment in their application. It is self-evident, therefore, that degree of performance for a pigment depends on the demands imposed upon it for its intended application.

1.3
New Candidates on the Catwalk of Color

Bearing in mind the limitation in the color of inorganic pigments, one has to be surprised at the numbers of new compounds introduced with good pigment performance. More and more, specialized physical effects appear to dominate over variation in chemical composition. In Table 1–1, for example, we must point out that mica-based effect pigments, being still a "young" pigment class, have already become well established since their "breakthrough" introduction. Again, while bismuth vanadate yellow is in the early stages of its growth potential, cerium sulfides are in their industrial infancy, and are attempting to carve out a niche for themselves in applications where the well-established cadmium sulfide family is no longer the pigment of choice. On the more experimental side, "nanoscale silicon", with particle size below five nanometers, is now available as a laboratory curiosity in microgram quantities as the first in the series of "quantum effect pigments" predicted by theoretical physicists[3]. Nearer to introduction is another new family, the calcium, lanthanum, tantalum oxide-nitrides[4]. Reproducibility, however, must be proven first. Their published properties, viz. brilliance of color coupled with non-toxicity, appear ideal for inclusion in the high performance category.

A study of the "old fashioned" and almost forgotten workhorse pigment ultramarine blue could also be significant in the light of its revival through recently introduced new manufacturing technology. And so it is possible that, in the future, development of new manufacturing processes for "old" pigments and enhancement of their properties might well revitalize these products to the point where they could also join the ranks of truly high performance pigments.

1.4
Challenges for the Future

This leads us to consider challenges for new high performance pigments, which can be designated as *Three Essential E's*:

Effectiveness = Technical performance
Economy = Benefits for the customer
Ecology = Environmental and toxicological safety

Better effectiveness could include higher tinting strength, greater ease of dispersion, better fineness of grind, higher saturation, and so on.

Better economy could include widening the fields of application for known high performance pigments by giving the customer enhanced value-in-use. And better ecology is today's task for industry as a whole, and is self-evident.

All three "E's" will be optimized further on. New inventions will be made, hand in hand with steady process and product development. And as we can learn from a study of today's lower-cost pigments, such as lead chromate, where the encapsulated specialties of yesteryear are now the norm for coatings application, the high performance pigments of today will become the conventional standards of tomorrow, with those of tomorrow having to be invented now. And so the development of High Performance Inorganic Pigments is, in reality, a never-ending story.

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2
Bismuth Vanadates

Hartmut Endriss

2.1
Introduction

Bismuth vanadate pigments are a relatively new pigment class that has gained steadily in importance over the last two decades. The pigments exhibit brilliant greenish-yellow to reddish-yellow shades, with compositions ranging from $BiVO_4$ (CAS No. 14059–33–7, EINECS No. 237–898-0) to the mixed pigment $4BiVO_4 \times 3Bi_2MoO_6$. They appear in the Colour Index as CI Pigment Yellow 184 without any statement as to chemical composition. To improve the properties, including the tendency to photochromism, bismuth vanadate pigments in paints contain several percent of organic stabilizers.

Color changes may occur when these pigments are used to color plastics, because of reduction of the vanadate ion in the polymer melt. Thermostable types suitable for coloring plastics are therefore protected by a dense, glass-like, multilayer coating composed of the oxides of aluminum, boron, silicon and zinc.

Bismuth vanadate pigments are lead- and chromate-free inorganic yellow pigments used in the coatings industry to manufacture brilliant yellow, orange, red and green shades with good gloss and hiding power. As thermostable types become more available, the plastics industry is also increasingly turning to these pigments. Bismuth vanadate pigments have benefited from the decline in use of lead chromate and cadmium pigments, especially in the coatings and plastics industries.

2.2
Historical Background

Bismuth vanadate or orthovanadate, $BiVO_4$, occurs naturally as tetragonal dreyerite in Hirschhorn, Germany, as monoclinic clinobisvanite in Yinnietharra, Western Australia, and as orthorhombic pucherite in Schneeberg, Germany. However, these deposits are of no practical importance to the pigment industry.

Bismuth vanadate was first reported in a medical patent in 1924 and synthesized as a solid substance in 1964. In 1976, Du Pont described the preparation and properties of “brilliant primrose yellow” monoclinic $BiVO_4$. Montedison developed numerous pigment combinations based on $BiVO_4$. Pigments containing other phases besides $BiVO_4$, for example Bi_2XO_6 (X = Mo or W) have been reported by BASF. In addition, Bayer and Ciba have published methods for the manufacture of pigments based on $BiVO_4$. Today there are several manufacturers, producing ca. 900 tonnes annually. The two leading producers are BASF AG and Ciba.

Bismuth vanadate pigments are high-quality yellow pigments. They lie in the higher price range for inorganic pigments because the raw materials are relatively expensive.

2.3
Manufacture

Bismuth vanadate pigments are obtained by a precipitation process in which caustic soda or sodium hydroxide is added to a solution containing bismuth nitrate, sodium or ammonium vanadate, sodium molybdate (where specified) and nitric acid. The precipitate of oxides and hydroxides is washed until it is free of salt. To form better crystals and hence improve the pigment properties, the intermediate product is tempered at 200 to 700 °C. Layers of stabilizer are then applied to the surface of the crystals in subsequent precipitation steps, and are sometimes also calcined. In the case of the thermostable type, these layers are dense, glass-like coatings composed mainly of silicates. Further washing, drying and milling operations follow. To produce free-flowing, low-dusting fine granules, the pigment suspension is spray-dried and automatically packed.

The wastewater from the production process is fed to a neutralization step in which soluble heavy metals are precipitated, and suspended pigment particles allowed to settle out. A denitrification step may be employed to lower the nitrate content.

2.4
Properties and Applications

2.4.1
Chemical Properties

Bismuth vanadate pigments are insoluble in water and alkalies. Only in strongly alkaline media, e.g. mixtures with cement, will they sometimes show instability and undergo a change in shade. Acid media with a pH of less than 2 cause perceptible solubilization, depending on how well the pigment has been stabilized.

2.4.2
Physical Properties

The most important physical properties are:

Density	5–7 g/cm^3
Mean particle size	0.4–0.8 μm
Specific surface area	12–4 m^2/g
Oil absorption	30–10 g/100 g pigment

Compared with organic pigments, the density and particle size are relatively high while the specific surface area and oil absorption are quite low. This means very high pigment loading is possible. However, precautions must be taken to prevent sedimentation in low-viscosity systems, due to the high density of the particles and the fact that they readily settle out.

2.4.3
Coloristic Properties

Bismuth vanadate pigments are characterized by brilliant, greenish-yellow to reddish-yellow shades of high color strength, high gloss and good hiding power. When they are compared with other inorganic yellow pigments, their coloristic properties are seen to resemble those of cadmium yellow and lead chromate. Figure 2–1 shows the reflectance curves of bismuth vanadate and other inorganic yellow pigments.

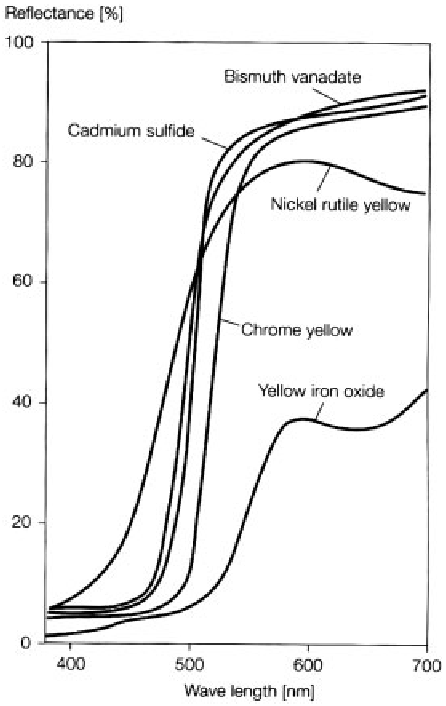

Figure 2–1: Reflectance curves of bismuth vanadate and other yellow pigments (cadmium sulfide, nickel rutile yellow, yellow iron oxide and chrome yellow).

Bismuth vanadate pigments have a much higher chroma than yellow iron oxide and nickel titanate pigments. In full shades and the palest tints, bismuth vanadate pigments show superlative fastness to weathering.
Unstabilized types tend to undergo substantial reversible color changes (photochromism) on exposure to intense radiation in the Suntest. Following additional stabilization, this effect is substantially reduced or becomes barely perceptible.

2.4.4
Dispersibility

The excellent dispersibility is typical for inorganic pigments of this type and is far superior to that of organic pigments.

2.4.5
Light Fastness and Weather Resistance

Bismuth vanadate pigments exhibit very good light fastness in both deep and pale shades. They show excellent weather resistance in full shades, and are superior to lead chromate in this respect. In full shades they are comparable with the best organic pigments and have the greatest durability in deep reductions.

2.4.6
Chemical and Solvent Resistance

The resistance of these pigments to organic solvents is excellent. Their ionic character may be a disadvantage with regard to acid/alkali resistance, but surface stabilization improves this significantly (see Sec. 2.5.1).

2.5
Applications

About 95 % of the total volume of bismuth vanadate pigments is used in paint manufacture and about 5 % in plastics processing. This ratio may change however in the future in favor of plastics coloration.

2.5.1
Coatings

Bismuth vanadate pigments are used to obtain brilliantly colored lead-free standard automotive finishes, automotive repair finishes and high-grade industrial paints. They are equally suitable for pigmenting solvent-based and solvent-free paints. They are of particular interest as a basis for brilliant, highly opaque orange, red and green shades, for which they are combined with organic pigments.

The chemistry of bismuth vanadate pigments makes them sensitive to acids. However, tests in which acids were applied to baking finishes under practical conditions have shown that the acid resistance of these pigments is normally comparable to that of a highly stabilized lead chromate. The application of bismuth vanadate pigments in powder coatings and coil-coatings should be tested in customer material, because in such cases – more than in standard liquid paint systems – the suitability depends on the total formulation.

2.5.2
Plastics

2.5.2.1 Properties

Thermostable bismuth vanadate pigments are available today with a heat stability of 260 to 280 °C. They exhibit very good fastness to light and weathering in plastics for outdoor use. In weathering tests on plastics pigmented with 0.5 % cadmium yellow or 1 % bismuth vanadate, the bismuth vanadate pigment was superior both under artificial conditions (Xenotest, 4000 h) and outdoors (5 years).

The pigments have outstanding fastness to migration in plastics, and are readily dispersible.

2.5.2.2 Applications

With their excellent heat stability, the thermostable types can be readily incorporated into polyolefins and ABS at 260–280 °C, and polyamide injection-molding materials at 280–300 °C. Even when they are applied in the manufacture of large injection-molded and extruded plastic parts, the product obtained is dimensionally stable and non-warping. Because of their excellent fastness to weathering, they are an ideal substitute for pigments containing lead or cadmium in outdoor applications (bottle crates, garden furniture, garbage bins, etc.)

2.5.2.3 Conformity of Pigments for Plastics Coloration to Food and Drug Regulations

The good insolubility of bismuth vanadate pigments is reflected in their fastness to migration. They can be used in typical commercial concentrations for coloring plastics for food packaging and other materials and articles in accordance with the purity requirements of the following countries for colorants in food packaging: Germany (RECOMMENDATION IX of the Federal Institute for Consumer Health Protection and Veterinary Medicine, BgVV), Austria, Belgium, Italy, the Netherlands, Spain and Switzerland. In addition, the purity requirements of European RESOLUTION AP(89) I of September 1989 are met. However, they are not included in the French and FDA positive lists (21 CFR, § 178.3297), nor have they yet been submitted for inclusion.

2.6
Toxicology

2.6.1
Acute Toxicity

No adverse toxicological effects were observed in animal tests involving oral and inhalational intake of the pigments.

LD50 rat, oral	> 5000 mg/kg
LC50 rat, inhalational	> 5.15 mg/L/4 hours
Skin irritation	Non-irritant (tested on rabbit)
Mucous-membrane irritation	Non-irritant (tested on rabbit's eye)
Mutagenicity (Ames test)	Negative (tested on five strains of bacteria with and without enzymatic activation)
Sensitization	Non-sensitizing (tested on guinea pig)

2.6.2
Chronic Toxicity

Animal trials with respirable dust gave some indication of inhalational toxicity, the effects of which were reversible at low concentrations. To alleviate the associated risk, some manufactures supply bismuth vanadate pigments in a free-flowing, low-dusting form, making them inaccessible to the lungs. The safety of these pigments is reinforced by their high density, which causes any airborne dust generated to settle very quickly. Even so, the usual precautions and industrial hygiene rules necessary for handling chemicals must be observed.

2.7
Ecology

Bismuth vanadate pigments exhibit low solubility in water. They can therefore be removed from wastewater largely by mechanical means, for example in wastewater treatment plants. An appreciable increase in water solubility occurs only at pH levels of less than 2.

They exhibit practically no toxicity to fish, daphnia or bacteria, as evidenced by the following values: fish (orfe, acute, 48 h, EC_0 10 000 mg/L), daphnia (EC_0 100 mg/L) and bacteria (*Pseudomonas pudita*, EC_0 10 000 mg/L).

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3

Cadmium Pigments

Paul Dunning

3.1

Introduction

Of all the inorganic pigments, cadmiums have the broadest range consisting of brilliant yellow and red colors. The yellows span from pale primrose to deep golden yellow. Reds vary from light orange, progressing to deep orange, light red, through crimson and maroon (see Figure 3–1).

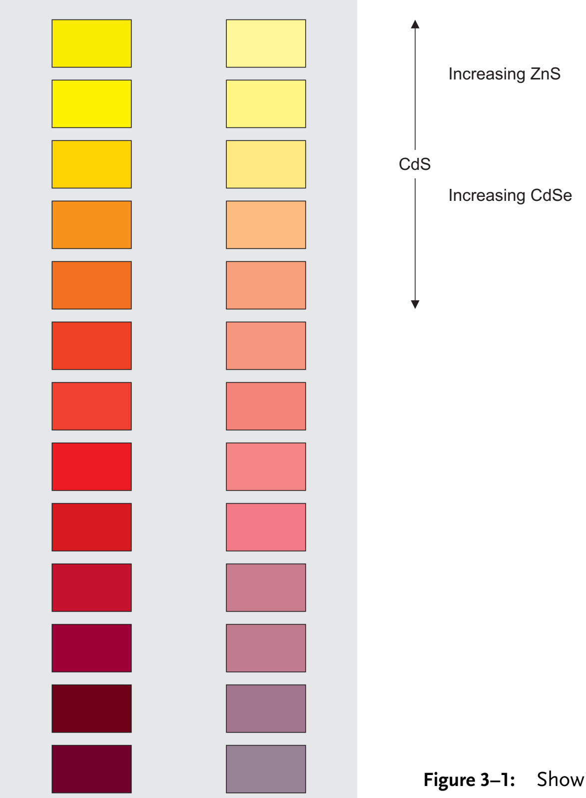

Figure 3–1: Showing mass tone and reduced tone (1 pigment: 9 titanium oxide).

Cadmium yellows are composed of cadmium sulfide or a mixture of cadmium sulfide and zinc sulfide, while reds are a mixture of cadmium sulfide and cadmium selenide (cadmium sulfoselenide).

Both reds and yellows can be made as a chemically pure type (C.P.), in which case they contain no extenders.

Cadmium lithopones, otherwise known as cadmoliths[1] are cadmium reds or yellows that contain barium sulfate coprecipitated with the pigment.

Although not discussed here, reds made with mixtures of cadmium sulfide and mercury sulfide, are known as mercadiums[2] and have also been produced as lithopones.

3.2
Pigment History

Cadmium compounds were first used as colorants shortly after the yellow compound cadmium sulfide was discovered by the German metallurgist Friedrich Stromeyer. The element cadmium was discovered by several chemists in 1817. Stromeyer was however the first to report it and is credited with its discovery. He recommended that the brightly colored yellow sulfide be used as an artists color.

In that same year, the Swedish chemist Berzelius identified a new element, called selenium, which was to become an essential component of cadmium reds.

While cadmium yellow pigment was at first very rare due to the scarcity of the metal, it became more available to artists in the 1830s after cadmium started to be produced commercially in Upper Silesia (now Poland). A reference to cadmium sulfide is made in George Field's Practical Journal of 1809, where a yellow cadmium water color sample is discussed. Cadmium yellow was also exhibited by today's well known Artist Supply company, Winsor and Newton, at the important Crystal Palace exhibition of 1851, in England.

In those days, cadmium pigments were expensive, but were highly regarded by artists because of their brilliance, opacity, ability to mix with other colors and, importantly, their permanence. Noteworthy was their reluctance not to darken in the presence of polluted industrial air containing hydrogen sulfide.

Cadmium yellows were also used in dyeing silks and cloths. "Steam cadmium yellow"[3] process was based on the fact that cadmium nitrate and sodium thiosulfate do not react in the cold, but produce cadmium sulfide on steaming.

Cadmium reds did not appear for some considerable time. Early reds and oranges were made by heating cadmium yellow with selenium to make red enamel pigments known as "fire red". However, it was not until 1919 that a German patent appeared for the production of cadmium orange and red pigments[4]. These were made by heating the precipitate resulting from mixing cadmium salt solutions with alkali and alkaline earth sulfides, including barium sulfide.

The 1920s saw the development of both cadmium oil colors and lithopones, which were designed to reduce the cost of the pigment. Lithopones are virtually the same as the pure pigments in mass tone, but have considerably less tinting strength because of the large amount of barium sulfate present.

Use of cadmium pigments then grew to applications other than artists' color and found favor in ceramic applications because of their heat stability. It was, however, their use in the rapidly expanding plastics industry in the 1950s that increased the demand for cadmiums. They exhibited excellent properties in the coloring of polymers, offering a broad range of bright, intermixable, dispersible and light fast shades. Unlike their organic counterparts they could withstand the rigorous processing temperatures demanded by engineering polymers.

3.2
Raw Materials

3.2.1
Cadmium

A naturally occurring but rare element, cadmium occurs as approximately 150 parts per billion of the earth's crust. Although cadmium sulfide does occur naturally as the mineral Greenockite (named after the Scottish coastal town Greenock), no commercially viable deposits of cadmium exist. It is derived primarily as a waste product from the refining of zinc ores and to a lesser degree from the smelting of copper and lead ores. Being more volatile than zinc, cadmium can be distilled from zinc furnaces. It is then concentrated and refined by distillation and electrolysis to a purity of 99.995 %, before being sold as rods, balls or ingots.

3.2.2
Selenium

An even rarer element, selenium is present at approximately 50 parts per billion of the earth's crust. It is much rarer than its neighbor in the Periodic Table, sulfur. The ratio of selenium to sulfur has been calculated to be about 1:6000!

Like cadmium, selenium is mainly derived from the purification of other mineral ores, although the world's first mine containing deposits of commercial grade selenium was opened in Wyoming in 1955. Most selenium is today obtained from anode slimes produced during the refining of nickel and copper sulfides.

The dark gray powder or pellets are sold as pigment grade selenium at typically 99.95 % purity.

3.3
Chemistry of Cadmium, Selenium and Cadmium Sulfide

3.3.1
Cadmium

Cadmium is positioned in Group IIb of the Periodic Table, which is sometimes known as the “zinc group”. It is positioned between zinc and mercury, and thus has some similar properties to these elements.

Cadmium metal is silvery white and reasonably soft. Although it does form some complexes, its pigment chemistry is entirely concerned with the +2 state.

An important property is that, because of its volatility (melting point 321 °C, boiling point 765 °C), cadmium metal can be burned in air to form a brown oxide (CdO). This is not stable in moist air and will slowly convert to the carbonate. However, CdO is readily soluble in mineral acids and is used as a starting point to make solutions of cadmium salts for pigment manufacture.

The sulfate, nitrate and chloride salts are all water soluble, but the white carbonate, hydroxide and phosphate salts of cadmium are insoluble in water.

Yellow cadmium sulfide is highly insoluble (more so than zinc sulfide) and can be precipitated from acidic solutions. Cadmium selenide is almost black and has no pigmentary properties, but is used in the semiconductor industry.

The solubility products of CdS and ZnS are 8×10^{-28} and 1.6×10^{-24}, respectively. It is this property that sets cadmium pigments apart from other cadmium salts.

Like zinc sulfide, cadmium sulfide has two forms, cubic (zinc blende, see Figure 3–2) or hexagonal (wurtzite, see Figure 3–3).

The cubic form is usually precipitated, but is not thermally stable and can be converted to the brighter, more stable hexagonal form on heating.

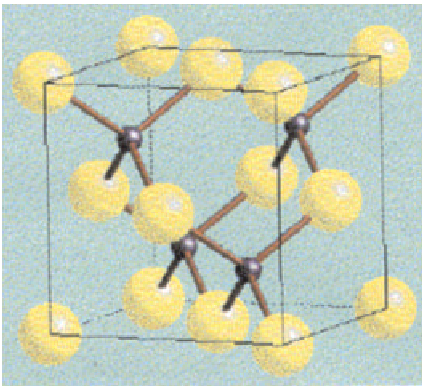

Figure 3–2: Zinc blende structure.

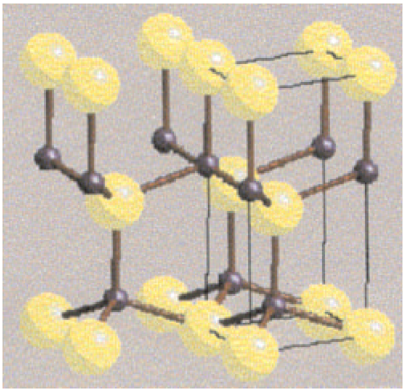

Figure 3–3: Wurtzite structure.

3.3.2
Selenium

Selenium is positioned between sulfur and tellurium in Group VIb (chalcogens) of the Periodic Table, and exhibits properties similar to both these elements. It is more metallic than sulfur but less so than tellurium.

Like other members of the group it exhibits allotropy and exists in red and gray forms.

It exhibits several valency states, –2 (selenide), –4 (selenite) and –6 (selenate). Pigment chemistry is concerned solely with the –2 state.

Selenium is quite volatile, with the gray form melting at 217 °C and boiling at 685 °C. This causes some selenium to be lost when pigments are calcined during manufacture.

Hydrogen selenide, like hydrogen sulfide, is gaseous, toxic and extremely pungent. Although selenides can be precipitated using hydrogen selenide, this route is never used in pigment manufacture because of its toxic nature.

As with sulfur, selenium is very soluble in alkali sulfides. This provides a convenient way to dissolve selenium and finely precipitate it in the manufacture of cadmium reds.

3.3.3
Substitution in the CdS Lattice

It is the very property that cadmium and sulfur can be lattice substituted to a considerable extent by members of their own Periodic Groups that gives rise to the broad range of colors possible in the cadmium palette.

This property, coupled with excellent insolubility and outstanding heat resistance, makes them truly high performance pigments.

The replacement of some cadmium with zinc ions in the CdS lattice produces a shift in color from deep yellow to pale primrose. Similarly, the partial substitution of sulfur for selenium in the lattice produces progressively deeper red shades.

Again, as already mentioned, mercury can also replace cadmium in the crystal lattice, giving rise to the former mercadmium range of pigments.

3.4
Method of Pigment Manufacture

3.4.1
General Points

Today's high performance pigments require the use of high grade starting materials and a controlled process to ensure the production of consistent colors. Early methods for cadmium pigments would appear crude by modern techniques, and would not be capable of producing the commercially required products of today.

The process route to cadmium pigments is reasonably lengthy, as it includes two filtration and two drying stages, with a significant proportion of the cost of the pigment taken up by the process costs. Today's manufacturers produce a range of yellows and reds, referred to as "standard bases" or "strike standards". From this range it is possible to blend the pigments to customer requirements and add extenders as necessary to control color and strength.

Cadmium pigments require to be made from pure grades of chemicals, especially as many common metal sulfides such as iron, nickel, copper and lead are darkly colored and would inhibit pigment brightness and acceptability.

The production of lithopones requires the use of barium sulfide, which coprecipitates barium sulfate with the pigment. Lithopone production has declined in recent years, being more expensive than mixing with blanc fixe at the final blending stage. Precipitation is undoubtedly the preferred route to producing today's high performance pigments, by providing an intimate mix of the ingredients and achieving close control over particle size.

Cadmium pigment manufacturers have over the years developed ways to improve pigment strength, brightness and dispersibility, and a reduction in the release of

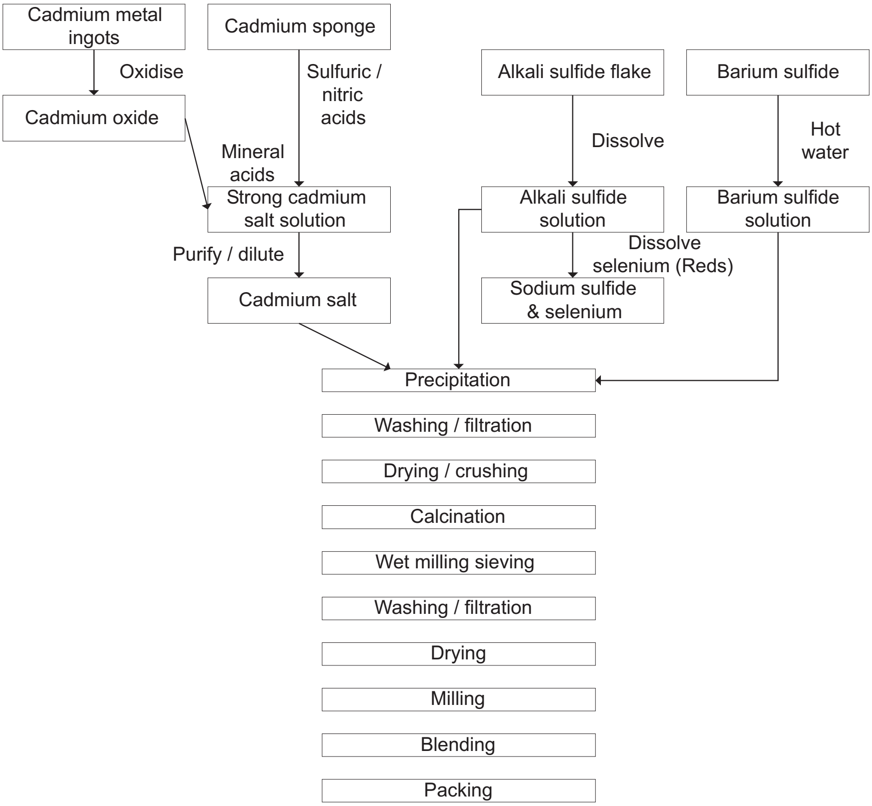

Figure 3–4: Typical production route.

soluble cadmium, but production is generally likely to consist of the following stages:

1. Formation of cadmium oxide (optional).
2. Formation of cadmium sulfate and other solution making.
3. Precipitation and production of the cubic form.
4. Calcination and pigment formation in hexagonal form.
5. Removal of soluble cadmium and production of a fine powder.

Blending and color matching to customer requirements.

A typical production route is illustrated in the process diagram above (Figure 3–4).

3.4.2
Cadmium Oxide Formation

Not all manufacturers produce cadmium oxide, as some prefer to dissolve cadmium metal directly in acid. However cadmium oxide is used in many other applications, including nickel cadmium batteries and stabilizers for polymers.

The oxide can be produced by first melting the metal, then allowing it to flow into a carbon or silicon carbide crucible where, at typically 800 °C, it will boil. The metal vapor is contacted with air by means of an extraction duct positioned over the crucible. A large air flow provided by a fan effects oxidation, and takes the oxide particles to a filtration unit, typically of the reversed jet type, which is a large series of filter bags arranged in a housing. The oxide collects on the outside of the bag while the gases pass through. Intermittent blasts of compressed air into the filter bags expand the bags and cause the oxide to fall off and collect in the bottom of the hopper.

The oxide is then packed and sold, or metered into water to form a slurry suitable for dissolving in acid. Sulfuric acid (50 %) is preferred, as the heat of solution is not too violent. In this way, a strong stock solution of about 300 g/L Cd^{2+} can be produced. The solution is treated as necessary to remove other undesirable metal contaminants, filtered and diluted down to the required strength prior to precipitation.

Clean air from the filter bag housing is typically passed to a scavenger unit to ensure that discharged gases are within permitted limits for cadmium emissions.

3.4.3
Cadmium Metal Dissolution

While cadmium will dissolve in sulfuric, hydrochloric and nitric acids, a mixture of sulfuric and nitric acids is preferred, to obtain a controllable reaction rate to avoid producing noxious fumes.

Sulfuric acid on its own does not dissolve cadmium metal well, as hydrogen bubbles produce a coating which prevents further attack.

Typically, cadmium moss or sponge is packed into a tower. The mixture of diluted acids (with sulfuric in excess) is recirculated through the tower. Cadmium ingots are avoided, as they provide insufficient surface area, and the solution reaction would be too slow. Purification and dilution to the required strength then proceeds as previously discussed.

3.4.4
Other Solution Making

Solutions of sodium sulfide are normally made from sodium sulfide flake ($Na_2S.H_2O$). If lithopones are required, a solution of barium sulfide is also necessary. The latter can be purchased as "black ash", which owes its name to a gray appearance, having been made from the reduction of barium sulfate with carbon. It is difficult to handle, and not as soluble as sodium sulfide. The solutions should be kept warm to prevent crystallization. Sodium sulfide solution is also required to dissolve selenium for the production of cadmium reds.

3.4.5
Precipitation

During precipitation, the above solutions are intimately mixed so as to form a mixture of stoichiometrically balanced sulfides that will form a pigment on firing. It must be remembered that the initial products formed on precipitation do not possess final pigmentary properties. Batch-wise production is the more common route for precipitation, although continuous precipitation has been used.

As with many other pigments, the choice of route and process conditions under which the products can be precipitated is extensive. Order of addition, concentration, temperature, pH and mixing conditions all have an effect on particle size and shape, and hence pigment properties. Each manufacturer has their own methods of manufacture, thus making their pigments slightly different from competition.

The following points are worth noting:

Cadmium sulfide can be formed under both acid or alkaline conditions.

Cadmium sulfide is more insoluble than most other cadmium salts. It can therefore be formed by reacting an alkali sulfide solution with an insoluble cadmium salt such as a carbonate, phosphate or hydroxide. For example:

$$CdCO_3 + Na_2S \rightarrow CdS\downarrow + Na_2CO_3$$

During precipitation of the red pigments, cadmium selenide is not precipitated. Instead, selenium dissolved in sodium sulfide is precipitated as the sodium sulfide is used up in the reaction. Cadmium selenide is then formed on calcining.

If lithopones are to be precipitated, an equimolar amount of barium sulfate will be precipitated for each mole of sulfide used. For example:

$$CdSO_4 + BaS \rightarrow CdS\downarrow + Ba\,SO_4\downarrow$$

3.4.6
Filtration and Washing

Separation of the solid particles from the liquid is most likely to be done by a filter press or belt filter, although decantation can be used for washing, as the product settles well. Soluble sulfate and /or nitrate salts, depending on the acid used to dissolve the cadmium, will also need washing out. This step is important, as the retention of excessive amounts of salts can have a detrimental effect on the product.

3.4.7
Drying

The filter cake can be oven dried, after which it requires crushing into small lumps prior to calcination. To reduce manual handling, the cake is often extruded into noodles onto a belt drier, where a flow of hot air through the pigment bed dries the product into small pellets.

3.4.8
Calcination

Calcination is one of the most important steps in cadmium pigment manufacture, since not only does the product become a pigment at this stage, but conditions used greatly affect the resultant pigmentary properties.

As stated previously for yellows, cubic cadmium and zinc sulfides are converted into hexagonal forms. Cadmium sulfoselenides are formed on calcining reds.

Rotary, tunnel, and static kilns using crucibles or "saggars" have all been used, with calcining sometimes carried out in a molten salt bath[5]. In the calcining process, sulfur dioxide, and (in the case of reds) selenium and some selenium dioxide are emitted, which requires careful fume removal through a gas scrubber or similar equipment. Temperature, residence time and calcining atmosphere all affect color properties and pigment texture. Ideally, cadmium pigments should be soft in texture, not too light or deep, have sufficient tinting power (strength) and chroma (brightness).

Generally, increased temperatures produce lighter and brighter shades, but with less strength, while lower temperatures have the opposite effect. The temperature range used is typically 500–650 °C, with deeper shades requiring a higher temperature. Slight changes in calcination temperatures are regularly made to obtain a balance of the required properties.

During calcination, cadmium and zinc sulfides are converted to their hexagonal form and cadmium selenide is formed. This is normally produced by reacting an insoluble cadmium salt with an equimolar amount of selenium. The cadmium selenide then forms a solid solution with the cadmium sulfide. For example:

$$3\,CdS + CdCO_3 + Se \rightarrow 3\,CdS.CdSe + CO_2\uparrow + \tfrac{1}{2}SO_2\uparrow$$

3.4.9
Wet Milling

Calcined cadmium pigments are relatively soft and easily form a slurry. Passing the slurry through a pin mill or hammer mill will break aggregates down. The slurry can then be passed through a fine mesh to exclude oversize agglomerates and ensure a product which disperses well when used in the desired application.

3.4.10
Removal of Soluble Cadmium

Calcination causes some oxidation of the product, resulting in the formation of soluble cadmium sulfate. Prevailing regulations require pigments or pigmented articles to pass tests for the extraction of heavy metals. In order to meet these tests any soluble cadmium must first be removed. This is achieved by acidification with dilute mineral acid, followed by decant /washing of the fired slurry, or filtration and washing by some other means.

3.4.11
Final Drying and Milling

The filter-cake of the calcined and washed pigment is re-dried, then milled using a pin or hammer mill, to give the final fine powder. Although relatively soft, as with most pigments, excessive shear during this operation can be detrimental. The choice and configuration of equipment is important. The pigment is now ready for blending with other shades as required to meet specific customer needs.

3.5
Physical Properties

The main advantages of cadmium pigments are:

- excellent temperature stability
- Insolubility in organic solvents (non-bleeding)
- light fastness and weather fastness
- chemical resistance
- non-migratory
- good dispersibility
- Polymers colored with cadmiums have good resistance to distortion and warpage
- high opacity
- can be recycled in polymers

Table 3–1: Colour index and typical properties.

Colour Index Name	***Pigment Yellow 35***	***Pigment Orange 20***	***Pigment Red 108***
Composition	CdS · ZnS	CdS · CdSe	CdS · CdSe
Colour Index No.	77 205	77 119	77 202
C.A.S. No.	8048-07-05	12656–57–4	58339–34–7
EINECS No.	232–466–8	235–758–3	261–218–1
Oil absorption w/w	21.8	20.7	20
Specific gravity	4.6	4.8	4.8–5.1
Bulk density g/cc	0.91	0.95	0.98–1.1
Residue on 300 mesh	<0.1	<0.1	<0.1
pH extract	6.5–7.0	6.5–7.0	6.5–7.0
Water soluble salts	<0.2 %	<0.2 %	<0.2 %

N.B. Lithopones have Colour Index names with the suffix 1. For example, Pigment Yellow 35:1 is the lithopone equivalent of Pigment Yellow 35.

Particle size measurements using electron microscopy show the primary particles to be 0.2–5 μm.

A slightly larger particle size will be found if the determination is done by other methods such as disc centrifuge or sedimentation techniques (Figure 3–5), depending on how well the pigment is dispersed.

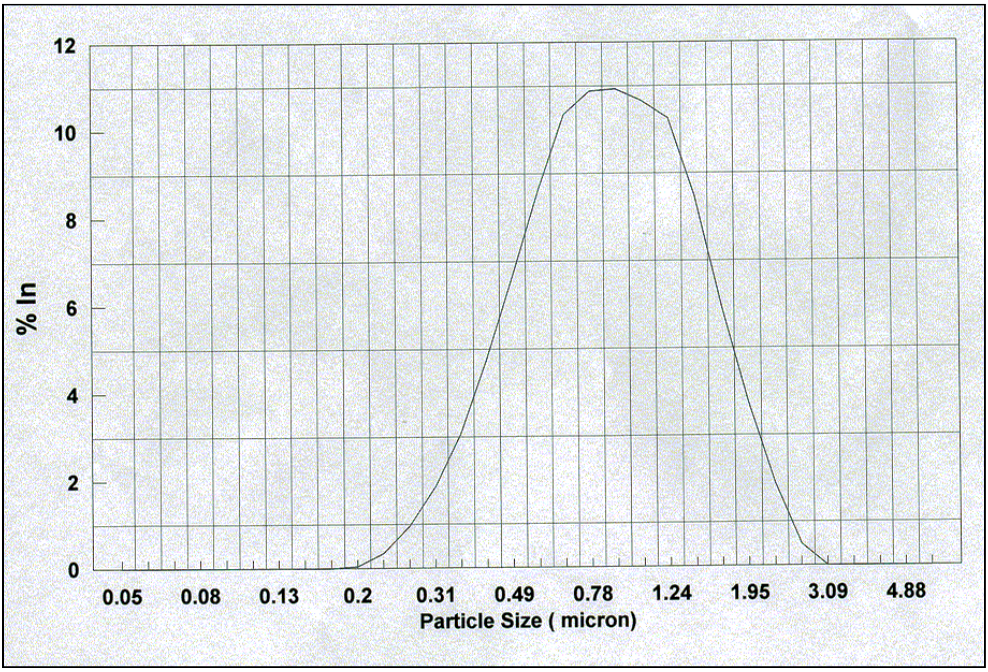

Figure 3–5: Typical particle size distribution

Cadmium pigments are stable to 400 °C with only minimal degradation, allowing them to be used in the majority of polymers, and also allowing colored articles to be recycled. They have limited use in some polymers, such as silicone molding compounds, acrylic molding compounds and acetals.

Chemical resistance is good, particularly to alkali, reducing agents and dilute acids. They are, however, susceptible to attack by concentrated mineral acids. Light fastness properties are also good (typically 7 by the Blue Wool Scale). In weathering tests, their performance is generally considered excellent in mass tone. However, the ability of the carrier resin to allow moisture to permeate, the presence of oxidizing agents and the presence of titanium dioxide when combined can all reduce performance. Thus, resistance to weathering in mass tone can be better than in reduced tone.

Because of the inorganic nature of the pigment, cadmiums are not soluble in organic solvents and polymers. They have therefore very low migration levels.

Much work has been done to determine levels of extractable cadmium leached from colored articles. This has been done to determine how much cadmium is likely to be released in food contact applications, and to predict cadmium release from waste products in landfill sites. It has been shown that in all but a few polymers insignificant levels of cadmium are leached out.

These properties, coupled with the broad color range, make cadmiums a preferred colorant.

3.6
Regulatory Issues

Since the 1950s, cadmium pigments have been used predominantly in the polymer industry. Regulations have, however, been introduced for some time to restrict their use in certain applications, because of concerns about the presence of cadmium in the environment. Pigment producers and users have always advocated strongly that pigments should be treated differently in environmental matters as compared with such products as electroplated cadmium, cadmium stabilizers for polymers, and other cadmium salts, on grounds of insolubility, inertness, low migration levels, and lack of bioavailability. At this time, no other substitute pigment is known to have been assessed for environmental risk to the same degree as cadmiums. However, arbitrary restrictions in some applications have already taken place where it has been decided that alternatives should be used. For example, Sweden and Denmark placed restrictions on the use of cadmium pigments in 1982. Next, the EU in 1992 issued a directive based on the “Precautionary Principle” (91/338/EEC), that included a list of polymers in which cadmium is to be excluded as a colorant. In 1995, this list was further extended. Since then, realizing its lack of credible scientific evidence, the EU commissioned an independent consultant to conduct a risk assessment from “cradle to grave” on the health and environmental effects of cadmium pigments. The report concluded that ”*for the entire pigment life cycle, emissions of cad-*

mium are negligible compared to emissions from all known sources and pose no significant risk to human health or the environment"[6].

Today, many different regions throughout the world have their own restrictions, classifications and labeling requirements for cadmium pigments.

3.7
Uses

Current annual world consumption of cadmium pigments is approximately 2,500 tonnes, used in the following applications:

Table 3–2: Applications of cadmium pigments.

Polymers	90 %	All grades of polymers and compound masterbatch
Ceramics	6 %	Glasses, enamels, porcelain, tile, china and glazes
	3 %	Oil colors, water colors, acrylics
Surface Coatings	1 %	Coil coatings, automotive paint, high temperature paint

Use of cadmium pigments in polymers is almost universal. Principal polymers of use include HDPE, polystyrene, polypropylene, nylon and ABS. Within Western Europe cadmium pigments are permitted for use in safety applications and in polymers that demand higher processing temperatures. They are also permitted in European toy applications, provided that the colored article conforms to soluble extraction limits of EN71: Part 3. Whereas in Europe the pigments are not permitted to be used in low-density polyethylene (LDPE), they can still be used in masterbatch, which can then be used to color unrestricted polymers.

In the USA, cadmium pigments must conform to TCLP (toxic characteristic leaching procedure) test limits to meet requirements for non-hazardous wastes.

Coloring ceramics can be considered the ultimate test for a pigment, where application temperatures can exceed 1000 °C, considerably beyond the performance limits of any organic pigment. Cadmium pigments offer a unique range of vivid and bright reds, oranges and yellow shades for ceramic applications such as glasses, porcelain and vitreous enamels where high temperature stability is an essential requirement.

The most demanding applications, which involve the highest temperatures for cadmium pigments are "inclusion stains", in which the pigments are mixed with zirconia and mineralizer to 1000–1100 °C. During this process, the pigment becomes completely encapsulated by a zircon (zirconium silicate) glass that forms a protective coating.

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4
Cerium Pigments

Jean-Noel Berte

4.1
Introduction

Pigment Name	***Formula***	***Colour Index***	***CAS#***
Cerium Sulfide Light Orange	Ce_2S_3/La_2S_3	PO 78 C.I. 772850	12014–93–6 / 12031–49–1
Cerium Sulfide Orange	Ce_2S_3	PO 75 C.I. 77283–1	12014–93–6
Cerium Sulfide Red	Ce_2S_3	PR 265 C.I. 77283–2	12014–93–6
Cerium Sulfide Burgundy	Ce_2S_3	PR 275 C.I. 772830	12014–93–6

Only a few truly high performance inorganic pigments are available today (with high performance in thermal, chemical, and UV stability) in the color range from red to yellow, such as cadmium sulfoselenide, lead molybdate and bismuth vanadate. Such products are currently used in applications for automotive coatings, engineering plastics, ceramic coloring and packaging, where high opacity, thermal stability, light-fastness and lack of warping are still difficult to obtain with organic or other inorganic pigments. The latter compounds have excellent performance characteristics, but their toxicity is environmentally questionable. Thus, driven by changes in legislation and government regulations, there is a growing need to develop new classes of inorganic pigments that are both non-toxic and environmentally unimpeachable, while preserving or even exceeding the optical, thermal, and chemical characteristics of present day high-performance pigments.

In the light of this situation, Rhodia saw an opportunity to develop a family of new pigments, called Neolor^{TM}, based on rare earth chemistry. The new pigments are rare earth cerium sulfides. Because cerium sulfide pigments possess good thermal stability, light-fastness, opacity and dispersibility, they are one of the most promising candidates as successors to today's families of heavy metal pigments[1, 2].

4.2
Rare Earth Sulfides and the Origins of their Color.

Rare earth sulfide materials have received considerable attention over past years, mainly because of their interesting optical and magneto-optical properties.

Rare earth elements and sulfur combine to form a wide range of compounds as sulfides or oxysulfides[3, 4]. Among them, sesquisulfides appeared to have the best potential as far as color is concerned (Table 4–1). We gave most of our attention to cerium sulfide, which was the most promising in terms of color intensity and purity.

Table 4–1: Color of some rare earth sesquisulfides in their γ-form.

La_2S_3	Ce_2S_3	Pr_2S_3	Nd_2S_3	Gd_2S_3	Tb_2S_3	Dy_2S_3
White yellow	Dark red	Green	Light green	Sand	Light yellow	Orange

Rare earth sesquisulfides exist in different allotropic forms (Figure 4–1). Cerium sesquisulfide is known to exist in 3 different allotropic forms: α, β, and γ, all stable at different temperatures and exhibiting different colors (Table 4–2).

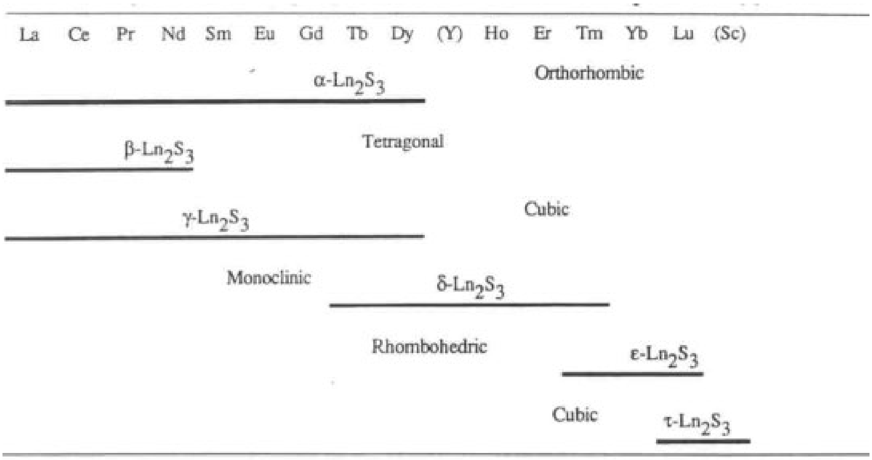


Figure 4–1: Different allotropic forms of the sesquisulfides of rare earth elements[5].

Table 4–2: Color and properties of rare earth sesquisulfide allotropic forms.

	$\alpha\text{-}Ce_2S_3$	$\beta\text{-}Ce_2S_3 = Ce_{10}S_{14}O_xS_{1-x}$ $(0 \leq x \leq 1)$	$\gamma\text{-}Ce_2S_3 = Ce_{3-x}\square_x S_4$ ($\square$ = cation vacancy)
Color	Black / brown	Burgundy	Dark red
Structure	Orthorhombic	Tetragonal	Cubic
Temperature of formation	< 900 °C	> 900 °C	> 1200 °C

The low-temperature α-Ce_2S_3 phase is exactly stoichiometric and is stable up to 900 °C in non-oxidizing atmospheres[6, 7]. This phase is readily produced, but has very little interest in terms of color because of its brownish-black shade.

The β-Ce_2S_3 phase is in fact an oxysulfide containing a minor amount of oxygen substituting sulfide atoms. Its formula can be written as follows: $Ce_{10}S_{14}O_xS_{1-x}$ with $0<x<1$[8–10] (Figure 4–2). It is burgundy in color, but it is possible to vary this from dark to light shades by adjusting the amount of oxygen in the molecule. The lower the oxygen content the lighter is the tint[11].

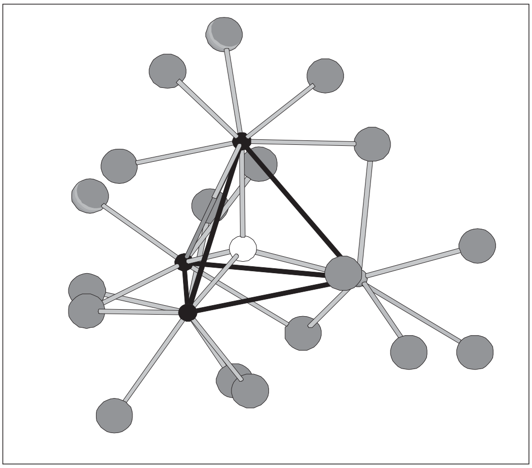


Figure 4–2: β-Structure: tetrahedric sites occupied either by oxygen atoms (white) or sulfur atoms (gray) in $Ce_{10}S_{14}O_xS_{1-x}$ (cerium atoms in black)[12].

The γ-Ce_2S_3 phase (Figures 4–3 and 4–4)[12] is dark red, but can only be produced at temperatures above 1100 °C, which makes it very difficult to prepare on the industrial scale. This phase is, in fact, isomorphous with Ce_3S_4 and has the ability to accommodate other cations in its metal vacancies, for example alkaline earth cations or other non-cerium lanthanides[13–17]. Its formula can be expressed as $Ce_{3-x}S_4$ where x stands for cationic vacancies.

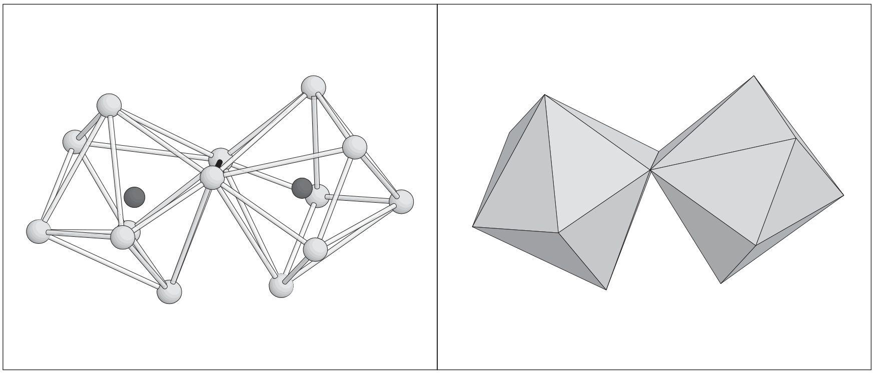


Figure 4–3: γ-Ce_2S_3 structure: dodecahedra joining at one edge[12].

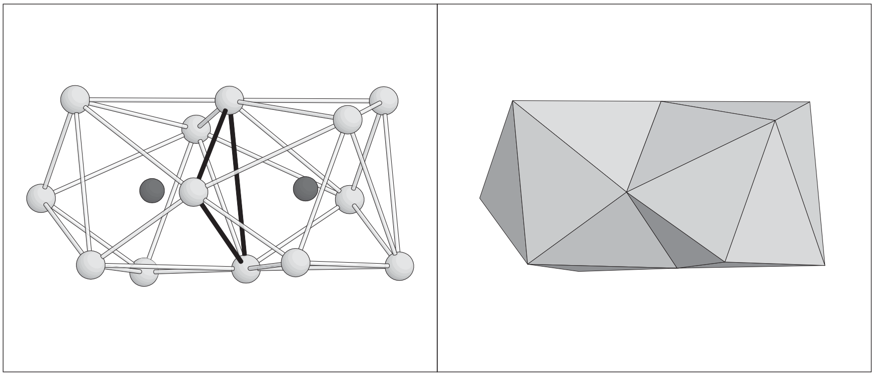


Figure 4–4: γ-Ce_2S_3 structure: dodecahedra joining at one face[12].

In the light of the above considerations, only the β- and γ- forms were chosen to be developed as pigments. This, however, limited the available color range to burgundy and red.

Research was thus carried out to study the possibility of enlarging the color range by considering modifications of γ-Ce_2S_3. Our results showed that the dark red color of γ-Ce_2S_3 was due to electronic transitions from the Ce4f level into the Ce5d conduction band, corresponding to an energy gap of about 1,9 eV (Figure 4–5). It was also found that the value of the 4f–5d energy gap correlates to the ionicity of the Ce–S bond[18]. This conclusion was important as it meant that it should be possible to enlarge the color range by modifying the ionicity of this bond.

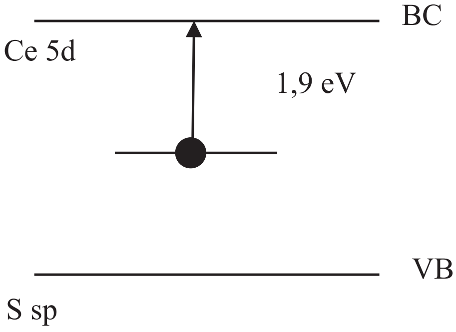


Figure 4–5: Electronic transition at the origin of the color for γ-Ce_2S_3.

It was next found that modification of the ionicity of the Ce–S bond could be achieved by incorporating dopants in the cationic lattice vacancies. The color of $Ce_{3-x}S_4$ doped with alkali cations (Li, K, Na) could thus be tuned from red (Eg=1.9 eV) to orange (Eg= 2.1 eV), depending on the nature and the amount of dopant used. This phenomenon was attributed to an increase of ionicity of the Ce–S bond due to the lower electronegativity of the alkali cation, compared to that of Ce^{3+}.

Because the amount of alkali cation dopant that could be incorporated within the vacancies is limited for structural reasons to a ratio of$^{[\Delta]}$ /$^{[Ce]}$ = 0.2, only a small modification of the Ce–S bonding ionicity could be induced, and only red/orange-doped γ-Ce_2S_3 materials could be obtained. A brighter orange shade (light orange) could however be obtained by partially substituting cerium atoms with lanthanum cations.

With this understanding of the properties of lanthanide sesquisulfides it was possible (by addition of alkali metal and/or alkaline earth elements) to enlarge the color range of cerium sesquisulfides from burgundy to light orange (Figure 4–6). Serendipitously, this chemical modification of the γ-phase Ce_2S_3 also permitted stabilization at lower temperatures (< 800 °C), thus making industrial production more practical[19].

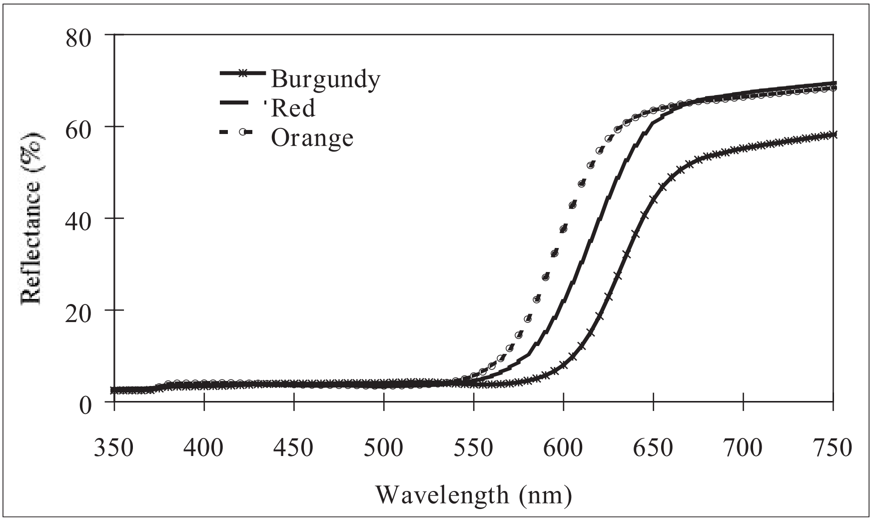


Figure 4–6: Reflectance curves of orange, red and burgundy cerium sulfide pigments.

Further research in this field is under way to extend the color range to yellow. Because of the limitations of the γ-Ce_2S_3 doping approach, other systems than cerium sesquisulfides are under study. Sm_2S_3 appears to be a good candidate[20].

4.3
Cerium Sulfide Pigment: Manufacture

The majority of processes aimed at obtaining rare earth sesquisulfides of high purity use solid/gas reactions.

Most of the methods of synthesizing lanthanide sulfides involve high-temperature gas-solid reactions between a sulfurizing agent (H_2S and/or CS_2) and lanthanide precursors at high temperatures or under high pressures[21, 22].

Various types of lanthanide precursors can be used: oxides, salts, alkoxides, or organic complexes like oxalates, carbonates, tartrates and malonates[23–27].

Solid-state reaction involving direct treatment of the precursor with elemental sulfur is also possible. In this case lanthanide metal can be used. Processes of this type have the disadvantage of being either difficult or impossible to be commercialized because:

1. They require excessive temperatures and/or pressure conditions.
2. They involve precursors incompatible with the production of sesquisulfides with good coloristic properties and particle size.

Rhodia has now developed and commercialized a special process to produce rare earth sesquisulfides, notably cerium sesquisulfides with the adequate purity and size necessary for pigment application.

Cerium sulfide pigments are prepared in three steps (Figure 4–7):

1. Synthesis of a cerium based precursor
   An acidic solution of cerium salt is transformed by a liquid process into a reactive cerium precursor as cited above. At this step, alkali metal and/or alkaline earth metal salts can be added depending on the color targeted. The resulting precipitate is not yet colored, and must next be transformed into a colored sulfide.
2. Sulfuration of the cerium precursor
   The transformation of the cerium precursor into the colored sesquisulfide is carried out at high temperatures (between 700 and 1100 °C) in a sulfurizing atmosphere. The resulting colored sesquisulfide is then cooled to room temperature.
3. Final treatment
   Once the colored powder is obtained it is ground in order to break all the agglomerates that may have been formed during the sulfurization process. This step is necessary to reveal the pigmentary nature of the pigment. A surface coating is then applied to the Ce_2S_3 particles by a wet process in order to increase the stability of the pigment and to optimize its compatibility with the final matrix. The coating can be mineral and/or organic (Figure 4–8). Finally, the pigment is filtered, dried, and sieved before packaging.

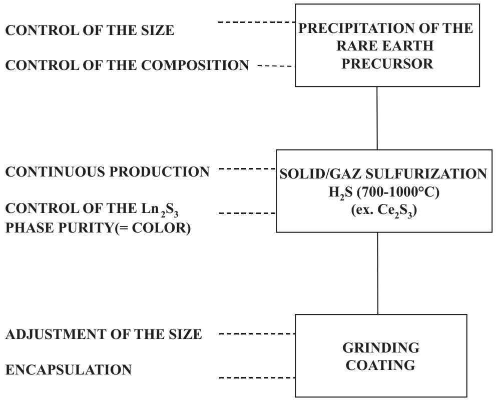


Figure 4–7: Processing of cerium sulfide pigment.

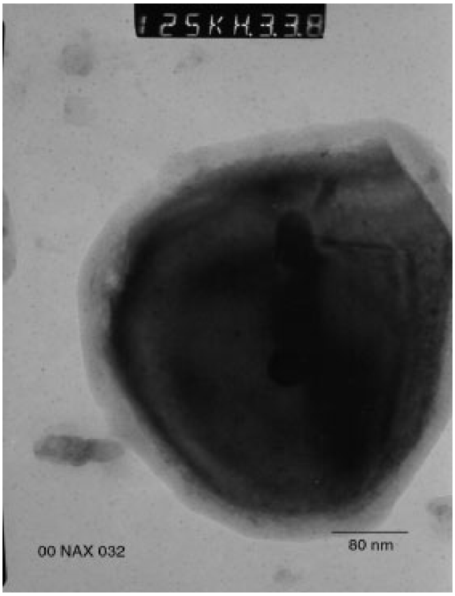


Figure 4–8: Coated cerium sulfide.

Typical products have the following characteristics:

Specific gravity (g/cm^3): 5
Apparent density (g/cm^3): 0.8
Refractive index n: 2.7
Specific surface area: 3m^2
Oil absorption (g/100g): 20–28
Hardness (Mohs): 4–5
Typical particle sizes (µm): 0.8–1.3
Thermal stability: 350–400 °C

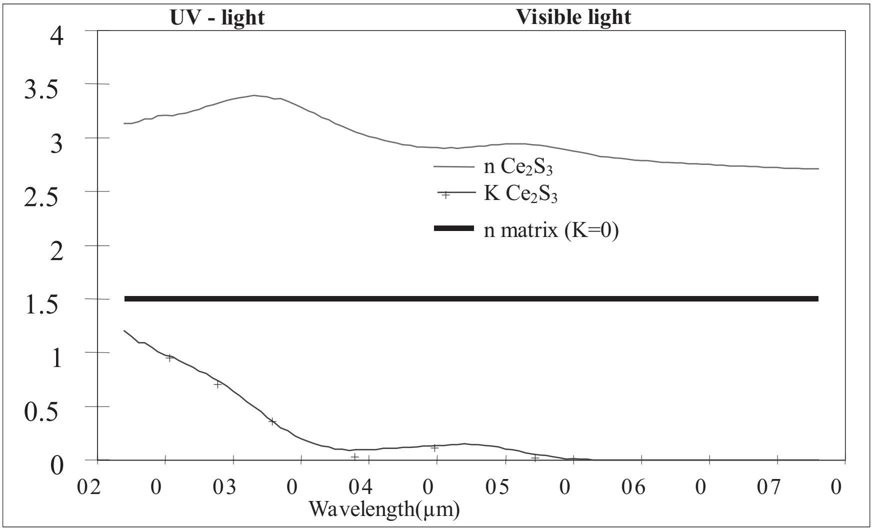


Figure 4–9: Absorption (K) and refraction (n) indices of cerium sulfide pigment.

Because of the affinity of metallic rare earths for sulfur, strong bonds are formed in the manufacturing process, inducing high refractory character and chemical inertness in many materials. In air, cerium sulfide pigments are stable up to 350–400 °C, which makes them good candidates for high-temperature processing applications.

Because of the orbital transition, Ce_2S_3 materials, like other cerium compounds, are naturally good UV absorbers (Figure 4–9). No photocatalytic effect is observed.

4.4
Properties and Applications

4.4.1
Coloration of Plastics

Cerium sulfide pigments have been developed primarily for the coloration of plastics. Shades of existing cerium sulfide pigments vary from light orange to dark red/burgundy. Colors obtained are less chromatic than with cadmium pigments, but are much brighter than with iron oxides.

The use of cerium sulfide in combination with white pigments leads to light salmon to pink shades. Their tinting strength is somewhat weaker than that of cadmium pigments, but is similar to that of lead pigments.

Table 4–3 indicates, for the range of existing cerium sulfide pigments, the typical quantity of pigment necessary to achieve a standard depth of shade of 1/25, when combined with 1 % rutile TiO_2 pigment.

Table 4–3: Tinting strength of cerium sulfide pigments in plastics.

Cerium sulfide pigment	*Light orange*	*Orange*	*Red*	*Burgundy*
g per kg of plastic	4	3	2.6	2

Cerium sulfide pigments provide relatively high opacity and hiding power, similar to cadmium and lead-based pigments.

Cerium sulfide pigments can be used either alone or in combination with other pigments and colorants to obtain orange and red shades. They are also successfully employed as shading pigments in pastels and beige tints.

Cerium sulfide pigments can be readily dispersed in a variety of polymeric resin systems using conventional plastics processing equipment. They are both non-dusting as well as dispersible (Figure 4–10).

Being inorganic, cerium sulfide pigments are not susceptible to migration when dispersed in a polymer matrix and are not soluble in thermoplastics. They do not cause blooming or bleeding, or show streaking effects during processing. They impart dimensional stability to molded parts because they are free from shrinkage or warpage. This is, of course, of prime importance in the coloration of crystalline or semi-crystalline polymers.

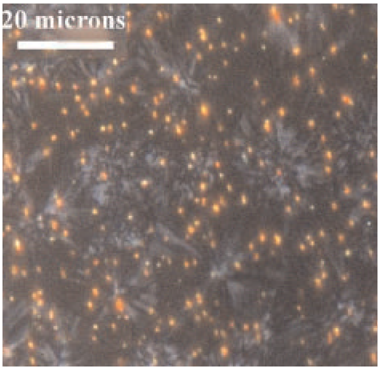


Figure 4–10: Image of a polypropylene sample pigmented with cerium sulfide obtained by optical microscopy.

When combined with other pigments or colorants, cerium sulfide pigments may even improve the dimensional stability of the resulting formulation, for example in high density polyethylene and polypropylene. Use of cerium sulfide pigments can even facilitate processing and allow reduction of cycle times in injection molding machines in comparison to organic based formulations. Cerium sulfide pigments have also only minimal effect on mechanical properties, for example, impact strength.

Besides the fact that they are compatible with most thermoplastics, cerium sulfide pigments can also be used in a wide range of other polymers including engineering plastics, thanks to their very good heat stability.

Table 4–4 gives results of heat resistance tests performed in various thermoplastics at 0.5 % pigmentation levels. Samples were obtained by injection molding at increasing temperatures with 5 min dwell time. The temperatures reported correspond to that at which an appreciable color change (DE* of 3) is observed.

Table 4–4: Heat stability of cerium sulfide pigments in various polymers.

Polymer	*PP*	*ABS*	*PC*	*PA6*	*PA6.6*
Heat Resistance	>320 °C	>290 °C	>320 °C	>320 °C	>320 °C

An additional benefit of such high levels of heat resistance is the potential for recycling pigmented material with limited color degradation.

Thanks to their strong UV absorption characteristics, cerium sulfide pigments are not only light-fast (Table 4–5), but can protect the medium in which they are incorporated from deterioration by UV light (Figure 4–11).

Table 4–5: Lightfastness of cerium sulfide pigments in various polymers.

Polymer	*PP*	*ABS*	*PC*	*PA6*	*PA6,6*
Color Change (BWS)	8	8	8	8	8

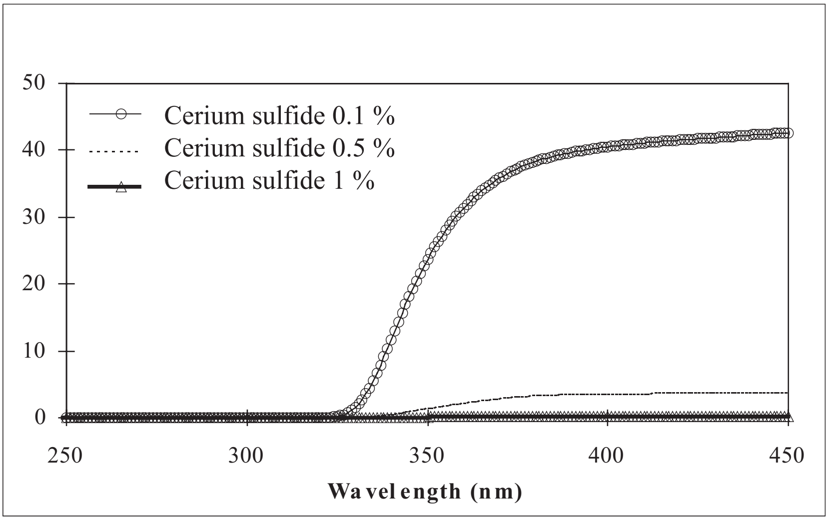


Figure 4–11: UV transmission curves of PP chips containing cerium sulfide pigments.

Hence, cerium sulfide pigments can be used advantageously in very demanding, high light-fastness applications such as automotive interiors.

Cerium sulfide pigments show outstanding weathering performance in most thermoplastics, including polyolefins, ABS, PC, PA and PMMA (Figure 4–12). However, cerium sulfide pigments are not recommended for durable PVC application, where discoloration is observed, probably related to the fact that the dehydrochlorination reaction typical for PVC degradation generates free HCl, which could attack cerium sulfide.

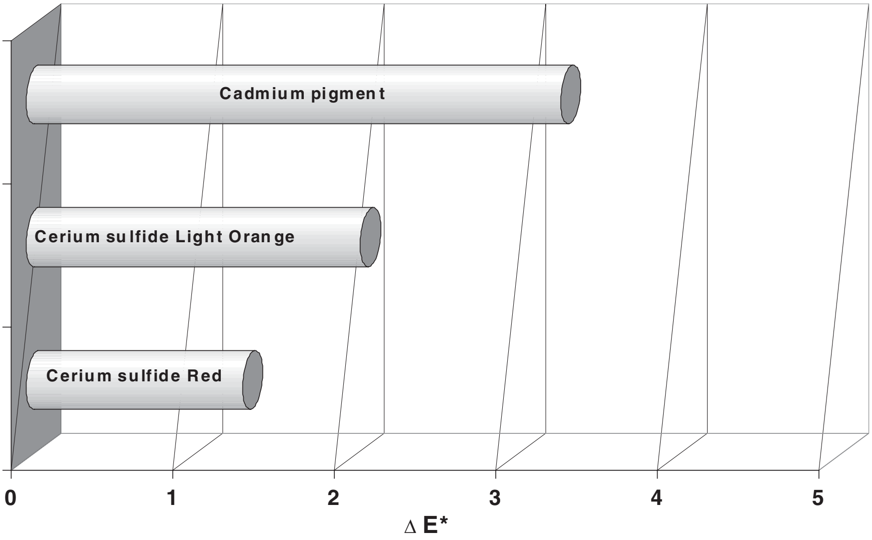


Figure 4–12: Color change of PC samples after 24 months natural weathering.

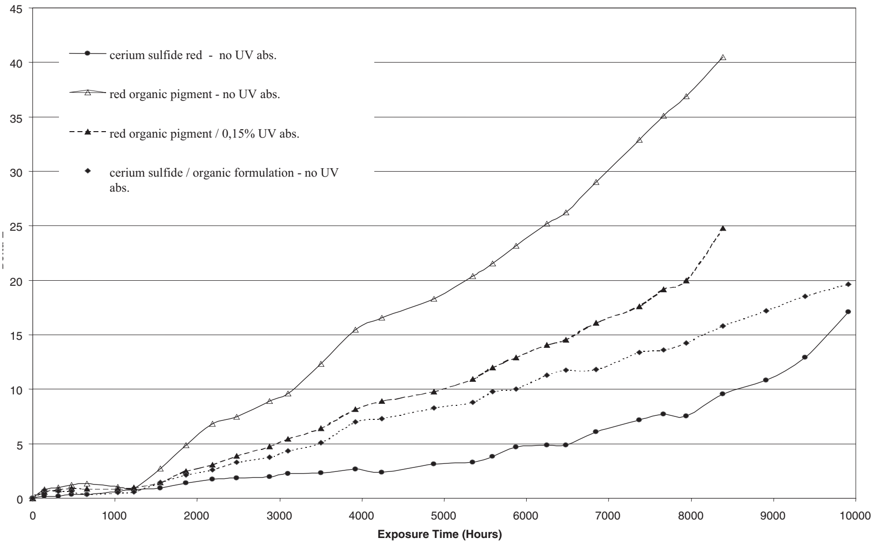


Figure 4–13: Color change of red HDPE samples (0.4 % HALS) during accelerated weathering (xenon arc).

Thanks to their UV screening effect, cerium sulfide pigments can have a beneficial effect on weathering performance in polymer systems. As shown in Figure 4–13, a combination of cerium sulfide pigments with red organic pigments is significantly more stable than the pure organic formulation. Furthermore, the addition of cerium sulfide pigment tends to allow reduction of traditional UV absorber level.

While pure cerium sulfide is sensitive to acidic species and moisture, its stability can be improved as a result of surface treatment.

During processing of polyamide under extreme conditions of temperature and shear in, for example PA6,6 with high levels of glass fiber reinforcement, the chemical stability of existing standard cerium sulfide pigments may be compromised, with some H_2S emissions detected. Further developments are in progress to obtain grades with improved stability.

The possibility of interaction with CuI stabilizer used in polyamide has also been reported as giving rise to unexpectedly darker shades.

Though processing in polymeric resins at moderate temperatures has proved successful, cerium sulfide is not recommended for the coloration of fluoropolymers, because of possible reaction and resulting discoloration in the presence of HF formed at high temperatures.

4.4.2
Paint and Coatings Application

A paint grade of cerium sulfide has also been developed. The pigment has been evaluated in several coatings formulations such as automotive refinish (acrylic-isocyanate binders), general industrial solvent-based systems (polyester-melamine binders), oil-based architectural coatings, and water-based paint. In the latter, performance may be improved by treatment with organics during formulation.

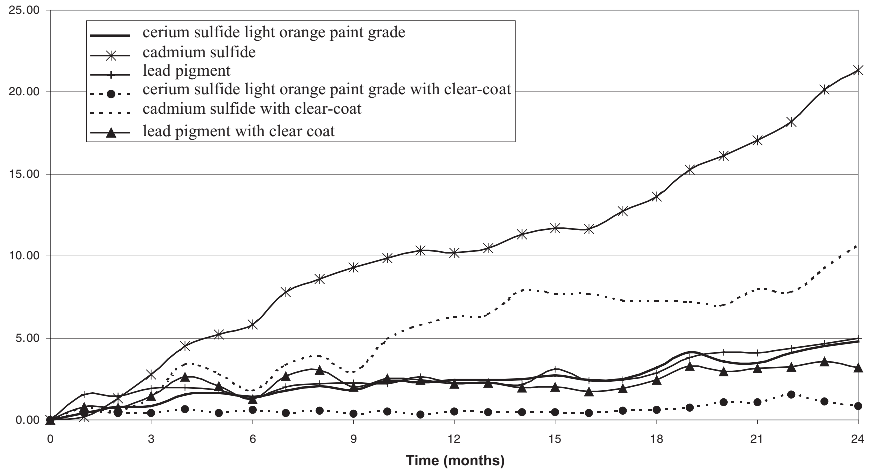
Paint grade cerium sulfide pigment has a very good wet point and flow point because of a significantly low oil demand in comparison with organic pigments. The low oil demand has a positive impact on the viscosity of the mill base; it induces a low energy cost for the milling process and provides a greater flexibility for the formulator by providing the possibility of working at high solids content with low viscosity levels.

In comparison to organic pigments, cerium sulfide formulations have a high "Persoz" level of hardness, coupled with good direct impact resistance. This produces very good gravel impact resistance. Chemical resistance (acid, base and solvent) has been evaluated in paint by the drop test. No specific problem was detected except for organic acids such as acetic acid.

Paint grade cerium sulfide pigments exhibit very good durability in both the xenon test and outdoor exposure. In QUV-A testing, however, the humidity conditions of the experiment are too severe to be representative of outdoor exposure.

Florida exposure has been evaluated (with a refinish acrylic-isocyanate formulation). Paint grade cerium sulfide outperforms cadmium sulfides, and is equivalent to that of lead pigments (Figure 4–14). In comparison with organic pigments, cerium sulfide paint grade also has a good durability.

Cerium sulfides may also be successfully used in powder coatings, thanks to their good weathering resistance.



Florida exposure (ASTM G7-97) refinish paint (acrylic-isocyanate) variation of tint (specular excluded)

Figure 4–14: Durability of paint grade in Florida exposure.

Cerium sulfide pigments are also good candidates for automotive paints, due to the IR reflectance properties of Cerium compounds (Figure 4–15).

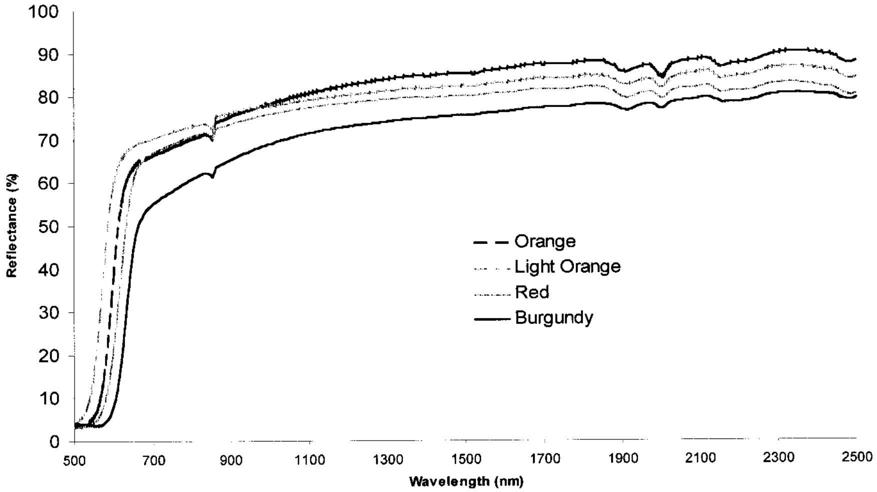


Figure 4–15: Visible and IR Reflectance curves of Light orange, Orange, Red and Burgundy.

4.4.3
Miscellaneous Applications

Cerium sulfide pigments are also used for some applications in printing inks and polyurethane foams, and are being evaluated in laminated paper.

4.5
Toxicology and Environmental Aspects

Cerium sulfide pigments (NEOLOR™) are almost completely insoluble in water, and the cerium ion shows effectively no toxicity (acute or chronic). As predicted, cerium sulfide pigments have shown no risk to humans or the environment. Acute oral toxicity: LD_{50} rat, oral >5000 mg/kg[28]. Tests for irritation to the skin, eyes, or mucous membranes have also shown no adverse effects, as have tests for potential skin sensitivity[29].

Cerium sulfide pigments also show no genotoxic or carcinogenicity effects. Bacterial and in vitro gene mutation assays (OECD 471 & 476) fail to show mutagenic activity. In vitro chromosomal aberration tests (OECD 473) show no clastogenic activity. Additionally, sub-chronic toxicity (28 day, OECD 407) studies show no significant adverse effects (dose of 150 mg/kg/day), unlike cadmium and some other pigments[30].

Cerium sulfide pigments show no harmful effects on the environment. The pigments are virtually completely insoluble. They show no mobility and readily form deposits in the soil. Further studies show they are not harmful to the aquatic environment: EC 50 (*Daphnia magna*, 48 h): >100 mg/L)[31].

4.6
Toxicological and Environmental Concerns during the Manufacturing Process

In the production process, inadvertent reaction with moisture, acids, and heat may result in the release of small amounts of hydrogen sulfide. Therefore, an exhaust air system is recommended for handling cerium sulfide pigments. The exhaust air might also require scrubbing for hydrogen sulfide removal, and state, local and national regulations should be carefully consulted.

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5
Complex Inorganic Color Pigments: An Overview.

James White

5.1
Introduction

An important family of high performance pigments is termed complex inorganic color pigments, or CICPs. Chemically, these pigments are synthetic crystalline metal oxides that have structures identical to those of naturally occurring minerals. They are called complex because they contain two or more different metals[1]. Complexity provides a range of metal combinations and in practice gives a wide range of colors for this class of pigments.

CICPs are used when outstanding color stability is required. Resistant to attack and dissolution by chemical agents and solvents, they do not bleed or migrate in application. They have heat stabilities hundreds of degrees higher than organic pigments, and are not discolored by exposure to ultraviolet (UV) light. The fact that these pigments absorb UV light without decomposition makes them good UV absor-

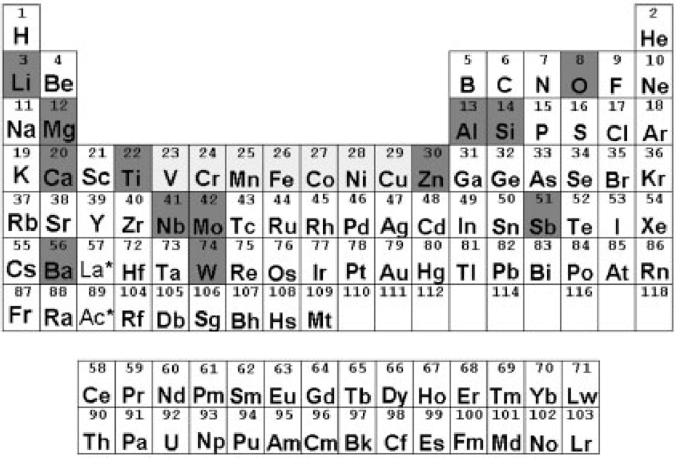

Figure 5–1: Elements commonly found in CICPs. Light shaded elements are those responsible for the primary color. Dark shaded elements are colorless and are present to balance charge and to modify color hues.

bers and opacifiers in their own right. They are the most stable and durable type of colorants commercially available – truly high performance products.

The elements typically found in CICPs are listed in Figure 5–1. Of these metal ions, only seven, all transition metals, are responsible for producing color[2]. Other metal ions in the pigments are colorless, and are added as modifiers to balance the charge of the crystal lattice, or to slightly modify the shade that the coloring ions produce.

Transition metal compounds are generally quite colorful, and CICPs are no exception. Color in CICPs is generated by electronic d–d transitions on the coloring metal ions in the crystal lattice, or from metal-to-conduction band transitions within the solids. These metal-based electronic transitions are spectroscopically unfavorable, resulting in relatively poor light absorption[3]. This means that CICPs have relatively weak coloring power when compared to other pigments. However, metal oxides are very stable entities and their color is very durable.

5.2
Structures of CICPs

CICPs are metal oxides, which can have a number of possible structures. The biggest determining factor in the structure is the oxygen/metal (O/M) ratio (Table 5–1). As long as the metal ions are of a comparable size, it is the O/M ratio that largely determines what the structure will be. Two crystal structures dominate the class of CICPs – those of rutile and spinel. The hematite and corundum structures are also observed, but are much less common.

Table 5–1: Structures and formulas of common CICPs.

Crystal type	*Basic formula*	*O/M ratio*
Rutile	MO_2	2.00
Hematite or corundum	M_2O_3	1.50
Spinel	M_3O_4	1.33

Rutile is the name of one of the crystalline phases of the mineral titanium dioxide, TiO_2. It is the most dense phase of naturally occurring titanium dioxide, with a stoichiometry of 2 oxygens to 1 metal, or O/M = 2. Formulations containing metal ions of similar size to Ti(IV) with an O/M ratio of 2 will often adopt the rutile structure. CICPs with this structure contain a large fraction of TiO_2 as a base oxide. Not surprisingly, rutile CICPs have many physical properties in common with titanium dioxide. Metal ions in rutile are octahedrally coordinated by six oxygen ions, as shown in Figure 5–2.

The spinel structure, named from the mineral spinel, $MgAl_2O_4$, is very common for many of the first row transition metal oxides. It has an O/M ratio of 1.33, and numerous transition metal oxides adopt this structure when they have this M/O ratio. In fact, the structure is so stable that even stoichiometries substantially differ-

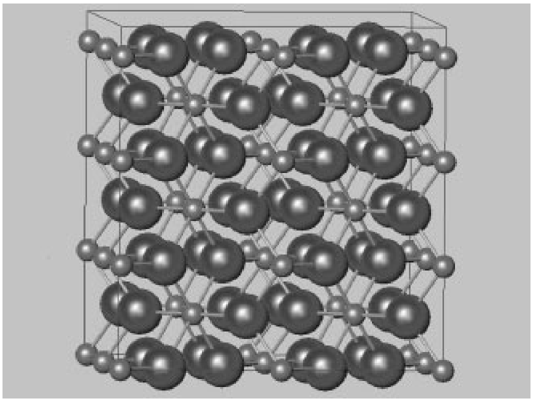

Figure 5–2a: A view of the rutile crystal structure. Oxide ions are large and metal ions are small spheres.

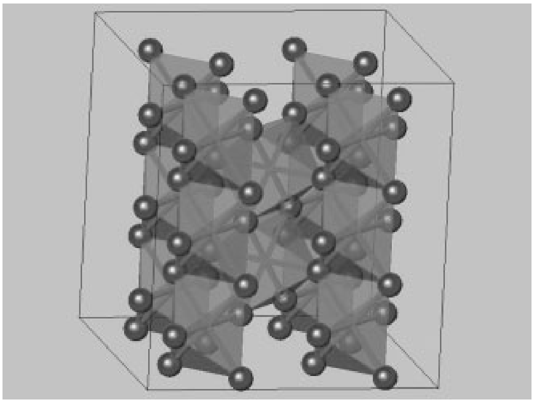

Figure 5–2b: Another view of the rutile structure showing the connectivity of the MO_6 octahedra. Metal ions, removed for clarity, reside at the center of each octahedron.

ent from M_3O_4 can retain the spinel configuration. In these cases, the solids generally contain metal ion vacancies.

The spinel structure contains metal ions in different oxidation states. Generally, there are divalent (+2) and trivalent (+3) metal ions in the structure, although other charged ions can be accommodated. There are two distinct coordination environments for metal ions in spinel. One site is octahedrally coordinated by the oxygen ions, while the other is tetrahedrally coordinated. An example of the spinel lattice showing these sites is displayed in Figure 5–3. Normal spinels have only divalent metal ions in tetrahedral sites and only trivalent metal ions in the octahedral ones. Inverse spinels also occur, where some divalent metal ions are 6-coordinated, with some trivalent ions in 4-coordinated sites.

The other structures of interest are those with the basic formula M_2O_3, $O/M = 1.5$. There are two of these structures found in CICPs, one being corundum, named after the α-alumina phase of Al_2O_3, and the other is hematite named after the mineral Fe_2O_3. There is a slight difference in spatial geometry between the two structures, but both are quite similar. Metal ions are trivalent and octahedrally coordinated in both.

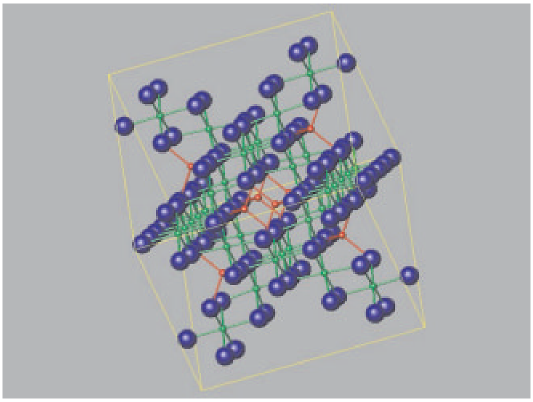

Figure 5–3: A view of the spinel crystal structure. Oxide ions are blue, octahedrally coordinated metals and their bonds are green, and tetrahedrally coordinated metals and their bonds are red. Some atoms and bonds have been removed for clarity.

5.3
Production of CICPs

CICPs are made by calcination (strong heating in air) of blends of metal oxides and/or oxide precursors such as metal salts, hydrates, and carbonates. Calcination temperatures typically range from 650 to 1300 °C. At relatively low temperatures, all the raw ingredients decompose to form the metal oxides. At higher temperatures, this oxide mix becomes reactive. Metal and oxide ions become mobile and interdiffuse to create a homogeneous solid. The ions in the solid then rearrange to a stable crystalline structure that is determined by the metals present, the O/M ratio, and the calcining temperature. This new structure is the color pigment. Following calcination, CICPs are milled to achieve a specific particle size, often washed, and finally blended for uniformity.

Three main groups of CICPs are commercially produced. Titanates, which use a titanium dioxide base, aluminates, which use an aluminum oxide base, and chromites and ferrites, which have chromium and/or iron oxide bases.

5.4
Titanate Pigments

Titanate-based pigments contain titanium dioxide as a base component. The different types are listed in Table 5–2[4]. Pigments using TiO_2 as a modifier are not included here. The important crystalline types are rutiles and spinels, with few other structures having commercial relevance. Titanates comprise the largest volume of CICPs in use today, and of these the greatest usage is of the rutile grades. Detailed information on titanate pigments can be found in Chap. 7 of this volume.

Table 5–2: Common titanate-based CICPs.

Chemical type	*C.I. Pigment*	*Color*	*Crystal Type*
CoTi	Green 50	Green	Spinel
BaNiTi	Yellow 157	Yellow-green	Priderite
NiSbTi	Yellow 53	Yellow	Rutile
NiNbTi	Yellow 161	Yellow	Rutile
NiWTi	Yellow 189	Yellow	Rutile
CrSbTi	Brown 24	Yellow-orange	Rutile
CrNbTi	Yellow 162	Yellow-orange	Rutile
CrWTi	Yellow 163	Orange	Rutile
FeTi	Black 12	Yellow-brown	Spinel
MnSbTi	Yellow 164	Brown	Rutile
MnNbTi	Brown 37	Brown	Rutile
MnCrSbTi	Brown 40	Brown	Rutile
MnWTi	Brown 45	Brown	Rutile

5.4.1
Rutile Titanates

Rutile titanates represent by far the largest commercial class of CICPs. Chromium antimony titanate yellows (C.I. Pigment Brown 24) are the most widely used, followed by nickel antimony titanate yellows (C.I. Pigment Yellow 53). Manganese antimony titanate browns (C.I. Pigment Yellow 164) occupy a much smaller market share, and the other rutile grades a significantly smaller fraction still.

Rutile CICPs contain a significant amount of titania as a base oxide. Typically they range from 70 to 90 % TiO_2 by pigment weight. Transition metal cations Ni(II), Cr(III), and Mn(III) are responsible for producing the color, while the colorless ions

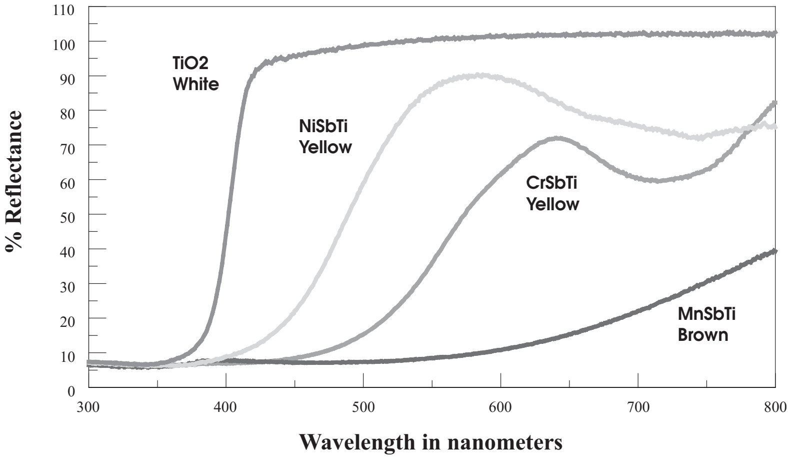

Figure 5–4: Reflectance spectra of selected rutile CICPs compared to rutile TiO_2.

Ti(IV), Sb(V), Nb(V), and W(VI) are present to maintain the MO_2 stoichiometry. Colors range from light yellow to dark brown. Reflectance curves for the three antimony titanates are compared to rutile TiO_2 in Figure 5–4.

It is well known that pure rutile titanium dioxide has a photoactive surface[5, 6]. When irradiated with UV light, highly reactive oxo radicals are formed that can photocatalytically degrade organic materials in contact with the pigment's surface. Commercial grades of rutile TiO_2 are passivated with coatings of other metal oxides such as those of aluminum, silicon, or zirconium to suppress this effect.

Rutile CICPs do not exhibit photocatalytic activity as do pure titanium dioxides. The act of doping the rutile structure with the transition metal and other ions eliminates the mechanism for formation of surface radicals via UV irradiation. Commercial grade rutile CICPs do not require surface coatings to make them inert.

5.4.2
Spinel Titanates

Titanate spinels form a much smaller class of pigments than the rutiles. The M_3O_4 stoichiometry of spinel is met by reacting two units of +2 metal oxide with one unit of TiO_2, according to Eq. (5–1).

$$\begin{array}{l} 2MO + TiO2 \rightarrow M_2TiO_4 \text{ spinel} \\ M = Ni(II), Co(II), Zn(II), Fe(II) \end{array} \qquad (5\text{–}1)$$

Titanates are inverse spinels, where a number of the +2 ions occupy octahedral coordination sites in the lattice. Commercially important grades are the cobalt titanate greens and iron titanate browns.

Cobalt titanate greens are generally modified by Zn(II) and Ni(II) oxides to produce their bright green colors. The greens can be in the same color space as chromium(III) oxide green, and compete somewhat since they have similar durability characteristics. However, cobalt titanate greens are usually formulated to give brighter and cleaner colors shades, some with bluer hues that are not otherwise available. Primarily as a result of the cobalt they contain, cobalt titanate greens are more expensive by comparison.

Iron titanates are formed from combinations of iron(II) oxide and TiO_2. These formulations are commonly modified by additions of iron(III) oxide, zinc(II) oxide, and aluminum(III) oxide. Like the cobalt titanates, these are inverse spinels structures. Iron titanate pigments yield light yellow-brown to dark reddish-brown hues. In many cases these pigments exhibit greater heat stability than zinc ferrite or iron oxide browns, and are generally used in applications for this purpose.

5.4.3
Other Titanates

The only other commercially important grade of titanate pigment, besides those listed above, is barium nickel titanium yellow priderite. The name priderite, just as with spinel and rutile above, refers to the crystal structure of this compound. These pigments provide a lighter, greener shade of yellow than is typically common for nickel titanate yellows. With that exception, other properties are similar to those of other CICPs. Yellow priderite has the basic formula $2NiO \times 3BaO \times 17TiO_2$.

5.5
Aluminate Pigments

CICPs that contain aluminum oxide, Al_2O_3, or alumina as a colorless base oxide are called aluminates. These almost always employ cobalt(II) oxide, CoO, as one of the coloring oxides. All of these pigments adopt the spinel crystal structure, and all have color hues in the blue to teal range.

5.6
Cobalt Aluminates

Combinations of cobalt(II) oxide and aluminum oxide in the spinel stoichiometry give cobalt aluminate blue spinels, $CoAl_2O_4$, C.I. Pigment Blue 28. Variations of this pigment include modification by zinc (C.I. Pigment Blue 72), magnesium, titanium, and lithium oxides. If lithium and titanium modifiers are added, a turquoise blue pigment is obtained.

Table 5–3: Common aluminate-, chromite-, and ferrite-based CICPs.

Chemical type	*C.I. Pigment*	*Color*	*Crystal Type*
CoAl	Blue 28	Blue	Spinel
CoCrAl	Blue 36	Blue-green to teal green	Spinel
CoCr	Green 26	Dark green	Spinel
ZnFe	Yellow 199	Yellow-brown	Spinel
	Brown 31	Yellow-brown	Spinel
MgFe	Brown 11	Red-brown	Spinel
ZnCrFe	Brown 33	Brown	Spinel
FeCr	Green 17 Brown 29	Brown-black	Hematite/corundum
FeCr	Brown 35	Brown-black	Spinel
CuCrFe	Black 23	Black	Spinel
FeMn	Black 26	Black	Spinel
CoCrFe	Black 27	Black	Spinel
CuCr	Black 28	Black	Spinel
CoFe	Black 29	Black	Spinel
NiCrMn	Black 30	Black	Spinel

Cobalt aluminate blues are the most durable blue pigments commercially available. They have excellent chemical and heat stability, and can be used in chemically aggressive environments and exterior durable applications without color fade. One drawback is that these blues are poor UV absorbers when compared to other CICPs.

5.7
Cobalt Chromium Aluminates

If some of the aluminum oxide in a cobalt aluminate is replaced with chromium(III) oxide green, the resulting compound is a cobalt chromium aluminate blue-green spinel (C.I. Pigment Blue 36), with basic formula $Co(Al_x,Cr_{1-x})_2O_4$, where x ranges from 0 to 1. These pigments can be further modified with zinc, magnesium, and titanium oxides to produce greener blues and teal shades.

Like the cobalt aluminates, cobalt chromium aluminates have excellent heat stability and weatherfastness. In many cases they have significantly better UV opacity than the Pigment Blue 28 grades.

5.8
Chromites and Ferrites

A large number of CICPs contain transition metal oxides without a significant amount of a colorless base oxide. These pigments, listed in Table 5–3, employ either green chromium(III) oxide, red iron(III) oxide, or a combination of the two as a base. They are thus referred to as chromites or ferrites[7], for the chromium and iron bases, respectively. Most adopt the spinel configuration, with the other important structures being those of corundum and hematite.

Chromite and ferrite pigments have physical properties similar to those of the titanates and aluminates. Nearly all pigments of this variety are of brown and black shades, with just a few greens and green-blues. Some have unique infrared spectral properties that make them of interest in addition to their durability and color stability.

5.9
Black CICPs

There are three types of black chromites and ferrites. These contain copper, cobalt, and nickel. The copper-containing blacks include C.I. Pigments Black 23, Black 26 (modified), and Black 28. Cobalt-containing grades include C.I. Pigments Black 27 and Black 29. There is one important nickel black, C.I. Pigment Black 30. All of these blacks have spinel crystal structures. The copper blacks are the most widely used, as they are excellent general purpose pigments. The cobalt and nickel blacks are used only in applications where their special properties are required.

Copper chromite blacks (C.I. Pigment Black 28) are spinels made from copper(II) oxide and chromium(III) oxide green, with a general formula of $CuCr_2O_4$. The presence of copper slightly distorts the usually cubic oxide lattice, and pure copper chromites are tetragonal spinels. The most common modifier in these blacks is manganese, which is present in many commercially available grades. Iron and molybdenum are the other modifiers of note.

Copper chromites are the most widely used CICP blacks. They offer a good jet-black color, excellent durability, and heat stability up to 1000 °C. These blacks are also excellent UV absorbers, and offer good UV opacity to the systems that employ them. Being chemically stable, copper chromite blacks are not prone to photocatalytically decompose in the presence of titanium dioxide white. Because of this, exterior durable grays and dark shaded colors are often formulated using these blacks. High heat systems such as silicone paints and glass enamels use copper chromites to make jet-blacks and grays.

When blacks of greater heat stability than copper blacks are needed, cobalt blacks must be used. Cobalt blacks have the general formula $(Co_x, Fe_{1-x})M_2O_4$, for $x = 0$ to 1, M = Fe, or Cr and Fe, and are described as C.I. Pigments Black 29 and Black 27, respectively. Nickel(II) oxide is the most commonly employed modifier. Because they contain a significant amount of cobalt, they are significantly more expensive that other CICP blacks. The higher cost restricts their use to porcelain and glass enamel systems that require the greater heat stability.

The only important nickel blacks are described as C.I. Pigment Black 30, and have the general formula $(Ni_y, Fe_{1-y})(Fe_x,Cr_{1-x})_2O_4$, where x and y range from 0 to1. The commercial grades are commonly modified with Mn(II) and Mn(III) oxides. These pigments are slightly more heat stable than the copper blacks, but not as heat stable as the cobalt blacks. They have a slight brown undertone compared to the

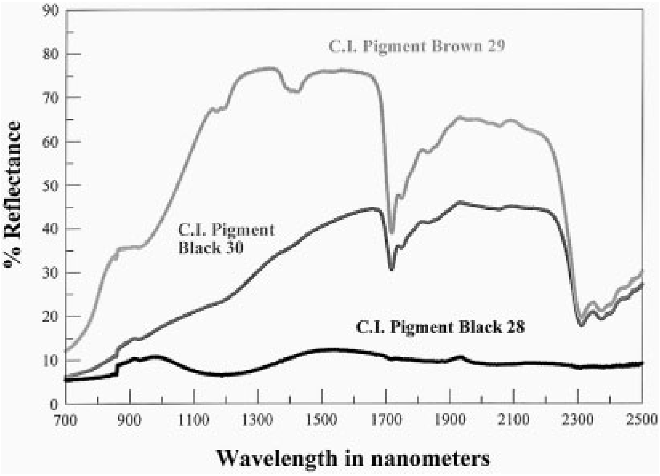

Figure 5–5: Reflectance spectra of two IR-reflective CICPs compared with a non-reflective Pigment Black 28. Dips in reflection centered at 1700 and 2300 nm are due to the polymer matrix.

other CICP blacks. These pigments are most commonly used for their infrared (IR) reflective properties.

In the near IR region, the nickel blacks reflect a significant amount of radiation compared with most other high performance blacks, as shown in Figure 5–5. More reflection causes less IR light to be absorbed. Exterior plastics and coatings pigmented with these blacks will therefore heat to a lesser degree in direct sunlight. Not surprisingly, the largest application for nickel blacks is in exterior coatings and PVC siding and window profiles, where durable color with minimal heating from the sun is desired.

5.10
Brown Pigments

There are three groups of commercially important ferrite and chromite browns. The first are pure ferrites defined by C.I. Pigments Brown 11, Brown 31, and Yellow 119, followed by the mixed chromite/ferrite browns which are C.I. Pigments Brown 33 and Brown 35. These are all spinels. The third type is mixed chromium iron pigments. These pigments adopt either the hematite or the corundum structures.

Pure ferrite spinels containing zinc, C.I. Pigments Yellow 119 and Brown 31, or magnesium, C.I. Pigment Brown 11, provide light yellow-brown to light red-brown colors. Zinc ferrites, and to a lesser extent magnesium ferrites, are widely used as heat-stable colorants for thermoplastics.

The mixed chromite/ferrite spinels, C.I. Pigments Brown 33 and Brown 35, provide darker browns than the pure ferrites, covering the color range from reddish-brown to nearly black. These products are used mainly in plastics and coatings to provide heat stable colors. In addition, Brown 35 spinels have good IR-reflective properties, and are used in low heat build-up plastics and coatings.

Pigments containing only iron(III) and chromium(III) oxides in an M_2O_3 stoichiometry are identified as either C.I. Pigment Green 17 or C.I. Pigment Brown 29. Both of these Colour Index descriptions denote the same pigment type, and the names can be used interchangeably. The pigments are not spinels, as they adopt either the corundum or hematite structures. They are dark red-brown to nearly black in color.

The great feature of these pigments is their good IR reflectivity. They generally have higher IR reflectivity than other dark IR-reflective CICPs, as demonstrated in Figure 5–5. These browns and blacks are primarily used to prepare dark exterior durable colors with low heat build-up.

5.11
Green Chromites

There is one commercially important chromite-based green pigment in this class. This is a cobalt chromite green, C.I. Pigment Green 26. These pigments are spinels made from cobalt(II) oxide and chromium oxide green, with the general formula

$CoCr_2O_4$. Common modifiers include aluminum, titanium, magnesium, and zinc oxides. The cobalt(II) ions in the spinel are tetrahedrally coordinated, providing the green chromium oxide base with a bluish hue. Generally these colors range from bright green-blue to a dark forest green.

The major use of cobalt chromite greens is in camouflage applications. In the near IR region (700 to 1000 nm), the pigments exhibit a reflectance similar to that of some natural backgrounds. Cobalt chromites have proved useful in preparing greenish colors that match ambient IR signatures.

References and Notes

1 Simple metal oxide colorants are those containing only one type of metal such as iron(III) oxide red, titanium dioxide white, and chromium(III) oxide green, according to this scheme.

2 The elements in the periodic table in which the d-electron shell is filled are all metals. These elements are referred to as the transition metals.

3 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., 1980, pp. 657–658, John Wiley & Sons, New York.

4 Pigment types are commonly referred to by their Colour Index (C.I.) designation, an internationally recognized nomenclature. These names are found in *Colour Index, International Pigments & Solvent Dyes,* Society of Dyers and Colourists, 3rd. edn., 1997, Bradford, West Yorkshire, England.

5 Peter A. Lewis, (ed.), *Pigment Handbook*, Vol. 1, Properties and Economics, 2nd edn., 1988, pp. 22–24, John Wiley & Sons, New York.

6 Swaraj Paul, *Surface Coatings Science and Technology* , 1985, pp. 324–326, John Wiley & Sons, New York.

7 The prefix ferri- in chemistry denotes iron in the +3 oxidation state, as it is in the red iron(III) oxide, Fe_2O_3. It is derived from the Latin word "ferrum" for iron.

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6

Titanate Pigments: Colored Rutile, Priderite, and Pseudobrookite Structured Pigments

John Maloney

6.1

Introduction

"Titanate" pigments typically refer to the colored rutile-structured pigments such as nickel antimony titanium yellow rutile. These pigments are heavily used in polymer and paint applications, especially for vinyl siding. In a broader context, several other TiO_2-containing pigments with similar applications can also be considered titanate pigments. This chapter will cover the synthesis, characterization, and uses of colored rutile, priderite, and pseudobrookite-structured pigments.

Discussions on the rutile pigments will cover primarily the various nickel titanium yellow, chromium titanium buff, and manganese titanium brown pigments. Since they are actually solid solutions of a dopant phase in the rutile lattice, the label *D*oped-*R*utile (DR) will be used to distinguish them from the white TiO_2 rutile pigments. Also to be covered are the yellow BaNiTi priderite pigments that have many similarities to the NiTi yellow DR pigments but possess a different crystal structure. Discussions of the pseudobrookite pigments will cover the FeTi and FeAlTi brown formulations that are often misclassified as spinels.

Other DR pigments, such as VSbTi gray, are less important and will not be specifically discussed. The CoTi green and ZnFeTi brown spinel pigments are more appropriately covered with the other spinel-structured pigments and will not be discussed. Finally, it should be mentioned that there is a series of doped-cassiterite (SnO_2) pigments with the same structure as the DR pigments. However, they do not contain titania and are typically used in ceramic applications.

Previous articles have reviewed the general chemistry, properties, applications, and market sizes for these pigments[1, 2]. In order to give a new perspective, this chapter is oriented more to the scientific understanding of these pigments. More specifically, this article covers:

1. updated information
2. corrected nomenclature and chemistry
3. in depth discussions of synthesis, characterization, and properties
4. other titanates (priderite and pseudobrookite)
5. a patent review

In the interest of brevity, some common conventions are used in this chapter. With the understanding that the subject concerns strictly metal oxide species, elemental symbols will be used to designate the pigment types, e.g. NiSbTi will represent the Nickel Antimony Titanium Yellow DR Pigments, $(Ni,Sb,Ti)O_2$. Also, M will represent a metal in general, whereby MSbTi represents either the NiSbTi yellow, the CrSbTi buff, or the MnSbTi brown DR pigments.

The synthetic oxide pigments containing more than one metal are now called *C*omplex *I*norganic *C*olor *P*igments (CICPs). These were formerly referred to as mixed metal oxide (MMO) pigments, a term that is still widely used today. In the 1920s, the major United States inorganic pigment manufacturers formed an organization that has since been renamed the *C*olor *P*igments *M*anufacturers' *A*ssociation (CPMA). This group, originally known as the Dry Color Manufacturers' Association (DCMA), recently categorized the CICP pigments according to the principal oxides comprising the phase, such as NiSbTi yellow rutile. These pigment classes were then grouped into 14 crystal classes according to their crystal structures. The 14 crystal classes were assigned mineral names of the naturally occurring minerals that represent the crystal structures, such as rutile and spinel. DCMA then published a handbook[3] with these classifications and pigment descriptions. This will be referred to as the DCMA Handbook as it was last published.

The family of titanate pigments are listed below in Tables 6–1 and 6–2 according to their listing in the DCMA handbook. They fall into three crystal classes: rutile, priderite, and pseudobrookite. Note that the Fe(III) pseudobrookite (Fe_2TiO_5) pigments were incorrectly categorized in the DCMA Handbook, as well as in company product literature, as FeTi-spinels. The spinel formula, Fe_2TiO_4, would require them to be Fe^{2+} species instead of Fe^{3+} species.

Tables 6–1 and 6–2 also present the Colour Index (C.I.) Pigment Names, Colour Index Constitution numbers, and the corresponding CAS numbers[4]. Surprisingly, the colors in the C.I. Pigment designations often misrepresent the actual colors! For example, CrSbTi buffs are classified as Pigment Brown 24, while MnSbTi browns are classified as Pigment Yellow 164.

Table 6–1: Doped-rutile (DR) pigments.

Dopants	***Color***	***C.I. Pigment***	***Constitution No.***	***CAS No.***
Ni,Sb	Yellow	Yellow 53	77788	8007–18–9
Ni,Nb	Yellow	Yellow 161	77895	68611–43–8*
Ni,W	Yellow	Yellow 189	77902	69011-05–8*
Cr,Sb	Buff	Brown 24	77310	68186–90–3*
Cr,Nb	Buff	Yellow 162	77896	68611–42–7*
Cr,W	Buff	Yellow 163	77897	68186–92–5*
Mn,Sb	Brown	Yellow 164	77899	68412–38–4*
Mn,Nb	Brown	Brown 37	77890	70248-09–8*
Mn,W	Brown	Brown 45	N/A	13463–67–7

Table 6–2: Titanate pigments.

Structure	*Color*	*C.I. Pigment*	*Constitution No.*	*CAS No.*
Priderite[a]	Yellow	Yellow 157	77900	68610–24–2*
Pseudobrookite[b]	Brown	Black 12	77543	68187-02-0*

[a] Base composition: $BaNiTi_7O_{16}$
[b] Base composition: Fe_2TiO_5

The three pertinent crystal classes are differentiated in Table 6–3 by their unit cell lattice constants. Rutile and priderite have tetragonal unit cells, while pseudobrookite has an orthorhombic unit cell. They are more thoroughly characterized in the PDF database[5].

Table 6–3: Lattice constants of the reference crystal structures.

Structure	*PDF No.*	*a(Å)*	*b(Å)*	*c(Å)*
Rutile	21–1276	4.59	4.59	2.96
Priderite	6–296	10.11	10.11	2.97
Pseudobrookite	9–182	9.81	9.95	3.73

Inorganic pigments are not as clean or as strong as organic pigments. It is their properties that recommend their use in preference to organic pigments. They offer greater stability (thermal, photochemical), hiding power (opacity), insolubility (bleed resistance), ease of dispersibility, and compatibility with aqueous systems. Because of their stability, they are extensively used in outdoor and higher temperature applications where organic pigments decompose.

6.2
History

A literature search on the specified titanate pigments yielded the 22 independent patents listed in Table 6–4. The majority of the patents deal with DR pigments. They cover compositions, processing, and improved properties. The older patents were concerned with ceramic applications, while the newer patents are primarily targeted at improved stability in polymers and paints.

6.2.1
Doped-Rutile (DR) Pigments

The patent literature shows that DR pigments date back to at least 1934. At that time their primary application was the coloration of ceramic ware. In the USA, however, it was the development of the vinyl siding market that created a large market for

Table 6–4: Patents for Titanate Pigments.

Ref.	Patent No.	Inventor	Company	Note	Title	Date	Secondary
Rutile Pigments							
6	US 1945809	Harbert	Harshaw	CrSbTi	Pigment Composition	02/06/34	
7	US 2231829	Harbert	Harshaw	CrWTi	Ceramic Pigment	08/05/41	
8	US 2257278	Schaumann	Du Pont	(Ni,Co,SB,TI)O2	Process for Colored Titanium Pigments	09/30/41	
9	US 3022186	Hund	Bayer	Rutile SS	Mixed Phases with a Rutile or Polyrutile Structure	02/20/62	
10	US 3832205	Lowery	Ferro	MNbTi	Pigments of Substantially Ternary System Having Oxides of Columbium and Transitional Elements	08/27/74	
11	US 3956007	Modly	Kewanee	NiWZnCeMgLiTi	Antimony-Free Yellow Pigments and Their Preparation	05/11/76	
12	BR 1541979	Mansmann	Bayer	Rutile nuclei	Production of Improved Chromium Rutile Pigments	03/14/79	
13	DE 2936746	Seitz	BASF	Coatings	Process for the Manufacture of Rutile Mixed Phase Pigments	03/19/81	
14	US 4450012	Messer	Bayer	Coated	Flocculation-resistant, Mixed Phase Pigments Having a Rutile Structure, Process for their Preparation, and Their Use	05/22/84	EP075197
15	US 4844741	Knittel	Lacke&Farben	0.1–2.0%Mg	Thermostable Rutile Mixed Phase Pigments	07/04/89	EP233601
16	US 4917735	Rademachers	Bayer	Indirect Rotary	Process for the Production of Rutile Mixed-Phase Pigments	04/17/90	
17	US 4919723	Wilhelm	Bayer	0.01–0.25%Li	Rutile Mixed Phase Pigments with Improved Coloristic Properties	04/24/90	EP318783
18	US 4919726	Rademachers	Bayer	Direct Rotary	Process for the Production of Rutile Mixed-Phase Pigments	04/24/90	
19	US 5006175	Modly	Engelhard	(MnWLiCe)Ti	High Infra Red Reflecting Brown Rutile Pigment Compositions	04/09/91	
20	US 5108508	Rademachers	Bayer	Spray Dry	Rutile Mixed Phase Pigment Microgranulates, a Process for Their Preparation and Their Use	04/28/92	
21	US 5192365	Modly	Engelhard	CoWLiCeTi	Buff Rutile Pigment Compositions	03/09/93	
22	EP 415478	Aderhold	Mitsui Mining +	Sb-doped SnO2	Electrically Conductive Rutile Mixed-Phase Pigment, Process for the Manufacture of these Pigments	01/12/94	
23	US 5496404	Gaedecke	BASF	Prep for rotary	Process for Preparing Inorganic Pigments of Particular Particle Size	03/05/96	
Priderite Pigments							
24	Br 1214361	Batchelor	HarrisonMayer	Priderite	Improvements in Pigments	12/02/70	
Pseudobrookite Pigments							
25	US 4036662	Rademachers	Bayer	PBrookite	Metal Additions to Pigments of Pseudobrookite-Titanium Dioxide Structure	07/19/77	
26	US 4084984	Hund	Bayer	PBrookite	Temperature-Stable Inorganic Yellow Pigments	04/18/78	
27	EP 949202	Katamoto	Toda Kogyo	PBrookite	Heat Resistant Yellow Pigment	10/13/99	

these pigments. Like the white TiO_2 rutile pigments, they have a combination of strong UV absorbance and high near-infrared (NIR) reflectance. These properties give them the excellent weathering characteristics needed for this outdoor application. The current commercial pigments have been significantly improved and optimized to meet the needs of this and similar markets. In fact, the MnSbTi DR browns of today are twice as strong as they were 20 years ago.

In 1962, Franz Hund was issued a patent on the preparation of DR pigments[9]. His patent demonstrated the ability of rutile to form solid solutions with many compounds. Three fundamental rules were given for the formation of a DR pigment:

1. Substitutional atoms must have ionic sizes similar to Ti^{4+} (0.68 Å) or O^{2-} (1.38 Å),
2. charge balance (electroneutrality) should be maintained, and
3. the cation:anion ratio should remain at 1:2, as in TiO_2.

More than 200 formulation examples are given in Hund's patent. An acceptable range of cation ionic radii from 0.46 to 0.91 Å is cited. However, use of a different set of ionic radii, specifically an average of Pauling's and Belov's[28], generates a more realistic range of ionic radii of 0.62–0.80 Å for the same list of cations. The patent also has many examples substituting F^- for O^{2-}.

The rules of electroneutrality and a 1:2 cation:anion ratio require the use of at least two dopants for the commercial pigments. For the NiSbTi DRs, partial substitution of Ni^{2+} for Ti^{4+} is accompanied by co-substitution of an ion with a valence greater than 4, such as Sb^{5+}, Nb^{5+}, or W^{6+}, so that the average valence is 4. For the NiSbTi pigments, an Sb^{5+}/Ni^{2+} mole ratio of 2 is required to maintain electroneutrality, while a W^{6+}/Ni^{2+} ratio of 1 is needed for the NiWTi pigments. These substitutions are simply solid solutions of either $NiSb_2O_6$ or $NiWO_4$ in TiO_2.

The CrSbTi buff DR pigment was previously studied by ESCA, EPR, and diffuse reflectance spectroscopy to determine the oxidation states of the Cr in the pigment[29]. It was concluded that both Cr^{3+} and Cr^{4+} can be contributing species in the pigment, with Cr^{4+} producing redder shades. Contamination by CrO_{3-x} species, where $x = 0.4–0.8$, was said to contribute a black color.

Finally, environmental and health concerns have prompted a number of agencies to develop lists and limits for regulated elements. Often referred to as "Heavy Metals", probably because Pb and Hg attracted most of the earlier attention, "Regulated Metals" is a more appropriate title. Originally, the regulations for food-contact applications precluded the presence of Sb in the pigments. This led to the development of "Heavy Metal Free" pigment product lines that included NiNbTi and CrNbTi DR pigments[10]. However, both NiSbTi and CrSbTi DR pigments have now been approved for most food contact applications at limited levels.

6.2.2
Priderite Pigments

The BaNiTi yellow priderite pigments are weaker and greener than the NiSbTi DR pigments. Their commercial formulas were developed mostly by empirical testing.

The DCMA handbook has their chemistry incorrectly listed as 2NiO × 3BaO × $17TiO_2$, which would result in the presence of secondary phases. Some of the stoichiometry confusion is due to complex composition of the naturally occurring mineral[30] that contains a large number of elements.

The priderite structure is related to the hollandite structure and can give a single-phase product over a considerable range of stoichiometries near $BaNiTi_7O_{16}$. These Sb-free pigments were initially sold as heavy metal free pigments.

6.2.3
Pseudobrookite Pigments

These brown to buff pigments are modified versions of pseudobrookite, Fe_2TiO_5. As seen in Table 6–2, they are surprisingly classified as C.I. Pigment Black 12. They possess a range of shades similar to that obtained for the ZnFe and ZnTiFe spinels. There are at least two chemistries in products seen in the marketplace. One uses excess TiO_2 and contains a rutile secondary phase. The other is an $(Fe,Al)_2TiO_5$ chemistry that partially substitutes Al for Fe, and usually has excess TiO_2 also. The FeAlTi version is generally lighter and yellower.

6.3
Synthesis

Titanate pigments are ultimately formed by solid-state reactions at high temperatures. Whether the process involves wet or dry blending of the raw batch, raw batch milling, or precipitation of the raw batch, the pigments are only formed upon high temperature calcination. They are then milled to fine and narrow particle size distributions. Other steps such as surface treatments or microgranulation may also be included for various purposes, depending on the manufacturer.

Solid-state reactions generally require high temperatures. In particular, bulk diffusion, such as the diffusion of Ni ions into a TiO_2 lattice, is a relatively slow process and will control the reaction rate for pigment formation. Therefore, ideal raw batches should consist of intimately blended nano-sized particles to minimize diffusion distances for the dopants and to generate homogeneous particles. Although manufacturers work towards this ideal, the perfect raw batch has yet to be achieved in a cost-effective manner.

There is a common misconception that coprecipitation generates a mix that is homogeneous on an atomic level. However, most coprecipitation reactions precipitate the metal ions sequentially, not simultaneously. Also, while atomically mixed batches would form crystals at much lower temperatures than mixtures of coarser particles, the coprecipitated batches seldom lower the reaction temperature by more than 100 Celsius degrees.

The raw materials for the raw batch can be simple metal oxides such as NiO or, alternatively, species that yield metal oxides upon thermal treatment, such as basic nickel carbonate. Since solid-state reactions are involved, the choice of these raw materials is critical. Considering that each 100 μm particle or agglomerate represents one million 1μm particles that could be much more intimately blended, the importance of raw material particle size and raw batch preparation cannot be overstated. Other ingredients for redox, particle growth control, or blending purposes may also be formulated into the raw batch. Depending on the manufacturer, either wet or dry blending of the raw batch is done. Of course, the wet-milled raw batches will need to be dewatered to a large degree before calcination.

The raw batch calcination can be accomplished in almost any kind of furnace. Tunnel kilns, box kilns, shuttle kilns, and rotary kilns have been used for many years, each with its own advantages, disadvantages, and limitations. In some instances, patents have been issued for the calcination technique[16, 18]. Special firing profiles have been developed for some pigments to guide the reaction chemistry.

Grinding can be done in a variety of different mills. A high degree of particle size classification is needed to minimize grit and achieve a high degree of gloss in coatings. Vibratory and jet mills are most commonly used.

6.3.1
DR Pigments

Numerous reactions occur during the synthesis of DR pigments. Some of the important reactions in the formation of an NiSbTi pigment are shown in Scheme 6–1. Note that A represents the anatase TiO_2 form and R represents the rutile TiO_2 form.

$Sb_2O_3 + O_2 \rightarrow Sb_2O_4$
$Sb_2O_4 + O_2 \rightarrow Sb_2O_5$
Sb_2O_3 melts
Sb_2O_x sublimes
$Sb_2O_4 + \text{A-}TiO_2 \rightarrow \text{A-}(Sb,Ti)O_2$
$\text{A-}(Sb,Ti)O_2 \rightarrow \text{R-}(Sb,Ti)O_2$
$NiCO_3 \rightarrow NiO + CO_2$
$NiO + Sb_2O_5 \rightarrow NiSb_2O_6$
$NiO + TiO_2 \rightarrow NiTiO_3$
$(Sb,Ti)O_2 + NiO + O_2 \rightarrow (Ni,Sb,Ti)O_2$ pigment
Particle faceting
Particle growth or agglomerate fusion

Scheme 6–1: Reactions that occur during the calcination process to form NiSbTi pigments.

Sb_2O_3 is the usual Sb source for the production of MSbTi pigments. Based upon the concept of electroneutrality presented in Hund's patent, oxidation of Sb_2O_3 to Sb_2O_5 is required for pigment formation. Equilibria between Sb_2O_3, Sb_2O_4, and Sb_2O_5 are dependent on the temperature and the partial pressure of oxygen. The equilibria need to be controlled to enable pigment formation and prevent any melt formation. Oxidation of Sb_2O_3 is usually accomplished with an adequate airflow (O_2

source), but is often assisted with added oxidizers. However, depending on the firing conditions, alkali and alkaline earth based oxidizers can also lead to the formation of metal antimonates, resulting in weaker pigments.

Formation of other secondary phases can also occur and need to be minimized. The phases $NiTiO_3$ and $MnSb_2O_6$ have been observed in NiSbTi and MnSbTi DR pigments, and can be somewhat difficult to eliminate once formed. Once again, the presence of secondary phases generally correlates to weaker pigment strength. In addition, the secondary phases can potentially be deleterious to the weathering properties of the pigment.

Anatase TiO_2 is generally the Ti source used for the production of DR pigments. The lower density of anatase enables a more facile formation of an Sb_2O_4:TiO_2 solid solution that precedes pigment formation. In some cases, rutile or titanium hydrates of various types can be used as the Ti source.

A new study has examined the reactions involved in the formation of the CrSbTi buff DR pigments[31]. Based on DTA/TGA results and XRD analysis of samples pulled at different temperatures, a proposed reaction sequence is given in Scheme 6–2. It was also observed that any free Sb_2O_x reduces and volatilizes at higher temperatures.

1. $Sb_2O_3 + O_2 \rightarrow Sb_2O_4$
2. $Sb_2O_4 + TiO_2(A) \rightarrow (Sb,Ti)O_2(A)$:expanded lattice
3,4. $Sb_2O_4 + O_2 \rightarrow Sb_2O_5$, and
   $(Sb,Ti)O_2(A)$:expanded lattice $\rightarrow (Sb,Ti)O_2(R)$:expanded lattice
5. $(Sb,Ti)O_2(R)$:expanded lattice + $Cr_2O_3 \rightarrow (Cr,Sb,Ti)O_2$:normal lattice

Scheme 6–2: Reaction pathway for the formation of CrSbTi-DR pigments

Anatase is capable of forming solid solutions containing up to 14 mol % SbO_2. The expanded anatase lattice that is formed slowly converts to an expanded rutile lattice in about the same time that the Sb_2O_4 undergoes further oxidation to Sb_2O_5. This oxidation can be observed as an exothermic peak and an increase in mass at ~920 °C, as seen in the DTA and TGA curves in Figure 6–1. The chromium appears to diffuse into the lattice after the oxidation has begun, in a partially concerted manner. As the chromium diffuses into the lattice, a lattice contraction is observed, and there is color development of the pigment.

In addition to the patent literature, there are journal articles that discuss the formation of DR pigments. Hund discusses mixed-phase DR pigments[32] based on his patent work. Krause discusses more specifically the NiSbTi DR pigments[33, 34]. Tavala discusses the CrWTi DR pigments[35] and NiMTi DR pigments[36]. Huguenin discusses new TiO_2 precursors for making DR pigments[37]. Solc discusses synthesis of VSbTi gray DR pigments[38]. Tena discusses MNbTi DR pigments[39].

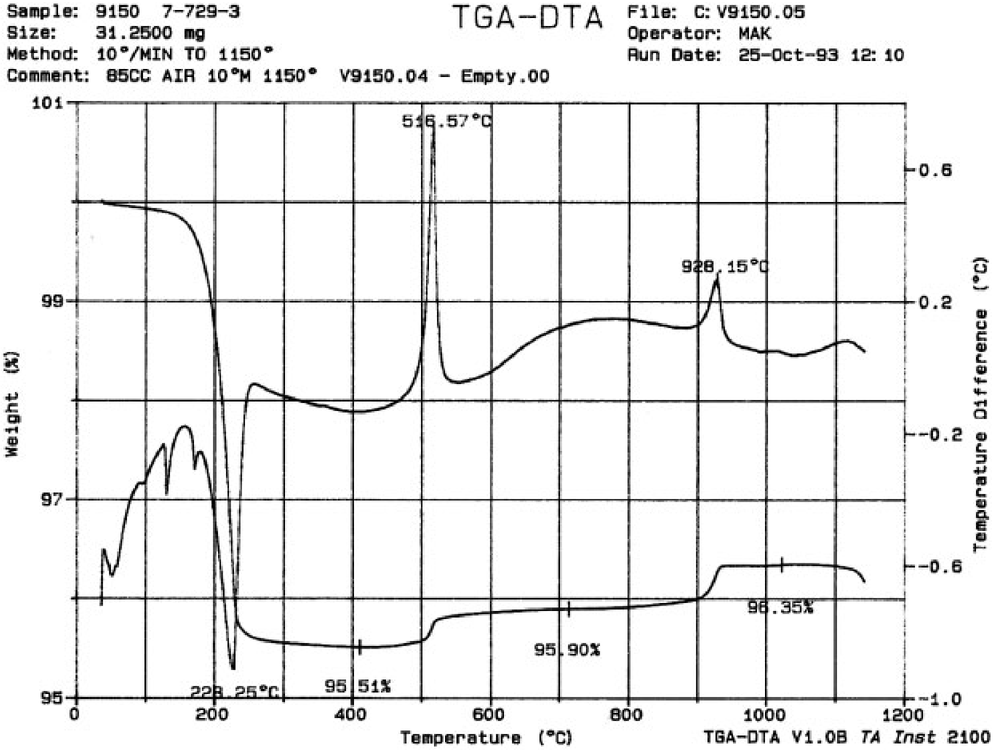

Figure 6–1: DTA and TGA curves of CrSbTi raw batch demonstrating stages of antimony oxide oxidation.

6.3.2
Priderite Pigments

BaNiTi yellow priderite pigments ($BaNiTi_7O_{16}$) are generally synthesized from $BaCO_3$, basic nickel carbonate, and TiO_2 in a high temperature reaction. One of the goals of the synthesis is to minimize the level of acid-soluble Ba in the product. The manufacturers have various techniques to accomplish this task. One difficulty is achieving complete $BaCO_3$ decomposition while avoiding a high temperature $BaO/BaCO_3$ eutectic. The reaction is further complicated by intermediate $Ba_xTi_yO_z$ species that form to various degrees during the calcination. Species such as $BaTiO_3$, $BaTi_2O_5$, and $BaTi_4O_9$ are sometimes seen in the product because of poor stoichiometry, coarse raw materials, or poor reaction.

Only one patent was found for a priderite pigment[24]. Ivan investigated the formation of Ni, Cu, and Cr versions of priderite[40]. It is believed that BaNiTi priderite is currently the only commercial product.

6.3.3
Pseudobrookite Pigments

Pseudobrookite, Fe_2TiO_5, is a stable structure that has even been observed as a decomposition product of overfired ZnFeTi spinel pigments. Despite this, it is difficult to make clean versions of this pigment.

The challenge in making high-quality pseudobrookite pigments (base formula Fe_2TiO_5) is obtaining complete reaction of the Fe_2O_3. This is a difficult reaction to force despite the availability of fine-sized pigmentary grades of Fe_2O_3 and TiO_2 for use as raw materials. Unfortunately, Fe_2O_3 can be found in the XRD spectra of most commercial pigments, and is surely present in significant amounts even when it is undetectable in the XRD patterns.

There are at least two pseudobrookite pigment chemistries in products in the marketplace. The first uses a large excess of TiO_2 to help force complete reaction of the Fe_2O_3. This results in a rutile secondary phase that is sometimes the dominant phase in the product. In fact, patents cover such composition with up to a 15 fold excess of TiO_2[25, 26].

The second chemistry is an $(Fe,Al)_2TiO_5$ formula that substitutes Al for some of the Fe. This partial substitution enhances reaction of the iron oxide and has less Fe_2O_3 in the formula that needs to react.

Fe(II) species such as $FeTiO_3$ ilmenite and Fe_2TiO_4 spinel will not form under normal conditions. Of coarse, addition of low-valent metals could allow formation of some spinel structure, but they would be Fe(III)-containing spinels. A study that characterized one Pigment Black 12 source as mostly spinel did not convey the complete chemistry[41].

6.4
Applications

Although the CrSbTi-DR pigments were originally designed for ceramic stain applications, polymer applications dominate the field today. DR pigments can be used in almost any polymer, including vinyl (polyvinyl chloride), high temperature engineering resins such as ABS and PPO, and fiber applications such as polypropylene and nylon carpeting. MnSbTi DR pigments are used almost exclusively in vinyl applications. They have been called Iron-Free Browns because they have much greater IR reflectance and much better weathering than the Fe-containing browns.

DR pigments are used in paint applications where their properties are required, such as high-temperature paints and coil-coating paint systems based on fluoropolymers, silicone-polyester, and plastisol. The NiSbTi and CrSbTi DR pigments are used in trade sale paints including acrylic house paints, general industrial paints in polyester systems, and fleet colors in thermoset acrylic, thermoplastic acrylic, and polyurethane systems. They are also used in polyester-based powder coating applications.

Several articles stress the use of titanate pigments in replacing cleaner and stronger heavy-metal lead and cadmium pigments. Enhancement of such inorganic replacement pigments with organic pigments gives improved color matching ability[42, 43].

Both NiSbTi and CrSbTi DR pigments were approved by FDA in 1999 for food contact (conditions B through H) applications at limited levels up to 1 or 2 % depending on the application[44, 45].

6.5
Properties

Many of the properties of titanate pigments need to be controlled or monitored to give good, reproducible performance in the various applications. The properties to be discussed are:

1. spectral properties: visible, UV/NIR
2. physical properties: particle size distribution, XRD phase characterization, specific gravity, oil absorption, specific surface area, powder flow and dusting
3. chemical properties: pH, weathering, particle chemistry

6.5.1
Spectral Properties

The color properties of pigments are derived from their reflectance spectra over the visible wavelength range (400–700 nm). This will be discussed in Sec. 6.5.1.1. The near-infrared (NIR) (700–2500 nm) and part of the ultraviolet (UV) (>300 nm) regions are important because they affect the heat build-up and weathering of pigmented systems. They are briefly discussed in Sec. 6.5.1.2.

6.5.1.1 Visible Spectral Characterization

It has been largely assumed that the spectral absorptions of the DR pigments are due to d-d transitions of the dopant chromophores, specifically the Ni^{2+}, Cr^{3+} and Mn^{2+} ions. However, it has also been proposed that the transition metal dopants have energy levels intermediate in the TiO_2 band gap, and that the optical response is due to charge transfer transitions. These transitions can either be from the occupied TiO_2 band to unoccupied M orbitals or from occupied M orbitals to the unoccupied TiO_2 band.

The charge transfer argument appears to be more logical. An article on calculated energy levels of Ru-doped TiO_2 supports this approach[46]. A CrNiSbTi-DR pigment shows a shift of the absorption band intermediate between that of a NiSbTi-DR and a CrSbTi-DR, and does not appear to be a composite of two separate absorption bands. However, more definitive evidence is needed.

There are two components to the reflectance spectra as defined by Kubelka-Munk theory, namely absorption and scatter. Rutile pigment particles exhibit maximum

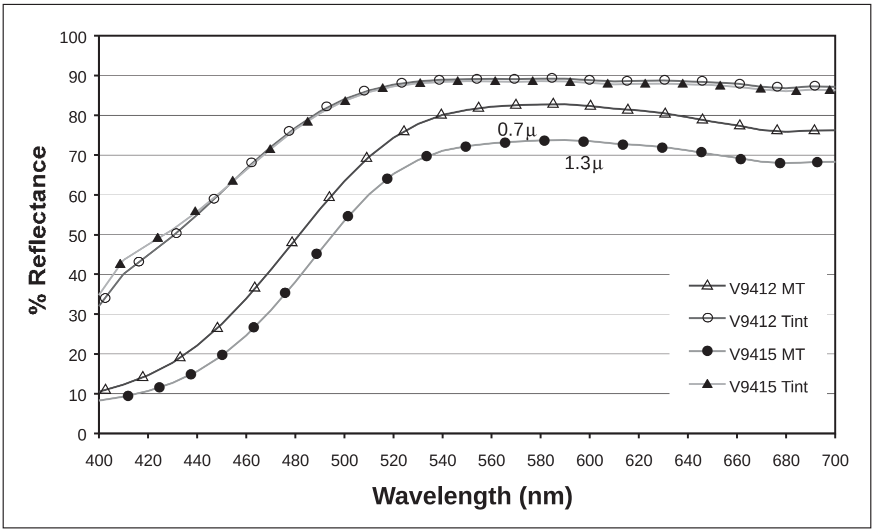

Figure 6–2: Reflectance spectra of two sizes of NiSbTi DR pigments in polystyrene.

scatter at approximately 0.2 μm. The scatter decreases slowly with increasing particle size, but drops off rapidly with finer particle size, the particles becoming transparent at sizes <50 nm. Therefore, the reflectance spectra will be a function of the particle size distribution of the pigment.

Color values are a derived set of numbers calculated from the reflectance spectra. A commonly used system is CIE L*a*b* with values calculated for Illuminant D65 and a 10° observer. The L value, with a range from 0(black) to 100(white), correlates to lightness, +a*=redness, –a*=greenness, +b*=yellowness, and –b*=blueness. Texts can be consulted for greater detail[47].

The effect of particle size on the reflectance curve is shown in Figure 6–2. It can be seen that the finer-sized pigment exhibits more scatter in the masstone, causing an increase in reflectance across the spectrum. This has a significant effect on the color values, increasing the lightness and decreasing the yellowness, as shown in Table 6–5. Therefore, coarser pigments can give brighter but more transparent mass tones.

Table 6–5: Color values of some DR pigments in polystyrene.

Pigment	*Size (μm)*	*Masstone*			*1:4 Tint*		
		L*	a*	b*	L*	a*	b*
V9412	0.80	89.5	–8.5	46.6	94.6	–6.5	20.3
V9415	1.25	85.0	–8.1	51.4	94.4	–6.3	19.5
V9416	0.80	84.1	1.1	49.8	92.6	–3.5	23.4
V9150	0.70	74.0	16.6	52.9	87.6	4.8	30.6

The effect of particle size on the tinting strength of the pigment can also be seen in Figure 6–2. For tints, the scatter of the two pigments is nearly equalized because it is dominated by the scatter of the TiO_2. On the other hand, the finer-sized pigment presents a larger absorption cross-section (per mass). This results in significantly greater absorption where it absorbs in the blue. Therefore, the tinting strength generally increases as particle size is reduced. However, this argument assumes perfect dispersions. Finer-sized particles form stronger agglomerates, making them more difficult to disperse and keep dispersed. This effect can reduce the expected increase in tinting strength of the finer-sized pigment.

For bright masstone applications, it is important to optimize the cleanness or color purity of a pigment. The cleanness can be roughly interpreted from the reflectance spectra by the difference between the maximum and minimum reflectances. A more accurate approach is to develop modified color values. Correlations can be developed from grind studies to account for changes in scatter due to differences in particle size distributions. For the NiSbTi yellows, a formula to calculate b’ values (e.g. $b' = b^* - 3\Delta L^*$) can be developed for a particular polymer system to account for the increased scatter and whiteness from finer-sized pigments.

The cleanness can also affect the tinting strength. Use of cap “Y” (a measure of lightness) to calculate tinting strength favors dirtier pigments. Therefore, while cleaner pigments will enable generation of a broader palette, dirtier pigments can still be used in many tint applications. However, secondary phases responsible for the dirtier pigment could deleteriously affect a crucial property such as weathering.

Figure 6–3 shows the reflectance spectra for an NiSbTi, an NiCrSbTi, and a CrSbTi DR pigment. The shade becomes redder as the absorption band moves

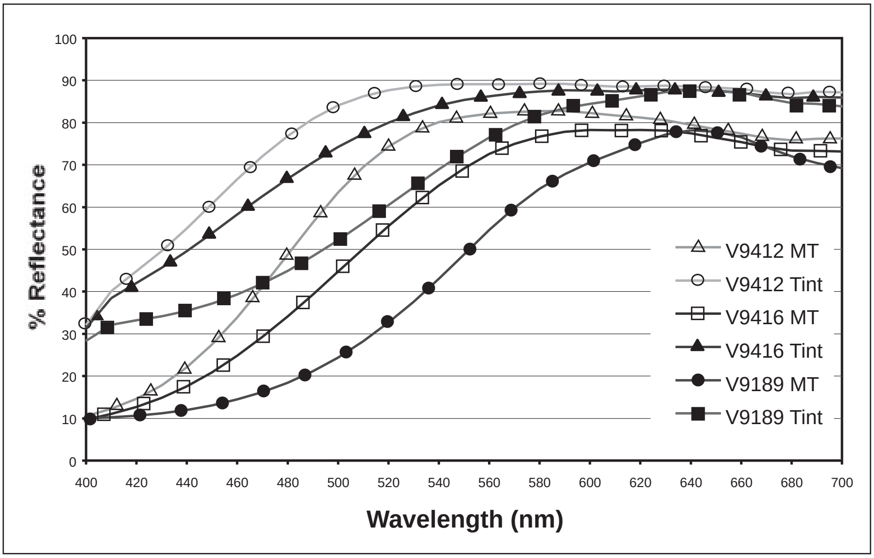

Figure 6–3: Reflectance spectra of some NiCrSbTi DR pigments in polystyrene demonstrating the effect of increasing Cr/Ni ratio.

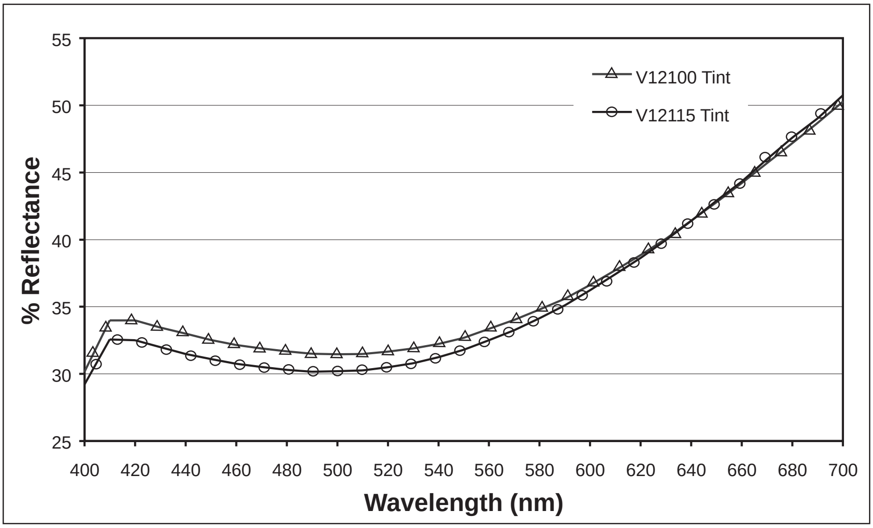

Figure 6–4: Reflectance spectra of two MnSbTi DR pigments exhibiting different curve slopes in the red.

towards lower energy (longer wavelength) in going from Ni to Cr. This behavior is similar to the CdSSe pigments that can be fine-tuned within a wide range of band gaps. However, unlike the cadmium pigments, the sharp rise in reflection is broadened and reduced going from yellow to buff.

Figure 6–4 exhibits the reflectance spectra of two different MnSbTi brown pigments. Note that the tilt of the reflectance line can be controlled to some degree. At the present time, four manufacturers have pigments of similar strength that exhibit slight differences in the tilt of the reflectance curve.

6.5.1.2 UV and NIR Spectral Characterization

Figure 6–5 shows UV-Vis-NIR reflectance spectra of some DR pigments. The DR pigments exhibit good UV absorbance and high IR reflectance – properties that enhance their performance in outdoor weathering systems.

6.5.2
Physical Properties

6.5.2.1 Particle Size Distributions

The antiquated Fisher Sub-Sieve Sizer (FSSS) has been largely replaced by instruments that employ light scattering techniques, such as the Horiba LA910. These modern instruments measure particle size distributions (PSDs) over a size range of 0.02–1000 μm (microns or micrometers). Given proper dispersion and operating techniques, very reproducible PSD results can be obtained. The titanate pigments have mean particle sizes ranging from 0.5 to 2.5 μm, many of them <1.0 μm. High performance pigments should have no measurable fraction >10 μm, and often have

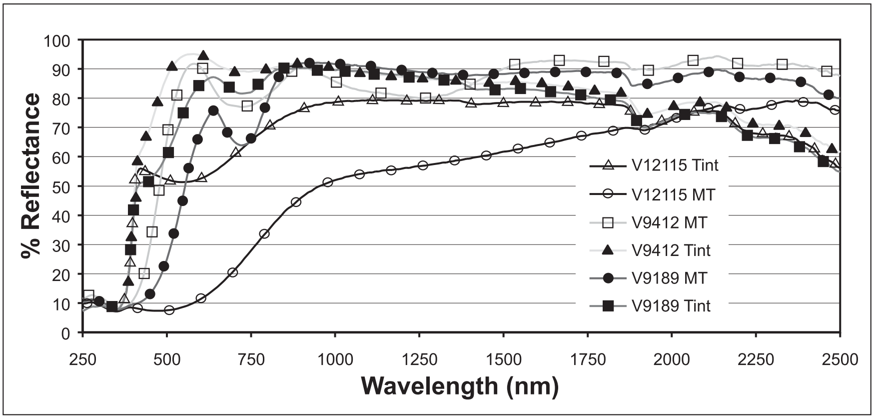

Figure 6–5: UV-Vis-NIR reflectance spectra of MSbTi DR pigments demonstrating strong UV absorbance and high NIR reflectance.

0 %>3 μm. These properties enable Hegman grinds of >7 to be achieved and high-gloss coatings to be produced.

It must be remembered that pigments are controlled for color properties. Although the particle size affects the color properties, so do other factors. Lot-to-lot variations in mean particle size of 10 % are not uncommon.

Although a modern instrument may indicate 100 %<3 μm, it is important to realize that there will still be a certain portion of particles >3 μm. In fact, most pigments show at least a trace of a residue on a 325 mesh (45 μm) screen, and a common 325 mesh residue specification is <0.1 %[1]. These coarse particles, as few as they may be, can be a problem for some of the newer applications. Test procedures to measure 400 mesh and 600 mesh residues have been developed to more critically characterize the coarse tails of the particle size distributions. Specifications as tight as <0.005 % (50 ppm) 600 mesh (20 μm) residue (V12100 MnSbTi brown, Ferro Corporation) can easily be met with modern processing techniques.

Optimum particle sizes can be calculated using Mie scattering theory. Such calculations show that the color properties of pigments could be significantly improved if a monosized pigment of the appropriate size could be made.

6.5.2.2 X-ray Diffraction Characterization

X-ray diffraction (XRD) is a very useful characterization tool in today's pigment industry. It is routinely used to verify RM quality and as a QC tool to control production. It can also be used to accurately measure lattice constants, study site-occupancies, measure crystallite size (when <100 nm), identify secondary phases, and quantify the concentrations of secondary phases.

A study of the effect of the various DR pigment chemistries on lattice constants in underway[48]. Surprisingly large variations of lattice constant changes have been observed that are dependent on both the low-valency cation (Cr,Mn,Ni) and the high-valency cation (Sb,Nb,W). The differences in the lattice constants affect the electronic states of the lattice, and have an impact upon the shade of the pigment. Some preliminary measurements are shown in Table 6–5.

Table 6–6: Lattice parameter changes (vs. pure TiO_2) in DR pigments.

DR	*Pigment*	*Δa(Å)*	*Δc(Å)*	*ΔV(Å^3)*
NiSbTi	V9415	0.0092	0.0161	0.59
NiNbTi	V9440	0.0179	0.0108	0.69
NiWTi	Exptl	0.0099	0.0030	0.33
CrSbTi	V9150	0.0013	0.0123	0.30
CrNbTi	V12107	0.0087	0.0080	0.40
CrWTi	V12110	0.0049	0.0023	0.18
MnSbTi	V12100	0.0308	0.0426	1.75

It can be observed from Table 6–6 that the Mn-DR pigments have much greater lattice expansions than the Ni and Cr analogs. This is partially, but not entirely, because of the higher substitution levels used in the MnSbTi pigments. Second, Nb curiously causes an increase in the ‘a’ constant, but a decrease in the ‘c’ constant relative to the Sb addition. W causes the least expansion in the ‘c’ lattice constant. W often forms distorted WO_6 octahedra[49] that can have a significant impact on the lattice and the color. It is observed that the W analogs are redder than the Sb or Nb analogs when they have similar particle sizes.

It has previously been reported that the Nb analogs give redder shades than the Sb analogs. However, it appears that this was mostly a particle size effect, and that an Nb analog of the same size as the Sb version will give approximately the same redness.

6.5.2.3 Specific Gravity

Specific gravities (SG) have historically been reported on pigment data sheets along with two derived values, solid weight and bulking value. Solid weight is simply the SG measured in different units (lbs/gal). Bulking value is simply the reciprocal of solid weight. These values are for completely densified materials and have no relation to the powder properties of the pigments. The significance of SG probably dates back to its requirement to measure particle sizes on the Fisher Sub-Sieve Sizer, and should be of little use today.

There are two good techniques for measuring SGs of fine powders: helium pycnometry and XRD. Accurate and reproducible values have been obtained on a Micromeritic’s 1305 Multivolume Pycnometer. However, given the submicron size of most of the powders, careful calibration, sealing, and extensive purging cycles (>50) are needed before the true values are asymptotically approached.

Given a known chemical formula, lattice constants measured by XRD can be used to calculate the SG. This technique should be more accurate and can give verification of the pycnometer values.

The DR pigments have higher SGs than pure rutile, with SGs ranging from 4.40 to 4.85 g/cc, compared to 4.25 g/cm^3 for rutile TiO_2. The SGs followed the trend

MNbTi<MSbTi<MWTi, as expected, since the high-valency dopant changes significantly in density.

The approximate SGs for the common MSbTi pigments are given in Table 6–7. The newer MnSbTi pigments have higher dopant levels than the older versions, and have therefore a higher SG.

Table 6–7: Typical specific gravities for DR pigments.

Pigment	SG (g/cm^3)
CrSbTi	4.50
NiSbTi	4.55
MnSbTi(old)	4.65
MnSbTi(new)	4.80
CrNbTi	4.40
CrWTi	4.85

6.5.2.4 Oil Absorption and Specific Surface Area

Oil absorptions are traditionally reported on pigment data sheets. However, this measurement is sensitive to the oil used and is somewhat operator dependent. At best, measurements are accurate to +/–5 % of the value with a single operator. In addition, pigments are controlled for color, so there will be some lot-to-lot variation.

ASTM D281–84 is the commonly accepted standard test. This test method standardizes the oil and much of the technique. The measurements are reported as % oil based on pigment weight.

A review of data for the DR pigments from several companies shows a range of oil absorptions from 10 to 27 %, i.e. lower than for organic pigments. It appears that the higher values correlate with older pigments, so it is likely that some remeasurements are needed, especially for any pigments reported to have values >20 %. These higher values may have been obtained using the ASTM 1483 test, which gives higher values. A data range of 10–20 % appears more reasonable, assuming the absence of highly absorptive additives or surface treatments. Likewise, data from different companies are not necessarily directly comparable.

As expected, good correlations are seen between mean particle size and oil absorption. However, significant changes in particle size have only a mild effect on the oil absorptions, as seen in Table 6–8.

Specific surface area (SSA) measurements are becoming more popular for pigments. Although this technique will measure surface areas of pores (that will be inaccessible to oils or polymer) in addition to the external surface area, these inorganic pigments have negligible internal porosity. Therefore, SSA measurements give good correlations to particle size and should give trends that correlate to oil absorptions.

SSAs are also subject to limited accuracy. The technique is quite sensitive to the degassing conditions, as well as calibration. Calibration standards are only certified to +/–10 %.

The range of SSAs for DR pigments is approximately 2–6 m^2/g for unadulterated pigments. These values are much more sensitive to particle size than oil absorption and may be more useful for those using the pigments. Some SSA data are given in Table 6–8 along with oil absorptions.

Table 6–8: Specific surface areas and oil absorptions of some DR pigments.

Pigment	*Chemistry*	*Size (μm)*	*SSA (m^2/g)*	*Oil abs. (%)*
V9412	NiSbTi	0.80	3.7	14
V9415	NiSbTi	1.25	2.1	12
V9150	CrSbTi	0.70	4.6	15
V9118	CrSbTi	0.90	3.5	15
V9156	CrSbTi	1.35	2.4	14

6.5.2.5 Powder Flow and Dusting

A more recent development is that of non-dusting, free-flowing pigments. Because of their highly cohesive nature, DR pigments have not presented much of a dusting problem, and dust collection systems are typically present in major plants. However, free-flowing powders facilitate the handling of these powders and are finding increasing applications.

Currently, some free-flowing DR powders are commercially available. They are microgranulated powders that withstand shipping without disintegrating. It is also critical that these microgranulates adequately redisperse back into their original fine particulate form during their process applications.

6.5.3
Chemical Properties

6.5.3.1 pH Measurements

pH values are typically made using 10 % pigment slurries in degassed distilled water (ASTM D1208 Procedure 6.1.1). Addition of a small, controlled amount of salt (e.g. reagent grade KCl) improves the electrode response. A blank should be run to verify proper degassing and technique. CO_2 absorption decreases the pH. In the absence of better techniques to prevent CO_2 absorption, measurements are only accurate to 0.5 pH units.

Most of the titanate pigments have neutral pH values. Treated pigments that utilize certain mineralizers, modifiers, oxidizers, or additives can have acidic or basic character and exhibit pH values in the range of 4–10. The pigment pH can be important in some applications such as acid-catalyzed paint systems.

6.5.3.2 Weathering

It is extremely important to realize that weathering involves multiple degradation mechanisms. These can be free radical mechanisms (photolytically or thermally induced), or acid or base-catalyzed chemistry, as well as physically based mechanisms. This makes weathering a difficult property to study.

Second, in general, inorganic pigments do not weather (degrade). It is the polymer systems that do so. However, inorganic pigments certainly affect the weathering of the polymer systems, both chemically and physically. Chemically, a component of the pigment, such as trace amounts of an unreacted raw material, can be involved in free radical generation or in acid-base chemistry. Physically, inorganic pigments have much lower thermal expansion coefficients than the polymer systems, and can therefore affect the physical structure of the polymer system over its numerous heating cycles.

Since it is the polymer system that weathers, the polymer system itself has a huge impact on weathering. In fact, a newer fluoropolymer paint system has been found to give unexpectedly good weathering results with some traditionally poor weathering pigments. On the other hand, alkyd paints are generally poor weathering systems.

The properties most commonly used to measure weathering are the color values. Certainly it is desirable to maintain the initial color as much as possible. However, the color values are most affected by surface weathering initially, especially surface roughness, and give no indication of bulk polymer degradation like strength or brittleness measurements do. In fact, the L* value is fairly sensitive to the exact part of the light or dark cycle in which the sample is removed for color measurement. In addition, ΔL^* values are seen to increase and decrease at random after the initial lightening effect has occurred.

Both indoor and outdoor weathering assessment is routinely performed on pigments. Accelerated indoor weathering is mostly done with either a Xenon-Arc apparatus or under UV-lamp irradiation. Outdoor weathering is usually required for verification.

DR pigments weather well because they possess both good UV absorptivity and IR reflectivity. Their UV absorbance removes the UV light so that it cannot degrade the polymer. Their IR reflectivity keeps the polymer at a lower temperature where the polymer degradation is slower. Their biggest drawback is that TiO_2 can photoinitiate free radicals. This is one reason why most of the white TiO_2 rutile pigments are coated.

Iron oxide has a notorious reputation for causing bad weathering. A recent study showed that the levels of free (acid-leachable) iron oxide correlated better to weathering than the levels of contained iron oxide[41]. The data presented in the plot showed no deleterious weathering effect from samples with <1 % free iron oxide. More detailed studies are needed to determine when free metal oxides such as iron oxide are detrimental to weathering. In addition, measurement of properties other than color values may provide a better understanding and correlations.

6.5.3.3 Particle Chemistry

Modern microscopic and surface analysis techniques can be used to get a better understanding of the pigment particles. In the case of a host pigment lattice such as the DR pigments, there is the question about the uniformity of the dopants throughout the particles. Some preliminary studies on some DR pigments indicate that the homogeneity of the dopants in a particle is dependent on the synthesis technique used. Some samples exhibited concentration gradients of the dopants across a sliced particle while others did not. For numerous reasons, great caution is needed before drawing definitive conclusions from the data.

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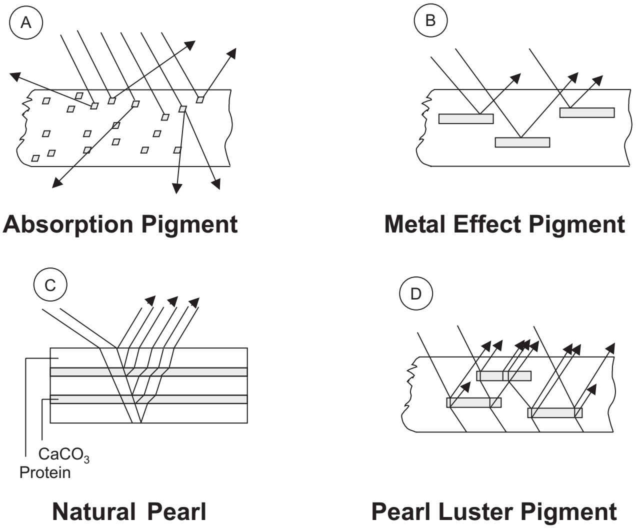
7
Special Effect Pigments

Gerhard Pfaff

7.1
Introduction

Pearl luster pigments, which can be natural or synthetic, show outstanding qualities of luster, brilliance and iridescent color effects based upon optically thin layers. This visual impression develops by reflection and scattering of light on thin multiple layers. In nature this is not limited to pearls and mussel shells alone; there are a multitude of birds, fish, precious stones and minerals, even insects which demonstrate a pearl luster effect. Experiments to understand the optical principles of natural pearl luster demonstrate that the brilliant colors are based upon structured biopolymers and upon layered structures which are developed by biomineralization.

Figure 7–1 illustrates the various optical principles of conventional pigments (absorption pigments), metal effect pigments, and pearls and pearl luster pigments. In the case of absorption pigments, the interaction with light is based upon absorp-



Absorption Pigment **Metal Effect Pigment**

Natural Pearl **Pearl Luster Pigment**

Figure 7–1: Optical properties of absorption pigments, effect pigments and natural pearls.

tion and/or diffuse scattering. A completely different optical behavior can be observed with the group of effect pigments including pearl luster and metal effect pigments. Metal effect pigments consist of small metal platelets (for example aluminum, titanium, copper) which operate like little mirrors and almost completely reflect the incident light.

Pearl luster pigments simulate the luster of natural pearls. These consist of alternating transparent layers with differing refractive indices. The layers consist of $CaCO_3$ (high refractive index) and proteins (low refractive index).

This difference in refractive indices, arising equally on the interface between air/oil film or oil film/water, is a prerequisite for the well-known iridescent color images in these media. Small highly refractive platelets of pearlescent pigments align themselves parallel in optically thin systems such as paints, printing inks, or plastics. Interference effects develop when the distances of the various layers or the thicknesses of the platelets have the right values.

Synthetic pearlescent pigments are either transparent or light-absorbing platelet shaped crystals. They can be monocrystalline as in $Pb(OH)_2 \times 2\ PbCO_3$ and BiOCl or possess a multi-layered structure in which the layers have differing refractive indices and light absorption properties.

7.2
Pearlescent and Interference Pigments

The use of pearls and nacreous shells for decorative purposes goes back to ancient times (e.g., in Chinese wood intarsia). The history of pearl pigments dates back to 1656, when the French rosary maker Jaquin isolated a silky lustrous suspension from fish scales (pearl essence) and applied this to small beads to create artificial pearls. It took more than 250 years to isolate the pearl essence material (guanine platelets) and understand the pearl effect. Attempts were made to create synthetic pearl colors as organic or inorganic, transparent, highly refractive coatings and pearl pigments as crystalline platelets. From 1920 onwards, hydroxides, halides, phosphates, carbonates, and arsenates of zinc, calcium, barium, mercury, bismuth, lead, and other cations were produced for this purpose. Only the traditional natural pearl essence, basic lead carbonate and bismuth oxychloride, is still of importance.

The strong demand for pearl effects came from the growing coatings and plastics industries, which wanted to improve the acceptance and popularity of their products. Furthermore, pearlescent pigments also allowed artists and designers to create new visual effects similar to those found in nature. The breakthrough for pearlescent pigments came with the invention of mica coated with metal oxides. Mica-based pearlescent pigments now account for > 90 % of the world market.

Pearlescent pigments are used to obtain pearl, iridescent (rainbow), or metallic effects, and in transparent color formulations to obtain brilliance or two-tone color, luster flops and color travel effects (changing with viewing angle). The most important applications are plastics, industrial coatings, printing inks, cosmetics, and automotive paints.

Table 7–1 shows an overview of pigments with luster effects. Effect pigments can be classified as metal platelets, oxide-coated metal platelets, oxide-coated mica platelets, oxide-coated silica and alumina flakes, platelet-like monocrystals, comminuted PVD films (PVD = physical vapor deposition), and liquid crystal polymer platelets (LCP-pigments)[1, 2]. Aims of new developments are new effects and colors, improvement of hiding power, more intense interference colors, increased light and weather stability, and improved dispersibility. Of special interest are pigments which are toxicologically safe and which can be produced by ecologically acceptable processes.

Table 7–1: Overview of effect pigments.

Pigment type	*Examples*
Metallic platelets	Al, Zn/Cu, Cu, Ni, Au, Ag, Fe (steel), C (graphite)
Oxide coated metallic platelets	Surface oxidized Cu-, Zn/Cu-platelets, Fe_2O_3 coated Al-platelets
Coated mica platelets	Non-absorbing coating: TiO_2 (rutile), TiO_2 (anatase), ZrO_2, SnO_2, SiO_2 selectively absorbing coating: FeOOH, Fe_2O_3, Cr_2O_3, TiO_{2-x}, TiO_xN_y, $CrPO_4$, $KFe[Fe(CN)_6]$, colorants Totally absorbing coating: Fe_3O_4, TiO, TiN, $FeTiO_3$, C, Ag, Au, Fe, Mo, Cr, W
Platelet-like monocrystals	BiOCl, $Pb(OH)_2 \times 2\ PbCO_3$, α-Fe_2O_3, α-$Fe_2O_3 \times n\ SiO_2$, $Al_xFe_{2-x}O_3$, $Mn_yFe_{2-y}O_3$, $Al_xMn_yFe_{2-x-y}O_3$, Fe_3O_4, reduced mixed phases, Cu-phthalocyanine
Comminuted thin PVD-films	Al, Cr(semitransp.)/SiO_2/Al/SiO_2/Cr (semitransp.)

7.2.1
Optical Principles of Pearlescent and Interference Pigments

The physical background of optical interference effects has been the subject of many publications[3–8]. The optical principles of pearlescent (interference) pigments are shown in Figure 7–2 for a simplified case of nearly normal incidence without multiple reflection and absorption. At the interface P_1 between two materials with refractive indices n_1 and n_2, part of the beam light L_1 is reflected (L_1') and part is transmitted (i.e., refracted) (L_2). The intensity ratios depend on n_1 and n_2. In a multilayer arrangement as found in pearl or pearlescent and iridescent materials (Figure 7–1d), each interface produces partial reflection. After penetration through several layers, depending on the size and difference between n_1 and n_2, virtually complete reflection is obtained, provided that the materials are sufficiently transparent.

In pigments that simulate natural pearl effects, the simplest case is a platelet-shaped particle with two phase boundaries P_1 and P_2 at the upper and lower surfaces of the particles, i.e., a single, thin, transparent layer of a material with a higher refractive index than its surroundings. For small flakes with a thickness of ca. 100 nm, the physical laws of thin, solid, optical films apply.

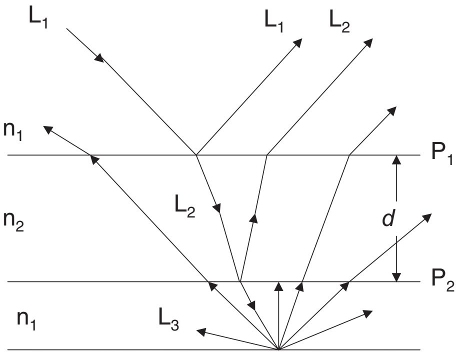


Figure 7–2: Simplified diagram showing nearly normal incidence of a beam of light (L_1') from an optical medium with refractive index n_1 through a thin solid film of thickness d with refractive index n_2. L_1' and L_2' are regular reflections from phase boundaries P_1 and P_2. L_3 represents diffuse scattered reflections from the transmitted light.

Multiple reflection of light on a thin solid film with a high refractive index causes interference effects in the reflected light and in the complementary transmitted light. For the simple case of nearly perpendicular incidence, the intensity of the reflectance (I) depends on the refractive indices (n_1, n_2), the layer thickness (d), and the wavelength (λ):

$$I = \frac{A^2 + B^2 + 2AB \cos\Theta}{1 + A^2B^2 + 2AB \cos\Theta}$$

$$A = \frac{n_1 - n_2}{n_2 + n_1} \quad B = \frac{n_2 - n_1}{n_2 + n_1} \quad \Theta = 4\pi \frac{n_2 d}{\lambda}$$

With given n_1 and n_2 the maximum and minimum intensities of the reflected light – seen as interference colors – can be calculated and agree well with experimental results. Values for the refractive index of the most important materials for pearlescent pigments are shown in Table 7–2.

Table 7–2: Refractive indices of materials.

Material	*Refractive index*
Vacuum/air	1.0
Water	1.33
Proteins	1.4
Organic polymers (plastics, lacquers, etc.)	1.4–1.7
Mica	1.5
$CaCO_3$ (aragonite)	1.68
Natural pearl (guanine, hypoxanthine)	1.85
$Pb(OH)_2 \times 2\ PbCO_3$	2.0
BiOCl	2.15
TiO_2 (anatase)	2.5
TiO_2 (rutile)	2.7
Fe_2O_3 (hematite)	2.9

In practice, platelet crystals are synthesized with a layer thickness d calculated to produce the desired interference colors (iridescence). Most pearlescent pigments now consist of at least three layers of two materials with different refractive indices. Thin flakes (thickness ca. 500 nm) of a material with a low refractive index (mica, silica, alumina, glass) are coated with a highly refractive metal oxide (TiO_2, Fe_2O_3, layer thickness ca. 50–150 nm). This results in particles with four interfaces that constitute a more complicated but still predictable thin film system. The behavior of more complex multilayer pigments containing additional, thin, light-absorbing films can also be calculated if appropriate optical parameters are known.

Color effects depend on the viewing angle. Pearlescent pigment platelets split white light into two complementary colors that depend on the platelet thickness. The reflected (interference) color dominates under regular (maximum) reflection, i.e., when the object is observed at the angle of regular reflection. The transmitted part dominates at other viewing angles under diffuse viewing conditions, provided there is a nonabsorbing (white) or reflecting background. Variation of the viewing angle therefore produces a sharp gloss (reflectance) peak, and the color changes between two extreme complementary colors. The resulting complex interplay of luster and color is measured goniophotometrically in reflection and at different angles. A pearlescent pigment is characterized by a minimum of three L*a*b* data sets (CIE L*a*b*-system) measured under different conditions (e.g., 0°/45° black background, 22.5°/22.5° black background, 0°/45° white background). An analysis of these data specifies a pigment on the basis of its hiding power, luster, and hue[7, 9, 10].

Against a black background or in a blend with carbon black, the transmitted light is absorbed and the reflected interference color is seen as the mass tone (i.e., overall color) of the material. In blends of nacreous pigments with absorbing colorants, the particle size of the latter must be well below the scattering limit, i.e., they must be transparent. The nacreous effect or iridescent reflection is otherwise quenched by the hiding pigments. This also applies to blends with strongly reflecting metal effect pigments (e.g., aluminum). Blends of pigments with different interference colors obey an additive mixing law, (e.g., blue + yellow = green).

7.2.2
Substrate-Free Pearlescent Pigments

7.2.2.1 Natural Pearl Essence

Natural pearl essence is isolated as a silky lustrous suspension from fish scales. The pigment particles in the suspension are platelet-shaped with a very high aspect ratio (0.05 μm × 1–10 μm × 20–50 μm), and consist of 75–97 % guanine and 3–25 % hypoxanthine[4, 6–8].

To date there is no commercial synthetic process for producing similar platelet-shaped products of such brilliance. One is therefore limited to a process based on the natural supply. An aqueous suspension of white fish scales is treated with organic solvents in a complicated washing and phase-transfer process to remove proteins and irregular guanine crystals. One ton of fish yields less than 250 g of guanine. The pigment particles show a high tendency to agglomerate and are, therefore, only handled as dispersions.

Natural pearl essence is very expensive but shows some advantages over synthetic pearlescent pigments. For example, it shows a high but soft luster ($n_D = 1.79$ (parallel) to 1.91 (perpendicular)), It is not brittle and has a relatively low density of 1.6 g/cm^3, which reduces settling in liquid formulations. It is almost exclusively used in expensive cosmetic applications.

7.2.2.2 Basic Lead Carbonate

The first commercially successful synthetic pearlescent pigments were hexagonal lead salt crystals, especially basic lead carbonate $Pb(OH)_2 \times 2\ PbCO_3$. Basic lead carbonate is precipitated from aqueous lead acetate with carbon dioxide under carefully controlled reaction conditions. The resulting platelets are less than 0.05 μm thick and show hexagonal dimensions of about 20 μm, yielding an aspect ratio of > 200. Because of their high refractive index of 2.0 and their even surface, they exhibit a very strong luster. If the thickness of the platelets is increased by slightly modified reaction conditions, interference colors can be obtained[4, 6–8].

The crystals are very fragile and are handled only in dispersions. They settle very fast because of their density of 6.14 g/cm^3. The use of basic lead carbonate is also limited by its low chemical stability, the toxicity of its by-products, and toxicological concerns in its application areas.

7.2.2.3 Bismuth Oxychloride

Bismuth oxychloride is produced by the hydrolysis of very acidic (pH < 1.0) bismuth solutions in the presence of chloride. The crystal quality can be varied by careful adjustment of bismuth concentration, temperature, pH, pressure, reactor geometry, and addition of surfactants. The usually tetragonal bipyramidal structure can be flattened to platelets with a high aspect ratio. Products with an aspect ratio of 10–15 show low luster and a very good skin feel and are used as fillers in cosmetics. Crystals with higher aspect ratios show an exceptional luster and are mainly used for nail polish[4, 6–8].

The low light stability, the fast settling caused by the high density of 7.73 g/cm^3, and the lack of mechanical stability limit the use of BiOCl in technical applications. Therefore, it is mainly used in cosmetics, but also in buttons and jewelry. The light stability can be improved to some extent by cerium doping and UV absorbers.

7.2.2.4 Micaceous Iron Oxide

Micaceous iron oxide consists of pure or doped hematite (α-Fe_2O_3). Its density is 4.6–4.8 g/cm^3. Micaceous iron oxide can also be obtained by hydrothermal synthesis in alkaline media. However, the dull dark color is as unappealing as that of the natural product. If substantial amounts of dopants are incorporated, the aspect ratio can be increased up to 100, resulting in a much increased luster. The color can be also shifted to a more attractive reddish brown so that the products can be used for decorative purposes[1, 11].

The most important dopants are Al_2O_3, SiO_2, and Mn_2O_3. These can enforce a spinel structure. SiO_2 yields thin small platelets, Al_2O_3 yields thin larger platelets, and Mn_2O_3 reduces the thickness.

The starting material $Fe(OH)_3$ or better FeOOH is heated in an alkaline suspension together with the dopants to temperatures above 170 °C, typically 250–300 °C. After several minutes to hours, platelets of doped iron oxide are obtained. In a second reaction phase, the pH is further increased so that platelets grow and form flat basal faces.

7.2.2.5 **Titanium Dioxide Flakes**

Titanium dioxide flakes are produced by breaking down a continuous film of TiO_2[8, 12]. The most efficient process is therefore a web-coating process involving a thermal hydrolysis of $TiOCl_2$ on the web. Alternative procedures are the application of titanium alkoxide on a smooth flat surface and cracking the resulting film into flakes by steam treatment or the application of a TiO_2 sol on a glass surface and scratching off the resulting film[13, 14].

The titanium dioxide flakes produced by these methods are not single crystals but quite porous and, lacking the mechanical support of a substrate, hence brittle. Therefore, they are not yet used in technical applications in which mechanical stress is exerted.

The TiO_2 flakes can be reduced to titanium suboxides yielding a dark bluish mass tone in addition to the interference color[15].

7.2.3
Pigments Formed by Coating of Substrates

7.2.3.1 **Metal Oxide-Mica Pigments**

The dominant class of pearlescent pigments is based on platelets of natural mica coated with thin films of transparent metal oxides[2–8, 16]. The mica substrate acts as a template for the synthesis and as a mechanical support for the deposited thin optical layers of the pearlescent pigments. Mica minerals are sheet layer silicates. Pearlescent pigments are usually based on transparent muscovite but some are based on natural or synthetic phlogopite. Although muscovite occurs worldwide, few deposits are suitable for pigments. Mica is biologically inert and approved for use as a filler and colorant.

Selection and pre-processing of the mica substrate is one of the key factors which determine the quality and appearance of nacreous pigments. The aspect ratio of the final pigment depends on the particle size distribution of the mica platelets, which have a thickness of 300–600 nm and various diameter ranges (e.g., 5–25, 10–50, 30–110 μm). Since light is regularly reflected from the planes of the metal-oxide-coated mica and scattered from the edges, brilliance and hiding power are inversely related to each other.

A mica pigment coated with a metal oxide (Figure 7–3) has three layers with different refractive indices and four phase boundaries P_1–P_4: (P_1) TiO_2 (P_2) mica (P_3) TiO_2 (P_4). Interference of light is generated by reflections of all six combinations of phase boundaries, some of which are equal: $P_1P_2 = P_3P_4$, $P_1P_3 = P_2P_4$, P_1P_4, and

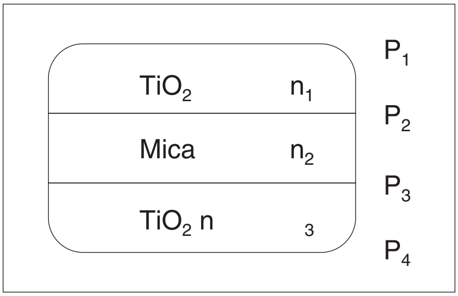


Figure 7–3: Structure of a titanium dioxide mica pigment with the four existing interphases.

P_2P_3. The thickness of the mica platelets varies in accordance with a statistical distribution. Consequently, interference effects involving the phase boundaries between the mica substrate and the oxide coating add together to give a white background reflectance. The interference color of a large number of particles therefore depends only on the thickness of the upper and lower metal oxide coating layers.

The development of the mica-based pigments started with pearlescent colors (Figure 7–4a, TiO_2–mica). This was followed by brilliant, mass-tone-colored combination pigments (i.e., mica TiO_2, and another metal oxide) with one color (interference color same as mass tone) or two colors (interference and mass tone different) that depend on composition and viewing angle (Figure 7–4b). In the 1980s further development was made by coating mica particles with transparent layers of iron(III) oxide (Figure 7–4c).

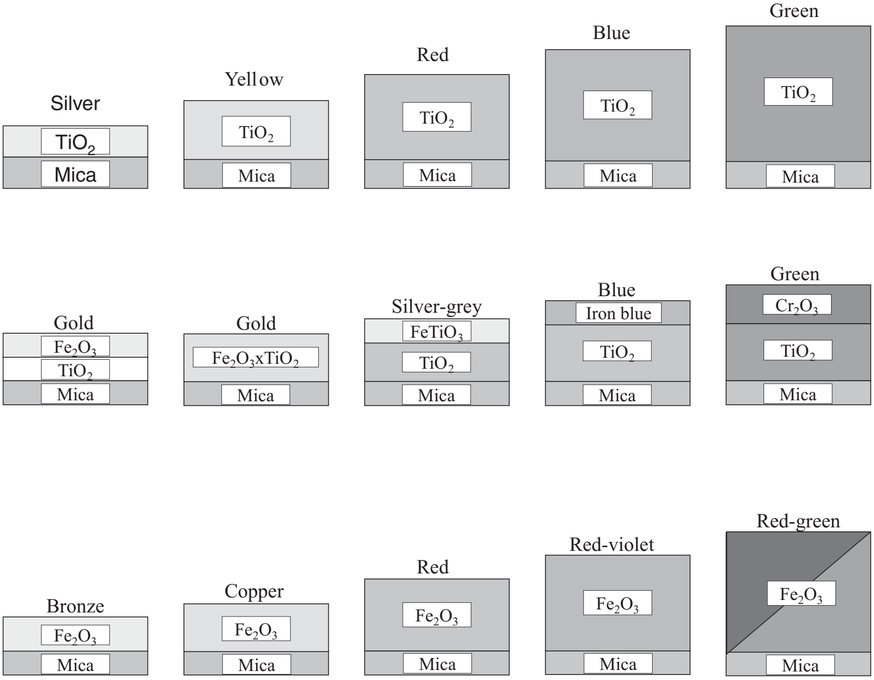


Figure 7–4: Schematic illustration of different metal oxide mica pigments.

Titanium Dioxide-Mica

The first multilayer pigments were marketed in the 1960s as TiO_2-coated muscovite micas. Two different processes are used for coating mica in aqueous suspension on a commercial basis:

(1) Homogeneous hydrolysis

$$\mathrm{TiOSO_4 + mica + H_2O \xrightarrow{100\,°C} TiO_2\text{-}mica + H_2SO_4}$$

(2) Titration

$$\mathrm{TiOCl_2 + 2\ NaOH + mica \rightarrow TiO_2\text{-}mica + 2\ NaCl + H_2O}$$

The pigments are then dried and calcined at 700–900 °C. The titration (chloride) process is preferred for interference pigments with thick TiO_2 layers because it is easier to control. Chemical vapor deposition in a fluidized bed has also been proposed:

$$\mathrm{TiCl_4 + 2\ H_2O + mica \xrightarrow{> 100\,°C} TiO_2\text{-}mica + 4\ HCl}$$

When TiO_2 is precipitated onto muscovite under reaction conditions unfavorable for side precipitation, e.g., pH > 1.5, only the anatase modification is formed. Even after annealing at 1000 °C, no rutilization is found in the layer, whereas the free titania turns completely into rutile at about 700 °C.

Rutile has a higher refractive index and therefore yields a stronger pearlescence than anatase. Therefore, processes have been developed to create a rutile layer on mica. A thin layer of SnO_2 is precipitated as a continuous layer onto the substrate,

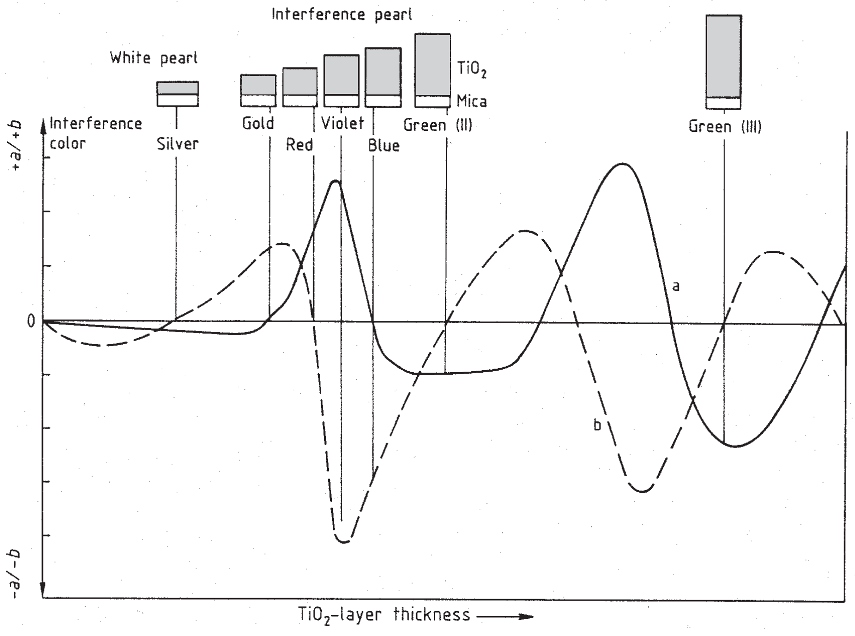


Figure 7–5: TiO_2-mica pigments: The dependence of interference colour according to titanium dioxide layer thickness.

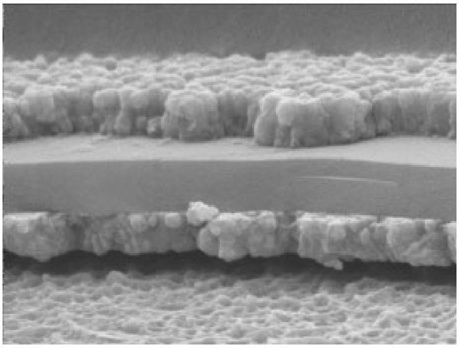


Figure 7–6: SEM photo of a cross-section through an anatase/mica pigment particle.

and then the TiO_2 layer is created using the usual process. $SnCl_2$ or better $SnCl_4$ can be used as precursors for the SnO_2 precoating. SnO_2 acts as a template because its lattice parameters are close to those of rutile.

The desired interference color determines the thickness of the titania layer. For a silver white pigment 50 nm of anatase is needed and for a blue interference color about 120 nm. The sequence of interference colors obtained with increasing TiO_2 layer thickness agrees with theoretical calculation in the color space (Figure 7–5). A cross section of a TiO_2-mica pigment is shown in Figure 7–6.

TiO_2-mica pigments are used in all color formulations of conventional pigments where brilliance and luster are required in addition to color, i.e., in plastics, coatings, printing, and cosmetics. Table 7–3 contains a comparative overview of TiO_2-mica, basic lead carbonate, bismuth oxychloride, and natural fish silver pigments. Some further physical data are summarized in Table 7–4.

Table 7–3: Properties and applications of pearlescent pigments.

Pearlescent pigment	*Advantages*	*Disadvantages*	*Main application field*
Natural fish silver	Very low density High luster Nontoxic Light stable	High price Low hiding power Limited availability	Nail lacquers
Basic lead carbonate	Very high luster Good hiding power Low price Light stable	High density Chemically and thermally of limited stability; toxic	Buttons Bijouterie
Bismuth oxychloride	Very high luster Good hiding power Nontoxic	Limited light stability High density	Decorative cosmetics Buttons Bijouterie

Table 7–3: Continued

Pearlescent pigment	*Advantages*	*Disadvantages*	*Main application field*
Titanium dioxide-mica	High luster Good hiding power (depending on the particle size) Highest thermal, chemical, and mechanical stability Nontoxic Low price Low density	Inferior luster in comparison with top qualities of basic lead carbonates and bismuth oxychloride	Plastics Lacquers Cosmetics Printing inks Ceramic products

Table 7–4: Technical data on pearlescent pigments.

Pearlescent pigment	*Shape*	*Particle size (µm)*	*Thickness (nm)*	*Density (g/cm³)*
Natural fish silver	Needles, longish platelets	10–40	40–50	1.6
Basic lead carbonate	Hexagonal crystals	4–20	40–70	6.4
Bismuth oxychloride	Flat tetragonal bipyramidal crystals	5–30	100–700	7.7
Titanium dioxide-mica	Platelets	1–200	200–500	3

Iron Oxide-Mica

Like titanium dioxide, iron(III) oxide is suitable for coating mica platelets. It combines a high refractive index (metallic luster) with good hiding power and excellent weather resistance. Commercial Fe_2O_3-mica pigments are produced by precipitation of iron(II) or iron(III) ions in aqueous mica suspensions and calcination of the resulting coated particles at 700–900 °C:

$$2\ FeCl_3 + \text{mica} + 3\ H_2O \rightarrow Fe_2O_3\text{-mica} + 6\ HCl$$

It is also possible to produce iron oxide-mica pigments by a direct CVD fluidized bed process in which iron pentacarbonyl is oxidized and Fe_2O_3 is deposited on the mica surface.

Independent of the synthesis route, iron(III) oxide crystallizes in the α-modification (hematite) after calcination. Brilliant, intense colors are obtained with 50–150 nm layers of Fe_2O_3 (hematite) on muscovite (see Figure 7–4c). Absorption and interference colors are produced simultaneously and vary with layer thickness. The red shades are especially intense because interference and absorption enhance each other. An intense green-red flop with different viewing angles is possible at a Fe_2O_3 layer thickness producing green interference.

Combination Mica-Based Pigments

Simple blending of transparent absorption pigments with pearlescent pigments is only one way to attain new coloristic effects. It is possible to produce pearlescent pigments coated with a layer of transparent absorption colorant to realize more pronounced brilliant colors with a sharper color flop. An additional advantage of such pigments is the elimination of dispersion problems associated with transparent absorption pigments due to their small particle size and high surface area.

One possibility for attractive combination pigments is the coating of TiO_2-mica pigments with an additional layer of an inorganic or organic colorant. The thickness of the TiO_2 layer is decisive for the brilliance or interference effect under regular viewing conditions, whereas the transparent colorant dominates at all other viewing angles. A deep, rich color with a luster flop at all angles is attained when the colorant and interference color are matched. If the interference color and the mass tone of the colorant are different, a color flop (two-tone pigments) is seen in addition to the luster flop.

Iron(III) oxide is the most important metal oxide for combination with titanium dioxide on mica flakes. Brilliant golden pigments result which can be applied for several purposes. Two routes are used to synthesize these pigments, and different

Table 7–5: Examples of mica-based pearlescent pigments with special coloristic properties.

Pigment composition	***Preparation***	***Remarks***
TiO_{2-x}/TiO_2/mica[17, 18]	TiO_2/mica + H_2 (Ti, Si) T > 900 °C (solid state reaction)	Gray, blue-gray
TiO_xN_y/TiO_2/mica[19]	TiO_2/mica + NH_3 T > 900 °C (solid state reaction)	Gray, blue-gray
$FeTiO_3/TiO_2$/mica[20]	Fe_2O_3/mica + H_2 T > 600 °C (solid state reaction)	Gray (ilmenite pigments)
Fe_3O_4 mica[19, 21]	Fe_2O_3/mica + H_2 T ≈ 400 °C (solid state reaction) Fe^{2+} + O_2 + mica (precipitation) $Fe(CO)_5$ + O_2 + mica (CVD-process)	Black Black Black
TiN/mica[1]	$TiCl_4$ + NH_3 + mica (CVD-process)	Gold
TiO_2/C/mica[22]	$TiOCl_2$ + C + mica (precipitation) calcination under N_2	Silver-gray, interference colors (carbon inclusion pigments)
$BaSO_4/TiO_2$/mica[7, 23]	Ba^{2+} + SO_4^{2-} + $TiOCl_2$ + mica (precipitation)	Low luster pigments
Fe_3O_4/mica (mica surface only partially coated)[7, 24]	Fe^{2+} + O_2 + mica (precipitation)	Transparent colors

structures are formed. In the first, a thin layer of Fe_2O_3 is coated onto the surface of a TiO_2-mica pigment. The overall interference color is the result of both metal oxide layers. The mass tone is determined by the Fe_2O_3 layer, and interesting gold pigments (e.g., reddish gold) are possible. In the second case, co-precipitation of iron and titanium oxide hydroxides on mica particles followed by calcination leads to greenish gold pigments. Interference and mass tone can be explained as above. The mass tone in this case is, however, further modified because of the additional formation of the highly refractive yellowish iron titanate phase Fe_2TiO_5 (pseudobrookite).

Other inorganic colorants used instead of iron oxide for combination pigments are Cr_2O_3 (green), iron blue, cobalt blue, Fe_3O_4 (black), and $FeTiO_3$. In the case of black colorants, the interference color is seen as the mass tone. There is an analogy to blends with black pigments in a color formulation where the transmitted part of the light is absorbed. Coating of TiO_2-mica with an organic colorant for a mass-tone or two-tone pigment is performed by precipitation or deposition on the mica pigment surface in aqueous suspension, assisted by complexing agents or surfactants. Another method is to fix the colorant as a mechanically stable layer by using proprietary additives.

Mica platelets can be coated with a variety of other compounds to produce further pigments. Solid-state reactions and CVD processes extend the possibilities for the synthesis of mica pigments. In addition, the calcination of the materials in the presence of inert (e.g., N_2, Ar) or reactive gases (e.g., NH_3, H_2, hydrocarbons) allows the formation of phases which are not producible by working in air. Table 7–5 contains a summary of pearlescent mica pigments with special coloristic properties.

Initially, metal oxide-mica pigments were developed purely for their excellent coloristic properties. Since then, they have also become of interest for functional uses. In coatings with a high content of platelet fillers, an advantageous overlapping roof-tile arrangement is possible that provides close interparticle contact, barrier effects, and dense covering. The composition and thickness of the oxide layer on the mica surface are always responsible for the physical properties like electrical conductivity, magnetism, IR reflectivity, and laser markability. Table 7–6 lists data on some functional metal oxide-mica pigments.

Table 7–6: Functional metal oxide-mica pigments.

Pigment composition	*Property*	*Application*
$(Sn,Sb)O_2$/mica $Sn(O,F)_2$/mica[22, 25, 26]	Electrically conductive	Conductive flooring, antistatic packaging materials, light colored primed plastic surfaces which can be electrostatically painted in further coating process, light colored conducting surfaces in clean room conditions for dust reduction
Fe_3O_4/mica[7]	Magnetic	Magnetic surfaces
TiO_2/mica[27]	IR-reflective	IR-reflecting plastic sheets, e.g. for domed and continuous roof lights
TiO_2/mica[22] $(Sn,Sb)O_2$/mica	Laser sensitive	Laser marking of plastics, coatings

7.2.3.2 Silica Flake Pigments

Instead of mica, SiO_2 flakes can be used as a substrate for pearlescent pigments. The SiO_2 flakes are produced by a web-coating process. Synthetic SiO_2 flakes offer three advantages over the use of natural mica: (1) the thickness of the SiO_2 substrate can be controlled in the preparation so that at the end a pigment with a true optical three-layer system is obtained, the interference color of those systems being stronger than that for the conventional mica pigments for which the effect of the mica is "wiped out" by a broad thickness distribution; (2) as synthetic substrates they do not have the small iron impurities that cause the slightly yellow mass tone of natural mica; (3) SiO_2 has a lower refractive index (1.46) than mica (about 1.58) and, therefore, leads to a stronger interference effect[28–30].

Figure 7–7 shows a cross-sectional diagram of metal oxide coated on mica and metal oxide deposited on silica flake pigments. The new properties available with silica flake pigments can be summarized as follows.

Improved substrate characteristics

- uniform and controllable substrate thickness
- smooth and uniform substrate surface

transparent substrate with no mass tone color

Improved reflection and refraction of light

- improved chromatic strength and purity
- new color travel behavior.

The silica flakes are manufactured by a web coating process as shown in Figure 7–8. The web, moving at a controlled speed, is wet with an aqueous solution of a silica compound. The film on the web is dried to form a stable coating layer that can be selected between 50 nm and 1000 nm thick by adjustment of process parameters. The layer is then removed from the web and processed further to generate flakes

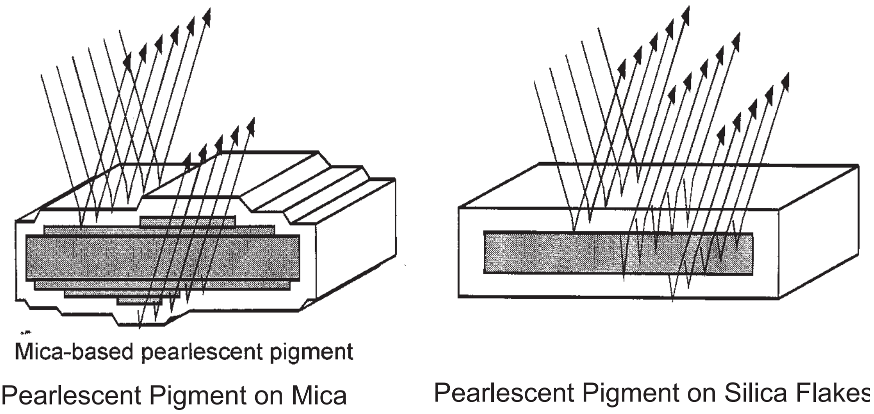


Figure 7–7: Schematic cross-section of metal oxide coated pigments.

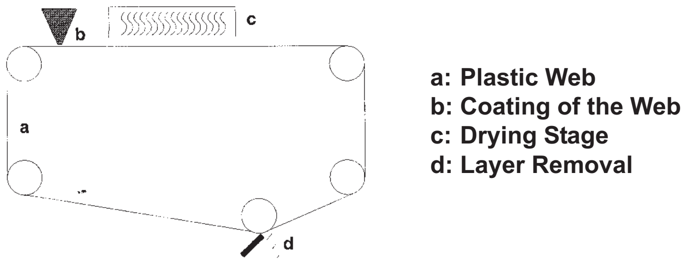


Figure 7–8: Manufacturing process of transparent silica flakes.

that are fractionated and coated. The transparent flakes have a relatively low refractive index. However, they provide an excellent substrate for coating with the relatively high index metal oxides such as titanium dioxide and iron oxide. The metal oxides are applied in a standard precipitation-coating process producing high performance pearlescent pigments.

Titania is deposited as hydrated titanium oxide on the surface of the SiO_2 flakes. The thickness of the layer is monitored and precisely controlled. After drying and calcining, anatase is formed and a specific color is produced corresponding to the film thickness. The anatase modification is used in the cosmetic industry. In principle, the manufacturing process is similar to the “anatase” procedure. However, a thin intermediate SnO_2 layer is applied to the surface of the SiO_2 flakes before the TiO_2 deposition. The SnO_2 layer has a rutile structure which seeds epitaxy of the TiO_2 rutile modification with its higher refractive index, brilliant color intensity and superior light stability. Consequently, the rutile pigments are preferred when these properties are advantageous.

SiO_2 can be coated not only with TiO_2 but also with other metal oxides that are deposited from hydrolyzable salts. Iron(III) oxide is deposited as hydrated iron oxide on the transparent silica flakes. Subsequent drying and calcining produces α-Fe_2O_3 (hematite) layers on the flakes. The high refractive index of iron oxide generates strong interference effects and, in conjunction with the mass tone, brilliant red pigments.

Figure 7–9 shows schematic diagrams of the three metal oxide/silica flake pigments. Two extraordinary optical effects are achieved by the combination of transparent silica flakes selected for precise uniform thickness and controlled depositions of metal oxide coating layers. The color of these pigments exhibits extreme angle dependence, and objects painted with them will change appearance with the direction of lighting and the location of the observer. Color changes from gold-silver to green, to green-blue, to dark blue are seen. The strong color travel is seen even under subdued lighting conditions. Figure 7–10 demonstrates how color travel is generated as a function of viewing angle with uniform silica substrates and metal oxide layer thickness. The angle-dependent color travel of three pigments through the “CIELAB” system is shown in Figure 7–11 for constant Fe_2O_3 deposition on SiO_2 substrates of different thickness.

Coating is possible with

- Titanium dioxide, TiO_2 (two modifications)
- Iron oxide, Fe_2O_3
- Other metal oxides (as used for mica pigments)

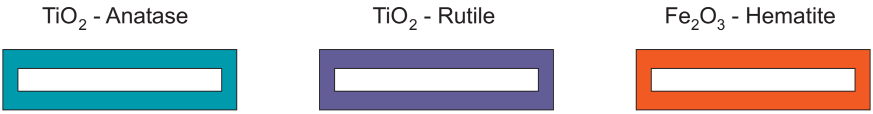


Figure 7–9: Coating of transparent silica flakes with various metal oxides.

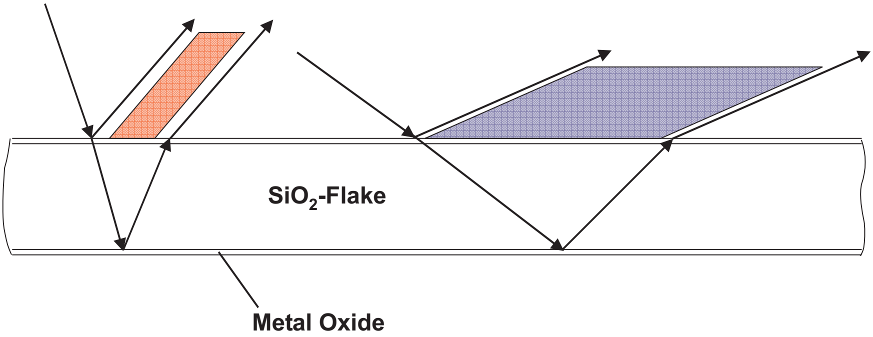


Figure 7–10: Colour variation vs. viewing angle of a SiO_2 flake pigment with a very thin metal oxide layer.

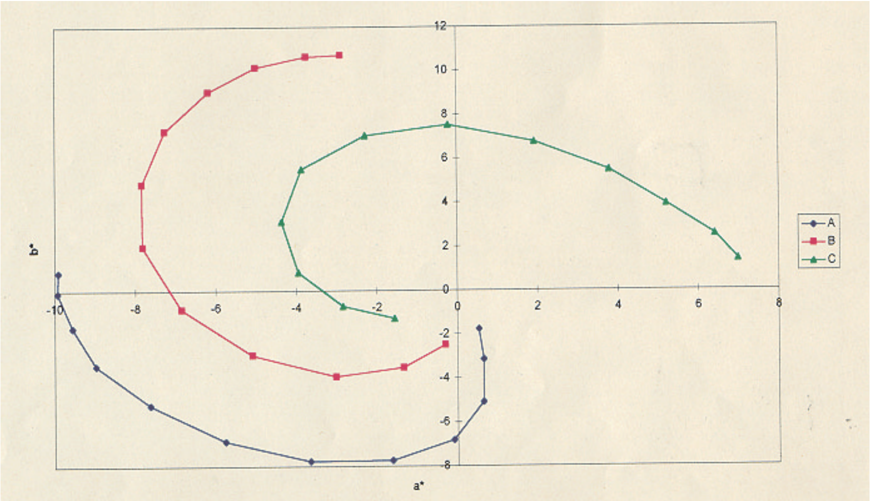


Figure 7–11: Angle dependent colour travel of Fe_2O_3 coated silica flakes of different thickness.

Improved color strength and very high luster are produced by the combination of precise thickness silica flake substrate materials, selected for their interference chromaticity, and by deposition of titania or iron oxide coating layers of the precise thickness required to generate the same interference color. These pearlescent pigments show stronger chromaticity L*a*b*-values than can be produced with mica-based designs.

A schematic diagram of the silica flake pigments is shown in Figure 7–12. The SEM micrograph in Figure 7–13 shows a cross section through a TiO_2 silica flake pigment. It shows clearly that both the SiO_2 flake and the TiO_2 layer thickness are precisely controlled.

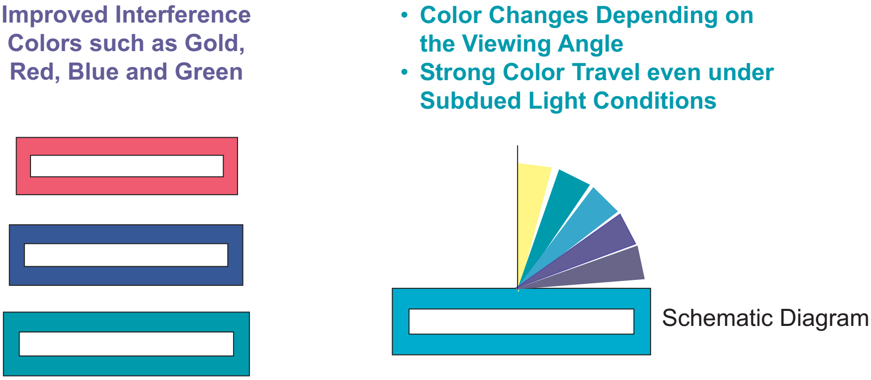


Figure 7–12: Properties of new pearl lustre pigments on silica flakes.

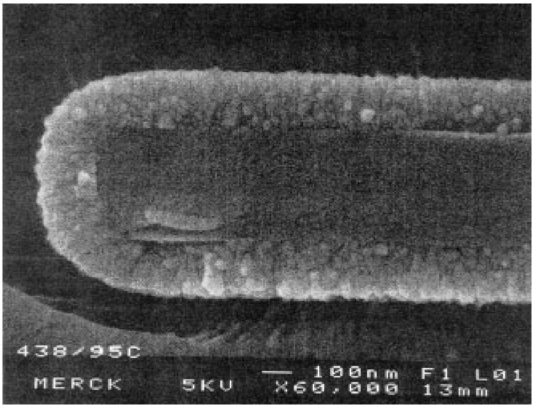


Figure 7–13: Cross-section through a silica flake coated with TiO_2.

7.2.3.3 Alumina Flake Pigments

Thin hexagonal monocrystalline Al_2O_3 flakes can be produced by hydrothermal processes[28–30]. The thickness of the resulting flakes is not uniform. Therefore, the resulting coated pigments merely assume a dull pearlescence.

Al_2O_3 flakes of a higher quality are produced by the following steps (Figure 7–14). An aqueous solution of an aluminum salt is mixed with small quantities of a titanium salt and phosphate. After neutralization, a sol or suspension is obtained,

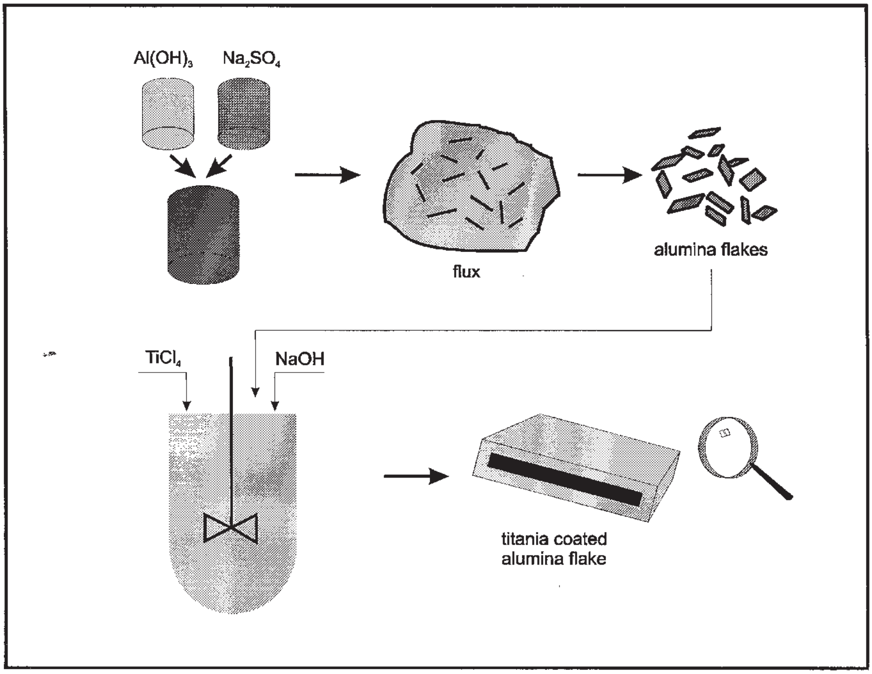


Figure 7–14: Process scheme for alumina pigments.

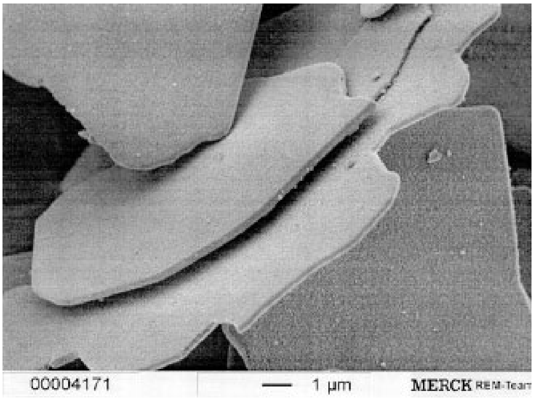


Figure 7–15: Electron micrograph of Al_2O_3 flakes.

which is then dried and heated to 900–1400 °C. After washing, very thin flakes are found which consist of corundum and show a high aspect ratio, a very narrow thickness distribution, and very smooth surfaces (Figure 7–15). The thickness can be controlled by the doping and reaction conditions. The resulting flakes are used as substrates in the aqueous-phase processes described above to prepare pearlescent pigments of very high luster. The advantage over a mica substrate lies mainly in the fact that all Al_2O_3 flakes have about the same thickness, which leads to true optical three-layer systems as for the SiO_2 flakes. A very interesting crystal-like effect can be achieved by using alumina flake pigments in application systems such as car paints.

7.3
Effect Pigments Formed by Coating of Metal Flakes

Metal effect pigments consisting of flakes or lamellae of aluminum (aluminum bronzes), copper and copper-zinc alloys (“gold bronzes”), zinc, and other metals have been well known for a long time[31]. Some of these metal flakes, especially aluminum platelets, can be coated with iron oxide in a CVD process[1, 11, 19]. These are commercially the most important pigments based on CVD. The metal flakes are fluidized in nitrogen gas at temperatures around 450 °C. Then the reagents $Fe(CO)_5$ and O_2 are injected into the fluidized bed. For a proper coating these must be highly diluted in an inert gas. Sometimes water vapor is added to reduce electrostatic charging. The thickness of the coating is controlled by the reaction time. The only side product is carbon monoxide, which is catalytically oxidized to CO_2. The resulting pigments show golden, orange and reddish metal-like effects.

The aluminum flakes can be coated with aluminum oxide and/or silicon dioxide in the liquid phase before the CVD process to reduce the reactivity of the metal and to create multilayer color effects. These pigments show strong angle-dependent coloristic effects (color travel)[32]. Metal halogenides are difficult to use as gas-phase precursors for metal oxide coating because of the reactivity of the metal flakes and the corrosion of steel in chloride atmospheres. The use of $TiCl_4$ and water vapor was described about ten years ago. However, no commercial products have, as yet, been introduced.

Mica flakes can also be coated in CVD processes using the same techniques as those discussed for metal flakes. In addition, one can also use metal chlorides as precursors for oxide coating on mica. However, essentially the same products can be obtained more easily by precipitating the oxides from the liquid phase.

7.4
Pigments Formed by Grinding a Film

Optical coatings that shift color with viewing angle have been adapted into optically variable films, pigments, and inks during recent years[8, 33]. These coatings are based frequently on metal-dielectric multilayer thin structures having large color shifts with angle, high chroma, a large color gamut, and light fastness. Different colors are produced by precisely controlling the thickness of the multilayers in the coating's structure. To maintain tight color tolerance, the layer thickness must be controlled to within a few atoms.

The metal layers frequently consist of chromium (semitransparent absorber metal) or aluminum (opaque reflector metal). Silicon dioxide or magnesium fluoride are the materials mostly used for the dielectric layers. In the case of pigment particles, there is a symmetrical arrangement of the layers, as shown in Figure 7–16, whereas optical coatings can also consist of a system of unsymmetrical layers. All these arrangements are the basis for an optical phenomenon called the Fabry-Perot effect.

Such multilayer interference configurations filter the spectrum into a sequence of high-reflectance regions surrounded by low-reflectance regions and thus lend themselves, in principle, to high-purity color production. The detailed spectral characteristics can be widely controlled by controlling the specific design parameters.

It has been found that for flaky pigment particles suitable for strong color-shifting effects, a symmetrical arrangement of the layers is necessary. A minimum of five layers and, for some optical purposes, even more may be required. The need for many layers tends to make such a design relatively impractical in any high-volume coating production. Therefore, for practical purposes, only the five-layer arrangement plays a role.

The pigment flakes can typically be manufactured sequentially in a series of specialized roll-coating machines. In the first machine a carrier film, the so-called release layer, is deposited on a moving polymer web (transfer foil). This release layer is soluble in organic solvents so that the later formed multilayer film can be removed from the web at the end of the process. After depositing this release layer, the transfer foil is placed in a vacuum deposition roll coater and the first metal layer (e.g., chromium) as the semitransparent absorber metal is deposited followed by the first dielectric layer (e.g., magnesium fluoride) and the opaque metal layer (e.g., chromium). The second dielectric layer and the second semitransparent absorber

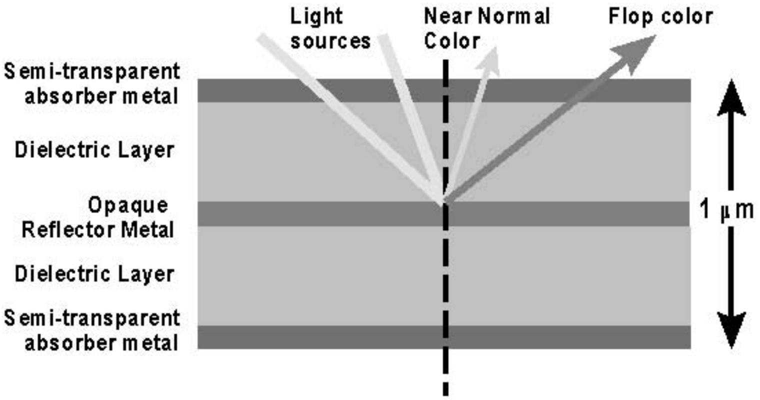


Figure 7–16: Scheme of design of optically variable pigments (OVP).

metal layer follow by the same deposition process. After this symmetrical multilayer interference coating has been deposited, the coated foil is removed from the vacuum chamber. In a subsequent step, the formed thin multilayer film is removed from the supporting transfer foil by dissolving the release layer. Transformation into pigment particles is done by grinding the removed part of the film into small platelets, which now show pigment dimensions (thickness 0.2–2 μm, diameter 1–100 μm).

Such types of effect pigments can be used for several applications and are on the market as so-called optically variable pigments (OVP). They have found a broad application especially in preventing counterfeiting of important documents such as banknotes, stock certificates, visas, passports, or car licenses. When incorporated into security inks and printed on bank notes and other documents of value, the pigments are effective against color copying by printers, copiers, or cameras and unauthorized lithographic reproduction[34].

7.5
Pigments Based on Liquid Crystal Polymers

Interference and angle-dependent color effects can also be achieved by layers or particles based on liquid crystal polymers (LCP)[8, 35]. Such effects can, for example, be produced by small plate-like substances which consist of an LCP material itself, or by small platelets which are uniformly coated with a cross-linked liquid crystalline polymer in a chiral-nematic arrangement[36].

Liquid crystals are organic compounds in a state of matter intermediate between that of an isotropic liquid and an anisotropic crystalline solid[37]. Most liquid crystalline molecules are markedly elongated and rod like. In nematic liquid crystalline materials, the directions of the long molecular axes (directors) are arranged parallel to each other. Adding a chiral molecule to a nematic phase causes a superstructure comparable to the steps of a spiral staircase. The structure can be understood as

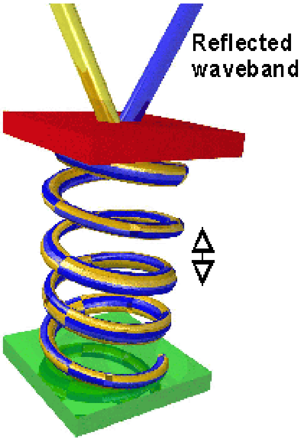


Figure 7–17: Scheme of a liquid crystal film.

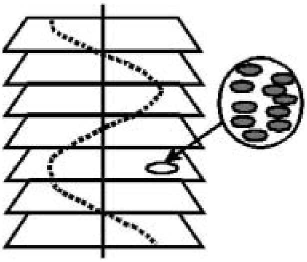


Figure 7–18: Chiral cholesteric (nematic) liquid crystal structure. The dotted line shows a helical path within the medium. Pitch length p = 360° rotation.

being composed of nematic layers having the director rotated by a certain angle with respect to an adjacent layer, eventually building up a helical array (Figure 7–17).

The thickness of a 360° turn of the director represents the pitch length p of the helix[35]. The color design of LCP pigments in paint films or of pure LCP films has its origin in an interference phenomenon. In this case, only incident light with a wavelength equal to the LCP lattice separation interferes and is reflected.

Because of the change of refractive index from layer to layer, the helical structure gives rise to interference effects (Figure 7–18). When white light is incident normally on a film or an oriented arrangement of platelet-like particles of a cholesteric material with the helical axis perpendicular to the substrate, selective reflection of a finite wavelength band occurs similar to Bragg X-ray reflection. The reflected band is centered about a wavelength l_0, which is related to the helical pitch length p of the phase and its average refractive index n by $l_0 = np$[35, 36].

On the other hand, a structure which has a helical superstructure with no change in the refractive index can also reflect light just like cholesteric phases[38]. In this case, it is not so much a change in the refractive index that gives rise to the optical effect but rather the superstructure.

The reflected light is circularly polarized with the same sense of polarization as the helical sense of the liquid crystal phase. Light circularly polarized in the opposite manner is transmitted through the sample together with those wavelengths of light not being reflected. Light experiences a double refraction as a result of the anisotropy of the system. The bandwidth $\Delta\lambda$ of the selectively reflected band is described by the relation $\Delta\lambda = p\Delta n$. The angular dependence for an incident and observed angle Θ is given by $\lambda_\Theta = \lambda_0 \cos \Theta$.

The reflected light waves from the layers increase the intensity of the total reflection. The maximum reflectivity of one polarization state requires at least 6 helices or a thickness of about 3 μm. The most efficient reflection is given by layers with a thickness of up to 10 μm.

Cholesteric materials are temperature sensitive and show a thermochromic effect. The reason for this is that the pitch length of the helix and the refractive index are temperature dependent[35, 36].

Liquid crystal polymer films are transparent to visible light, including when they are in the form of platelets and coatings on substrates dispersed in a transparent paint film. These films need to be deposited on a dark base coating. Light is transmitted through the liquid crystal polymer, but some wavelengths are absorbed by the dark substrate or base coating. The liquid crystal polymer will be aligned parallel to the substrate, either as a film coating or on the interference pigment platelets within the paint film. This will then show a particular color in the orthogonal view and another color when observed at an angle. Such angle-dependent color phenomena give a very striking effect, which is of great interest for security applications. Paint coatings incorporating such pigments must be constructed of several layers with the liquid crystal materials in one of the inner layers only.

A number of interference pigments of this type are based on polysiloxanes. They are formed first as a thin cross-linked film of liquid crystalline polymers, and these are then ground to small platelets. The interference pigments themselves are colorless and transparent. The color effect is based on the regular structure and on the uniform arrangement of the liquid crystalline molecules. This gives rise to the reflection and subsequently interference with light of a particular wavelength. The other parts of the light go through the pigment particles. Very interesting color effects are possible based on these optical principles.

Liquid crystalline siloxanes are limited with respect to the glass transition in comparison to other backbone systems, such as poly(meth)acrylates. Glass transition temperatures of up to 80 °C can be achieved, but there is a limit for the variations of the mesogenic groups[39]. Therefore, cross-linking is the preferred method. The presence of at least some polymerizable moieties within the side chain groups is necessary. Typical examples for these groups are epoxides, cinnamates, or methacrylates.

After polymerization and crushing, the liquid crystal polymer platelets can be used as iridescent pigments[40]. Such platelets can be suspended in inorganic and organic media, especially lacquers. The spray technique is mostly used for the application in paint films. The color effects are very strong if black substrates are used to ensure the absorption of the transmitted light. Very interesting colors can be obtained when combined with other effect pigments or in mixtures with conventional pigments[41].

Interference pigments based on liquid crystalline materials are prepared by a doctor-blade coating of the polymers in the liquid or liquid crystalline state on an even surface. The doctor-blade process leads to a thin film wherein a homogeneous orientation of the molecules takes place. It is only after this orientation process that the film shows an interference color. The films are then cured and crushed by special techniques to yield platelets of liquid crystalline polymers showing interference effects.

7.6
Pigments Based on Holography and Gratings

Grinding of holographic films, when done in a suitable manner, can lead to small holographic particles[8, 42]. These so-called holographic or hologram pigments are relatively new materials for attaining special optical effects in different application media. A structure of a holographic pigment particle is shown in Figure 7–19. Gen-

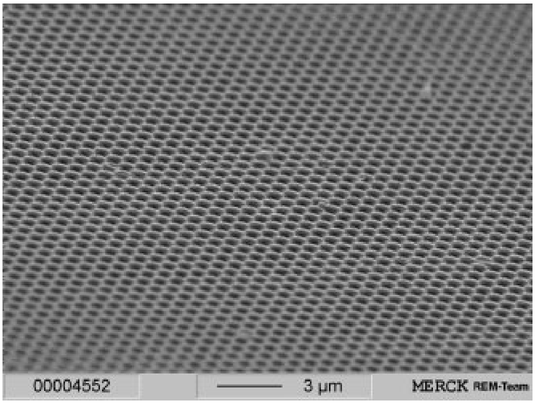


Figure 7–19: SEM photo of a holographic film made by aluminum metal deposition on a polymer film to be used for the production of holographic pigments. The average distance between the peaks of the structure is about 800 nm.

erally, any hologram base material on which an interference band corresponding to the wave face of light from a substance is formed as a hologram image may satisfactorily be used with no specific limitation for the production of holographic flake pigments. For practical use, holographic mirrors are preferred for the manufacture of those pigments. A holographic mirror is the simplest reflection hologram. It can be created by splitting a laser beam and recombining the beams at a photosensitive layer on the thermoplastic film (two-beam method). Alternatively, it can be created by projecting a laser beam through the photosensitive layer onto a mirror (single-beam method).

Holographic flake pigments frequently have a band-centre wavelength of about 380–1100 nm and an effective bandwidth of about 10–200 nm. The pigment particles have a thickness of about 1–100 µm, an average diameter of about 10–300 µm, and a thickness-to-diameter ratio from about 1:2 to about 1:60. Holograms can be converted to pigment particles of the desired size by any conventional means, such as grinding, ball milling, attritor grinding, or two-roll milling. One possibility that can be used is to cool the hologram below its glass transition temperature, for example in liquid nitrogen, before grinding. It is also possible to grind the hologram in cold water, such as ice water. As an alternative, the grinding equipment can be refrigerated to cool the hologram to below its glass transition temperature.

Holographic flake pigments are useful for the preparation of decorative coatings that can be used to emphasize the lines and contours of a three-dimensional surface. Another possibility is the application in molded plastics to provide a decorative appearance, e.g., in tiles.

7.7
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8
Crystal Design of High Performance Pigments

Peter Erk

8.1
Introduction

With few exceptions, pigments exist as crystalline solids, and all of their essential properties depend on structural and morphological features associated with the solid state. For an efficient design of high performance pigments it is necessary to analyze and to understand the molecular reasons behind those solid properties which give rise to the technical performance of these materials (Table 8–1).

Table 8–1: Microscopic (molecular and crystal) and solid state properties of crystalline materials related to their technical performance.

Molecular	***Crystal properties***	***Solid***	***Technical performance***
		Hardness	Agglomeration / flocculation
	Lattice energy	Refraction	Wetting / dispersibility
Crystal structure	Particle size	Cohesion	Thermal stability
Polarizability	Crystal habit	ξ-potential	Color / optical properties
Dipole moment	Density	Solubility	Weatherfastness
Conformation	Defects	Absorption	Filtration / caking
Constitution	Surface structure	Conductivity	Dispersion rheology
	Band structure	Magnetism	Compaction properties
		Brittleness	Powder flow / density

Crystal design covers aspects of crystal engineering[1] (designing the bulk structure), morphology control[2] (designing particle size and shape), and interfacial engineering of pigment particles. Computational tools are the backbone of crystal design, and most of them have just become available because of the dramatic increase of computing power over the last decade. With their help, general properties of crystalline solids can be investigated by statistical analysis[3], structural features may quickly be visualized, and computational simulations can help to analyze and to interpret the observed features. Guidance for the design of new pigments may then be drawn by combining these insights with chemical and crystallographic knowledge, experience and intuition[4].

For conceptual reasons this chapter is restricted to organic pigments. Although there are some fundamental differences between organic and inorganic pigments which originate from the different bonding situations in the solids, many of the principles outlined here for organic pigments may be applied to inorganic pigments as well.

8.2
Crystal Engineering of Organic Pigments

8.2.1
Close Packing

The molecules in organic crystal structures are usually close packed. The ratio of the volume occupied by the molecules to the cell volume, the Kitaigorodskii packing coefficient C_K, ranges from ca. 0.65 to 0.8[5]. Organic pigments usually can be found in the regime above 0.74, thus packing more efficiently than equally sized spheres (Table 8–2, Figure 8–1).

The reasons behind close packing are the molecular shapes and the intermolecular forces. In a first approximation, medium-range isotropic forces define close packing. Long-range anisotropic forces of mainly electrostatic nature lead to specific molecular arrangements like centrosymmetry, herring-bone stacking and polar structures. Molecular shapes must support close packing by forming a space filling pattern if oriented according to the long range forces.

All crystal structures of high performance pigments are characterized by an excellent match of their molecular shapes to form close packed solids and to simulta-

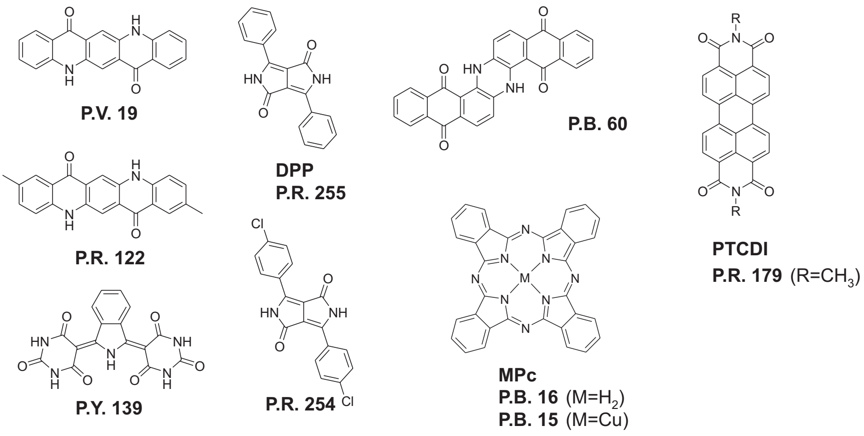

Figure 8–1: Chemical structures of the pigments listed in Table 8–1.

Table 8–2: Crystallographic data, packing coefficient C_K, calculated packing energy PE and specific packing energies SPE1 (PE/molecular mass), SPE2 (PE/molecular volume) of organic pigments.

	PY 139	***PR 255***	***PR 254***	γ-***PV 19***	β-***PV 19***	***PR 122***	***PB 60***	***PR 179***	β-***PB 16***
Formula	$C_{16}H_9N_5O_6$	$C_{18}H_{12}N_2O_2$	$C_{18}H_{10}Cl_2N_2O_2$	$C_{20}H_{12}N_2O_2$	$C_{20}H_{12}N_2O_2$	$C_{22}H_{16}N_2O_2$	$C_{28}H_{14}N_2O_4$	$C_{26}H_{14}N_2O_4$	$C_{32}H_{18}N_8$
Mass [a.u.]	367.3	288.3	357.2	312.3	312.3	340.4	442.4	418.4	514.6
Space group	C mca	$P\,\bar{1}$	$P\,2_1/n$	$P\,2_1/c$	$P\,2_1/n$	$P\,\bar{1}$	$P\,2_1/a$	$P\,2_1/c$	$P\,2_1/a$
Z	8	1	2	2	2	1	2	2	2
Mol. V [å^3]	275.0	250.6	283.0	267.1	267.1	301.2	362.9	344.4	440.8
Surface [Å^2]	310.4	280.5	316.4	295.6	295.6	335.4	385.3	365.5	472.9
Reference	X								
Cell V [Å^3]	2800.2	334.4	720.8	708.6	685.1	392.5	926.5	873.2	1181.2
ρ [g/cm^3]	1.742	1.432	1.646	1.464	1.514	1.440	1.586	1.591	1.447
C_K[a)] [%]	80.0	77.3	80.4	77.5	80.7	79.3	80.6	82.0	77.0
PE [kcal/mol]	–86.4	–56.8	–77.2	–60.0	–59.3	–62.5	–69.2	–69.1	–57.5
MLRA[b)]	–62.4	–42.5	–	–45.3	–45.3	–48.1	–61.1	–53.8	–57.7
SPE1[c)]	0.235	0.197	0.216	0.192	0.190	0.184	0.156	0.165	0.112
SPE2[d)]	0.278	0.202	0.244	0.203	0.201	0.186	0.180	0.189	0.122
vdW	–30.7	–28.7	–31.5	–31.2	–35.2	–40.8	–56.2	–49.4	–56.0
Cb[e)]	–42.0	–20.9	–38.2	–21.6	–17.9	–16.6	–13.0	–19.7	–1.5
H–bond	–13.7	–7.2	–7.5	–7.2	–6.2	–5.1			

a) $C_K = 1$ – free volume in cell / cell volume; free volume has been determined by a probe of 1.0 Å diameter.

b) Packing energy calculated according to multilinear regression analysis from[20], see also Eq. (8–1).

c) SPE1 = PE / molecular mass.

d) SPE2 = PE / molecular surface.

e) Coulomb energy based on charge equilibration[16] derived atomic point charges.

neously maximize their intermolecular forces. In many cases molecular symmetry supports the formation of close packed solids by coinciding with symmetry elements of the crystal lattice (see Figure 14–11 in Chap. 14). But molecular symmetry is not a stringent necessity for close packing, as examples of benzimidazolone and isoindoline pigments demonstrate (for good examples see Figures 10–5a and 10–5b in Chap. 10, and Figure 14–10 in Chap. 14).

8.2.2
Crystal Energy

In general, the low solubility and high thermal stability of pigments are indicative of large packing energies due to the strong intermolecular attractive forces within crystals. These intermolecular forces may be evaluated using various molecular modeling methods. For practical reasons, lattice or packing energies of molecular crystals are calculated by force field methods.

The packing or lattice energy PE of a molecular crystal is defined as the sum of all intermolecular potentials, i.e. van der Waals plus Coulomb energy (Eq. 8–1). In this chapter the van der Waals energies have been calculated using the 6–12 potential Lennard-Jones type function and the common and universal Dreiding 2.21 parameter set[15]. Atomic point charges were derived from charge equilibration within the packing[16]. The Coulomb energy has been calculated by the Ewald summation method. All calculations have been performed using the modeling package CERIUS2©[17].

$$PE = \sum AR_{ij}^{-12} - BR_{ij}^{-6} + \sum \frac{q_i q_j}{R_{ij}} \qquad (8\text{–}1)$$

For a series of high performance pigments, packing energies have been found to be in the range of $-56.8 \geq PE \geq -86.4$ kcal/mol (Table 8–2). In the case of P.B.16 the calculated value of the packing energy of –57.5 kcal/mol corresponds reasonably to the experimentally determined sublimation enthalpy of 50 ± 2 kcal/mol[18]. Experimentally determined sublimation enthalpies for pigments are rare, but, as a rule, for calculated packing energies, an error of ca. 10–15 % (roughly the same as for experimental data) must be considered.

Analyses of large sets of structures have shown that the packing energy correlates reasonably with the molecular volume and also with the number of valence electrons in the molecule[19]. In another approach, neural network techniques have been used to identify a correlation between molecular composition and sublimation enthalpy based on 60 compounds[20]. The correlation is based on a 3-parameter model involving the number of carbon atoms C, the number of hydrogen bond donors HBD and hydrogen bond acceptors HBA (Eq. 8–2).

$$\Delta H_{sub} = 3.47 + 1.41 \times C + 4.55 \times HBD + 2.27 \times HBA \qquad (8\text{–}2)$$

According to Eq. (8–2), atoms which induce polarity and which are capable of hydrogen bonding contribute considerably more to the packing energy than carbon atoms. The specific packing energies SPE2 (per mol. surface) which are based on the force field derived packing energies in Table 8–2 clearly confirm this trend. They increase with the ratio of hetero to carbon atoms in the molecule.

The empirical correlations do not differentiate between configurational isomers or polymorphs, but they are useful in order to estimate the overall expected values of PE. As can be seen from Table 8–2, the values derived from the multilinear regression analysis (MLRA) are at average 28 % (!) lower than the PEs calculated by the force field, which indicates a likely overestimation of polar forces by the chosen charge model. In contrast, the values for the least polar molecule listed in Table 8–2, P.B.16, are almost identical.

From the statistical regression analyses of homologous sets of crystal structures (e.g. hydrocarbons, oxo and aza hydrocarbons), the SPE2 may roughly be estimated to range from 0.10 to 0.16[19]. Regardless of the method for calculating the packing energy, specific packing energies SPE2 of most pigments in Table 8–2 exceed these average values significantly, pointing to outstanding thermodynamic properties of these solids. For the moment, the limited number of high performance pigment crystal structures and the diversity of their chemical constitution do not allow for a more detailed and comprehensive analysis of the thermodynamic data of the structures.

8.2.3
Specific Interactions

Creative concepts in crystal engineering make use of supramolecular synthons to define specific interactions in molecular solids, which may be employed to design crystal packings[1, 4]. The synthon approach has been used to produce close packed structures, and, on the contrary, to build open network structures[21]. In the packing motifs of high performance pigments several types of specific interactions (synthons) can be identified.

The chlorine-chlorine interaction is somewhat controversially discussed in the literature[22]. In high performance pigments it supports the packing energy and hence the stability, as can be seen by comparing P.R.255 to P.R.254 in Table 8–2. Excessive and favorable use of chlorine-chlorine interactions is made in P.G.7, P.G.36, P.Y.110 and P.Y.138 (Figure 8–2a).

However, chlorination does not in all cases lead to an improvement of the pigmentary character. Tetra- and octachlorinated derivatives of perylenetetracarboxylic acid are twisted and exhibit packing in many cases less favorable than that with planar unsubstituted perylene pigments (Figure 8–2b above)[23].

Hydrogen bonds deserve special emphasis. Their strength depends on the acidity of the H-donor and the basicity of the hydrogen-bond acceptor involved. Supramolecular synthons based on hydrogen bonds can be found in many organic pigments. Quinacridone pigments of the α-type (P.R.122, P.R.202)[10, 11], the perylene pigment P.V. 29 and DPP pigments[7, 8] form ladder-like arrangements induced by the two-point recognition of the molecules via hydrogen bonds (Figure 8–3a). The similarity

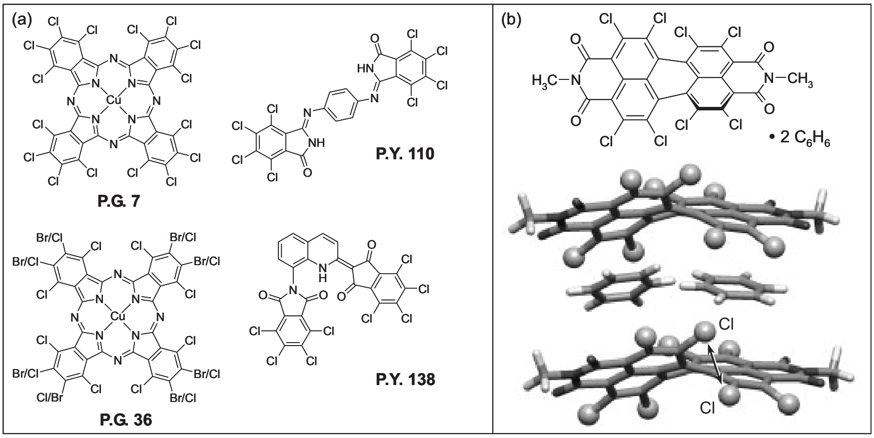

Figure 8–2: a) Chemical structures of chlorinated pigments (left); b) stacking of the bis-benzene-solvate of octa-chlorinated P.R. 179 (right).

of the hydrogen bond motifs and the molecular shapes of DPP and quinacridone have been used to produce solid solutions of both pigments[24].

Other pigment classes, where hydrogen bond functionality was introduced in order to achieve lower solubility, are the Naphthol AS and benzimidazolone pigments. A striking example for combining hydrogen bonds with proper molecular symmetry is P.Y.139[6] (Figure 8–3b, see also Figure 14–11, in Chap. 14). All hydrogen bond donors and acceptors in the molecule participate in an extensive hydrogen bond network, which is essential for the superior properties (e.g. temperature stability) of this isoindoline pigment.

The packing of aromatic hydrocarbons has been subjected to intense investigations[25]. Many organic pigments are derived from polycyclic aromatic hydrocarbons, and their basic packing behavior often reflects this relationship.

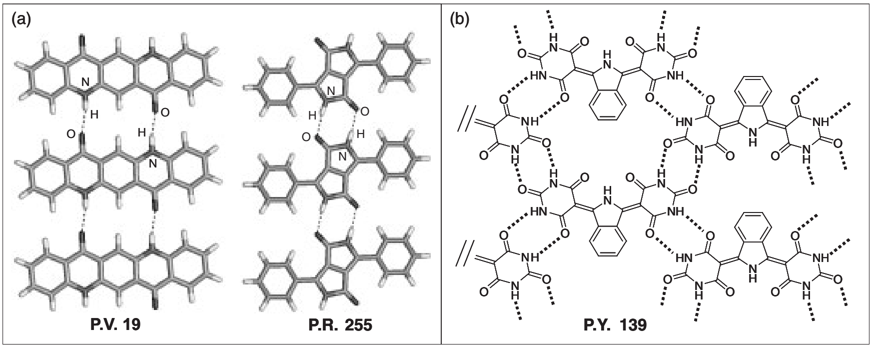

Figure 8–3: Hydrogen bond recognition within pigments: a) hydrogen bond-directed ladder-like arrangements of P.V. 19 and P.R. 255 (left); b) hydrogen bond network of P.Y. 139 (right).

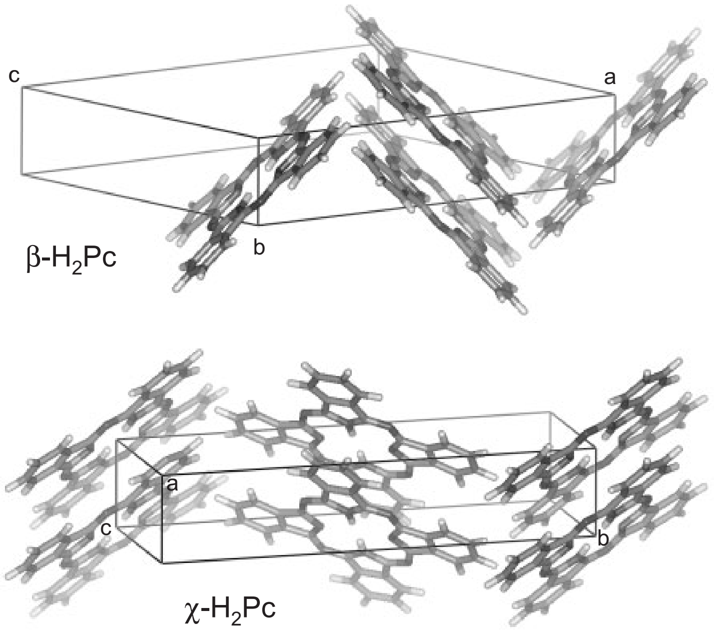

Figure 8–4: Herringbone-type interactions in phthalocyanines: edge-on-face arrangement in β-H_2Pc (upper); corner-on-face arrangement in χ-H_2Pc (lower).

Generally, aromatic systems either form stacks with strong interactions of the π-systems or are arranged herringbone-like with close contacts between the π-system of one molecule and the peripheral hydrogen atoms of adjacent molecules[26]. π-Stacking is common for polycyclic pigments and contributes largely to the packing energy. In contrast, herringbone-like interactions contribute only marginally to the packing energy of large molecules. Various phthalocyanine polymorphs differ mainly in herringbone-type interactions (Figure 8–4). However, this type of interaction occurs rarely among other pigments and can be found e.g. in P.B.60[12] and P.V.19[9].

Connecting heteroatoms to aromatic systems changes the polarity of the molecules considerably. This is also reflected by preferences in the stacking arrangement of large polycyclic systems. In order to find out which stacking arrangement in PTCDI pigments is preferred energetically, the interaction energy of two unsubstituted PTCDI molecules was calculated. This was done by plane-parallel alignment of the molecules at a distance of 340 pm (picometers) and moving them relative to one another in the molecular plane. Van der Waals and Coulomb energies (derived from the electrostatic potential[27]) of the molecular pair were calculated after each 2 pm shift.

As expected, van der Waal interactions merely reflect the degree of overlap between the molecules, whereas the addition of Coulomb interactions gives rise to a structured interaction map (Figure 8–5), which yields information about the stacking arrangement of minimum energy preferred by the perylene fragments.

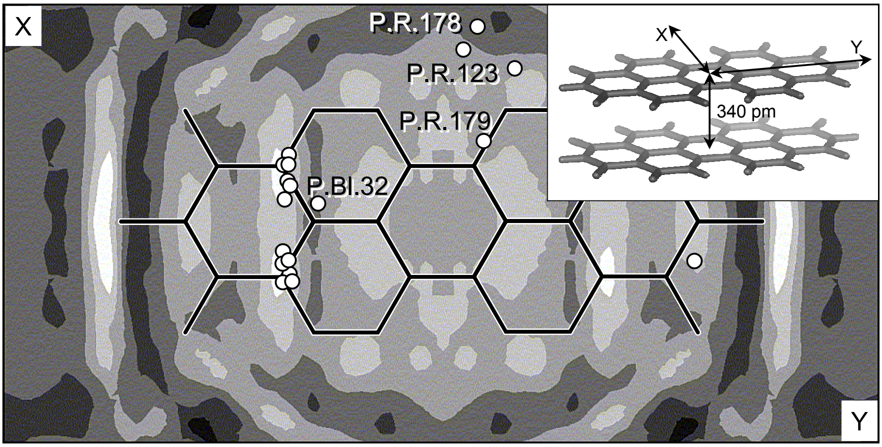

Figure 8–5: Interaction energy map of two parallel stacked PTCDI molecules (R=H). Different gray shades denote zones of 10 kcal/mol. Open circles illustrate the position of known crystal structures.

Apparently, for most of the 22 known perylene structures, the PTCDI fragments actually do determine the molecular arrangement in the stacks (see Figure 8–5). It is noteworthy that this is not true of the technical pigments used in commercial products (e.g. Pigment Red 123, 178 and 179). Stacking arrangements with highly attractive interactions between perylene systems yield mainly bluish-red pigments. However, throughout the coloristic evolution of perylenes "brilliant red" or black pigments (e.g. Pigment Black 32) were of course selected. In order to engineer solids of that type, predictions of full 3-dimensional crystal structures are needed.

8.3
Crystal Structure Determination

In the process of mapping molecular functionality to the physical and technical properties of a pigment, crystal structure is key information which can be looked at as a molecular property itself. Therefore, the determination and simulation of crystal structures provide core know-how for all aspects of designing high performance pigments. About five dozen crystal structures of organic pigments are published in the literature, but many more are kept as proprietary know-how in the archives of pigment manufacturers.

Most crystal structures of organic pigments have been solved classically from single crystal X-ray diffraction data. However, because of their limited solubility and high sublimation enthalpy, single crystals of pigments suitable for crystal structure determination are difficult to grow, or require special techniques such as high vacuum / high temperature sublimation[14], controlled cooling crystallization from high boiling solvents[13, 28], or gel crystallization.

In cases of metastable polymorphs (susceptible toward crystal growth conditions), twinned crystals, and materials of extreme insolubility, electron diffraction or X-ray powder data can be used as a basis for structure determination.

Electron diffraction has been used to investigate bulk structures of pigments[29] as well as thin layers. A strength of this method is the spatial resolution which allows the structural characterization of single microcrystals even in mixtures of polymorphs[30]. Even more striking, the occurrence of two polymorphs in the same submicron crystal may be analyzed, as in the case of α/β copper phthalocyanine[29].

Throughout past decades, the number of methods giving access to structure solutions from polycrystalline powders has been grown significantly[31]. However, all of these methods still require samples of appropriate crystallinity, yielding high resolution X-ray powder patterns suitable for indexing. At present, indexing of lower-resolution powder patterns in real-life situations limits the access to structure information, because of low quality of data obtainable from routine samples by routine diffraction methods. To obtain high resolution powder data, considerable effort must be put into the crystallization (usually ripening) of the material and in the diffraction experiments. Again, electron diffraction is an alternative tool to determine unit cell constants from microcrystals, and is in many ways complementary to X-ray powder diffraction.

Despite such restrictions, real space crystallographic methods based on genetic algorithms[32], Monte-Carlo methods[33], or simulated annealing techniques[34] have proved to be powerful means for structure solutions from X-ray powder patterns. Provided with the unit cell, the composition and configuration of the asymmetric unit, and sufficiently texture-free diffraction data, refinable structure models can be obtained within minutes on a personal computer, even for molecules with multiple internal degrees of freedom[35]. The resulting structure models are then refined by Rietveld techniques, which use the whole profile of the X-ray diffraction pattern for refinement[36].

A polymorph of the quinoid red crystal form of fluorescein was one of the first examples of a complex molecule whose structure was determined by a real space approach based on the Monte-Carlo method[37]. The same method has more recently been used to solve the structure of the β-form of the latent pigment boc-DPP (Figure 8–6). The kinetics of the thermal fragmentation to DPP differs for both forms. The more reactive α-form crystallizes (less ordered) with three conformationally different half-molecules in the asymmetric unit. This structure was initially solved from single crystal data. However, it could be improved substantially by Rietveld refinement, thus demonstrating the potential of this technique[38].

Apart from purely diffraction-based structure determinations, minimization of the packing energy offers an alternative route to the solution of structures from indexed powder patterns (Figure 8–7). In addition to R-factors, packing energy may be taken as an additional criterion for the correctness of a structure model. Packing energy minimizations within fixed lattices yield structure models of high geometrical accuracy. This approach has been successfully applied to a variety of pigments, e.g. x-H_2Pc[39], the perinone DHP[40], PY13 and PY14[41] (Figure 8–6). In the case of the perinone DHP, minimum energy packings have been calculated for all possible conformations of the hydroxyl functions in two space groups ($P\ na2_1$, $P\ 2_12_12_1$). The experimental structure corresponds to the lowest energy packing in space group $P\ na2_1$. However, several minima in space group $P\ 2_12_12_1$ were found to be lower in energy, which may be explainable by inadequacies in the force field.

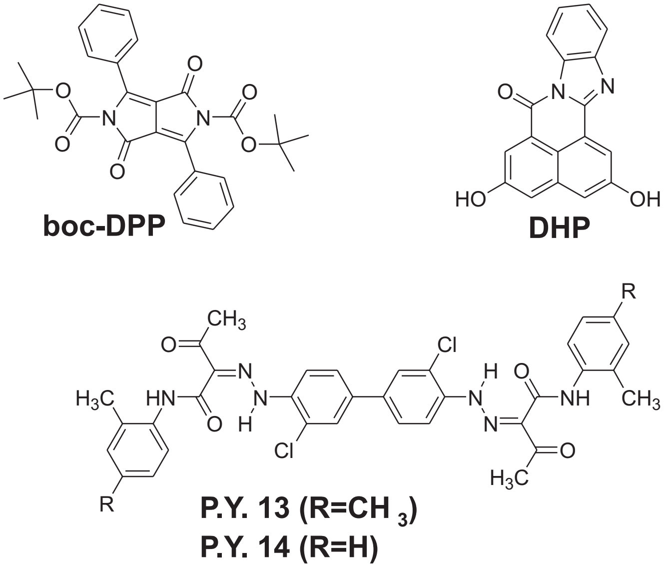

Figure 8–6: Examples of pigments whose structures have been solved with the aid of packing energy calculations.

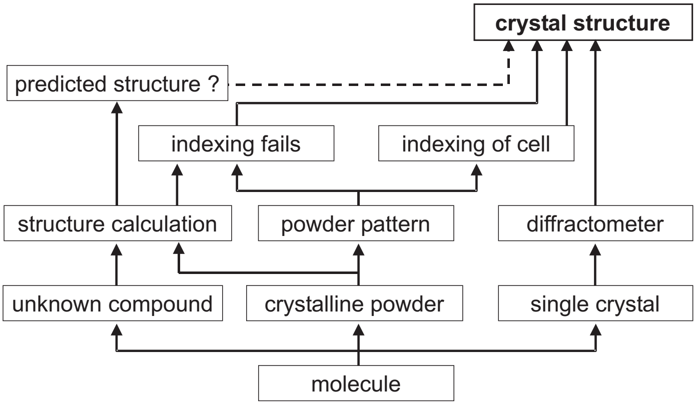

Figure 8–7: Scheme of the possible ways to determine crystal structures.

8.4
Crystal Structure Calculation

8.4.1
General Methods

"Are crystal structures predictable?[42]" This question is still a "Holy Grail" for crystallographers, solid-state physicists and solid-state chemists, and has been the subject of controversial discussions for more than a decade.

In order to calculate a crystal packing, it must first be constructed from molecules of specific shape to obtain a maximum of lattice energy, resulting from molecular interactions. To date there is no analytical mathematical solution to this problem.

However, several research groups are even now trying to close this gap and develop methods for the ab initio calculation of crystal structures on the basis of chemical composition and molecular structure, without any additional experimental data[43]. The main problems here are to locate global energy minima within the numerous possible low energy crystal packings, and then select possible polymorphs by means of accurately calculated physical criteria, e.g. packing energy or density.

In general, all methods of global minimization follow the same principles. In a first step, possible structures (usually several thousand structures per space group and per molecular conformation) are generated using systematic or random techniques. At this stage only intermolecular interactions are taken into account. Secondly, the optimization of the generated structures by energy minimization of a force field leads to all possible close packed structures representing local energy minima (with respect to the force field parameters in use). As a rule, the final optimization of the structures using force field methods is the most time-consuming step. Here, depending on the individual problem, either the intermolecular interactions alone in the crystals are taken into account, or the molecular geometry plus the crystal packing are optimized.

Generally, several hundred unique crystal packings remain after optimization. They must then be evaluated with respect to either calculated physical properties such as density and lattice energy, or by means of empirical scoring functions[44].

Absolute predictions of crystal structures require that calculated criteria, i.e. packing energies, are accurate enough and allow for a judgement of the stability order of the virtual polymorphs. At this time, however, no force field or quantum mechanical method fulfills this requirement. The multipurpose force fields now in use just do not yield reliable predictions of the thermodynamic stability of a crystal packing, and even specifically tailored force fields may lack transferability. Nevertheless, correctly predicted structures can often be found in the top spots of the energy ranking list, which had been calculated using force field methods. Thus, methods to calculate crystal structures certainly do have a degree of predictive success[45].

8.4.2
Crystal Structure Calculations of Pigments

Pigments are comparatively large molecules. The relationship of the number of atoms versus the computation time for a crystal structure calculation is approximately linear. However, pigment molecules are fairly rigid and have limited conformational flexibility, which reduces computational expenses if only one or a few conformations must be considered. In many cases, even distinct low energy conformations may be obtained from molecular or quantum mechanical calculations.

Crystal structure calculations have been successfully employed to obtain the structures of DPPI[46], BTI[47] (Figure 8–8), the α-form of quinacridone[48], and the α-form of copper phthalocyanine[49]. Because of low crystallinity and excessive peak overlap, the powder patterns of these compounds could not be indexed. In all cases global minimization techniques yielded structure models, which subsequently could be refined by Rietveld methods to solve the structures.

In the case of DPPI, two symmetrical rotamers were taken into account with dihedral angles of 60° and 90° between the perylene plane and the phenyl substituent. According to the expected probability of occurrence, centrosymmetric space groups (P $\bar{1}$, P 2_1/c, C 2/c) were selected for the calculation. Possible structures were generated systematically and the energy of each structure minimized considering full

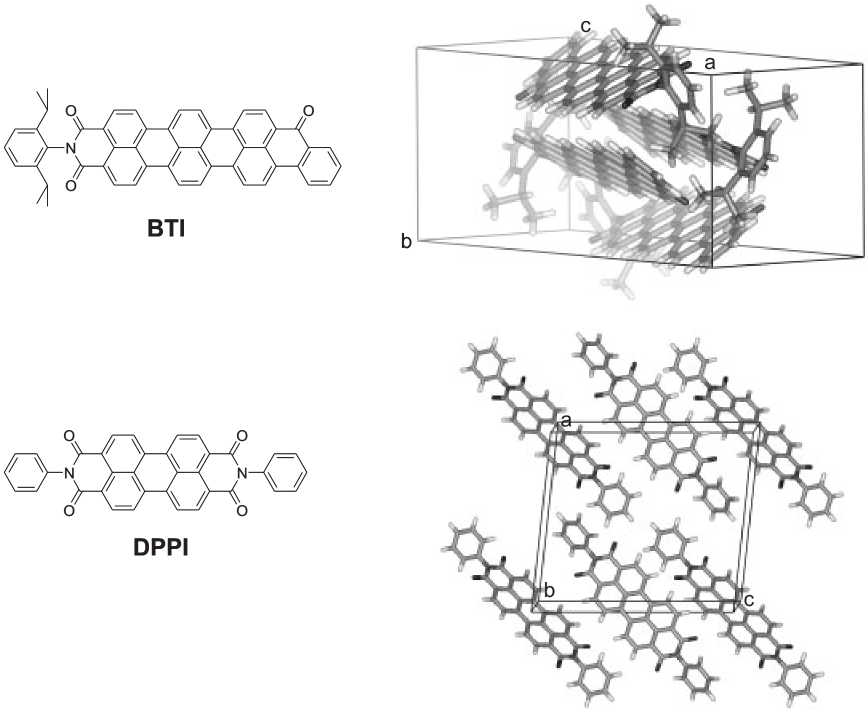

Figure 8–8: Crystal structures of pigments which have been solved by ab initio crystal structure calculation.

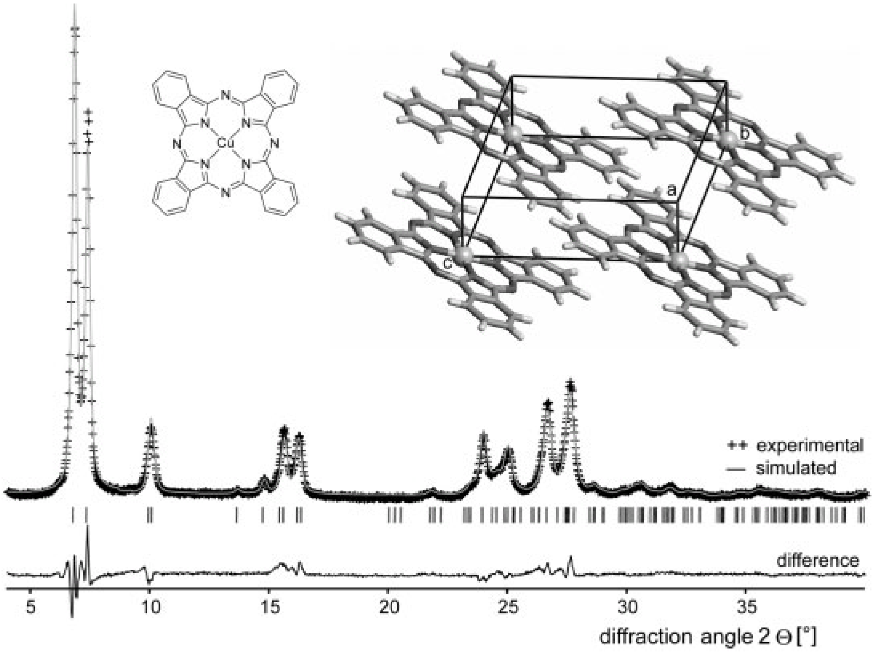

Figure 8–9: Rietveld plot and crystal packing of the α-form of copper phthalocyanine; $R_{wp} = 0.068$.

molecular flexibility. Automated comparison of the resulting packings to the experimental powder pattern[50] yielded a structure model in space group P $2_1/c$ suitable for refinement. However, this model, which could be refined to $R_{wp} = 0.229$, was only ranked fourth by packing energy.

A similar procedure was used to determine the structure of the α-form of copper phthalocyanine, P.B. 15 (Figure 8–9). This structure determination helped to clarify contradictory statements in the previous literature[51, 52], which have over time led to a somewhat enigmatic status of what is called an α-phase of phthalocyanines in the literature and in textbooks.

8.4.3
Crystallochromy

Even in the days before X-ray crystallography, color chemists have recognized polymorphism by color changes. In contrast to molecularly dissolved dyes, excitations in pigment crystals are affected by supramolecular interactions in the solid state. As a consequence, the absorption spectrum of a pigment crystal differs from the spectrum of the isolated pigment chromophores (Figure 8–10). This phenomenon is widely known as crystallochromy, and examples of many pigment classes are well documented in the literature, e.g. the polymorphs of phthalocyanine and of quinacridone.

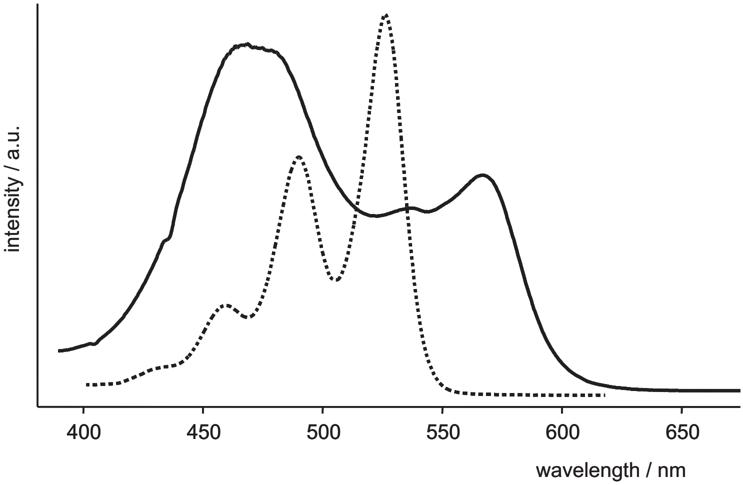

Figure 8–10: Absorption spectra of P.R. 179 in solution (dashed line) and in the solid state (solid line).

For several pigments, the origins of crystallochromy could be derived from accurate structure data in combination with spectroscopic investigations. Primarily, the distortion of the molecule due to packing effects may change the absorption spectrum of the solid. Molecular distortions have been identified to be the reason for the solid state absorption properties in various phthalocyanines, especially in titanyl phthalocyanine[14, 53].

Perylene pigments (PTCDIs) probably show the phenomenon of crystallochromy in its most pronounced form. PTCDI molecules form regular stacks in the crystal with an average distance of 340 pm (picometers) between them. For different substituents of the imido nitrogen the overlap between the chromophores varies within the stacks (Figure 8–5). As a consequence, the solid state colors of PTCDIs range from orange to black depending on the stacking arrangement in the crystal packing, while the color in solution always stays orange.

Firstly, Klebe et al. established an empirical correlation for uniformly stacked perylene pigments[54]. Later, a 1d-band-structure based explanation derived from extended Hueckel calculations was published by Hofmann and Kazmaier[55]. Recently, Mizuguchi has investigated crystalline films of perylene pigments by temperature dependent spectroscopy. These experiments demonstrate the excitonic nature of the longest wavelength absorption band[56]. Similar analyses allow for the explanation of the absorption properties of diketopyrrolopyrroles, which can be correlated to the molecular arrangement in the crystal structure[57].

8.4.4
Morphology Calculation

Elucidating crystal structures paves the way to understanding and controlling all properties of high performance pigments. This involves the control of particle morphology and the tailoring of the interfacial properties of the pigment particles.

Crystal morphology has a crucial influence on the properties of most crystalline products. It determines handling, mechanical, optical and even chemical properties of the crystals.

Because of their insolubility, pigments are used in the form of dispersed submicron particles. Interfacial and scattering properties of the pigment particles determine their in-use and optical properties. As a consequence, the optical properties of pigments can be controlled by the size and the shape of their particles.

Crystal morphology describes both the size and the shape (habit) of a crystal. Crystal polyhedra develop according to the growth rates of their surfaces. Crystal growth is controlled by kinetic effects such as diffusion and heat transfer in crystallizing solutions or melts as well as by supramolecular recognition processes at crystal surfaces.

Ever since three-dimensional crystal structures have been known, researchers have been searching for a relationship between morphology and crystal structure. From a purely thermodynamic perspective, this relationship can be elucidated by measuring or calculating the surface energy of the individual crystal faces. The thermodynamically most stable crystal polyhedron is the one possessing the lowest overall surface energy.

Knowing the crystal structure also enables one to calculate the surface energies of organic molecular crystals using force field methods[58]. Thus the thermodynamically most stable morphology can be calculated rapidly and easily by determining the attachment energies of the various crystal faces. The attachment energy of a crystal face corresponds to the energy which is gained if two parts of a crystal which were cleaved parallel to this face are brought together from infinite separation (Figure 8–11). Attachment energies give access to “equilibrium morphologies” which

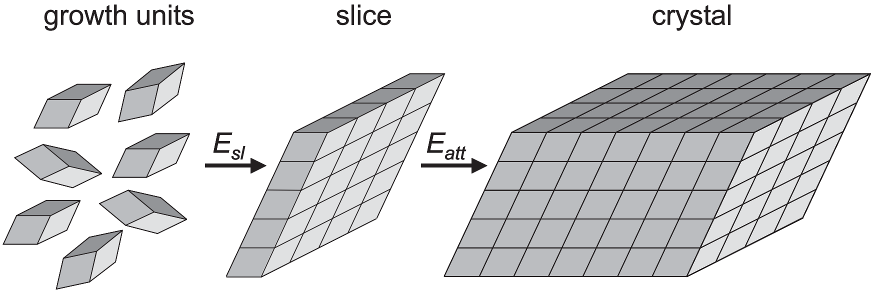

Figure 8–11: Calculation of the attachment energy E_{att}. Building a slice from growth units (molecules or dimers) yields the slice energy E_{sl}. Attachment of stable slices to growth faces yields the attachment energy E_{att}, which is proportional to the surface energy and may be used to derive the crystal habit.

are formed if the crystallization process is carried out close to equilibrium conditions without the influence of perturbing factors such as during slow sublimation or ripening (e.g. during a pigment finishing procedure).

Computational methods are particularly valuable in determining the morphology of pigments since it is difficult, time-consuming and often impossible to determine crystal habit using electron diffraction. In contrast, the calculations yield reliable and comprehensive information about both observed and potential growth faces.

8.4.5
Pigment Morphologies

As a rule of thumb, pigments whose intermolecular interactions are mainly defined by π-π-interactions within stacks tend to form needles or rods parallel to the stacking direction. Typical examples are the phthalocyanines (Figure 8–12a). Only P.B.15:3 may be obtained in the form of platelets by defined control of supersaturation during the pigment synthesis[59].

According to attachment energy calculations, the equilibrium crystal habit of P.R.179 is represented by a prismatic rod with an aspect ratio of ca. 3 (Figure 8–12b). These results correspond with experimental observations on crystals grown from xylene or phenol (see below, Figure 8–15). As expected, the main growth direction is parallel to the stacking direction along the a-axis. Consequently, the {011} face accounts for more than 80 % of the crystal surface.

The presence of one other directional interaction in addition to π-stacking leads to the formation of “platy” morphologies. Prominent examples are P.R. 255[7], P.V. 19[9] and P.R. 122, which show pronounced growth rates in the directions of π-stacks and hydrogen bonds (Figure 8–13). For these pigments the plate-faces represent ca. 60 % of the crystal’s total surface area. Similarly for P.R. 255 and for P.V. 19, aromatic C–H groups are exposed on the plate-faces giving them a predominantly hydrophobic character. As a consequence, both pigments interact with polymer

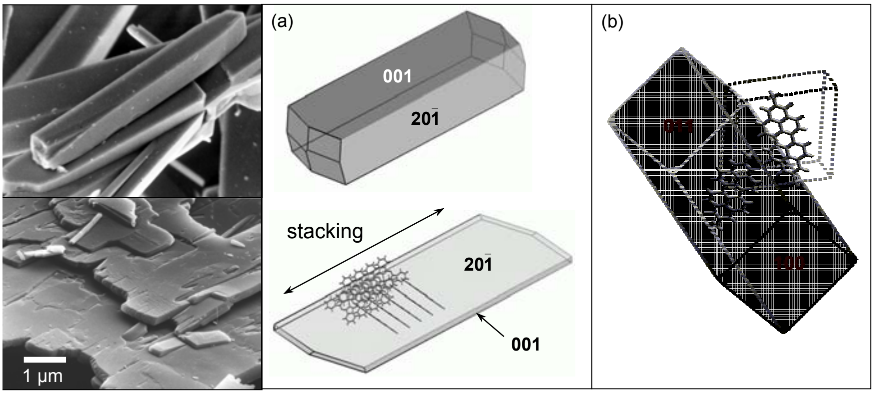

Figure 8–12: Calculated and experimental crystal morphologies of a) needle-like and platy β-copperphthalocyanine (left) and b) calculated crystal habit P.R. 179 (right).

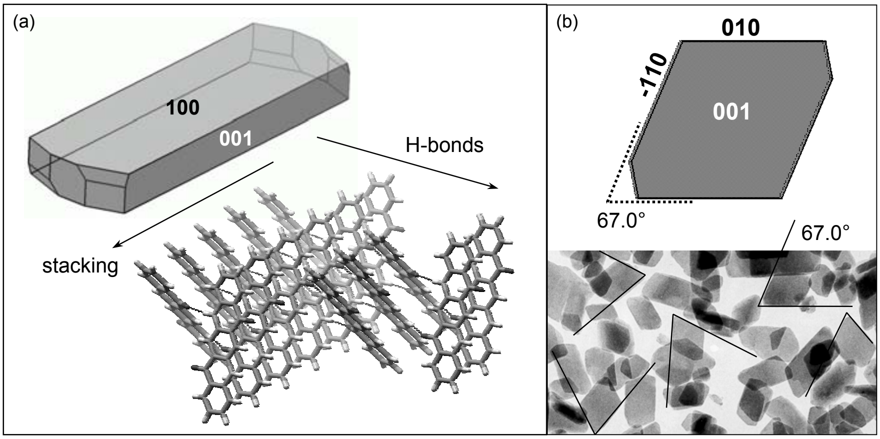

Figure 8–13: Crystal habits of quinacridone pigments:
a) calculated habit and surface structure of γ-P.V. 19;
b) comparison of calculated and experimentally observed crystal morphology of P.R. 122.

melts via these hydrophobic faces. As an example, P.V. 19 nucleates the β-form of isotactic polypropylene[60]. Again, P.R. 255 causes warping of injection-molded polyethylene parts, which may be lowered by treating the surface with appropriate additives, as has been shown for P.R. 254[61].

8.5
Control of Interfacial Properties Through Tailor-made Additives

That crystal faces differ with respect to rates of growth and dissolution as well as wetting and adsorption behavior is vital for the processing and coloristic properties of pigments. Light scattering, which is dependent on particle size and refractive index, also plays a significant role in determining the optical properties of pigments. It is therefore important to stabilize primary particles from flocculation, as this increases the effective particle size, and induces a color shift and loss of brilliance. To avoid flocculation, modern high performance pigments are enhanced with surface modifiers, which counteract the attraction between the particles.

In order to be effective, it is important that surface modifiers are strongly adsorbed onto an available crystal face of a particle[62]. Nature uses such mechanisms in biomineralization, e.g. in the formation of mussel shells or in the protection of hardy plants against frost. In both cases, additives control the crystal growth of either calcium carbonate[63] or ice through selective adsorption of tailor-made proteins on certain crystal faces[64].

This principle can be copied if the structures of the crystal faces are known. Then it is possible to search for or to design molecules which fit into the face according to the “lock and key” principle, thus stabilizing it (Figure 8–14) and actively inducing changes in morphology by the use of such tailor-made additives[65]. In the field of

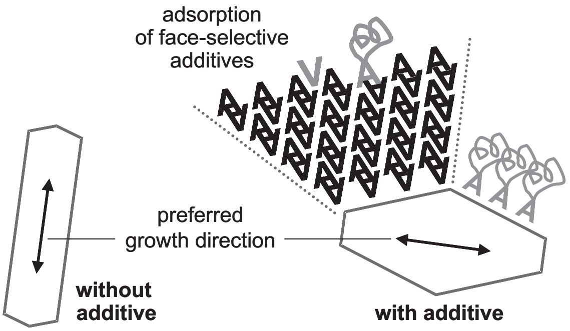

Figure 8–14: The concept of tailor-made additives to control crystal growth.

pigment technology, tailor-made additives have been designed to fit surface topologies and successively applied to control crystal growth of pigments[66] to stabilize metastable polymorphs, e.g. P.B. 15:6[67], and to prevent warping of pigmented polyolefin parts[62].

Face-selective additives can today be designed to fit into the structures of single crystal faces. Their effectiveness is determined by the energy of interaction between the additive and the crystal face. In simple cases, this energy can be calculated for different positions of the additive on the crystal face.

As an example, the crystal growth of P.R.179 can be drastically inhibited (Figure 8–15) by the addition of a few percent of perylene dicarboxylic acid imide (PDCI)[68]. The changes in particle size are accompanied by significant modifica-

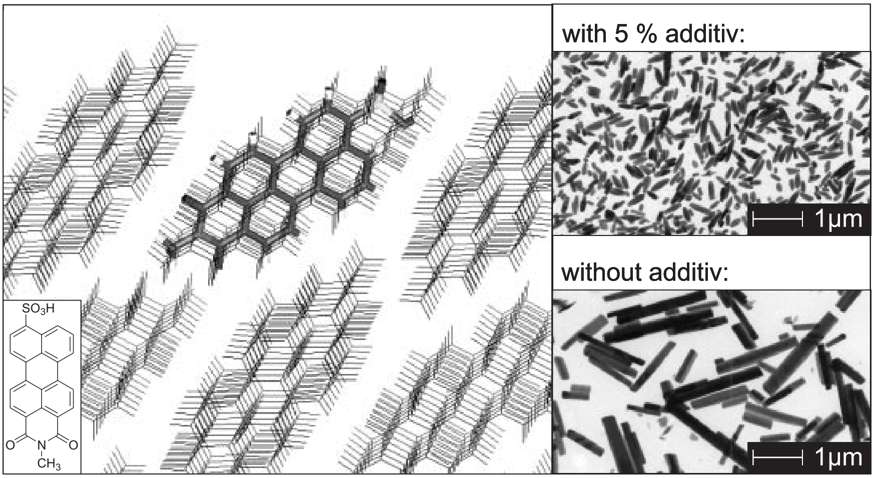

Figure 8–15: Inhibition of crystal growth of P.R. 179 by a PDCI-type additive (insert lower left corner); minimum energy structure of the additive embedded in the [011] -face of P.R. 179 (left); samples of P.R. 179 grown in the presence (top) and absence (bottom) of a PDCI-type additive (right).

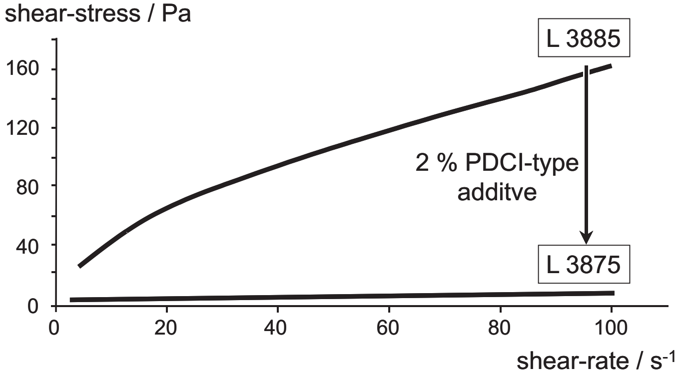

Figure 8–16: Rheology of a grinding formulation of Paliogen Red L 3875 in a typical high-solid system compared to Paliogen Red L 3885 with similar particle size.

tions of the crystal habit. Crystals grown or ripened in the presence of MePDCI have the overall shape of rice-grains. Assuming that the elongated axis in these grain-like crystals corresponds to the needle axis of P.R.179, the rounded ends should be terminated by a series of medium energy faces, presumably of the type h, k, l > 0. These faces are rough on the molecular scale and are covered, by their nature, with plenty of "step and kink" sites supporting a strong adsorption of the PDCI additive onto the surface. Conversely, the PDCI additive causes the appearance of these rough faces by stabilizing them. Usually only molecularly (more or less) flat surfaces are stable; the rough faces are unstable and would grow fast and disappear. One can now look at the phenomenon from two sides: the growth in the direction perpendicular to the face is hindered or the face, rough as it is, is stabilized.

If a sulfonated PDCI is used, then the sulfonate anion acts as an electrostatically stabilizing agent on pigment faces by attributing like charges to the pigment particles. With a sulfonated PDCI-based additive, Paliogen® Red L 3875, a transparent form of P.R. 179 has been developed for use in solvent- and waterborne coating systems.

Shear-stress measurements reveal an extremely low yield value for Paliogen Red L 3875 combined with standard dispersants in a typical high-solids mill base formulation (Figure 8–16). In addition to the higher solids (pigments) content at application viscosity, the improved colloidal stability of the pigment particles in Paliogen Red L 3875 offers a yellowish shade and a high chroma. The humidity resistance, overspray fastness and weatherability are not influenced by the strongly adsorbing additive and maintain the same high level, characteristic of other perylene pigments.

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9
The Global Market for Organic High Performance Pigments

Fritz Brenzikofer

9.1
Introduction

To characterize the market volume for High Performance Pigments (HPPs), we must first of all define what we understand by this term. Unfortunately, at this time there is no unique definition because the value-in-use of a pigment can differ depending on the technical or commercial view. From the technical aspect, Hugh Smith's definition of an HPP as "a colored, black, white, pearlescent, or fluorescent particulate organic or inorganic pigment that demonstrates high performance properties in its end use application"[1] is probably the most appropriate one. However, there are organic pigments which have excellent fastness properties yet are positioned in the market as low cost "classical" or "commodity" products because little or no confidential know-how is required to produce such pigments. As a consequence, there are today many suppliers of such pigments, with major consequences at the market price level. The best-known example of this is phthalocyanine pigments.

For this reason, my conclusion at the 1998 High Performance Pigment Conference[2] was that the definition of an HPP should be "The right pigment selection for a specific use with well-defined quality criteria at optimized pigment cost." Today, however, I am more and more convinced that classification into "specialties" and "commodities" would better describe how pigment products are positioned in the market.

In the following sections I will apply the same rule, which means that I will count only 5 % of all phthalocyanine pigments as HPPs, i.e. approximately 3500 tons of the total volume of approximately 70 000 tons. This principle seems also to be accepted indirectly by the protagonists of the "fastness property criteria"; otherwise they would have to contest the overall well-accepted estimations of the proportion of HPP in the total organic pigment market (Table 9–1).

9.2
The 1999 Market for Organic High Performance Pigments[1)]

I estimate the total market for organic HPPs at:

- Approximately 19 000 tonnes or approximately 9 % of the total organic pigment volume of 220 000 tonnes
- Approximately 1.2×10^9 USD or 30 % of the total organic pigment market of 4.2×10^9 USD

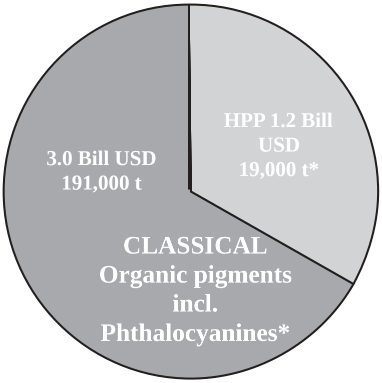

Figure 9–1: Organic pigments world market 1999 (4.2×10^9 USD, 210 000 t). *Phthalocyanines: 5 % of the total 70 000 tonnes considered as HPP.

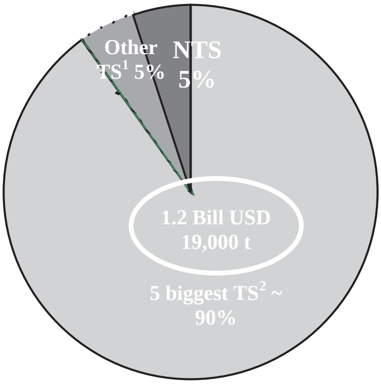

Figure 9–2: HPP market by types of producers. [1]TS: Traditional Suppliers (pigment manufacturers which have traditionally been many years in the business), NTS: Non-Traditional Suppliers. [2]The five biggest TS: BASF, Bayer, CIBA, Clariant, DIC/Sun.

These figures are slightly higher than indicated in my former presentations at the 1997 and 1998 HPP Conferences and at the 1999 CPMA Conference[3]. I believe today that I have previously underestimated the captive use of the main HPP producers for their own printing ink and masterbatch activity.

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1) Based on published data and discussions at recent conferences about Organic Pigments

By volume and value the most important HPP pigment classes are:

- special azos (benzimidazolone, disazo-condensation)
- quinacridones
- diketopyrrolo-pyrroles (DPP)
- carbazole Violet
- perylenes
- other polycyclic pigments (isoindolinones, quinophthalones, anthraquinones)
- HP naphthols
- phthalocyanines with special properties

Let us have a look at the supply side (producers) and the demand by market segments and regions.

9.3
The Producers of High Performance Pigments

I will use two terms to indicate the types of pigment producers. Traditional Suppliers (TS) and Non-Traditional Suppliers (NTS). By “traditional suppliers” I mean those international chemical companies which have been producing organic pigments for many years. From the beginning, the locations of HPP production plants have always been located in the country of these companies’ headquarters. For HPPs, Germany, Switzerland, USA and Japan have been and still are by far the most important production countries.

I estimate that today’s traditional suppliers produce approximately 75 % of the total organic pigment demand. For HPPs they have an even larger share. CIBA and Clariant are the leading suppliers, followed by BASF, DIC/SUN and BAYER. These five “majors” produce together approximately 90 % of the HPP volume! Although these figures appear to show an oligopolistic supply side, in reality this is absolutely not the case. In recent years, prices for HPP have been under constant pressure due to increased production capacities and the fact that some other manufacturers have started to produce certain types of HPPs.

Nevertheless, the question remains as to why so few producers dominate this market. I see mainly two reasons:

- confidential production know-how
- heavy investment requirements

This will be discussed below.

9.4
The Demand for HPP by Consumer Market Segments

With a total market of 9000–10 000 tonnes, the coatings industry is the main consumer market segment (Figure 9–3). Of this volume, 50 % is used in the automotive sector for OEM and refinish coatings. Industrial and decorative paints are also important segments.

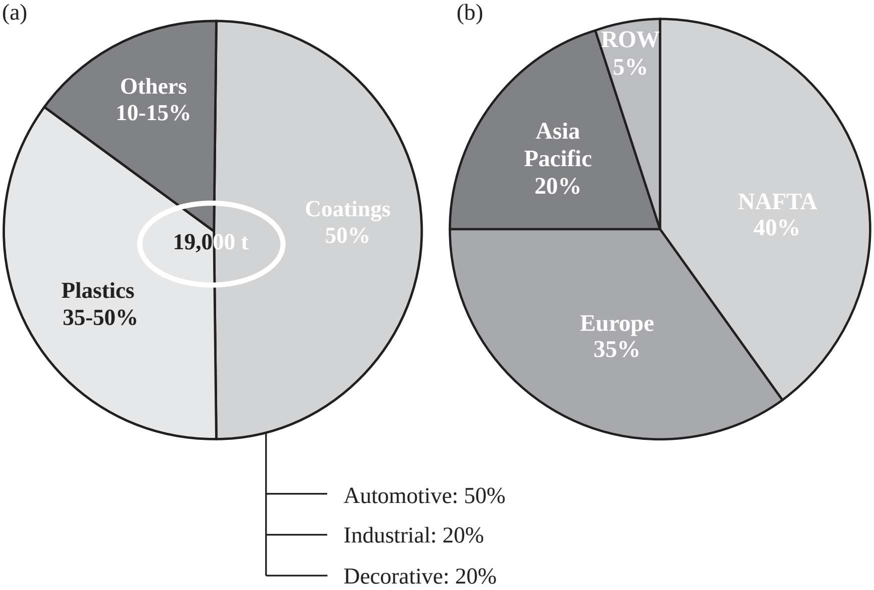

Figure 9–3: HPP-consumption 1998 by a) segments and b) regions.

As the demand for HPP continues to grow in the plastics and non-impact printing field, the market share of coatings is expected to decrease. Utilization of HPP for printing inks and textile printing is best considered under “others”. Printing ink is the biggest market segment for organic pigments in general, but, as the quality of lower cost “classical” azo pigments is often sufficient, use of HPP is rather limited. There are of course exceptions, such as Carbazole Violet (C.I. Pigment 23), which is a very important product for printing inks.

9.4.1
The Demand by Regions

As Figure 9–3 shows, NAFTA countries have the biggest demand, followed by Europe. Asia Pacific with 20 % and “rest of the world” (ROW) with 5 % are quite a lot smaller, but as more and more global paint companies are building up production units in China, Southeast Asia and India, these regions will become increasingly important.

9.4.2
The Trade Balance of HPP among these Regions

How is the worldwide "trade flow" for High Performance Pigments?

In order to establish a trade balance we need, in addition to the consumption figures, a "guestimate" of the production volume by regions (Table 9–1).

Table 9–1: Production site of main HPP producers.

Producers	*Main pigment classes*
BASF	Perylene, isoindolines/isoindolinones, quinophthalone, phthalocyanine specialties, anthraquinones
Bayer	Quinacridones, dioxazines, perylenes, phthalocyanine specialties
Clariant	Quinacridones, dioxazines, perylenes, special azos, hp naphthols
Ciba	Quinacridones, dioxazines, perylenes, special azos, other polycyclic pigments, phthalocyanine specialties
DIC/SUN	Quinacridones, dioxazines, perylenes, special azos, hp naphthols, phthalocyanine specialties

The major part of these pigment segments are manufactured in Europe, USA and Japan.

Based on the consumption by regions (Table 9–2), we have:

Europe 6600–6800 tonnes (approximately 35 %)
NAFTA 7600–7900 tonnes (approximately 40 %)
Asia Pacific 3500–3800 tonnes (approximately 20 %)
ROW (Inc. India) 800–1000 tonnes (approximately 5 %)

We can now estimate the product volumes in each region, to establish the trade balance. Our best guess about such production volumes is shown in Table 9–2.

Table 9–2: Trade balance of HPPs by regions.

	Europe	**NAFTA**	**Asia Pacific (incl. Japan)**	**ROW (incl. India)**
Production	> 8000 t	> 8000 t	< 3000 t	< 500 t
Consumption	6600–6800 t	7600–7900 t	3500–3800 t	800–1000 t
Trade balance	Net exporter	Slightly net exporter	Net importer	Net importer

These figures clearly show that developing countries like China and India do not yet play an important role as producers. Will this change next year? Will the scenario for textile dyes be repeated? Certainly, it is not easy to predict the future, but the following comments can be made. First of all, it is evident that the main HPP producers are themselves the key as to whether China and India will become increasingly important or not. Four reasons are given for this statement:

1. The capital investment to produce HPPs is significantly higher than that for classical azo pigments and textile dyes. To fund such investment, local companies (sometimes government-controlled) are active in looking for joint ventures with well-known pigment producers.
2. The quality of certain HPPs produced in the two above-mentioned countries does not yet correspond to global market requirements.
3. The more certain pigment specialties are perceived of as "commodities", the more the major players will be forced to produce in locations at the cheapest possible price. However, we must also consider that labor costs to produce HPPs are in general not higher than 10 % of the total production costs. Is it worthwhile for the "majors" to risk their current strong positions for a small saving? The "commoditization" of certain products is therefore another driving factor for the production move to developing countries.
4. The success rate of research and development. The commoditization process can of course be delayed if also in the future new and modified HPPs can be successfully launched, because it is more or less certain that such innovations will be first produced in well-established plants in Germany, Switzerland, USA and Japan.

Of course, there are other factors like

- trade barriers
- availability of raw materials and intermediates
- governmental regulations about ecological and toxicological issues, etc., which also influence a possible change in the trade balance of HPPs.

In conclusion, taking all possible factors into account, it appears that the developing countries will ultimately become more important for production and consumption of HPPs, but that this process will be rather slow.

9.5
Demand Factors for HPPs

For the total organic pigment market the growth rate is estimated at 2–3 %. For HPPs there seems to be a common belief that the future demand will grow around 5 % per annum.

What are the factors which are driving this demand?

9.5.1
Market Requirements and Trends

In this group I include governmental and environmental regulations as they directly influence the market situation. By market segments, the following demand factors appear determinant for the future growth of HPPs.

9.5.1.1 Industrial / Decorative Paints

- There is a continuing switch from inorganic pigments to HPPs for quality and environmental reasons (for example, the ban in some applications of lead chromate pigments). In these applications there is also a growing demand for brilliant colors, and this leads to further replacement of the duller inorganics by organic pigments.

9.5.1.2 Plastics

- Replacement of cadmium pigments and diarylide pigments is due to toxicological limitations in certain applications.
- Engineering plastics with outstanding technical properties need pigments with high heat stability.
- Highly sophisticated manufacturing machines are commonplace, so as to ensure a high output. Such machines require pigments with excellent heat resistance.
- Increased use of polypropylene (PP) fibers in the textile industry. PP-fibers are mainly ”dyed” with organic HPPs.

9.5.1.3 New Markets

Several new market segments are becoming more and more attractive for HPP suppliers. Well-known examples are non-impact printing (Ink Jet), high tech security printing, and pigments for optical storage (compact disc, digital versatile disc, etc.). Other new technologies will certainly emerge requiring the use of more High Performance Pigments.

Several other driving factors can shift the demand for organic HPP to inorganic HPPs or vice versa, e.g. trends in color shades for automotive coatings. In 1998 and 1999 the most fashionable shades in Europe were metallic silver and grey colors. For this reason the actual demand for silver flakes is booming, whereas a reduced demand for reddish shades has significantly influenced the utilization of DPP, quinacridone and perylene pigments.

9.5.2
Marketing Strategies of Main HPP Producers

As in the case of textile dyes, lower cost azo pigments are acquiring more and more the character of “commodities”. For this reason it is logical that the major pigment producers focus their research and development activity on HPPs. The goal of finding new or modified HPPs is the reason why BASF, CIBA and Clariant all maintain their research activity at quite a high level (2–4 % of sales).

These companies very actively promote their HPPs in order to further strengthen their positions in the pigment market. Thus, the suppliers become their own driving factor!

9.5.3
Globalization Process

I believe that for quality reasons the big paint producers in Europe and USA are more likely to consume HPPs than the small and middle size paint producers in developing countries.

However, because of the merger and acquisition policy of the major paint producers, these companies are extending their presence into Asia, India and South America. And in order to have a worldwide quality standard, they transfer their production formulations and raw material requirements to these countries, with the effect that the use of HPPs will increase there.

9.6
Conclusions/Outlook

For the specialty chemical business and especially for the organic pigments segment, organic HPPs remain an attractive business. The fact that five major suppliers continue to dominate the market is another reason why most pigment producers would like to get at least a minimum share.

However, entry barriers are much higher than for example with textile dyes and classical azo pigments. This is the chief reason why the "commoditization process" will not be fast. But by fixing their own strategy concerning R & D activity and the possible transfer of production know-how, the major HPP producers will significantly influence their own future. It is therefore quite difficult to accurately predict the future HPP supply structure. On the demand side, the forecast is perhaps easier, as there seems to be a common belief that the future growth rate for HPPs will remain above the average growth in the specialty chemical business.

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2 Fritz Brenzikofer, High Performance Pigment Conference, Intertech, Barcelona, 1998

3 Fritz Brenzikofer, North American Color Pigments Business in a Global Marketplace, CPMA, Philadelphia, May 19–20, 1999.

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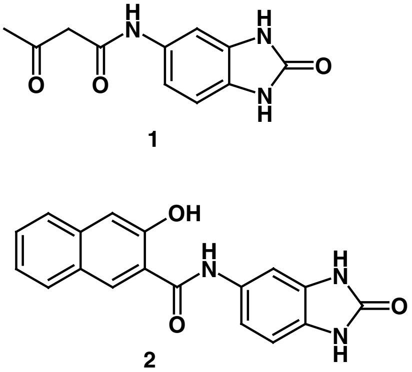
10
Benzimidazolone Pigments and Related Structures

Hans-Joachim Metz and Frank Morgenroth

10.1
Introduction

Benzimidazolone pigments are azo colorants that derive their name from the benzimidazolone group which is introduced as part of the coupling component. Apart from one exception[1] there are two coupling components of commercial importance: 5-acetoacetylaminobenzimidazolone (**1**) and 5-(2′-hydroxy-3′-naphthoylamino)-benzimidazolone [Naphtolon™] (**2**) (see Figure 10–1).



1

2

Figure 10–1: The two commercially relevant coupling components for benzimidazolone pigments.

While the acetoacetyl derivative **1** provides greenish yellow to orange products, the naphthoylamino compound **2** affords colorants having medium red to carmine, maroon, bordeaux or brown shades. Figure 10–2 summarizes the Colour Index data[1], shades and structural formulae of commercial available benzimidazolone pigments.

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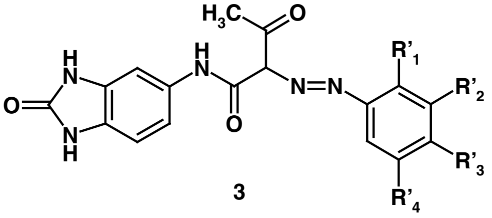
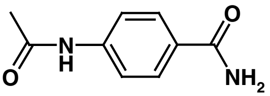
[1] P.O. 64 is prepared by coupling diazotized 5-amino-6-methylbenzimidazolone onto barbituric acid.

Figure 10–2a: Colour Index data, shades and structural formulae of commercially available benzimidazolone pigments (yellow and orange).

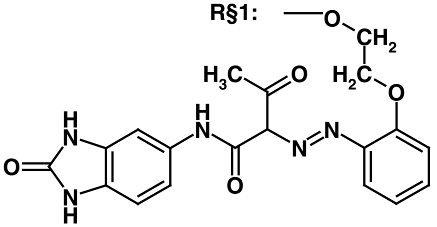


3

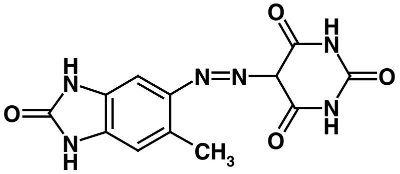
R§2:



R§1:



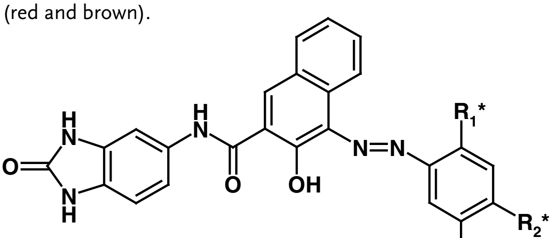
P.O. 64:



C.I. name:	*C.I. const. no. / CAS no.:*	*1st known product:*	*Shade:*	*R′₁*	*R′₂*	*R′₃*	*R′₄*	*CAS index name / chemical formula:*
P.Y. 120	11783 / 29920-31-8	PV Fast Yellow H2G	Yellow	-H	$-COOCH_3$	-H	$-COOCH_3$	1,3-Benzenedicarboxylic acid, 5-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]-,dimethyl ester / $C_{21}H_{19}N_5O_7$
P.Y. 151	13980 / 31837-42-0	Hostaperm™ Yellow H4G	Greenish yellow	-COOH	-H	-H	-H	Benzoic acid, 2-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]- / $C_{18}H_{15}N_5O_5$
P.Y. 154	11781 / 68134-22-5	Hostaperm™ Yellow H3G	Greenish yellow	$-CF_3$	-H	-H	-H	Butanamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo-2-[[2-(trifluoromethyl)phenyl]azo]- / $C_{18}H_{14}F_3N_5O_3$
P. Y. 175	11784 / 35636-63-6	Hostaperm™ Yellow H6G	Very greenish yellow	$-COOCH_3$	-H	-H	$-COOCH_3$	1,4-Benzenedicarboxylic acid, 2-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]-, dimethyl ester / $C_{21}H_{19}N_5O_7$

C.I. name:	***C.I. const. no. / CAS no.:***	***1st known product:***	***Shade:***	R'_1	R'_2	R'_3	R'_4	***CAS index name / chemical formula:***
P.Y. 180	21290 / 77804-81-0	PV Fast Yellow HG	Greenish yellow	R§1	-H	-H	-H	Butanamide, 2,2′-[1,2-ethanediylbis(oxy-2,1-phenyleneazo)]bis[N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo- / $C_{36}H_{32}N_{10}O_8$
P.Y. 181	11777 / 74441-05-7	PV Fast Yellow H3R	Reddish yellow	-H	-H	R§2	-H	Benzamide, N-[4-(aminocarbonyl)phenyl]-4-[[1-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-oxopropyl]azo]- / $C_{25}H_{21}N_7O_5$
P.Y. 194	11785 / 82199-12-0	Novoperm™ Yellow F2G-A	Bright yellow	$-OCH_3$	-H	-H	-H	Butanamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-2-[(2-methoxyphenyl)azo]-3-oxo- / $C_{18}H_{17}N_5O_4$
P.O. 36	11780 / 12236-62-3	Permanent™ Orange HL	Orange	$-NO_2$	-H	-Cl	-H	Butanamide, 2-[(4-chloro-2-nitrophenyl)azo]N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-oxo- / $C_{17}H_{13}ClN_6O_5$
P.O. 62	11775 / 52846-56-7	Novoperm™ Orange H5G	Yellowish orange	-H	-H	$-NO_2$	-H	Butanamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-2-[(4-nitrophenyl)azo]-3-oxo- /$C_{17}H_{14}N_6O_5$
P.O. 64	12760 / 72102-84-2	Cromophtale™ Orange GP	Reddish orange	-	-	-	-	2,4,6(1H,3H,5H)-Pyrimidinetrione, 5-[(2,3-dihydro-6-methyl-2-oxo-1H-benzimidazol-5-yl)azo]- / $C_{12}H_{10}N_6O_4$
P.O. 72	-/-	PV Fast Orange H4GL 01	Orange			-/-		not published

Figure 10–2b: Colour Index data, shades and structural formulae of commercially available benzimidazolone pigments (red and brown).



4

C.I. name:	*C.I. const. no. / CAS no.:*	*1st known product:*	*Shade:*	R^*_1	R^*_2	R^*_3	*CAS index name / chemical formula:*
P.R 175	12513 / 6985-92-8	Permanent™ Red HFT	bluish red	-$COOCH_3$	-H	-H	Benzoic acid, 2-[[3-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-hydroxy-1-naphthalenyl]azo]-, methyl ester / $C_{26}H_{19}N_5O_5$
P.R. 176	12515 / 12225-06-8	Permanent™ Carmine HF3C	bluish red	-OCH_3	- H	-$CONHC_6H_5$	2-Naphthalenecarboxamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxy-4-[[2-methoxy-5-[(phenylamino)carbonyl]phenyl]azo]- / $C_{32}H_{24}N_6O_5$
P. R. 185	12516 / 51920-12-8	Permanent™ Carmine HF4C	bluish red	-OCH_3	-SO_2NHCH_3	-CH_3	2-Naphthalenecarboxamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxy-4-[[2-methoxy-5-methyl-4-[(methylamino)sulfonyl]phenyl]azo]- / $C_{27}H_{24}N_6O_6S$
P.R. 208	12514 / 31778-10-6	PV Red HF2B	bright red	-$COOC_4H_9$(n)	-H	-H	Benzoic acid, 2-[[3-[[(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)amino]carbonyl]-2-hydroxy-1-naphthalenyl]azo]-, butyl ester // $C_{29}H_{25}N_5O_5$

C.I. name:	***C.I. const. no. / CAS no.:***	***1st known product:***	***Shade:***	***R*₁***	***R*₂***	***R*₃***	***CAS index name / chemical formula:***
P.V. 32	12517 / 12225-08-0	PV Fast Bordeaux HF3R	reddish violet	$-OCH_3$	$-SO_2NHCH_3$	$-OCH_3$	2-Naphthalenecarboxamide, N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-4-[[2,5-dimethoxy-4-[(methylamino) sulfonyl]phenyl]azo]-3-hydroxy- // $C_{27}H_{24}N_6O_7S$
P.Br. 25	12510 / 6992-11-6	Hostaperm™ Brown HFR	reddish brown	-Cl	-H	-Cl	2-Naphthalenecarboxamide, 4-[(2,5-dichlorophenyl)azo]-N-(2,3-dihydro-2-oxo-1H-benzimidazol-5-yl)-3-hydroxy- / $C_{24}H_{15}Cl_2N_5O_3$

10.2
Historical Background

Since 1950, particular efforts have been made to develop new azo pigments that combine excellent overspray fastness and bleed resistance with high fastness to light as well as weathering. As a result of this work, two different concepts found by Ciba and Hoechst, respectively, proved to be very successful:

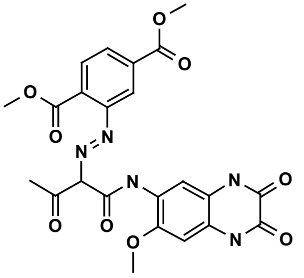
1. Enlarging the pigment molecule, as done with disazo condensation pigments by Ciba[2].
2. Introduction of substituents which lower the solubility of the pigment molecule, as first introduced by Hoechst[3].

Taking advantage of the second principle, it was found that carbonamide moieties in the pigment molecules reduce their solubility. Pursuing this path, pigments were developed that contain five- or six-membered heterocyclic carbonamides such as tetrahydroquinazoline-2,4-dione, tetrahydroquinoxalinone-dione, or benzimidazolone. In contrast to an open carbonamide group, the cyclic moieties improved the fastness to light considerably. Among the various ring structures considered, benzimidazolone based colorants have been the most successful.

Regarding pigment shades, the development of benzimidazolone pigments occurred during two eras: the mid 1960s to the early 1970s, with occasional introduction of new products in subsequent years. During this first period, mainly red pigments appeared on the market. In 1960, Hoechst applied for patent protection for water-insoluble mono azo benzimidazolone dyestuffs[3a]. The pigments had been synthesized by diazotization of aminobenzoic acid amides and subsequent coupling of the resulting diazonium compounds with 2-hydroxy-3-naphthoic acid derivatives of 5-aminobenzimidazolone. Later, the use of alkoxy-substituted aminobenzoic acid amides as diazo components provided bluish red pigments[4]. Among the diazo components claimed in other disclosures were amino benzene sulfonic acids[5], simple anilines such as nitro- or chloroanilines[3a] and ester functionalized aromatic amines[6].

The second period in benzimidazolone development focused on the application of acetoacetylamino benzimidazolone derivatives as coupling components, resulting in the formation of yellow or orange pigments. The first yellow benzimidazolone pigment on the European market was PV Fast Yellow H2G. This pigment was obtained by coupling diazotized 5-aminoisophthalic acid dimethyl ester with acetoacetylated 5-aminobenzimidazolone[7]. The marriage of the two concepts described above has been accomplished with PV Fast Yellow HG (P.Y. 180), introduced several years ago. P.Y. 180 represents a benzimidazolone disazo pigment. Cromophtal™ Orange GP (P.O. 64) is a reddish orange pigment synthesized from 6-methyl-5-aminobenzimidazolone as diazonium salt and barbituric acid as coupler. However, P.O. 64 is the only benzimidazolone pigment of commercial relevance that is not based on couplers **1** or **2**.

After the discovery of the benzimidazolone pigments, Hoechst was the only manufacturer in the 1960s and 1970s. Today, however, there are numerous manufacturers of such pigments, including Clariant, Ciba Specialty Chemicals, and Dainippon Ink & Chemicals (see Sec. 10.6, Pigment Manufacturers, Economics), providing a wide range of benzimidazolone pigment types for printing inks, paints and plastics. Originally applied in azo pigments, the benzimidazolone concept has been extended to create improved heterocyclic pigments, such as Pigment Yellow 192 (Sandofil™ Yellow S-RL, CAS-No. 56279-27-7) and, very recently, Hostaperm™ Blue R5R (Clariant), the first commercial example of a property-enhanced triphendioxazine comprising this structural feature. (For further information, see Chap. 20.) Recent research by Clariant led to the expansion of the benzimidazolone ring system by one carbonyl group. This effort yielded new yellow quinoxalinedione-based azo pigments with outstanding properties, for example Hostaperm™ Yellow H5G (P.Y. 213)[8].



Hostaperm™ Yellow H5G (P.Y.213)

10.3
Method of Manufacture

All commercial benzimidazolone azo pigments are produced by classical azo coupling, commonly carried out in aqueous media. As mentioned already above, in yellow and orange pigments the coupling component is 5-acetoacetylaminobenzimidazolone (**1**) (apart from one exception, P.O. 64). In red pigments the naphthol derivative 5-(2′-hydroxy-3′-naphthoylamino)-benzimidazolone (**2**) serves as coupling

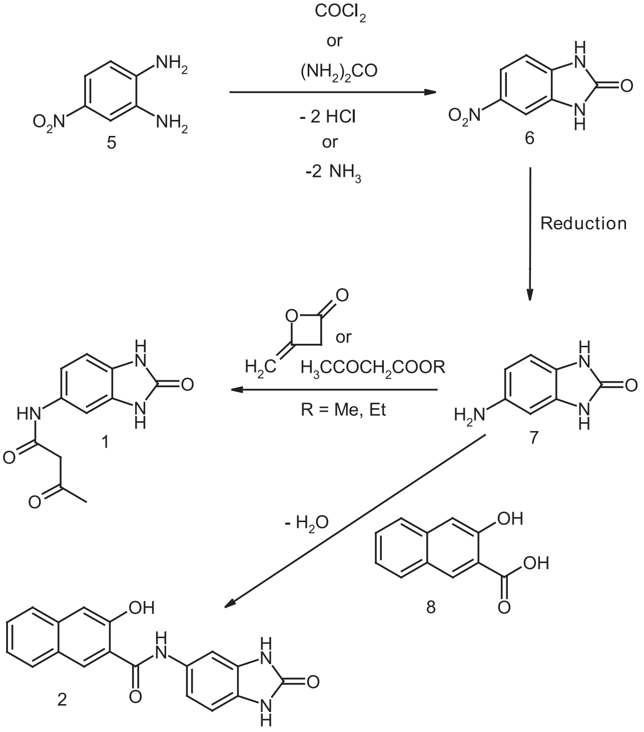


Figure 10–3: Manufacture of the coupling components for yellow, orange and red benzimidazolone pigments.

compound. Both coupling components are prepared from 5-aminobenzimidazolone (**7**) (compare Figure 10–3). This amine is obtained advantageously by the reaction of 4-nitro-1,2-diaminobenzene (**5**) with phosgene or with urea (in melt) which results in 5-nitrobenzimidazolone (**6**). Reduction of the nitro compound **6** leads to the required aminobenzimidazolone **7**. The coupling component **1** for yellow pigments is produced by reacting diketene or acetoacetic ester with **7**. Again, the condensation of 2-hydroxy-3-naphthoic acid (**8**) with 5-aminobenzimidazolone **7** in the presence of phosphorus trichloride in an organic solvent yields the coupler **2** for red pigments.

For the coupling reaction itself the coupling components **1** or **2** are dissolved in alkali and reprecipitated with acetic or hydrochloric acid, optionally in the presence of a surfactant. This procedure is necessary to facilitate the coupling reaction by conversion of the coupling compound into an “activated form”. This means that it consists of small particles which readily react with the diazonium salt. In certain cases, auxiliary agents are added during the coupling process. However, regarding the demands of today’s technical applications, the crude pigments are usually in an unsatisfactory physical form. Therefore the initially obtained pigments are subject to a post-coupling, thermal aftertreatment called “finishing”. Typically, an aqueous suspension of the crude pigments is heated (under pressure) to temperatures of 100 to 150 °C. The purpose of the finishing is to control the physical properties of the pigments, such as crystal shape, crystal phase, crystal size and grain size distribution, since these characteristics determine the application properties of the colorants. In conclusion, finishing provides the basis for pigments with tailor-made application properties including shade, tinctorial strength, transparency/hiding power, light fastness, weather fastness, fastness to solvents and migration resistance as well as dispersibility.

The considerable impact of the finishing on the resulting pigment properties may be best illustrated by comparing two examples from German patent DE1179908. In the patent, it is shown that the pigment prepared by the azo coupling of diazotized 3-amino-4-methoxybenzoic acid anilide with 5-(2′-hydroxy-3′-naphthoyl-amino)-7-chloro-benzimidazolone has quite different properties depending on the coupling conditions and aftertreatment. One approach was to carry out the coupling step in the presence of an additive obtained from tributylphenol and ethylene oxide. After the coupling was complete, *o*-dichlorobenzene was added to the resulting pigment suspension prior to heating to 97 °C (207°F). The usual workup yields a bluish red pigment with very soft grain texture. In contrast, the chemically identical pigment manufactured without additive and thermal aftertreatment has a hard texture and exhibits inferior fastness properties. The attempt to process the untreated pigment into a printing ink resulted in unsatisfactory tinctorial strength and insufficient flow properties.

Following the finishing process, the pigments are isolated, washed, dried at moderate temperatures between 70 to 85 °C, and milled. The same techniques and equipment are thus used as for other azo pigments, such as, for example, plate-and-frame filter presses, drying chambers or continuous drying belts and air mills.

10.4
Typical Properties and Major Reasons for Use

Benzimidazolone pigments cover a broad spectral range from very greenish yellow through orange, red and violet to brown. The tinctorial strength of the pigments prepared varies considerably because of their different physical characteristics. This fact does not surprise us, as the median of the particle size distribution ranges from 50 nm to 1000 nm (compare Table 10–1). Typical pigment loadings for printing inks range from 7.5 to 25 % to obtain 1/3 standard depth, depending on intrinsic color strength and particle size distribution. Generally, the tinctorial strengths of yellow and the orange benzimidazolone colorants are similar to those found for classical yellow monoazo pigments. The same analogy in terms of color strength can be observed for the red series of Naphtolon™ and Naphtol AS™ derived pigments.

All benzimidazolone pigments exhibit outstanding light fastness and weather resistance combined with excellent solvent, overpainting and bleeding fastness. In this respect benzimidazolone pigments are markedly superior to their coloristic counterparts in the monoazo yellow or red Naphtol AS™ series. In fact, the class of benzimidazolone pigments contains colorants matching high-performance polycyclic pigments in terms of light fastness and weatherability.

Table 10–1: Technical properties of some benzimidazolone pigments.

Pigments for the paint industry	*Hostaperm™ Yellow H4G (P.Y. 151)*	*Hostaperm™ Yellow H3G (P.Y. 154)*	*Hostaperm™ Yellow H6G (P. Y. 175)*	*Novoperm™ Yellow F2G (P.Y. 194)*	*Novoperm™ Orange H5G 70 (P.O. 62)*	*Novoperm™ Orange HL 70 (P.O. 36)*	*Novoperm™ Red HFT (P.R.175)*	*Novoperm™ Bordeaux HF3R (P.V. 32)*	*Hostaperm™ Brown HFR (P.Br. 25)*
Hue angle at 1/3 SD:[1]	97.4	95.1	97.9	92.5	68.1	39.8	28.5	339.5	43.5
Density [g/cm^3]:	1.57	1.57	1.49	1.47	1.49	1.62	1.48	1.43	1.51
Specific surface area [m^2/g]	23	18	30	20	9	17	62	45	90
Particle size distrib. (median) [nm]:	230	280	140	280	1000	300	100	180	65
Tinctorial strength:[2]	1:3.0	1:2.0	1:2.1	1:4.5	1:1.5	1:2.5	1:6.2	1:9.5	1:6.4
Light fastness:[3]	8	8	8	7	7–8	8	8	5–6	8
Fastness to weathering:[4]	4–5	5	4–5	3–4	4–5	4–5	3–4	2–3	4–5
Heat resistance [°C]:	200	160	180	200	180	160	200	200	200
Overspray fastness:[5]	5	5	5	5	5	4–5	5	5	5
Chemical resistance:[6]									
Acid	5	5	5	5	5	5	5	5	5
Alkali	3	5	5	5	5	5	5	5	5
Solvent fastness:[7]									
Butanol / ethyl glycol	4–5 / 4	4–5 / 3–4	4–5 / 3–4	4 / 3	4–5 / 3–4	5 / 4–5	4–5 / 4	5 / 4–5	4–5 / 2
Butyl acetate / MEK[8]	4–5 / 4–5	4–5 / 3–4	4–5 / 3–4	3–4 / 3	4–5 / 4	5 / 4–5	4–5 / 4–5	5 / 4–5	4 / 3–4
Xylol / white spirit	4–5 / 5	5 / 5	5 / 5	3 / 4–5	5 / 5	5	4–5 / 5	5 / 5	4–5 / 4–5

The performance of the pigments considerably depend on the system in which they are processed and applied.

1) Hue angle at 1/3 standard depth SD (German standard: DIN 6174).

2) Parts TiO_2 required to reduce 1 part of pigment to 1/3 SD (1:x TiO_2). These data represent guide values that can be influenced by the binder used and the dispersion status.

3) Light fastness was tested in air drying paint at 1/3 SD. Assessment was made against the 8-step Blue Scale (DIN 54003) in which rating 8 denotes excellent and rating 1 very poor light fastness.

4) Evaluation was made by comparison with the 5-step 'change of shade' Grey Scale (DIN 54001) after 12 month outdoors weathering of an air drying paint. Rating 5 is the best, rating 1 the poorest.

5) Assessment of bleeding into a white nitrocellulose combination laquer against the 5-step 'bleeding' Grey Scale (DIN 54002) in which rating 5 is the best and rating 1 the poorest.

6) Assessment against the 5-step 'change of shade' Grey Scale.

7) Assessment against the 5-step 'bleeding' Grey Scale (DIN 54002).

8) Methyl ethyl ketone.

Table 10–1: Continued

Pigment for plastics colouration	***PV Fast Yellow H2G 01 (P.Y. 120)***	***PV Fast Yellow HG (P.Y. 180)***	***PV Fast Yellow H3R 01 (P.Y. 181)***	***PV Fast Orange H4GL (P.O. 72)***	***Cromophtal™ Orange GP (P.O. 64)***	***Graphtol™ Carmine HF3C (P.R. 176)***	***Graphtol™ Carmine HF4C (P.R. 185)***	***Graphtol™ Red HF2B (P.R. 208)***	***Graphtol™ Bordo HF3R (P.V. 32)***
hue angle at 1/3 SD:[1]	97.0	88.7	66.5	56.7	–	2.1	358.0	17.9	341.5
density [g/cm^3]:	1.50	1.42	1.48	1.57	1.59	1.42	1.45	1.42	1.45
specific surface area [m^2/g]:	29	24	27	37	–	61	45	65	56
particle size distribution (median) [nm]:	130	320	560	140	–	120	180	50	120
tinctorial strenght:[2]	10.42	5.54	14.59	2.4 (PE)	2.5 (PE)	5.35	4.49	5.08	3.58
light fastness:[3]	8	6–7	8	8	7–8	7	7–8	7	7–8
heat resistance [°C]:[4]	260	290	300	290	300	270	250	–	–
fastness to bleeding:[5]	5	5	5	5	5	5	5	4–5	5

Pigment for printing inks	***Novoperm™ Bordo HF3R (P.V. 32)***
hue angle at 1/3 SD:[1]	341.49
density [g/cm^3]:	1.45
specific surface area [m^2/g]:	56
paticle size distribution (median) [nm]:	120
tinctoral strenght:[8]	7.9
light fastness:[10]	5
heat resistance [°C]:[12]	200
chemical resistance:[6]	
acid	5
alkali	5
solvent fastness:[7]	
solvent mixture[9] / ethanol	5 / 5
ethyl acetate / MEK	4 / 4
toluene / white spirit	4 / 5

1) Hue angle at 1/3 standard depth SD (German standard: DIN 6174), determined in HDPE.

2) Indicated is the amount of pigment needed to reach 1/3 SD in 5% rutile titanium dioxide white reductions in PVC unless indicated.

3) Against the 8-step Blue Scale (DIN 54003). The evaluation was done according to DIN 53388. Pigment concentration: 0.1%.

4) 1/3 SD was tested to determine the heat resistance in PE injection moulding (DIN 53772).

5) The fastness to bleeding was determined at 100 °C / 15 h against the 5-step ‚bleeding' Grey Scale (DIN 54002).

6) Assessment against the 5-step ‚change of shade' Grey Scale (DIN 54001).

7) Assessment against the 5-step ‚bleeding' Grey Scale.

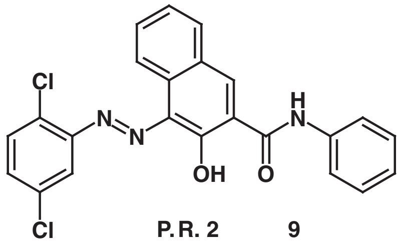
8) Indicated is the pigmentation level of a printing ink (in percent) applied at 1.0 g/m^2 to reach 1/3 SD.

9) 60 vol% ethanol, 30 vol% ethyl acetate, 10 vol% 1-methoxy-2-propanol.

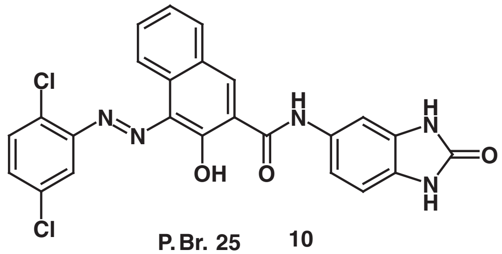
10) Against the 8-step Blue Scale.

11) Methyl ethyl ketone.

12) Print on a metal sheet; start at 140 °C, steps of 20 °C / 10 min.



P.R. 2 **9**

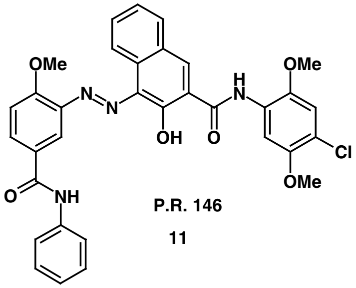


P.Br. 25 **10**

Figure 10–4a: Comparison of the fastness properties of benzimidazolone and Naphthol AS™ pigments; P.R. 2 and P.Br. 25.

	Permanent™ Red FRR (P.R. 2)	***Hostaperm™ Brown HFR 01 // PV Fast Brown HFR 01 (P.Br. 25)***
Hue angle at 1/3 SD[1]	21.4	43.5
Density [g/cm^3]	1.45	1.51
Specific surface area [m^2/g]	33	90
Particle size distrib. (median) [nm]	160	65
Light fastness[2]		
1/1 SD (print)	5	7
1/3 SD (print)	4–5	7
Full shade	6 (paint)	8 (PVC)
Heat resistance [°C][3]	< 140	240
Solvent fastness[4]		
Solvent mixture[5] / white spirit	4 / 4–5	5 / 4–5
Ethanol / ethyl acetate	5 / 3–4	5 / 5
MEK[6] / toluene	3–4 / 3	5 / 5
Chemical resistance[7]		
Alkali	5	5
Acid	5	5
Fastness to bleeding[8]	Not recommended for plastics	4–5 (PVC)

1) Hue angle at 1/3 standard depth SD (German standard: DIN 6174).
2) Assessment against the 8-step Blue Scale.
3) Print on a metal sheet; start at 140°C, steps of 20°C / 10 min.
4) Assessment against 5-step Grey Scale.
5) 60 vol% ethanol, 30 vol% ethyl acetate, 10 vol% 1-methoxy-2-propanol.
6) Methyl ethyl ketone.
7) Assessment against the 5-step "change of shade" Grey Scale.
8) The fastness to bleeding was determined at 100 °C / 15 h against the 5-step "bleeding" Grey Scale (DIN 54002).



P.R. 146

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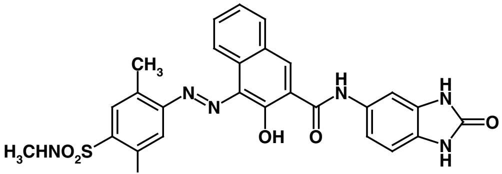

P.R. 185

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Figure 10–4b: Comparison of the fastness properties of benzimidazolone and Naphthol™ AS pigments; P.R. 146 and P.R. 185.

	Permanent™ Carmine FBB 02 (P.R. 146)	*Novoperm™ Carmine HF4C // Graphtol Carmine HF4C (P.R. 185)*
Hue angle at 1/3 sd[1]	357.1	358.0
Density $[g/cm^3]$	1.41	1.44
Specific surface area $[m^2/g]$	36	45
Particle size distrib. (median worth) [nm]	110	180
Tinctorial strength[2]	10	7.5
Light fastness[3]		
1/1 SD on the print	5	6–7
1/3 SD on the print	5	5
Heat resistance [°C][4]	200	220
Solvent fastness[5]		
Solvent mixture[6] / white spirit	5 / 5	5 / 5
Ethanol / ethyl acetate	5 / 4–5	5 / 5
MEK[7] / toluene	4–5 / 4–5	5 / 5
Chemical resistance[8]		
Alkali	5	5
Acid	5	5
Fastness to bleeding[9]	2 (PVC)	5 (PVC)

1) Hue angle at 1/3 standard depth SD (German standard DIN 6174).

2) Indicated is the pigmentation level of a printing ink (in percent) applied at 1.0 g/m^2 to reach 1/3 SD.

3) Against the 8-step Blue Scale (DIN 54003).

4) Print on a metal sheet; start at 140°C, steps of 20°C / 10 min.

5) Assessment against 5-step Grey Scale.

6) 60 vol% ethanol, 30 vol% ethyl acetate, 10 vol% 1-methoxy-2-propanol.

7) Methyl ethyl ketone.

8) Assessment against the 5-step 'change of shade' Grey Scale.

9) The fastness to bleeding was determined at 100 °C / 15 h against the 5-step 'bleeding' Grey Scale (DIN 54002).

Figure 10–4 compares important application properties of the benzimidazolone P.Br. 25 (data from Hostaperm™ Brown HFR01 and PV Fast Brown HFR 01) with the Naphtol AS™ pigment P.R. 2 (Permanent™ Red FRR). From a chemical point of view P.Br. 25 can be considered as a Naphtol AS™ pigment wherein the anilide function derives from 5-amino-benzimidazolone instead of aniline. The effect of this difference is tremendous. With respect to the fastness properties, the better fastness to light and solvents of the benzimidazolone pigment compared to the Naphtol AS™ species is striking. Thus, the fastness to light, measured using the 8-step wool scale according to German standards, equals step 7 for the benzimidazolone and only step 5 for the Naphtol AS™ pigment. This result is remarkable since a difference of two steps on the wool-scale corresponds approximately to a four-fold exposure time. Furthermore, Figure 10–4 contains data reflecting the solvent fastness as well as fastness to alkali and acids. The evaluation has been done according to a five-step scale, in which rating 5 is the best and rating 1 the poorest. P.Br. 25 is thus completely resistant to solvents such as ethyl acetate, methyl ethyl ketone (MEK) or toluene, as well as to acids and alkali (all step 5), while P.R. 2 tolerates acids and bases (both step 5) but is sensitive to the above solvents (steps 3, 3–4). In addition, P.Br. 25 has a 39 % higher color strength than P.R. 2. Owing to these properties, P.R. 2 is primarily used in water based printing inks, because it does not show sufficient performance in other fields. In contrast, the application properties of P.Br. 25 qualify this benzimidazolone pigment for use in printing inks and plastics, as well as in paints.

Chemical similarities between classical monoazo and benzimidazolone pigments are of academic interest only. The positioning of a pigment is determined by its coloristics and fastness properties as well as the price/performance ratio, as when we compare Naphtol AS™ Pigment Red 146 with the somewhat more yellowish benzimidazolone Pigment Red 185 (see Figure 10–4). As expected, the benzimidazolone type pigments Novoperm™ Carmine HF4C and Graphtol™ Carmine HF4C, respectively, show better fastness properties than the Naphtol AS™ derived Permanent™ Carmine FBB 02 (e.g. bleed fastness 5 versus 2).

It is well known that classical azo as well as benzimidazolone pigments are stabilized by intramolecular hydrogen bonds. These bonds are stronger than the ubiquitous van der Waals forces that hold together molecules within a crystal. As revealed by X-ray studies, the exceptional properties of benzimidazolone pigments can be explained by the supportive function of their intermolecular hydrogen bonds. These bonds remarkably stabilize the pigment crystals, thereby improving the fastness properties[9]. Like other azo pigments (e.g. monoazo yellow, β-naphthol and Naphtol AS™ -types), benzimidazolone pigments are almost planar molecules that exist as oxohydrazone tautomers in the solid state. Figure 10–5 shows a two-dimensional scheme as well as crystal structures[9b, 9d, 10] from both a yellow and a red benzimidazolone pigment. The molecules form “flat bands” by hydrogen bonds. These bands in turn are held together by van der Waals forces only. Polycyclic pigments, e.g. quinacridones and diketopyrrolopyrroles, are also known to form intermolecular hydrogen bonds in their crystals.

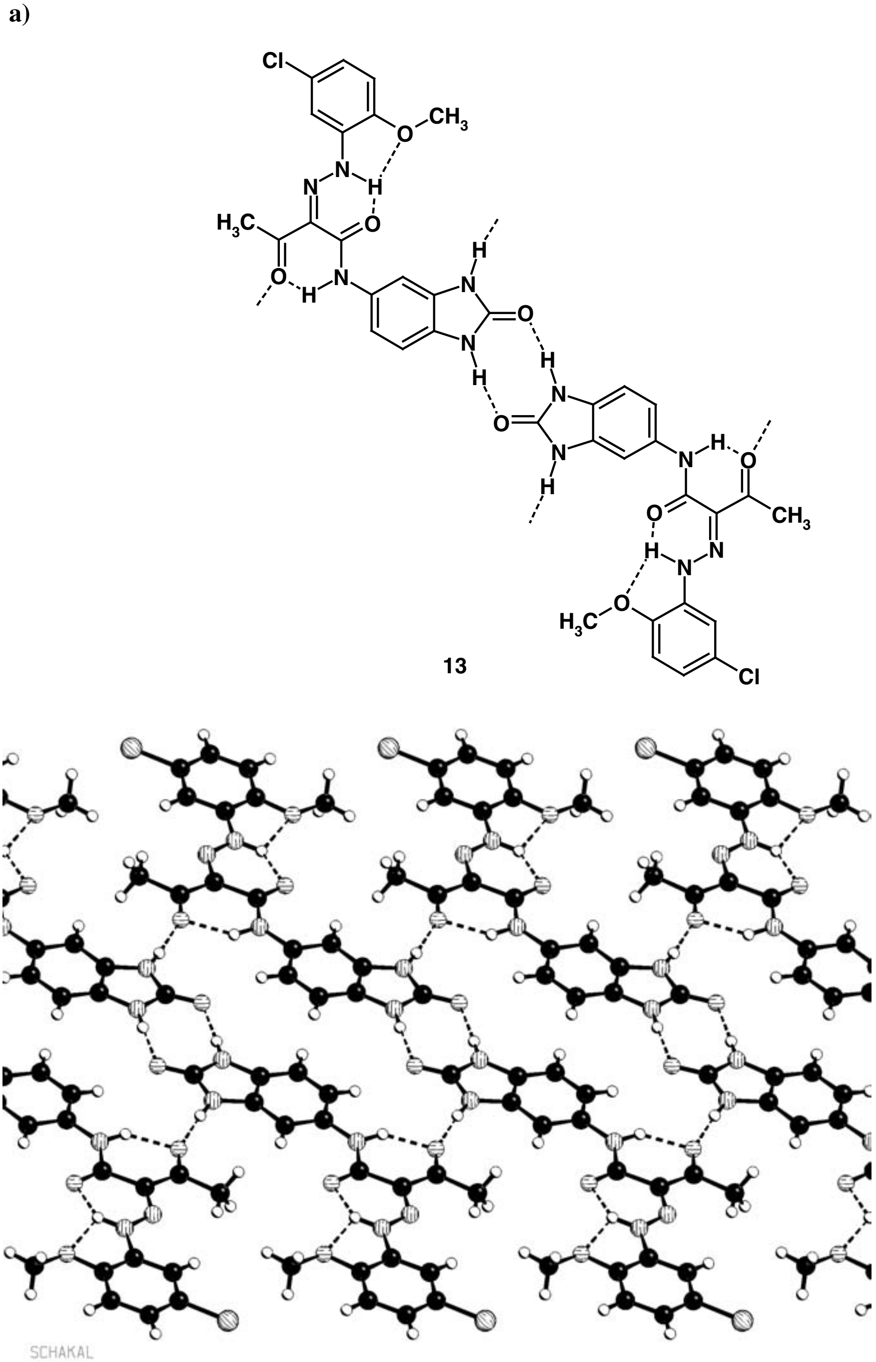

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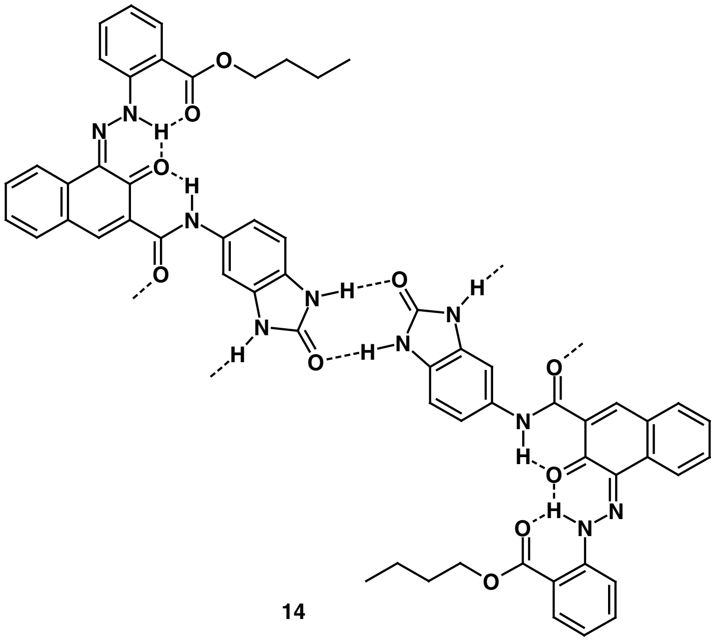
Figure 10–5a: Structure of yellow benzimidazolone pigment: schematic illustration and structure from X-ray diffraction[9d] (view along crystallographic y-axis, showing one double-chain of molecules).

b)



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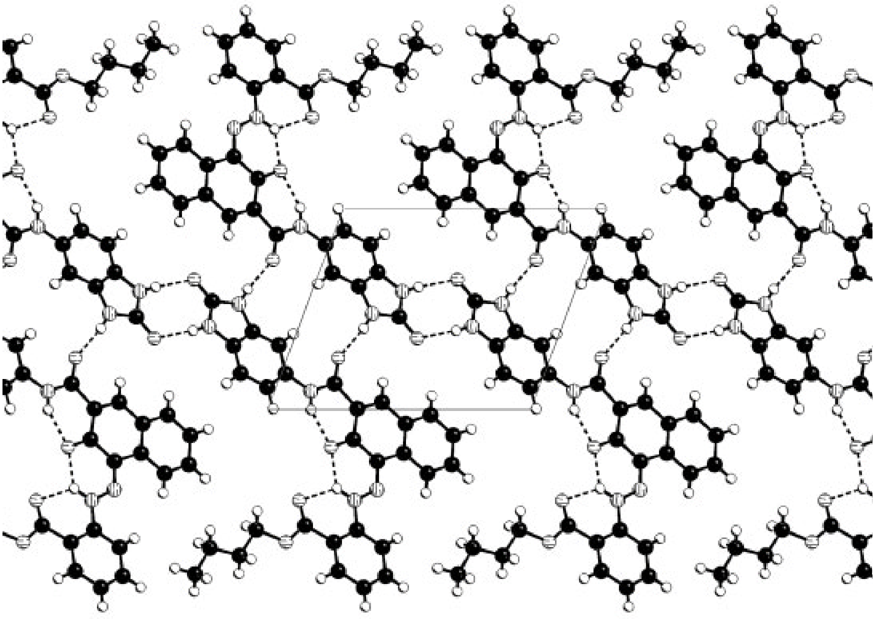

Figure 10–5b: Structure of red benzimidazolone pigment: schematic illustration and structure from X-ray diffraction[9b] (view along crystallographic z-axis, showing one double-chain of molecules).

10.5
Pigment Grades, Discussion of Individual Pigments

The properties described qualify benzimidazolone pigments for applications such as high quality industrial paints, including automotive finishes and special effect paints, plastics and high performance printing inks. The colorants are available in the form of powders, masterbatches, liquid dispersions, pastes and granules (see Table 10–4).

Table 10–2: Spectrometric data of five commercially available benzimidazolone pigments.

Pigment / titanium dioxide ratio 10:90.	***Tristimulus value***			***Chromaticity coordinates***		***Munsell renotation***		***λ_{max} [nm]***	***Excitation purity [%]***
	X	Y	Z	X	Y	Hue	Value/chroma		
Novoperm™ Yellow H2G (P.Y. 120)	75.0	84.6	28.0	0.400	0.451	1.0GY	9.3 / 9	572	60.5
Novoperm™ Red HFT (P.R. 175)	46.3	32.0	17.6	0.483	0.334	6.3R	6.2 / 12	605	50.8
PV Red HF2B (P.R. 208)	42.5	25.9	16.8	0.499	0.304	2.9R	5.6 / 14	631	47.3
Graphthol™ Carmine HF4C (P.R. 185)	41.0	23.3	22.3	0.474	0.269	8.9RP	5.4 / 16	494	50.3
PV Fast Brown HFR (P.Br. 25)	41.6	31.9	14.1	0.475	0.364	1.5YR	6.2 / 10	595	56.8

Whether or not a pigment fits the technical requirements of a certain target application is determined by its application properties, which in turn depend on the chemical constitution and the physical parameters of the pigment. Some important physical data, including hue angles, densities and median particle size distributions for some commercially available pigments are given in Table 10–1. Figures 10–6 and 10–7, respectively, show the reflectance and particle size distribution curve for a representative benzimidazolone pigment (Hostaperm™ Yellow H3G). Detailed spectrometric data for five commercial benzimidazolone pigments are given in Table 10–2.

The particle size distribution curve of Hostaperm™ Yellow H3G (P.Y. 154, see Figure 10–7) was determined using a transmission electron microscope. The data are presented as differential and as cumulative distributions, respectively. The excellent fastness and flow properties of Hostaperm™ Yellow H3G are in good accordance with the small proportion of particles less than 0.1 μm in diameter and the general observation that extremely fine particles exert a detrimental effect on fastness and flow properties.

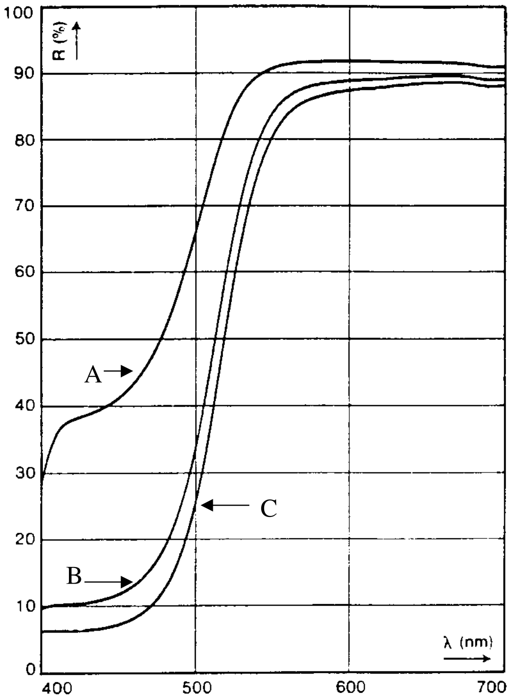

Figure 10–6: Reflectance curve for a representative benzimidazolone pigment (Hostaperm™ Yellow H3G). Reductions with titanium dioxide:
A: 1/25 SD
B: 1/3 SD
C: 1/1 SD

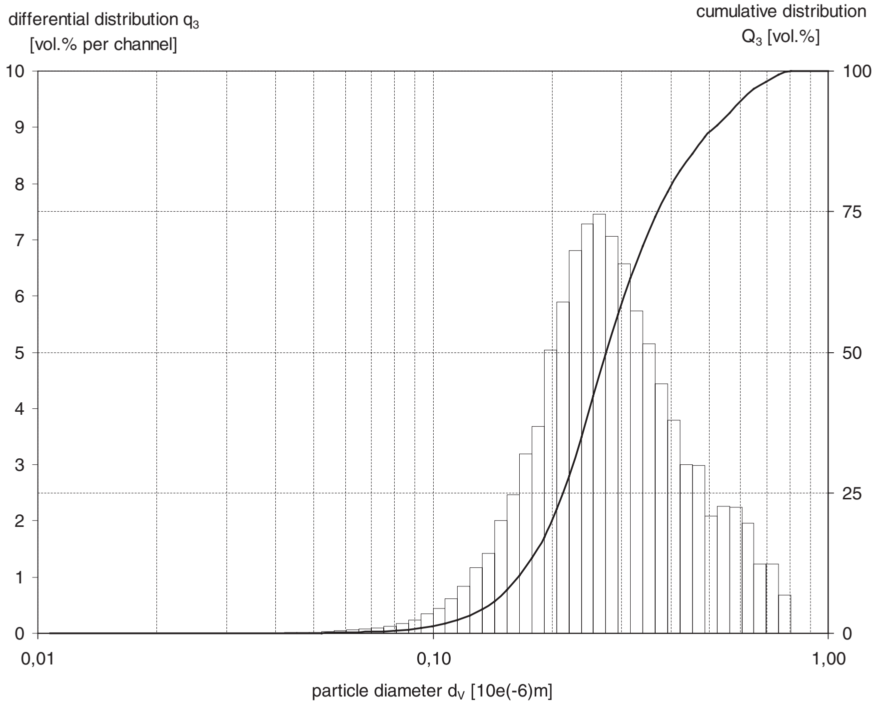

Figure 10–7: Particle size distribution curve for a representative benzimidazolone pigment (Hostaperm™ Yellow H3G).

The reflectance curve of Hostaperm™ Yellow H3G between 400 nm to 700 nm (Figure 10–6) reveals that the pigment "absorbs" violet, blue and blue-green light while it reflects the green, the yellow and red range of the spectrum. Thus, the colorant appears greenish yellow.

As mentioned above, techniques to influence and control the application properties of a given pigment have been developed enormously, in particular within the last two decades. While it is true to say that a pigment is "suitable" for a certain application, it is also true to say that today's pigments are tailor made (or modified) to satisfy the demands of a given application. Consequently, a pigment cannot be characterized like a classical chemical compound, which is described by fixed physical data and chemical composition. Instead, a pigment should be considered as material that lends its individual profile to potential applications. Bearing this in mind, the following brief overview of commercially available benzimidazolone pigments is given below (compare also Table 10–4). One should also recall that few azo pigments are suitable for the coloration of polyamide.

P.Y. 120 is a very bleed resistant medium yellow pigment that combines good thermal stability with high tinting strength and excellent fastness to light. It is primarily used in plastics.

P.Y. 151 has a clean greenish yellow shade. The pigment provides access to very lightfast and durable coatings and shows excellent fastness to migration in plasticized PVC. It is used in particular for high grade industrial paints but also plays a role in the coloration of plastics and lightfast prints.

P.Y. 154 is a somewhat greenish yellow pigment having outstanding fastness to light and weathering. In fact it is one of the most weatherfast organic yellow pigments available. P.Y. 154 is used throughout the coatings and paints industry, including automotive finishes. The pigment also exhibits excellent fastness properties in printing ink and plastics. However, because of its unsatisfactory tinctorial strength it has not gained much importance for these applications.

P.Y 175 has a very greenish yellow shade. It combines very good fastness to light and weathering with good flow properties in paints. The pigment is used in high performance coatings, such as automotive finishes and refinishes. It is of interest for high grade inks and plastics, where excellent light- and weatherfastness properties are required.

P.Y. 180 is a very heat stable greenish to medium yellow disazo pigment that does not affect the shrinkage of plastics. Thus, it is primarily used in plastics, including polymers such as PVC, polycarbonate, polyester, and polystyrene. Additionally, P.Y. 180 is of interest in polypropylene spin dyeing and in heat stable printing inks or paints.

P.Y. 181 represents a reddish yellow pigment with excellent heat stability and lightfastness. It is especially suitable for polymers that are processed at higher temperatures. P.Y. 181 plays a role in the coloration of such plastics as polyacetals, polystyrene or polyester, as well as in spin dyed viscose rayon and viscose cellulose.

P.Y. 194 is a yellow pigment of high tinctorial strength with good flow properties in paint. It is mainly applied in industrial coatings and in the coloration of plastics. For such applications, P.Y. 194 is preferred due to its advantageous price/performance ratio.

P.Y. 213 was released most recently onto the market. This greenish yellow quinoxalinedione pigment combines outstanding weatherability and overspray resistance with an excellent fastness to solvents, acid and alkali. These properties render P.Y. 213 particularly suitable for modern car finishes, especially water based coating systems[11].

P.O. 36 affords a reddish orange shade. Because of its very good light-, weather- and overcoating fastness it is used mostly in high grade plastics and in high quality paints, including automotive finishes. It is also of interest throughout the printing ink industry, wherever stringent demands concerning light- and weatherfastness have to be satisfied.

P.O. 62 is a very opaque, extremely yellowish orange pigment that produces deep, clean, light- and weatherfast shades. It is used throughout the paint industry including automotive finishes as well as in refinishes and in general industrial paints.

P.O. 64, a very heat stable yellowish orange, is used mainly in plastics. It does not affect the shrinkage of partially crystalline polymers. For special applications it is also used in printing inks.

P.O. 72 is a yellowish orange of high heat stability and excellent light fastness. It does not induce warping in partially crystalline plastics and can be used for spin dying as well.

P.R. 175 is a somewhat dull red pigment with good fastness properties. Its field of application includes paint as well as plastics. P.R. 175 plays a role in transparent metallic automotive finishes and in the dyeing of PVC, for example.

P.R. 176 affords a bluish red shade. This pigment exhibits excellent fastness to migration and light. It is primarily used in plastics (e.g. PVC, polyolefins, polyacrylonitrile) and in laminated papers.

P.R. 185 is a heat stable bluish red pigment of very high tinctorial strength that has excellent solvent fastness and migration resistance. Its main applications comprise graphics printing and mass coloration of plastics such as PVC and polyolefins. P.R. 185 is also used in general industrial finishes.

P.R. 208, a bleed resistant medium red pigment with high tinctorial strength, is mainly applied in the mass coloration of plastics and in packaging gravure printing.

P.V. 32 is a somewhat dull, very bluish red heat stable pigment of very high tinctorial strength which is resistant to overpainting. The pigment is used in paints, plastics and printing inks as well as in spin dyeing.

P.Br. 25 provides a reddish shade of brown. It has excellent fastness properties in paints as well as in plastics, and does not cause warpage in HDPE. Because of its high transparency it is especially suitable for metallic and pearlescent effect coatings, to which it lends a beautiful copper tone.

Table 10–3: Economic aspects.

C.I. Name	*Pigment*	*Year*
P.O. 36	Permanent™ Orange HL	1964
P.R. 176	Permanent™ Carmine HF3C	1965
P.V. 32	PV Fast Bordeaux HF3R	1965
P.R. 175	Permanent™ Red HFT	1965
P.Br. 25	Hostaperm™ Brown HFR	1966
P. R. 185	Permanent™ Carmine HF4C	1967
P.Y. 120	PV Fast Yellow H2G	1969
P.R. 208	PV Red HF2B	1970
P.Y. 175	Hostaperm™ Yellow H6G	1971
P.Y. 151	Hostaperm™ Yellow H4G	1972
P.Y. 154	Hostaperm™ Yellow H3G	1972
P.O. 62	Novoperm™ Orange H5G 70	1973
P.Y. 181	PV Fast Yellow H3R	1979
P.Y. 180	PV Fast Yellow HG	1980
P.Y. 194	Novoperm™ Yellow F2G	1993
P.O. 72	PV Fast Orange H4GL 01	1997
P.Y. 213	Hostaperm™ Yellow H56	2000

10.6
Pigment Manufacturers, Economics

Benzimidazolone pigments first appeared on the German market in 1964. The relative order in which the seventeen generic structures, still available as pigments from Clariant, were launched in Europe, is listed in Table 10–3. As mentioned above, there are numerous manufacturers of benzimidazolone pigments today. Since the introduction of this pigment class, they have successfully competed in the replacement of heavy metal-containing inorganic pigments in paints and plastics, and now form a most important group of organic yellows, oranges and reds. Table 10–4 provides an overview of known suppliers and the physical form in which the pigments are offered. The data are adopted from the Colour Index[1].

Table 10–4: Known pigment brands and manufacturers of benzimidazolone pigments (as of 1997)[1].

C.I. name/ Trademark	*Manufacturer*	*Main applications*	*Physical form*
P. Y. 120			
Novoperm Yellow H2G	Clariant Intern. Ltd., CH	paint	powder
PV Fast Yellow H2G 01	Clariant Intern. Ltd., CH	plastics	powder
P.Y. 151			
DCC 7151 Benzimidazolone Yellow	Dominion Colour Corp., Canada	paint, plastics, printing inks	powder

Table 10–4: Continued

C.I. name/ Trademark	*Manufacturer*	*Main applications*	*Physical form*
Foscolor Yellow 151	Foscolor Ltd., UK	printing inks	masterbatch
Highlite Yellow 1205	Engelhard Corp., USA	paint, plastics	powder
Hostaperm Yellow H4G	Clariant Intern. Ltd., CH	paint	powder
Kenalake Yellow 4GO	Hays Colours, UK	paint	powder
Pigment Yellow 151	Member(s) of Color Pigments Manufacturing Association, USA	paint, plastics, printing inks	powder
PV Fast Yellow H4G	Clariant Intern. Ltd., CH	plastics	powder
Symuler Fast Yellow 4GO	Dainippon Ink & Chemicals Inc., JP	paint, plastics, printing inks	powder
Symuler Fast Yellow 4GO-E	Dainippon Ink & Chemicals Inc., JP	plastics	powder
Symuler Fast Yellow 4GT	Dainippon Ink & Chemicals Inc., JP	printing inks	powder
P.Y. 154			
Chromofine Yellow 2080	Dainichiseika Color & Chemicals, JP	paint	powder
Colanyl Yellow H3G 100	Clariant Intern. Ltd., CH	paint	liquid dispersion
Flexobrite Yellow L3GA	Yorkshire Chemicals plc., UK	paint	powder
Hostaperm Yellow H3G	Clariant Intern. Ltd., CH	paint	powder
Symuler Fast Yellow 4192	Dainippon Ink & Chemicals Inc., JP	paint, printing inks	powder
P.Y. 175			
Hostaperm Yellow H6G	Clariant Intern. Ltd., CH	paint	powder
Pigment Yellow 175	Member(s) of Color Pigments Manufacturing Association, USA	printing inks	powder
P.Y. 180			
Hostaprint Yellow HG 31	Clariant Intern. Ltd., CH	pastics (PVC films and mass coloration)	powder
Hostasin Yellow HG	Clariant Intern. Ltd., CH	plastics (rubber)	granule
Novoperm Yellow P-HG	Clariant Intern. Ltd., CH	printing inks (solvent based package inks)	powder
PV Fast Yellow HG	Clariant Intern. Ltd., CH	plastics	powder
Toner Yellow HG	Clariant Intern. Ltd., CH	colour toners	powder
Yellow EMD-352	Sumika Color Co. Ltd., JP	plastics	powder
Yellow KG	Keystone Aniline Corp., USA	plastics, printing inks and other	powder
Yellow PEC-352	Sumika Color Co. Ltd., JP	plastics (polyolefins)	granule
P.Y. 181			
PV Fast Yellow H3R	Clariant Intern. Ltd., CH	plastics	powder

Table 10–4: Continued

C.I. name/ Trademark	*Manufacturer*	*Main applications*	*Physical form*
Yellow K3R	Keystone Aniline Corp., USA	plastics	powder
P.Y. 194			
Novoperm Yellow F2G	Clariant Intern. Ltd., CH	paint, printing inks	powder
PV Fast Yellow F2G	Clariant Intern. Ltd., CH	plastics	powder
P.O. 36			
DCC 7036 Benzimidazolone Orange	Dominion Colour Corp., Canada	paint, plastics, printing inks	powder
Kenalake Orange HP-RLOX	Hays Colours, UK	paint	powder
Lysopac Orange 3620C	Cappelle, NV, Belgium	paint	powder
Novoperm Orange HL	Clariant Intern. Ltd., CH	paint	powder
Novoperm Orange HL 70	Clariant Intern. Ltd., CH	paint	powder
Novoperm Orange HL 70-NF	Clariant Intern. Ltd., CH	paint	powder
Pigment Orange 36	Member(s) of Color Pigments Manufacturing Association, USA	paint, plastics, printing inks	powder
Sudaperm Orange 2915	Sudarshan Chemicals Ind. Ltd, India	paint, plastics and other	powder
Sunfast Orange 36 (271–9036)	Sun Chemical Corp., USA	paint	powder
Symuler Fast Orange 4183H	Dainippon Ink & Chemicals Inc., JP	paint, printing inks	powder
Yorabrite Orange HL	Yorkshire Chemicals plc, UK	paint, plastics, printing inks and other	liquid dispersion
P.O. 62			
Kenalake Orange HP-3GO	Hays Colours, UK	paint, printing inks	powder
Novoperm Orange H5G 70	Clariant Intern. Ltd., CH	paint	powder
P.O. 64			
Cromophtal Orange GL	Ciba Speciality Chemicals Inc., CH	printing inks	powder
Cromophtal Orange GP	Ciba Speciality Chemicals Inc., CH	plastics, printing inks	powder
Hornapol Orange PO-536-T	Ciba Speciality Chemicals Inc., CH	plastics	masterbatch
Orange EMD-218	Sumika Color Co. Ltd, JP	plastics	powder
Orange GP	Keystone Aniline Corp., USA	plastics, printing inks	powder
Orange PEC-218	Sumika Color Co. Ltd, JP	plastics	granule

Table 10–4: Continued

C.I. name/ Trademark	*Manufacturer*	*Main applications*	*Physical form*
Pigment Orange 64	Member(s) of Color Pigments Manufacturing Association, USA	plastics, printing inks	powder
P.O. 72			
PV Fast Yellow H4GL 01	Clariant Intern. Ltd., CH	plastics	powder
P.R. 175			
Novoperm Red HFT	Clariant Intern. Ltd., CH	paint	powder
PV Fast Red HFT	Clariant Intern. Ltd., CH	plastics	powder
P.R. 176			
Aquanyl P Carmine HF3C 13–3166	Clariant Intern. Ltd., CH	paint	powder
Flexonyl Carmine HF3C-LA	Clariant Intern. Ltd., CH	decorative laminates, paper	liquid dispersion
Graphtol Carmine HF3C	Clariant Intern. Ltd., CH	printing inks	powder
PV Carmine HF3C	Clariant Intern. Ltd., CH	plastics	powder
P.R. 185			
Epsilon Red LB-1TO28	Sumika Color Co. Ltd, JP	rubber	masterbatch
Hostaprint Carmine HF4C 31	Clariant Intern. Ltd., CH	plastics	powder
Microlith Red 4C-K	Ciba Speciality Chemicals Inc., CH	paint, printing inks	powder
Novoperm Carmine HF4C	Clariant Intern. Ltd., CH	printing inks	powder
Pigment Red 185	Member(s) of Color Pigments Manufacturing Association, USA	paint, printing inks	powder
Graphtol Carmine HF4C	Clariant Intern. Ltd., CH	plastics	powder
Simperm Red AHE	WS Simpson & Co., UK	printing inks and other	powder
P.R. 208			
Hostaprint Red HF2B 31	Clariant Intern. Ltd., CH	plastics	powder
Hostasin Red HF2B	Clariant Intern. Ltd., CH	Plastics (rubber)	granule
Novoperm Red HF2B 01	Clariant Intern. Ltd., CH	printing inks	powder
Graphtol Red HF2B 01	Clariant Intern. Ltd., CH	plastics	powder
Renol Red HF2B-HW	Clariant Intern. Ltd., CH	solvent based wood stains, marker inks	powder
P.V. 32			
Hostaprint Bordeaux HF3R 31	Clariant Intern. Ltd., CH	plastics	powder
Novofil Bordeaux BB	Clariant Intern. Ltd., CH	colouration of viscose	liquid dispersion
Novoperm Bordeaux HF3R	Clariant Intern. Ltd., CH	printing inks	powder

Table 10–4: Continued

C.I. name/ Trademark	*Manufacturer*	*Main applications*	*Physical form*
Graphtol Bordeaux HF3R	Clariant Intern. Ltd., CH	plastics	powder
P.Br. 25			
Hostaprint Brown HFR 31	Clariant Intern. Ltd., CH	plastics	powder
Microdis Brown PSR	Colorom SA, Romania	other	paste
Microdis Yellowish Brown IGT	Colorom SA, Romania	other	paste
Novofil Brown HFR	Clariant Intern. Ltd., CH	colouration of viscose	liquid dispersion
PV Fast Brown HFR 01	Clariant Intern. Ltd., CH	plastics	powder
Renol Brown HFR-HW	Clariant Intern. Ltd., CH	solvent based wood stains and marker inks	powder

10.7
Safety, Health and Environmental Aspects

Because of their physicochemical properties benzimidazolone pigments represent an extremely low toxicological and environmental risk. Like other azo pigments, the benzimidazolone pigments have very high oral LD_{50} values. Exposure to fine dust should however be avoided in the workplace, and normal industrial hygiene procedures for handling chemicals should be practiced.

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11

Diketopyrrolopyrrole (DPP) Pigments

Olof Wallquist

11.1

Introduction

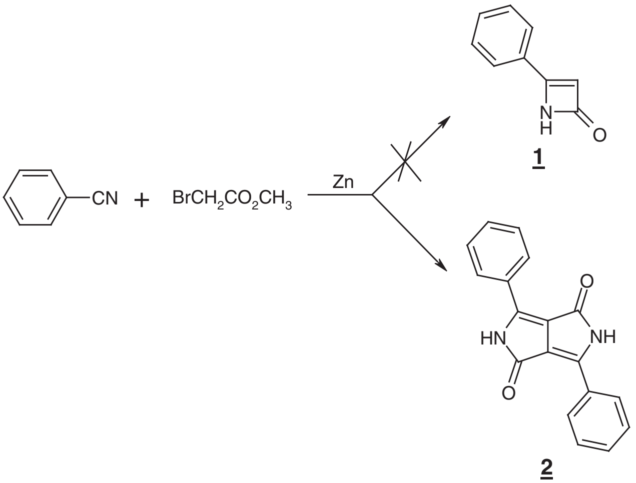
This chapter summarizes the scientific, technological and applicatory know-how on Diketopyrrolopyrrole (DPP) Pigments available in the literature since their first appearance in 1974 up to about July 2000. Emphasis is placed on the chemistry, properties and applications.

11.1.1

History

In 1974, Farnum, et al.[1] briefly reported on the attempted synthesis of 2-azetinones (**1**), in accordance with Scheme 11–1.

The proposed reaction failed, however, to produce the target lactam **1**. Instead, the authors isolated in 5–20 % yield the diphenyl DPP derivative **2**, in addition to several other by-products.



Scheme 11–1

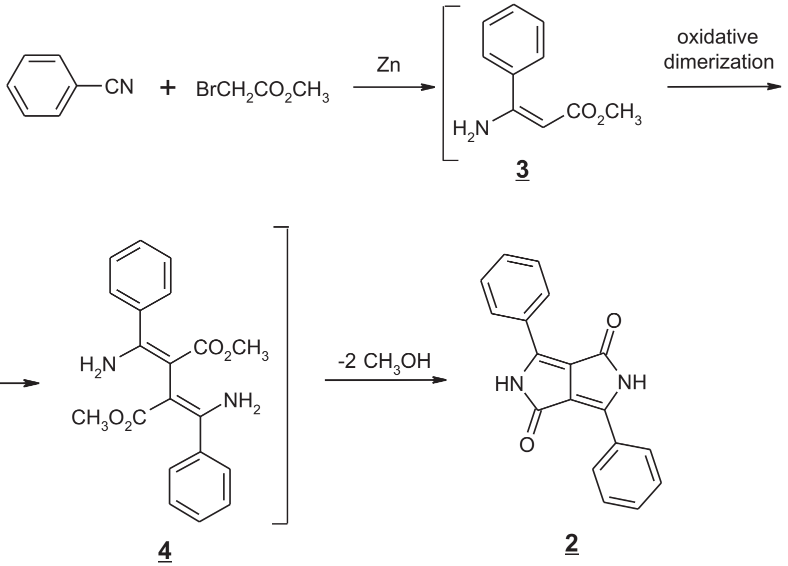
The physical properties of the DPPs such as its mp (> 350 °C), high insolubility and red color remained unremarked until researchers from Ciba-Geigy (now Ciba Specialty Chemicals) took notice of this reaction in a compilation of interesting reactions published by Ranganathan in 1980[2]. The chemistry and the applicatory properties were developed[3–4], and in 1986 the first DPP Pigment was introduced to the market. Since then, several other DPP Pigments have been developed and introduced to the market for conventional pigment applications like paints, plastics, fibers and inks. In recent years, interest in the DPP chromophore for non-conventional applications ("high tech" applications) has grown increasingly, and a large number of patent applications in different areas have been filed.

11.2
Syntheses

Several syntheses of the diketopyrrolopyrrole skeleton have been described in the literature. In the following sections, the different syntheses published are summarized.

11.2.1
Reformatsky Route

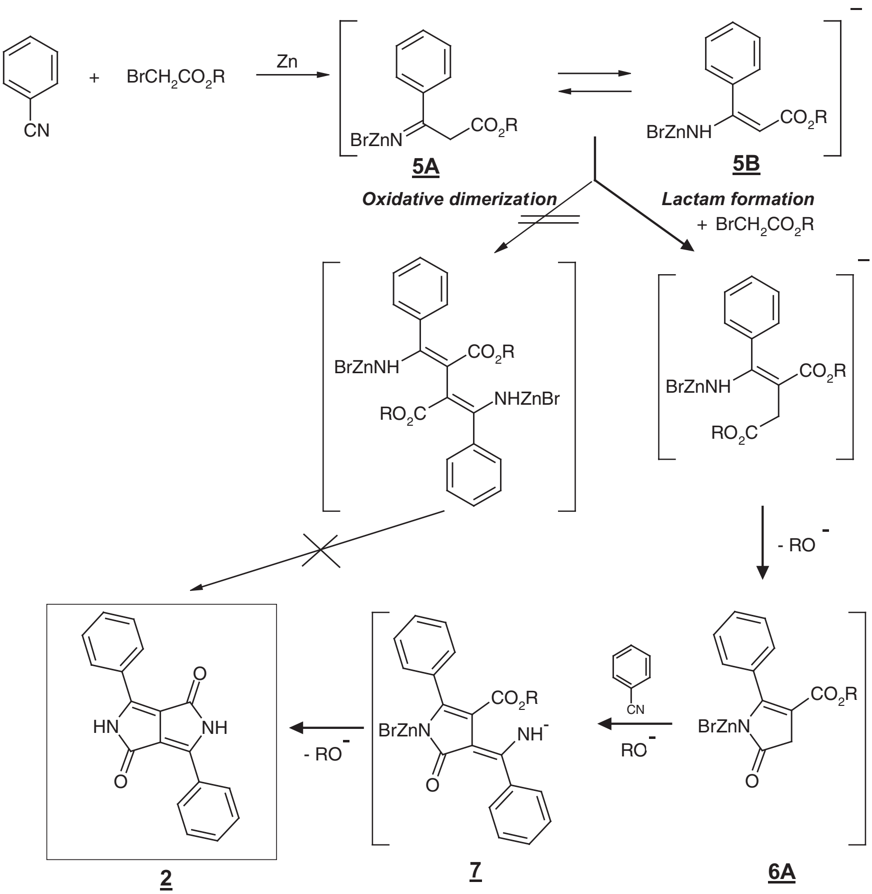
In the original publication[1] describing the first DPP synthesis (Scheme 11–1) via a Reformatsky reaction, the authors postulated that the formation of the DPP **2** proceed via an oxidative dimerization as depicted in Scheme 11–2.



Scheme 11–2: DPP formation mechanism proposed by Farnum et al.[1]

In 1988, new investigations on the Reformatsky route were published[5]. Synthesis of crucial intermediates and crossing experiments using two different benzonitriles strongly indicated that the reaction did not proceed via an oxidative dimerization mechanism and the intermediate **4**. Instead, it could be shown, that the lactam **5** is formed during the reaction, and a new mechanism was postulated involving a sequential build up of the DPP via the pyrrolinone ester **6A** as the crucial intermediate (Scheme 11–3).

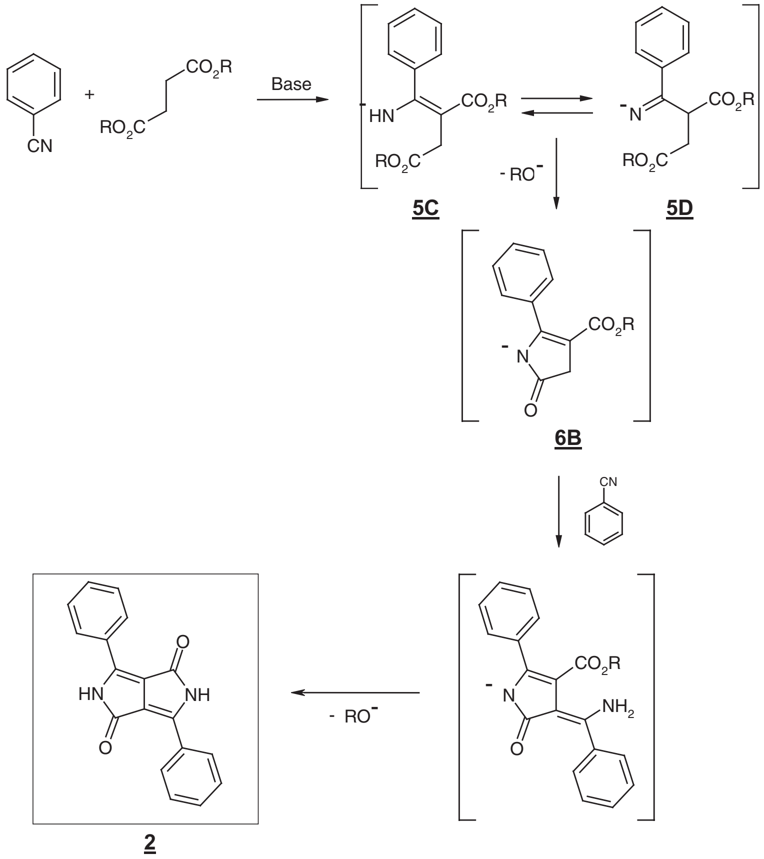
The first step is considered to involve the condensation of the Reformatsky reagent with benzonitrile to yield the Zn-salt **5**. C-alkylation by bromoacetate, followed by ring closure, is believed to lead to the hitherto elusive key intermediate **6A**, a pyrrolinone ester. Condensation with a second molecule of benzonitrile and subsequent cyclization of intermediate **7**, which could be isolated and was also mentioned by Farnum, finally affords the DPP **2**.



Scheme 11–3: Reformatsky reaction: possible reaction pathways.

11.2.2
Succinic Ester Route

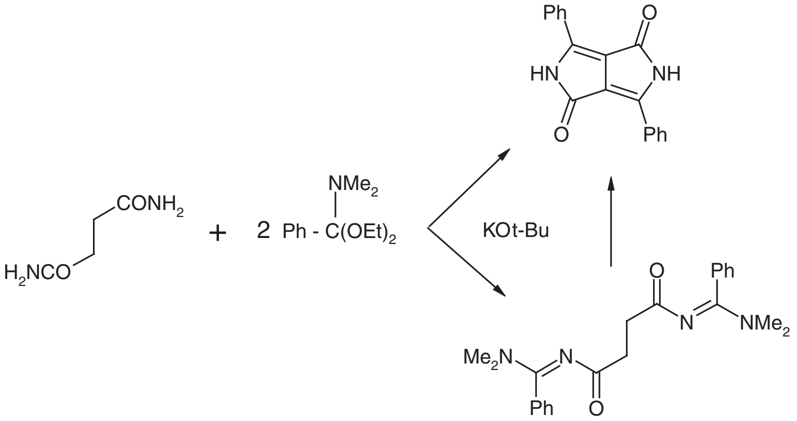
A second new route to DPP Pigments was developed and published 1983[5, 6]. In this route, succinic ester is condensed in a pseudo-Stobbe condensation with an aromatic nitrile in the presence of strong base to afford the desired DPP in good yield (Scheme 11–4). Mechanistically, the formation of a DPP unit from succinic esters is believed to proceed along the pathway shown in Scheme 11–4. The initially formed enaminoesters **5C/5D** cyclize to the pyrrolinone esters **6B**, which further react under basic conditions with another benzonitrile. Subsequent ring closure affords the DPP **2**.



Scheme 11–4: Mechanism of DPP formation via the succinic ester route.

11.2.3
Succinic Amide Route

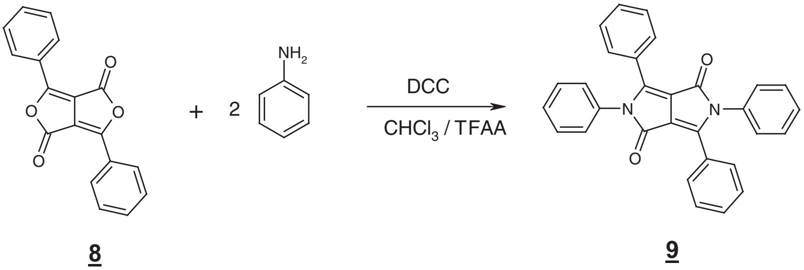
Yet another synthesis has been described by Prof. R. Gompper[7], involving the reaction of succinamide with *N*,*N*-dimethylbenzamide diethylacetal (Scheme 11–5).



Scheme 11–5

11.2.4
Miscellaneous Routes

During investigations to synthesize *N*,*N*′-dimethyl-DPP, Langhals et al. have been able to condense the diketofurofurane **8** with anilines in the presence of dicyclohexylcarbodiimide and isolate the tetraphenyl DPP **9** in 46 % yield (Scheme 11–6)[8].



Scheme 11–6

11.3
Molecular Structure and Properties

11.3.1
Spectral Properties

The diketopyrrolopyrrole is a bicyclic 8π electron system containing two lactam units. The characteristic physical properties of DPP **2** are the high melting point (>350 °C), low solubility (< 110 mg/l in DMF at 25 °C[3]) and an absorption in the visible region with a molar extinction coefficient of 33 000 (dm^2mol^{-1}). In solution, DPP **2** gives a yellow fluorescing solution, whereas in the solid state it is a vivid red. The absorption spectra of **2** in solution (dimethylsulfoxide) and in the solid state (of an evaporated film) are shown in Figure 11–1[5, 9].

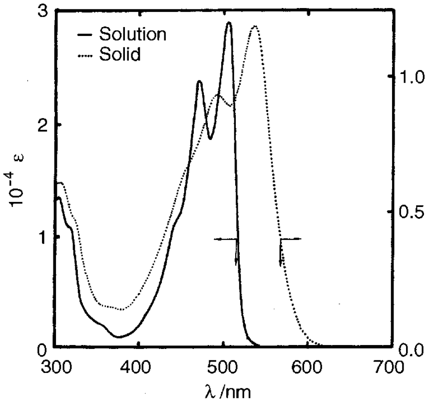


Figure 11–1: Absorption spectra of DPP **2** in solution (DMSO) and in the solid state (evaporated film).

Table 11–1 below shows the absorption maxima (λ_{max}) of differently substituted DPPs measured in solution together with the ε values, as well as the absorption maxima in the solid state, obtained by reflectance measurement on PVC-white reductions.

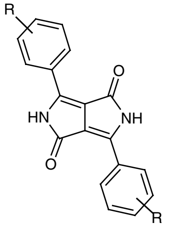


Table 11–1: Influence of substituents on shade and absorption (λ_{max}) of diaryl-DPPs.

DPP	*R*	*Shade*^{a}	*Absorption maxima λ_{max} (nm)* *In solution*^{b}	 *In solid state*^{c}	$\Delta\lambda_{max}$	$\varepsilon_{max}{}^d$
11	*m*-CF_3	Orange-yellow	509	518	9	21.500
12	*m*–Cl	Orange	512	528	16	27.000
2	H	Yellow-red	504	538	34	33.000
13	*p*-Br	Blue-red	515	555	40	35.000
14	*p*-$N(CH_3)_2$	Violet-blue	554	603	51	81.500

a) in plasticized PVC pigmented with 0.2 % DPP derivative;
b) measured in *N*-methylpyrrolidone;
c) obtained via reflectance measurements on PVC white reductions and subsequent computation after Kubelka-Munk;
d) molar extinction coefficient at wavelength of maximum absorption in solution

As with many other classes of pigments, all DPP pigments show a bathochromic shift of the maximum absorption in the solid state with respect to the maximum absorption in solution. The solid state absorption maxima of DPP depend strongly on the nature and position of the substituent. In comparison with the unsubstituted DPP **2**, the λ_{max} of *m,m'* substituted DPP often show a hypsochromic shift and the λ_{max} of *p,p'* substituted DPP a bathochromic shift.

The large bathochromic shift of the λ_{max} in the solid state compared to that in solution is due to the strong intermolecular interactions, i.e. the hydrogen bonding, π-π- and van der Waals interactions in the solid state. The extent to which the different interactions contribute to the bathochromic shift is not known. Detailed investigations of the influence of the intermolecular hydrogen bonding on the spectral properties of DPP have been published[5, 10]. The spectroscopic (^{1}H-, ^{13}C-NMR, UV-Vis and IR), thermogravimetric and conductivity investigations on DPP, *N*-methyl-DPP and *N,N'*-dimethyl-DPP lead to the conclusion that intermolecular hydrogen bonding is the predominant interaction, and the reason for the strong bathochromic shift of the λ_{max} in the solid state of the DPP molecule compared to the λ_{max} in solution.

Theoretical considerations and calculations have been done as well to explain the strong bathochromic shift of the DPP molecule[11]. In semiempirical MO INDO/S calculations, the authors investigated the influence of the geometry of aggregates on the electronic and spectral properties. The results of these calculations were in accordance with the previous investigations, which indicated, that the source of the above bathochromic shift is the intermolecular hydrogen bonding. In addition, the calculations also found that the π-π-stacking would result in a small hypsochromic shift.

11.3.2
Spectral Properties – Fluorescence

Like many other pigment classes, DPP pigments fluoresce in solution. The Stokes shifts are in the range 10–15 nm and the fluorescence quantum yields ca. 60 %[12]. In the solid state, some DPPs show a minor fluorescence. Through N substitution, both the solubility and the Stokes shift can be increased.

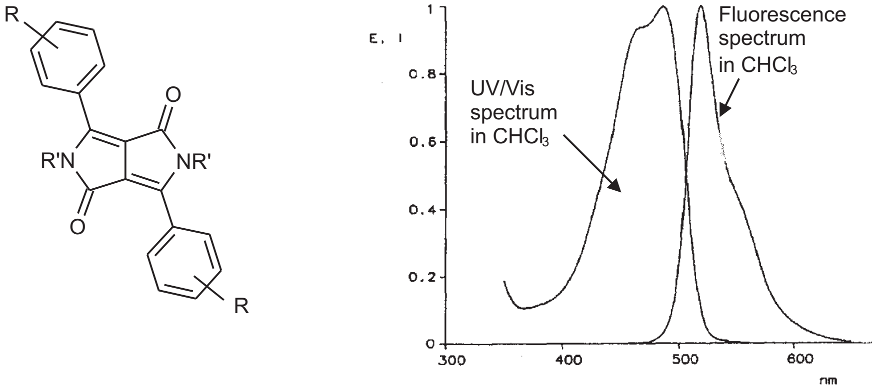


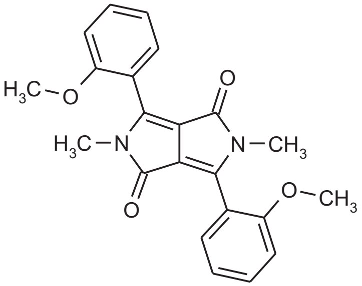
Figure 11–2: Absorption and emission spectra of DPP **2** in solution and solid state[13].

Table 11–2: Absorptions and emissions of DPP[13, 14].

DPP	*R*	*R′*	*λ_{max} a) Absorption (nm)*	*λ_{max} a) Fluoresence (nm)*	*φ b) (%)*
2	H	H	496	509	–
15	4-*t*-Bu	H	502	513	63
16	3,5-*t*-Bu	H	500	513	63
17	2-Me	H	448	518	64
18	H	CH_3	474	523	54
19	4-*t*-Bu	CH_3	485	528	53
20	3,5-*t*-Bu	CH_3	484	525	56
21	2-Me	CH_3	439	489	95
22	H	Ph	484	520 (555 sh)	

a) In chloroform
b) Fluorescence quantum yields in $CHCl_3$ in comparison to 3,4,9,10-perylenetetracarbonic acid tetramethylester

Some specifically substituted N-substituted DPPs also show a solid state fluorescence. One interesting case has been described by H. Langhals[14] where the DPP **23** can crystallize in two different crystal modification, one strongly fluorescing and the other showing only a very weak fluorescence. The two modifications showing different optical properties can be interconverted through a heating / crystallization process, thus being principally interesting for information storage applications[15]. Another use as a light guide concentrator has been described[16].



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Further photophysical studies on fluorescing DPPs have been conducted by Johansson[17] including spectroscopic studies of a DPP in a lyotropic nematic liquid crystal and a comparison of the molecular symmetry of the ground state versus the first excited state.

11.3.3
Single X-ray Structure Analysis

The intra- and intermolecular arrangements of the DPP molecules in a DPP crystal have been investigated by single X-ray structure analysis[18–24]. Angles and bond distances in the diphenyl DPP **2** are shown in Figure 11–3.

The DPP molecule is practically planar, the phenyl rings being twisted out of the heterocyclic plane by 7°. The distance between the two hydrogen atoms at N2 and C6 is 2.08 Å, while that between the hydrogen atom at C10 and O11 is 2.24 Å. For both cases, the sum of the corresponding van der Waals radii is substantially larger, being 2.4 Å and 2.6 Å respectively, thus implying resonance interaction between the DPP chromophore unit and the phenyl rings. This appears to be confirmed by a C3–C5 bond length of 1.43 Å, which is shorter and hence possesses even more pronounced double bond character than the bond (1.496 Å) between the two aromatic rings of biphenyl. Such resonance interactions, amongst others, would explain the electronic influence of substituents on the earlier mentioned wavelength shifts (see Table 11–1) of maximum absorption, and hence of color of different diaryl DPP derivatives in solution.

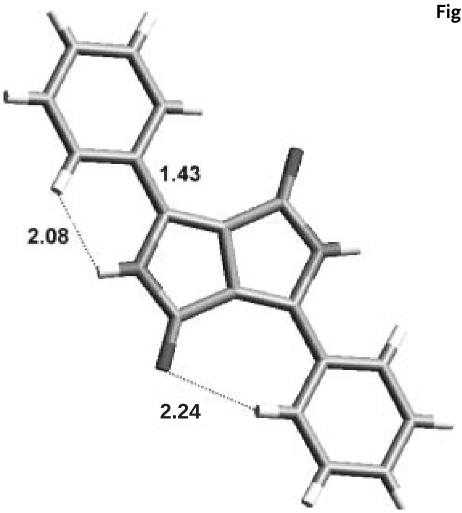


Figure 11–3: Perspective view of diphenyl-DPP **2**

Figure 11–4 depicts the projection of the crystal packing on the crystallographic (b,c)-plane, highlighting the intermolecular hydrogen bonding between neighboring lactam NH and carbonyl O atoms. This in turn determines the molecular packing along the a-b diagonal of the crystal lattice. In addition, the weak van der Waals contact between the terminal phenyl group atoms can be viewed.

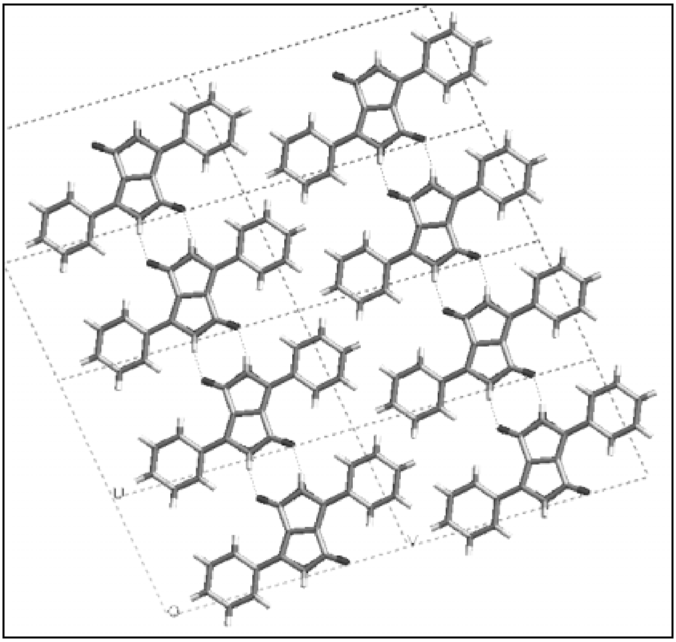


Figure 11–4: Projection of diphenyl-DPP crystal **2** on the (b,c)-plane and illustration of the hydrogen bond interaction.

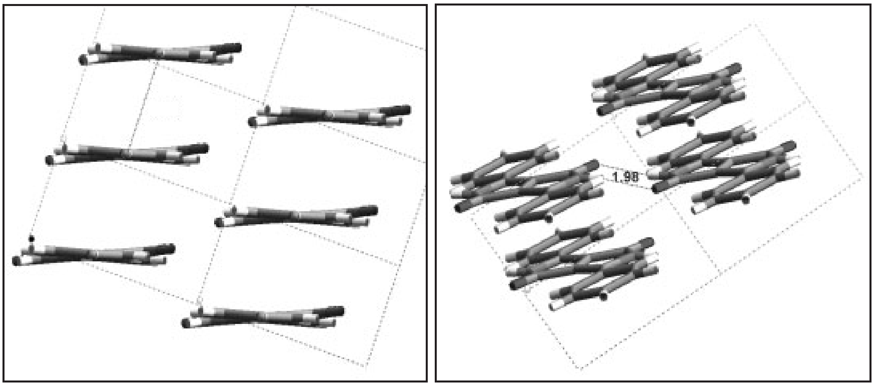


Figure 11–5: Illustration of the hydrogen bond and the π-π interaction.

Figure 11–5 illustrates the geometry of the hydrogen bond between two DPP molecules viewed through the phenyl ring at two slightly different angles. The hydrogen bond is slightly angled since the two interacting DPP molecules are not in the same plane. In addition, the π-π interaction between the layers of two DPPs is illustrated.

The crystal packing along the a-axis is determined by π-π interactions between layers of molecules. In Figure 11–6 the π-π interactions are viewed through the H–N bond, giving a good illustration of the distances in the crystal.

The optimum interlayer distances between chromophore planes (3.36 Å) and between phenyl ring planes (3.54 Å) are short enough to warrant significant π-π interactions, the growth of crystals investigated being also the strongest along this direction.

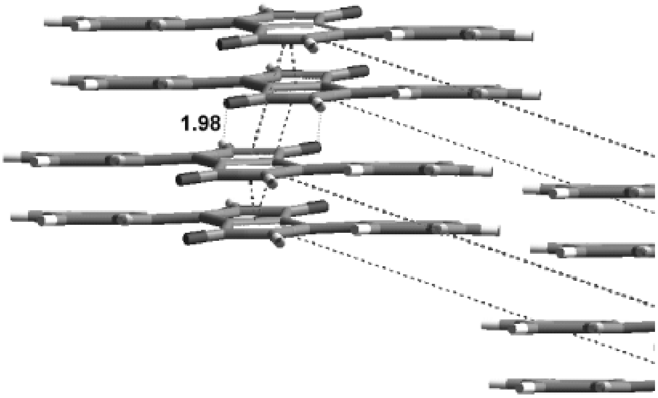


Figure 11–6: Projection of diphenyl-DPP 2 crystal on the (a,b)-plane.

11.4
Chemical Properties

A qualitative inspection of the diaryl-DPP molecule (Figure 11–7) reveals several centers of reactivity in the molecule.

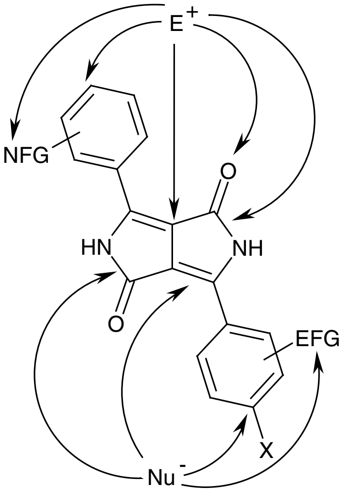


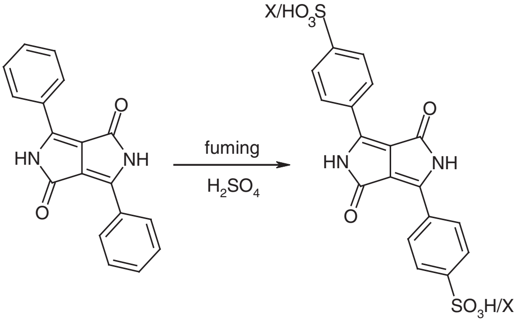
Figure 11–7: Potentially reactive centers in a diaryl-DPP derivative.
EFG: electrophilic functional group, e.g. CN, COOR
NFG: nucleophilic functional group, e.g. OH, SH, NHR
X: e.g. halogen

While the appropriately substituted phenyl rings should be capable of undergoing diverse electrophilic and nucleophilic aromatic substitution reactions, the bicyclic lactam chromophore unit incorporates three different functional groups, namely double bonds, carbonyl, and NH groups, each of them being potentially amenable to chemical transformation. Since concomitantly forming part of the diarylbutadiene and aminocinnamic ester substructures of the DPP molecule, the bicyclic lactam double bonds might also be expected to react in analogy with the double bonds in diphenyl butadiene and cinnamic ester itself.

11.4.1
Electrophilic Aromatic Substitution

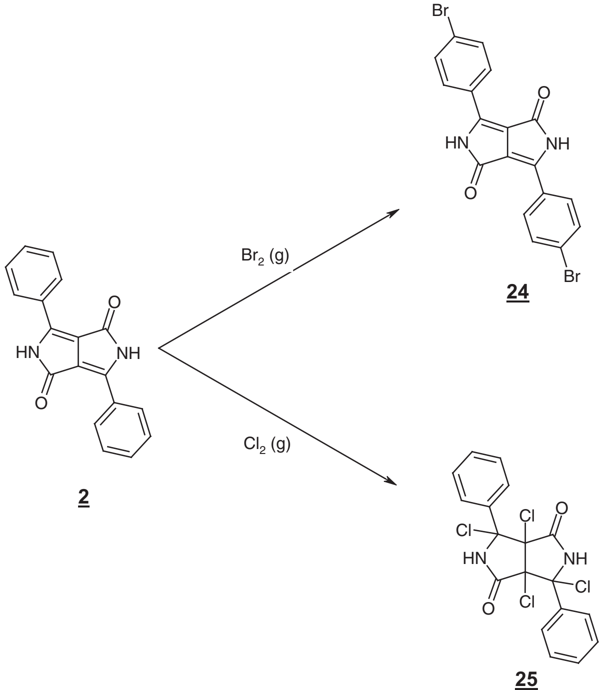
Diphenyl-DPP **2** was smoothly sulfonated to the corresponding disulfonic acid and acid salts **23** according to Scheme 11–7. Group II metal and ammonium salts of **23** proved to be thermally highly stable compounds and also useful pigment surface treating agents, frequently warranting rheological improvement of DPP pigment dispersions in various paint media[25–26].

The aromatic halogenation of diphenyl-DPP **2** did not however proceed as unambiguously as the sulfonation reaction. Bromination of the unsubstituted DPP **2** gave the electrophilic aromatic substitution product 4,4’-dibromophenyl DPP (**24**), whereas the corresponding chlorination gave the fairly unstable addition product **25** (Scheme 11–8)[27].



2 **23**

Scheme 11–7



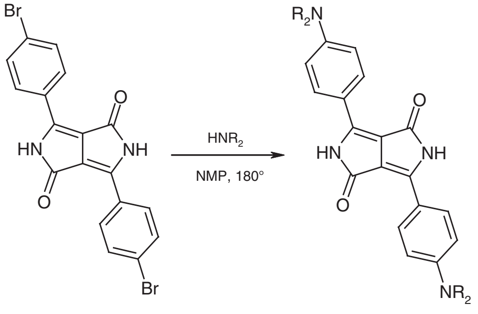
2 **24** **25**

Scheme 11–8

The different reaction pathways of bromine and chlorine was explained by a pre-equilibrium addition reaction to the double bonds allowing for a differentiation between the bromine being a better leaving group and a better nucleophile compared to the chlorine[5].

11.4.2
Nucleophilic Aromatic Substitution

In analogy to other aromatic systems, nucleophilic aromatic substitution can also take place, depending on the substituents on the aromatic ring. 4,4'-Bromophenyl DPP (**24**) can react with amines at high temperatures in polar solvents to give 4,4'-diaminosubstituted DPP (**26**) as illustrated in Scheme 11–9[28].

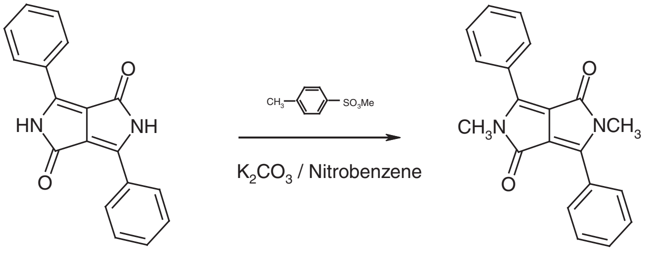


24 26

Scheme 11–9

11.4.3
N-Alkylation

The alkylation of the heterocyclic DPP moiety by alkyl halides or alkyl sulfonates yielded only N- and no O-alkylated products, as exemplified by the N-methylation of diphenyl-DPP **2** (Scheme 11–10)[29].



2 27

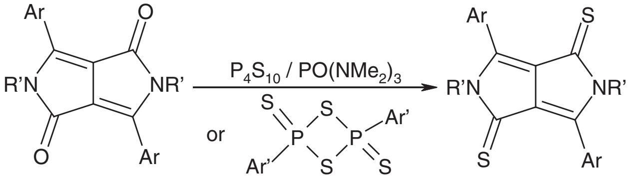
Scheme 11–10

As a direct consequence of N-alkylation excluding the possibility of intermolecular hydrogen bond formation in the solid state, the solubilities of diaryl-DPPs were drastically raised upon N-substitution (e.g. solubility in DMF at 25 °C: 100 mg/l for **2** but 3300 mg/l for **27**). Most of the N-substituted DPP derivatives fluoresced strongly, and with appropriately substituted derivatives *Stokes' shifts* of up to 70 nm at fluorescence quantum yields of up to 95 % have been reported (see Sec. 11.3.2).

11.4.4
Transformations at the Carbonyl Group

Nucleophilic transformation at the carbonyl group of DPP without cleavage of the bicyclic ring system corresponding to a formal replacement of O by S, N and C have also been investigated[6].

Attempts at direct reaction of nucleophiles with diaryl-DPPs were foiled by the low reactivity of the carbonyl group. However, replacement of O by S could be achieved by reacting diaryl-DPPs with P_4S_{10} or the Lawesson reagent (Scheme 11–11)[30].



29

Scheme 11–11

Derivatives of the type **29** have also proved to be more suitable starting materials than the corresponding O-analog for condensation reactions with carbanions like malodinitrile, ultimately enabling the formal replacement of O by C[31].

In order to achieve a formal displacement of the oxygen with a nucleophile, an activation of the carbonyl group with $POCl_3$ was necessary. The phosphorylated DPP could be transformed to the corresponding DPP imines by reaction with aniline[5, 32].

In the presence of $POCl_3$ / PCl_5, Prof. Gompper has transformed the DPP **2** to the corresponding imminium chloride, which could react further with N,N-dimethylaniline[33].

11.5
Solid State Properties

11.5.1
General Properties

A broad spectrum of solid state shades ranging from yellow to blue-violet have been accomplished by exchanging the substituents in the phenyl rings of the DPP chromophoric unit. Most DPP pigments display high color strength, the high ε_{max} values being additional testimony to this. The level of light- and weatherfastness of such pigments is in general excellent both in full shades and white reductions, making the DPP pigments very suitable for automotive and industrial coatings. Despite their low molecular weights, the diaryl-1,4-diketopyrrolopyrroles are highly insoluble and remarkably resistant to migration, even when carrying otherwise solubilizing alkyl substituents such as the tertiary butyl group. The DPP pigments also show good to excellent thermal stability, surpassing 400 °C (TGA) and allowing for use in plastics and fibers applications, mainly polyolefins. A major and striking feature of many DPP pigments compared to other pigment classes is the high chroma observed in the applications, which is related to the high purity of the compounds and the relatively sharp absorption bands.

11.5.2
Particle Size Control

DPP pigments with different particle sizes can be made by several methods. Classical conditioning (particle growth) in different solvents give rise to larger particles with different morphology depending on the solvent characteristics[34]. Large particles can also be achieved directly in the synthesis through a heat treatment after the protonation of the intermediate pigment sodium salt. Small particles are obtained either through classical mechanical diminution of the pigment particles through wet milling, dry milling or kneading, or through an acidic or basic reprecipitation. In addition, new methods are now known by which small particle size DPP Pigments can be formed in situ[35–40].

Typical examples of an opaque and a transparent DPP are shown in the Figure 11–8.

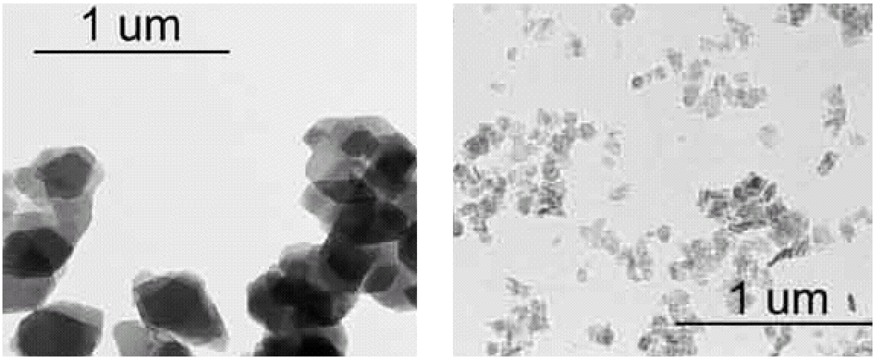


Figure 11–8: Transmission electron micrographs of C.I. Pigment Red 254 in an opaque (left) and a transparent form (right).

11.5.3
Polymorphism

As in many other pigment classes such as copper phthalocyanines and quinacridones[41], different crystal modifications of DPP pigments have been identified[42–45].

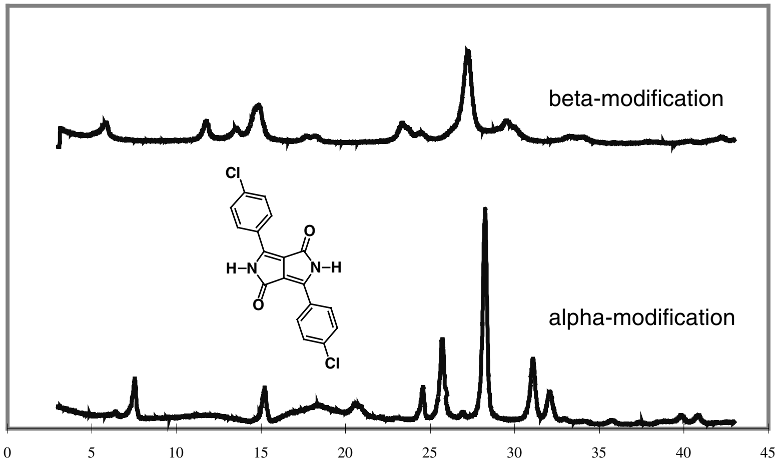


Figure 11–9: XRD of the α and the β modification of C.I. Pigment Red 254.

C.I. Pigment Red 254 for example exists in two different crystal modifications, as illustrated in Figure 11–9. The α modification is a medium to slightly bluish shade of red and the thermodynamically more stable modification, whereas the β modification is a more yellowish red.

11.5.4
Solid Solutions

Solid solution formation, where two or more components form one crystal lattice over a continuous range of compositions, is frequently observed in dye and pigment chemistry[46]. As a consequence, the X-ray diffraction pattern of such a solid solution is the same or very similar to that of one of the components, the host. In analogy to liquid solutions, the "guest" molecules are dissolved into the crystal lattice of the "host". In some cases this can also lead to a variation of the coloristic and other properties compared to a physical mixture of the individual pigments. A special case of solid solutions is a mixed crystal, where a specific composition containing two components results in a unique diffraction pattern different from the XRD of either of the components. In this case, a loose analogy can be drawn to the formation of azeotropes in the liquid state. Both cases have been observed within DPP chemistry.

Solid solution formation between different DPPs can be achieved through a DPP synthesis using two (or more) nitriles[5, 47–48], giving rise to a ternary solid solution, in which the components accommodate the crystal lattice of one of the symmetric DPPs or the crystal lattice the asymmetric DPP. The formation of a solid solution is sometimes accompanied by a bathochromic or a hypsochromic shift of the solid state hue.

Alternatively, binary DPP-DPP solid solutions or mixed crystals can also be formed through an acidic or basic reprecipitation or through a milling process of two (or more) DPPs[49–51]. Depending on the size and the interaction of the components in the solid solutions or mixed crystal, coloristic shifts and changes of the pigmentary properties can be observed as well.

Figure 11–10 illustrates both a ternary and a binary solid solution. The ternary solid solution of **AA**, **AB** and **BB** accomodates the lattice of the asymmetric DPP **AB**. A binary combination of equimolar amounts of the DPP **AA** (C.I. Pigment Red 255) and the symmetrical DPP **BB** (C.I. Pigment Red 254) can be combined and form an entirely new binary mixed crystal in the lattice of the asymmetrical DPP **AB**. The asymmetric DPP **AB** and the mixed crystal show a hypsochromic shift compared to the single components **AA** and **BB**.

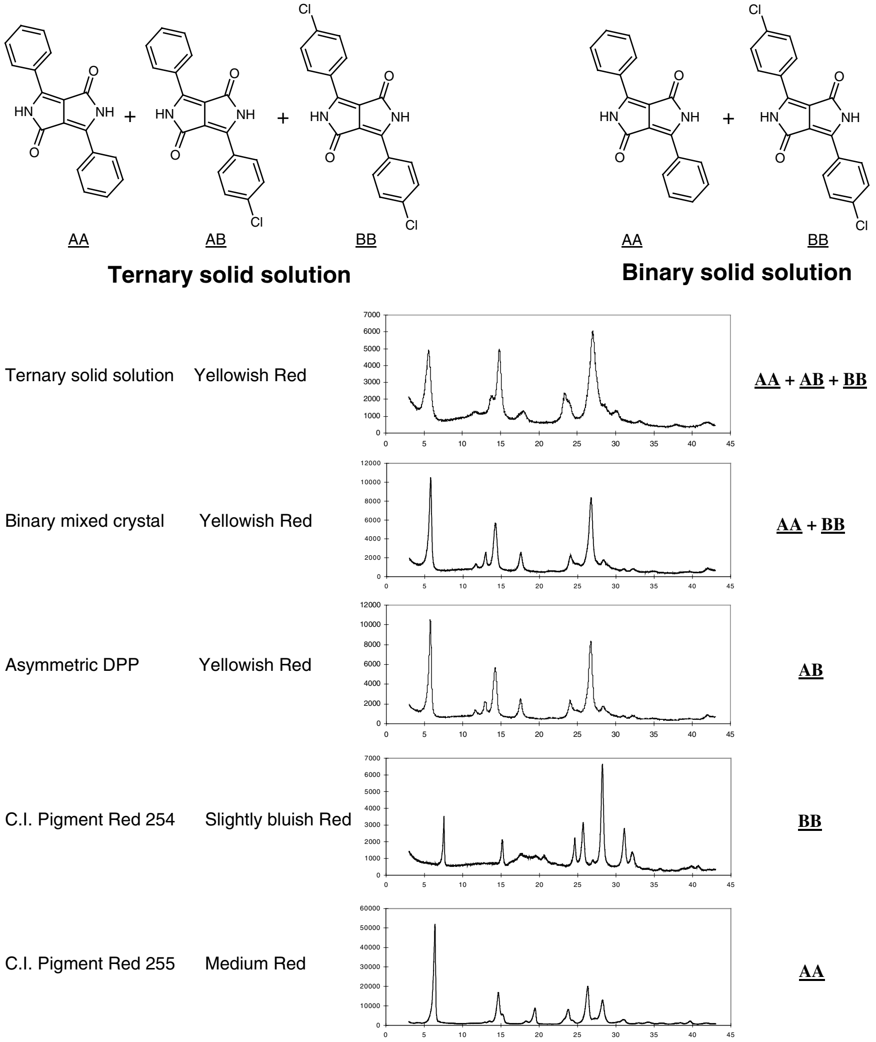


Figure 11–10: XRD and coloristics of a ternary and a binary solid solution (mixed crystal).

Figure 11–11 illustrates how equimolar amounts of the symmetrical DPP **AA** (C.I. Pigment Red 255) and symmetrical DPP **B’B’** (C.I. Pigment Orange 73) can be combined and form an entirely new binary mixed crystal in the lattice of the asymmetrical DPP **AB’**, again accommodating the coloristics of the asymmetric DPP. In this case, however, the asymmetric DPP and the solid solution show a bathochromic shift compared to the single components **AA** and **B’B’** and the corresponding physical mixture of **AA** and **B’B’**[52].

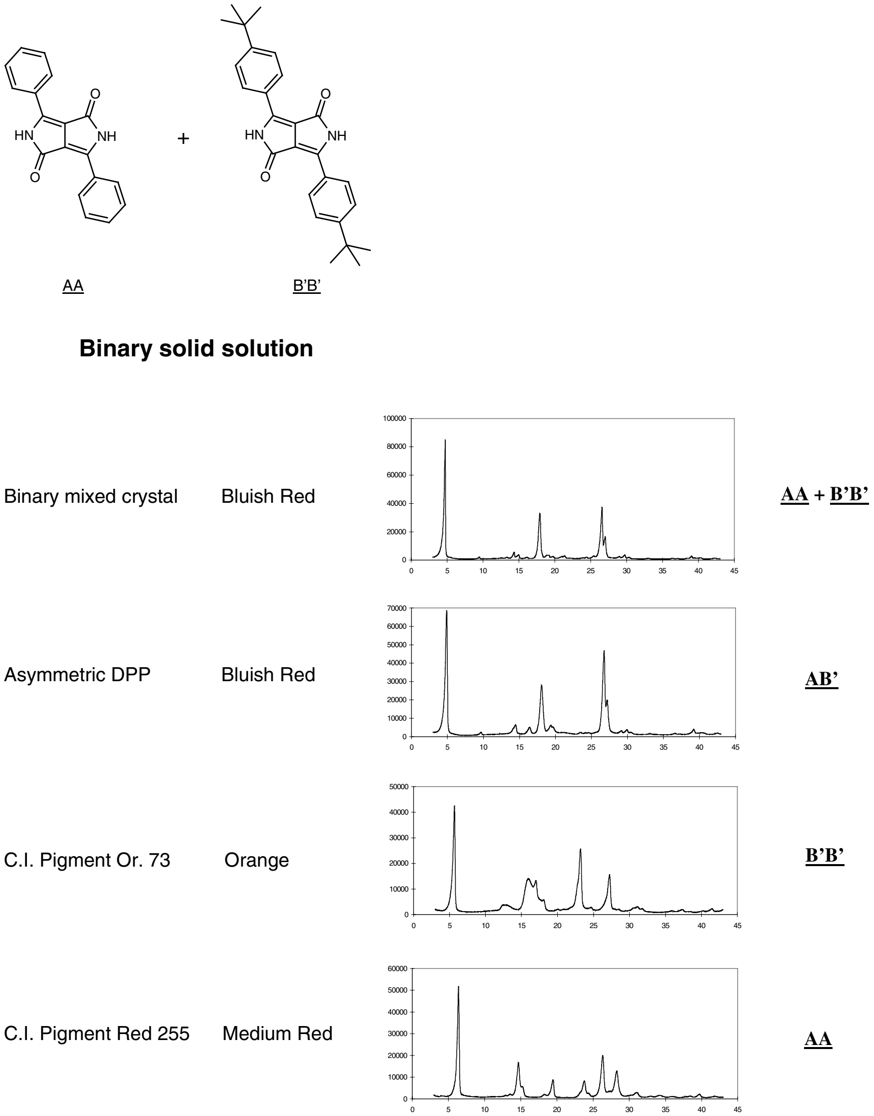


Figure 11–11: XRD and coloristics of a binary solid solution (mixed crystal) of **AA** and **BB.**

Solid solutions between a DPP and some other pigments have been investigated as well. Because of their similar structure and rigidity, DPPs frequently form solid solutions with quinacridone pigments[53–57]. Often, the solid solution shows a shift in color compared to a physical mixture of the individual components.

Recently, combinations[1] of DPP Pigments with yet other pigments like thiazine indigo, benzimidazolone triphenodioxazine, anthraquinones, azo pigments, benzimidazolones, isoindolinones[58–60] have appeared in the literature. The value of these new combinations has yet to be established.

11.5.5
Surface modifications

Since pigment properties are dependent not only on the chemistry and solid state properties of the pigment, but to a large extent also on the application in which the pigment is being used and how it is applied in a defined application, the interaction between a pigment and a specific application media is of the utmost importance. This interaction depends to a large part on the surface characteristics of the pigment. In order to achieve the desired properties of a pigment in a given application, the surface characteristics of the pigment must first be optimized.

The surfaces of DPP Pigments have been modified to optimize their properties for both coatings and plastics applications. Many patents and some publications have appeared in the literature on this subject[2].

In general, different types of surface modifications of DPP have been investigated and can be summarized as follows:

Surface Modification			*References*
Organic	Pigment derivative	DPP derivatives	[61–78]
		QA derivatives	[79–84]
		Perylene derivatives	[85]
	Misc. derivative		[86–88]
	Polymer		[89–92]
Inorganic	Metal oxide		[93]
	Metal oxide modified		[94–95]
Grafting			[96–106]

The purpose of modifying the surface of pigments for paint applications is to improve the rheological properties of the paint millbase and thereby improve the aesthetic value (gloss) of the resulting coating[107], reduce the VOC (volatile organic compounds) and improve the economics of the paint formulations through an increase of the pigment concentration. Several DPPs with improved rheology and gloss have been introduced to the market involving C.I. Pigment Red 254, C.I. Pigment Red 264 and C.I. Pigment Orange 73.

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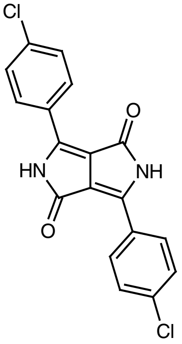
[1] In many cases no true solid solutions are being formed and designations such as combinations or hybrid pigments are used.

[2] Because of their abundance, not all references have been cited.

Specific surface treatments of pigments for plastics applications can be done to improve properties like dispersibility, warping and crystallization behavior. The warping (distortion) of polyethylene is strongly related to the crystallization of the polymer[108]. Through specific surface treatments, a reduction of the distorting properties of polyethylene can be achieved. DPPs have been surface treated to reduce the distortion, and commercial products based on C.I. Pigment Red 254 are now present on the market.

11.6
Conventional Applications

Many DPP pigments have been introduced to the market since the launch of the first DPP (C.I. Pigment Red 254) in 1986. The current3) commercial DPP pigments range coloristically from orange to bluish reds, with particle sizes allowing for both opaque and transparent colorations and with specific forms and surface modifications for inks, paints, plastics and fibers applications.



C.I. Pigment Red 254

C.I. Pigment Red 254 was introduced to the market in 1986 as the first representative of this new class of pigments. It is a highly saturated medium shade red pigment with good hiding power, excellent fastness to organic solvents and outstanding light and weather fastness. Because of its interesting properties, it has developed into a widely used high performance pigment for automotive and industrial paint applications, especially suited also for aqueous systems. A new type with improved gloss and rheological properties has just been introduced to the market. Several other types of P.R. 254 are finding increasing use in general industrial and architectural applications, permitting also lead- and cadmium-free formulations. A transparent type for metallic and effect finishes is available as well, allowing for the formulation of new saturated metallic shades.

Because of its brilliant shade, high color strength, opacity and saturation, different types of P.R. 254 are also being widely used in plastics applications, especially in polyolefins, PVC, and PS, where they offer excellent all-round properties and out-

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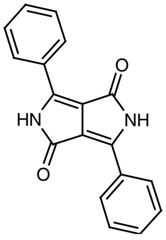
3) End of year 2000

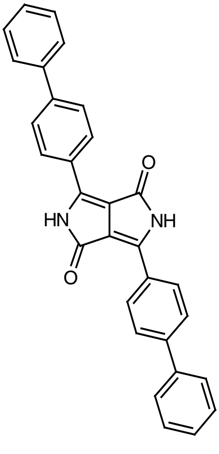
standing heat resistance. Major uses include transportation crates, caps, blow-molded containers and films. For injection molded HDPE, new types have become available enabling warp-free formulations to be produced. Selected grades are suitable for food packaging and toys, and meet national and international regulations including FDA (USA), FPL (France), BgVV (Germany) JHP/JHOSPA (Japan), TOYS and CONEG, EEG 94/62.



C.I. Pigment Red 255

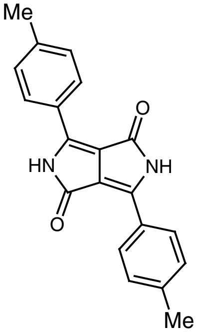
C.I. Pigment Red 255 is a yellowish Red DPP with excellent hiding power and outdoor durability. It is used for automotive OEM, refinish and general industrial paint applications including tinting applications and is recommended for lead-free formulations. Its solvent fastness is slightly inferior to that of P.R. 254.

Further, P.R. 255 can be used in PVC and in different inks applications. A less high-performing grade is available as well.



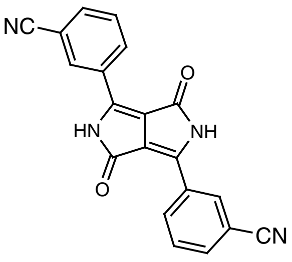
C.I. Pigment Red 264

C.I. P.R. 264 is a bluish shade, transparent red DPP with very high color strength, excellent durability, migration- and solvent-fastness as well as very high thermal stability. The pigment is being used in many different applications. It is especially suitable for metallic and effect finishes where it gives colorations with excellent durability and overpaint resistance, and allows for a broad coverage of red to bluish shade reds. The high tinctorial strength makes it also suitable as a shading component in many different applications including automotive and general industrial finishes. A new type with improved rheological properties has recently been commercialized. Its high thermal stability combined with insolubility makes it very suitable also for use in powder and coil coatings. It is also a very attractive pigment for many plastics and PP fiber applications, offering extremely high color strength and high transparency. It can be used for shading as it shows a high heat stability also at low concentrations. In injection molded HDPE it allows for formulations with low warping. There are grades available which meet several national and international regulations for food packaging and toys materials.



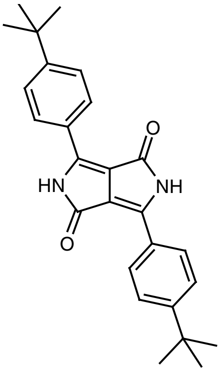
C.I. Pigment Red 272:

C.I. P.R. 272 is a slightly yellowish shade red with high chroma, very good hiding power and color strength. It offers good heat, light and migration resistance in plastics like PVC and polyolefins including PP fibers. Injection molded HDPE can be formulated warp free using this pigment. There are grades available which meet several national and international regulations for food packaging and toys materials. In general industrial paint application, it is recommended for lead- and cadmium-free formulations, due to its outstanding opacity.



C.I. Pigment Orange 71:

C.I. P.O. 71 is a very transparent orange with excellent heat stability and migration fastness in plastics applications like polyolefins, PP fibers, PVC and some engineering plastics. In injection molded HDPE it also allows for low warping formulations. Another grade with high tinctorial strength and chroma is being used for inks applications, both oil and liquid inks, including packaging, PVC and aqueous inks.



C.I. Pigment Orange 73

C.I. P.O. 73 is a brilliant medium shade orange with outstanding chroma, medium opacity and acceptable overpaint and solvent fastness. Because of its very high chroma, a broad range of shades including new color space can be formulated. It is recommended for general industrial, automotive OEM and refinish coatings, where it shows good durability. Since P.O. 73 has a good heat stability, it is also being used in plastics applications like PVC and polyolefins.

DPP-Quinacridone solid solutions

Two types of DPP-quinacridone solid solution pigments are available on the market. One is a yellowish, very transparent red for metallic and effect finishes with an unusual flop behavior. The durability in organic systems is good. The other type is a bluish shade transparent red for effect shades.

Specific information about properties and applications of individual pigments can be found in the commercial booklets.

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12

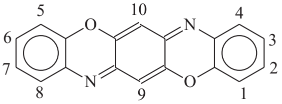
Dioxazine Violet Pigments

Terence Chamberlain

12.1 Introduction

The general class of compounds known as dioxazines, or more systematically as triphenodioxazines, exhibit colors ranging from yellow to violet, in the solid state, as a manifestation of their respective chemical and crystallographic structures[1].

The class is characterized by the parent of the series **1**, a condensed pentacyclic structure in which two oxazine rings with opposite orientation are sandwiched between three aromatic carbocycles of which the central one is quininoid:



1

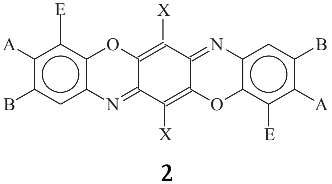
The symmetrical planar and conjugated quininoid structure is a very efficient chromophore, thus imparting intense coloration to those compounds of which it is a structural component.

The sulfonated derivatives of the parent structure, discovered in 1928 (Kranzlein et al., Farbewerke Hoechst), afford colorants which can be used as direct dyes on cotton, but the parent triphenodioxazine, an orange solid, has no technical importance as a colorant. It was not until 1952, however, that a tinctorially strong violet pigment derived from a 9,10-dichlorotriphenodioxazine was patented[2] and ultimately designated as Pigment Violet 23.

12.1.1

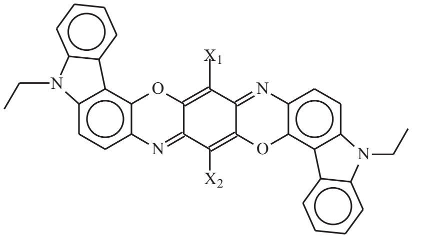
The Chemistry of Dioxazine Pigments

Dioxazine pigments are represented by the general structure **2**:



2

The technically important pigments possess the substitution pattern displayed in the general structure. Typically, A represents an acetylamino or a benzoylamino group, B represents an ethoxy group and X is a chlorine atom or an $HNCOCH_3$ moiety. Since production of Pigment Violet 34 and Pigment Violet 35 was discontinued several years ago there are currently only two dioxazine violets of commercial importance – Pigment Violet 23, which is used in considerable volume for miscellaneous applications including inks, plastics and coatings, and Pigment Violet 37, which is more of a specialty product and consequently used in somewhat lower volumes. Pigment Violet 37 corresponds to the general structure **2**, where A and B represent a benzoylamino group and an ethoxy group respectively, E = H and X is an acetylamino group. The more commercially successful product, Pigment Violet 23 (also referred to as Carbazole Violet), is an exception to the general structural format since A and B or A and E are combined as part of a fused indole moiety formally resulting in the impressive polycyclocondensed structures, where $X_1 = X_2 = Cl$:



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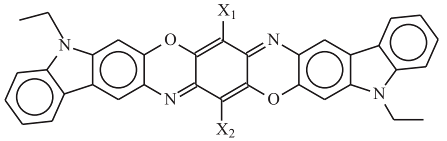

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Traditionally, the product has been assumed to possess the linear molecular structure **4**. However, comparison of the commercial product to one synthesized specifically to adopt the linear structure[3] exhibited differences between their respective visible spectra and other physical properties. Although speculative at that time, the data did imply the possibility that the actual molecular structure of Pigment Violet 23 was represented better by the “S” configuration resulting from angular ring fusion.

More recently[4], it has been demonstrated unequivocally, by single crystal X-ray diffraction analysis, that the molecular structure of Pigment Violet 23 does possess the angular configuration **3**, the result of an A-E fusion. In conjunction with that same research it has been demonstrated also that the linear structure affords a blue shade product that apparently has no commercial importance as a pigment.

12.2
Synthesis

Dioxazine synthesis involves two distinct stages: dianil formation and dianil cyclization.

12.2.1
Dianil Formation

The primary intermediate (generically referred to as the dianil), a 2,5-diarylamino-1,4-benzoquinone (**5**), where X = H or Cl or $NHCOCH_3$, is obtained by the reaction of an appropriately substituted aromatic primary amine with a suitably functionalized quinone. An acid scavenger (e.g. sodium acetate) is included in any process utilizing a chlorinated quinone to neutralize the cogenerated hydrogen chloride, which otherwise would proportionately deplete the amine component.

For example, the dianil of Pigment Violet 37 (**5**, B = D = OCH_2CH_3, A = NHCOPh, E = H, X = $NHCOCH_3$) is formed by the reaction of 2,5-diethoxy-4-benzoylaminoaniline (**6**), (B = D = OCH_2CH_3, A = NHCOPh) with 2,5-diacetylamino-3,6-dichloro-1,4-benzoquinone (**7**), (X = $NHCOCH_3$). Similarly the reaction between 3-amino-9-ethylcarbazole (**9**) and 2,3,5,6-tetrachloro-1,4-benzoquinone (**10**) affords the dianil precursor of Pigment Violet 23 (**5**), where A and E correspond to the fused indole moiety and B = D = H, X = Cl.

The solvent employed in the first stage may be different from that used in the second (cyclization) stage. In a process of that type the dianil is isolated prior to dioxazine formation being conducted in the second solvent. Obviously, overall efficiency is improved by conducting each stage sequentially as a one-pot process in a common solvent (e.g. *o*-dichlorobenzene).

12.2.2
Cyclization of the Dianil

Dioxazines are obtained by the cyclization of the corresponding dianils (**5**), a process that may be conducted by means of:

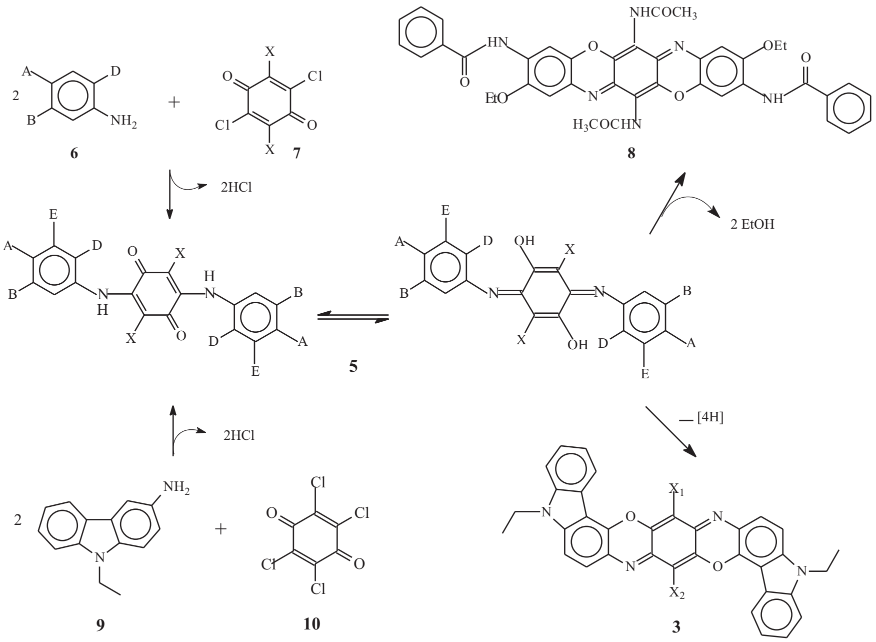
(a) Cyclocondensation (dealcoholation) of **5** when D = OR (R usually methyl or ethyl) (Scheme 12–1).

The reaction probably proceeds through the enol form of the dianil **5**, subsequently generating the cyclic ether by displacement of ethanol (when D = OCH_2CH_3). Since cyclization is regiospecific, directed by the nucleofugic alkoxy group, this synthetic method is selected for the preparation of specifically substituted dioxazines[3]. Cyclizations of this type are normally performed by heating at 170–175 °C for 4–5 h in solvents like *o*-dichlorobenzene in the presence of acidic agents such as benzoyl chloride. For example, the crude form of Pigment Violet 37 (**8**), is produced by this method[5] from its corresponding dianil **5**, (B = D = OCH_2CH_3, A = NHCOPh, E = H, X = $NHCOCH_3$).

Cyclization can be effected in the absence[3] of acidic agents, but substantially higher temperatures (> 200 °C) typically are required.

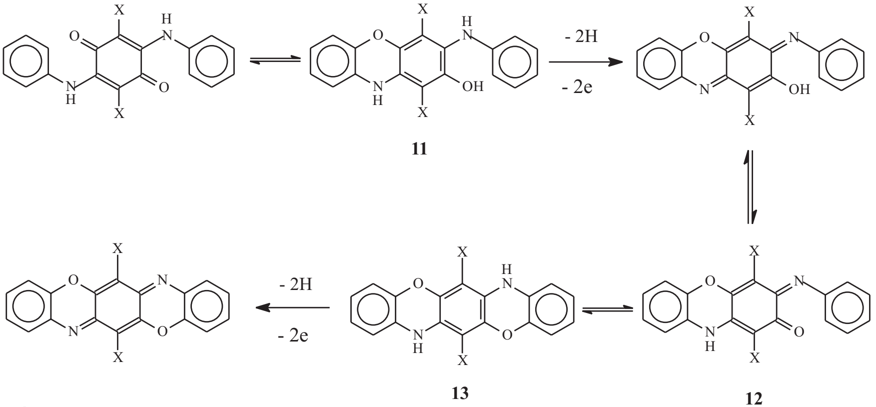
(b) Oxidation (cyclodehydrogenation) of **5**, when D = H.

This process, also conducted in solvents like *o*-dichlorobenzene, at similar temperatures (170–175 °C), in the presence of acidic agents, usually arylsulfonyl chlorides, is the typical method of synthesis for Pigment Violet 23 crude. However, the nature of this cyclization reaction is more complex than the cyclocondensation process, but can formally be represented as shown in Scheme 12–2.



Scheme 12–1.

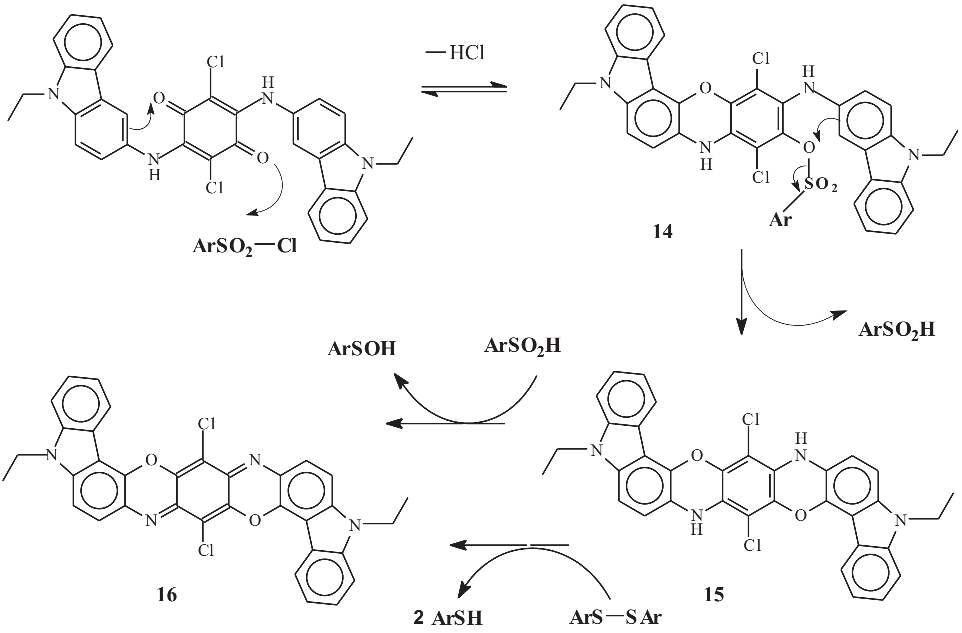
The process is probably initiated by cycloisomerization of the dianil to the diphenoxazine **11**, which oxidizes (dehydrogenates) to the azaquinone **12**. Cycloisomerization of the latter to the dihydrotriphenodioxazine **13**, followed by its oxidation, (dehydrogenation) then affords the corresponding triphenodioxazine in the final step.



Scheme 12–2.

Arylsulfonyl chlorides are typically employed as the cyclization agents in the oxidative route to dioxazines. In the manufacture of Pigment Violet 23 crude the most commonly employed agents are benzene- or *p*-toluene-sulfonyl chloride. Some literature articles describing the synthesis of dioxazines refer to the sulfonyl chlorides as catalysts, however, since they are consumed during the reaction, a more accurate description is cyclization agent.

Generally, sulfonyl chlorides are not considered as oxidizing agents, but some examples involving *p*-toluenesulfonyl chloride are known[6]. Therefore, during the cyclooxidation of the dianil **5** the sulfonyl chloride must be reduced. Since hydrogen chloride is a by-product of the reaction it is reasonable to assume the formation of an arylsulfonate ester (**14**) during the initial cyclization. Subsequent oxidation/cyclization, during which the sulfonate is reduced and expelled as an arylsulfinate (the oxidation state of S changing from +5 to +3), affords the dihydrotriphenodioxazine **15** (Scheme 12–3).

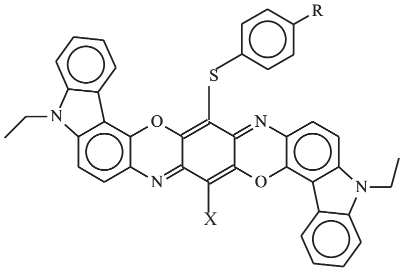


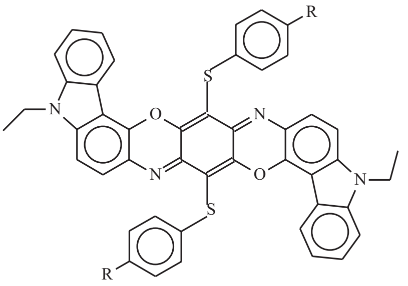
Scheme 12–3.

Although the composition of the oxidizing species involved in the dehydrogenation of **15** is not known with certainty, the participation of the arylsulfinic acid is clearly implicated by the formation of several specific by-products. The most probable structures, based on analysis by mass spectrometry, are the following thioether derivatives of the parent dioxazine (where X = H or X = Cl)[7]:

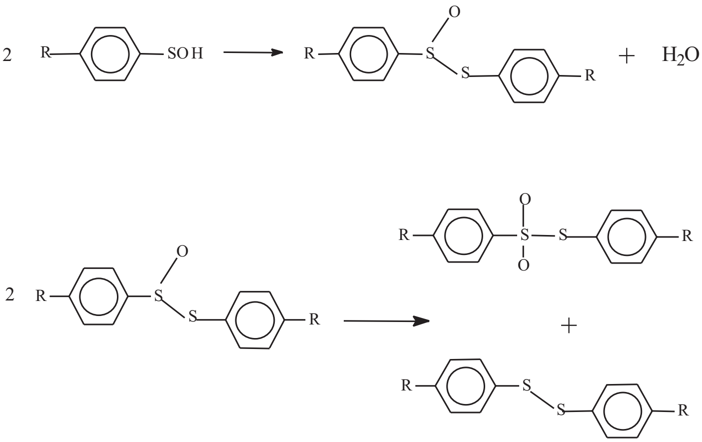
When the cyclizing agent is benzenesulfonyl chloride, R = H; when *p*-toluenesulfonyl chloride is used, R = CH_3. Consequently, the composition of the thioether group indicates which sulfonyl chloride has been employed in the synthesis.

Formation of the thioethers may be rationalized by assuming that some oxidation is effected by the arylsulfinic acid, which subsequently is reduced to the corresponding sulfenic acid (the oxidation state of S changing from +3 to +1). The inherent instability of the sulfenic acid is manifested [8] by its self-condensation to a thiosulfi-





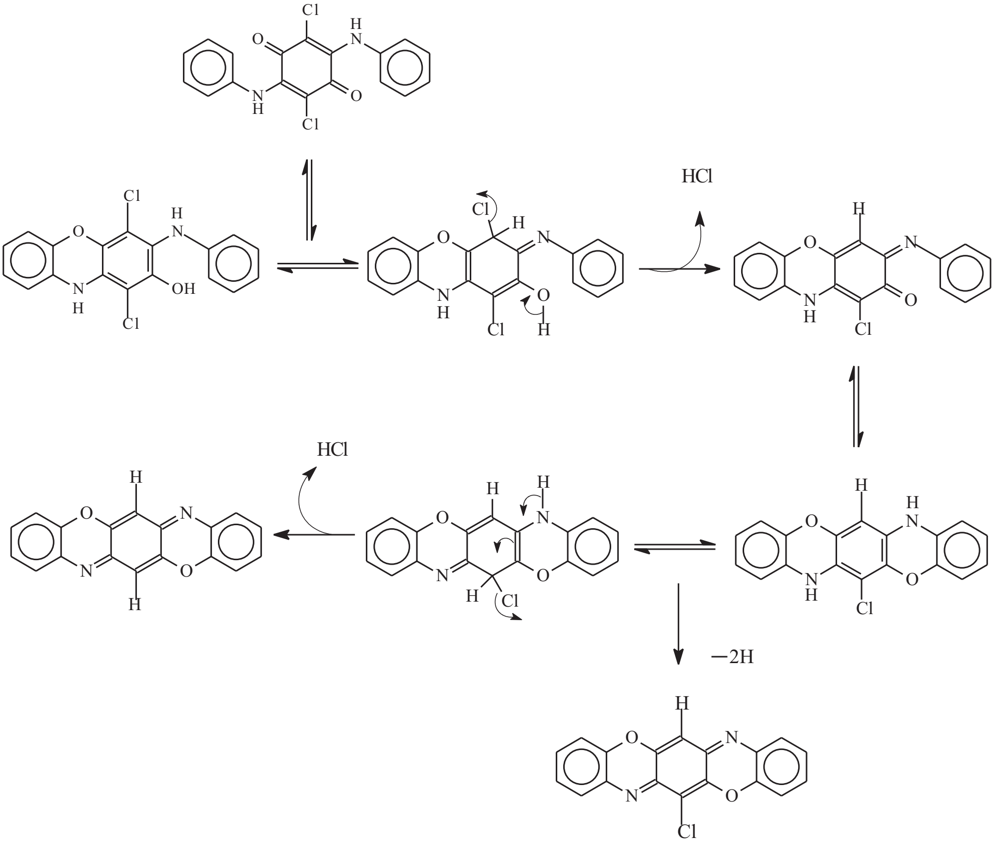
nate which, under the reaction conditions, disproportionates to afford a thiosulfonate and corresponding disulfide (as illustrated below Scheme 12-4). Since a disulfide will promote oxidation (dehydrogenation) during the facile reduction to its thiol components (the oxidation state of S changing from 0 to –1), the aryldisulfide probably competes with the arylsulfinic acid during the oxidation of the dihydrotriphenodioxazine **15**. The relatively nucleophilic arylthiol then can lead to the formation of a thioether by reaction with an appropriate species of the dianil-dioxazine reaction sequence (presumably involving one of the more soluble species), most likely by substitution of chlorine. The probability that a process like this occurs during dioxazine synthesis is supported by the odor of methyl mercaptan that becomes very evident when methanesulfonyl chloride is employed as the cyclizing agent[7].



Scheme 12–4.

(c) Oxidation/cyclization by dehydrochlorination.

A dioxazine nucleus may also be formed, in principle, from its dianil precursors **5** or **11**, where X = Cl, by an alternative route involving dehydrochlorination, generating a product devoid of chlorine. This is illustrated in the following generic outline. The azaquinone, formed by elimination of HCl from the tautomer of the cycloisomerized dianil, is in equilibrium with the isomeric dihydrotriphenodioxazine,



Scheme 12–5.

which can eliminate a second molecule of HCl through the intermediacy of its equilibrating tautomer, to afford the dechlorinated product. In addition, it is interesting to observe that a monochlorinated dioxazine may also form during the sequence shown in Scheme 12–5 if dehydrogenation occurs at the dihydrotriphenodioxazine stage.

A process, presumably related to this, dominates during the synthesis of carbazole violet when the arylsulfonyl chloride cyclizing agents are replaced by the corresponding sulfonic acids[9] (or by various carboxylic acids). The resulting product is not completely dechlorinated, indicating that some oxidation by the dehydrogenation route is occurring also. A product with a chlorine content of approximately 4 % (theoretical chlorine content of Pigment Violet 23 ≈ 12 %), consisting mainly of **3**, $X_1 = X_2 = H$, with appropriate contributions from **3**, $X_1 = Cl$, $X_2 = H$ and $X_1 = X_2 = Cl$, respectively, to afford that composition, is produced.

The value of this mode of cyclization is demonstrated by the shade of the finished products; as the chlorine content decreases the subsequent pigments exhibit increasingly redder shades of violet. Thus the product containing chlorine at the

4 % level (available in crude form as Sandorin Violet 2R-CSA) affords the reddest shade version of Pigment Violet 23 available commercially.

It is important to note that regular Pigment Violet 23 typically contains a small proportion of both the monochloro and the dechlorinated compounds, indicating that even under normal synthesis conditions some of the alternative cyclization is competing to a minor extent.

12.3
Pigmentation and Properties[10, 11]

The crude product is converted to a finished pigment by means of various comminution techniques. These include ball milling in the presence or absence of a solvent, attrition by kneading, acid swelling, or acid pasting. The application properties of the finished product and its ultimate shade (a function of particle size and shape as well as size distribution) are determined to a large extent by the technique selected.

12.3.1
Pigment Violet 23

The pigment exhibits a unique blue shade violet color of exceptional intensity. It is employed in virtually all applications including inks, plastics, coatings, textiles and other special purpose media such as contact lenses. The printing ink industry is the largest consumer of this pigment. Most grades possess high specific surface areas, some in the region of 100 m^2/g. Therefore, to achieve good dispersion and to avoid flocculation, it is necessary to maintain an adequate pigment to binder ratio, which in this case is higher than that for most other organic pigments.

The high tinctorial strength of Pigment Violet 23 ensures that it is an excellent shading pigment. For example, as a shading component for paints it provides a reddish tinge to the shade of copper phthalocyanine blue pigments. As it is lightfast and weatherfast, even in very light shades, and fast to overcoating, it is used in architectural, general and high grade industrial finishes including metallic ones. However, as a result of the more stringent requirements (external durability) now demanded by the automobile industry its use in automotive paints has greatly diminished.

Widely employed in the coloration of plastics, Pigment Violet 23 generally exhibits very good properties in terms of heat stability and lightfastness provided its concentration in the polymer is not too low (the fastness properties tend to diminish as the amount of white pigment increases). Although not entirely migration resistant, in plasticized PVC it still exhibits excellent weatherfastness and is suitable for long term exposure in that medium.

12.3.2
Pigment Violet 37

Generally weaker in most media and with a much redder shade than Pigment Violet 23, its use is restricted to more specialized applications. Within the printing ink industry its main application is in metal deco printing. It is used also to a significant extent in packaging inks (nitrocellulose), where it exhibits high tinctorial strength and excellent gloss. Its fastness properties in application equal those of Pigment Violet 23.

Pigment Violet 37 also exhibits a considerably more reddish shade and reduced tinctorial strength in paints compared to Pigment Violet 23, with equivalent fastness properties.

Similar observations apply to its coloristic and fastness properties in polymers. However, in plasticized PVC it has the advantage of being almost entirely fast to migration. Like Pigment Violet 23 it dissolves to some extent in polymers; therefore much of its heat stability is lost as the white pigment concentration in a system is increased.

For more comprehensive information it should be noted that the relative properties and applications of Pigment Violet 23 and Pigment Violet 37 have been described authoritatively in a recent text on pigments[10].

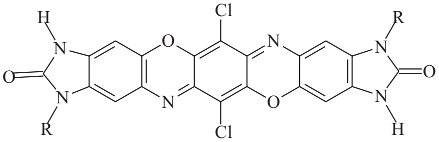
12.4
Recent Developments

12.4.1
Preparation/Production Methods

Methods to improve the efficiency of the synthesis of Pigment Violet 23 have been the subject of several patents. The most recent describes the replacement of the traditional sulfonyl chlorides by tertiary amine N-oxides[12]. According to the authors the subsequently formed tertiary amines (the by-products of the oxidation/cyclization process) then may be recovered by distillation during the final stage of the synthesis. The recovered amines (e.g. pyridine) then may be reoxidized to the corresponding N-oxides and reused. This innovative recycling of the oxidant reportedly results in a significant reduction in the amount of waste generated during product synthesis. In a further refinement, a catalytic quantity of a suitable quinone (2,3,5,6-tetrachloro-1,4-benzoquinone is preferred) is added to the reaction at the cyclization stage. Employing the optimum quantity in combination with the appropriate tertiary amine N-oxide, an improvement in the efficiency of the cyclization/oxidation stage is effected, resulting in an almost quantitative yield of product. All other things being equal, the impact of this technology improvement on economic and environmental factors is expected to be favorable.

12.4.2
New Products

Exploitation of the inherent color strength of the dioxazine chromophore while improving the durability properties relative to Pigment Violet 23 and Pigment Violet 37 is the subject of another patent[13]. By combining it with the benzimidazolone nucleus, well known for its facility to form exceptionally stable and insoluble supramolecular crystalline structures due to intermolecular H-bonding between the cyclic urea groups, a new class of dioxazine pigments has been developed. Unlike Pigment Violet 23, the structures of the new pigments have been demonstrated to possess the linear annellation shown[13].



The shade displayed is reported[14] to vary from bordeaux through reddish violet to reddish blue by simple changes of the substituent R. The new pigments are claimed to possess better heat stability and durability properties than those of the quinacridones, while exhibiting up to three times their color strength.

These products are described in more detail in Chap. 20 of this book.

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13
Disazocondensation Pigments

Fritz Herren

13.1
Introduction

Disazocondensation pigments form a very special class of azo pigments. As indicated by their name, they not only contain two azo groups but also structural units condensed onto the actual chromophoric system. They thus constitute the structurally most complex class of high performance organic pigments, with molecular weights ranging above 1000. On the other hand they belong to the oldest high performance pigments family, as they basically constitute a logical, but not easy to achieve, structural extension of azo and disazo pigments.

This chapter deals exclusively with disazocondensation pigments in the traditional sense, i.e. disazo pigments synthesized by condensing a (di) amine with an azocarbonic acid. Other disazo pigments containing carbonamide units, such as Pigment Blue 25 or Pigment Red 164, are not further considered.

13.2
Historical Background

The first half of the 20th century saw an impressive number of yellow, orange, red and brown azo pigments developed. From the simple Naphthol Reds and Hansa Yellows to Naphthol AS, (dichloro)benzidine-based disazo pigments and metal complex pigments including sulfonamide and metal salt derivatives, new pigments were (and continue to be) developed in a constant effort to improve fundamental pigment properties such as heat stability, fastness to acids, bases and organic solvents, and durability on exposure. While many of the simple azo pigments showed insufficient migration resistance, due to intrinsic solubility, disazo pigments obtained by coupling acetoacetarylides with (substituted) benzidines brought about significant improvement in this respect.

Further improvements in pigmentary character were sought along the following lines

- salt formation, i.e. pigment lakes mainly with alkaline earth metals
- increasing the molecular weight of the pigment

- introducing additional solubility-decreasing moieties into the pigment molecule, for example carbonamide groups (often combined with the above).

The latter two of these approaches encountered synthetic difficulties, as the intermediates employed (for example monoazo components) very often already had too low a solubility making it impossible to produce materials with the purity needed for migration-resistant pigments. Only in the early 1950s was an elegant and widely applicable synthetic route proposed by M. Schmid and co-workers[1], using an alternative to the traditional sequence of condensation and coupling reactions (see below). Since then, disazocondensation pigments have constituted a very important class of high performance pigments, and a significant number of the early examples of these products are still used in large quantities today.

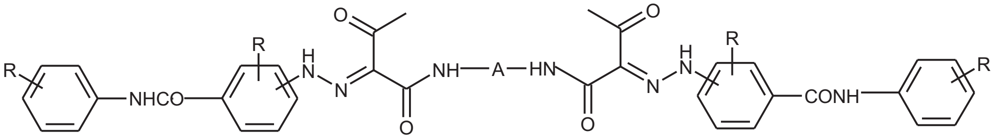
13.3
Chemistry

The general goal of increasing molecular size and incorporating carbonamide groups is achieved in two ways:

1. Extension of bisacetoacetarylide disazo pigments by condensation of an anilide onto the diazobase unit carrying a carboxylic group to yield type I yellow pigments (**1**).
2. Condensation of two monoazo acetoacetarylide or naphthol units, each carrying a carboxylic acid function with a diamine, to yield type II yellow (**2**) or red to brown pigments (**3**).

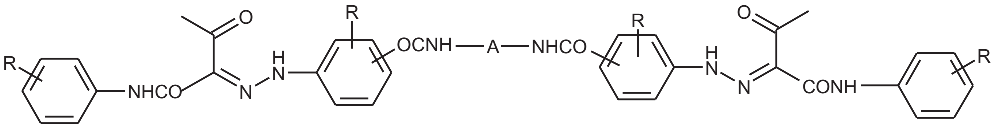
General structural formula of disazocondensation pigments are thus

Yellow type I



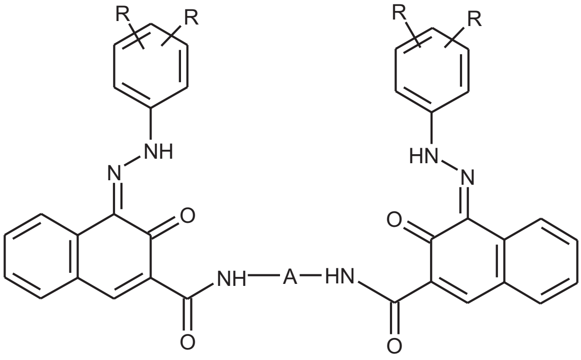
1

Yellow type II



2

Reds, Browns and Oranges



3

(In all cases the commonly accepted “hydrazo” form is depicted, even though no explicit proof for this tautomeric form has been disclosed for disazocondensation pigments. This form was however shown to be the energetically favored configuration for many monoazo pigments[2]).

All these molecules are built up using two aromatic amines in different ways: one to be diazotized and coupled, traditionally called the diazo base, and one to be condensed with the carboxylic acid function, traditionally called the condensation base. An enormous variety of compounds of the above generic structures has been synthesized since their first discovery. While Chemical Abstracts only lists some 550 CA Registry Numbers, the actual number of compounds synthesized by far exceeds 10 000, with most of the work carried out in industrial laboratories[3].

Out of this wealth of molecular entities, only about 20 have ever been launched on the market. Today[4], some 14 pigments are still being used, the latest chemical constitution to be added to the Colour Index being Pigment Red 262.

13.3.1
Commercialized Pigments (Past and Present[4])

The following is a complete compilation of chemical structures of disazocondensation pigments with an assigned Colour Index (CI) Pigment Name. Also given are Chemical Abstracts Registration Numbers, as well as CI constitution numbers (if known).

All commercial yellow pigments are of type I and contain 3-amino-4-Cl-benzoic acid as diazobase.

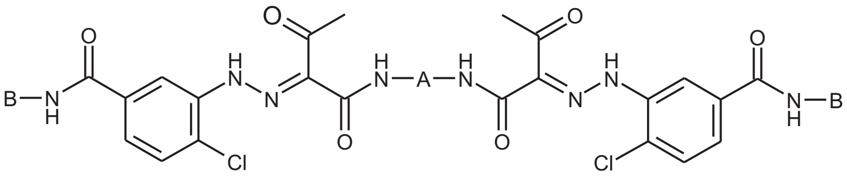
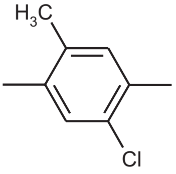
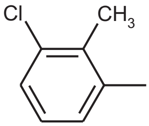
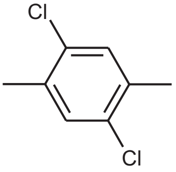
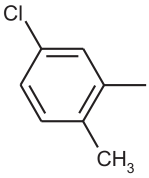
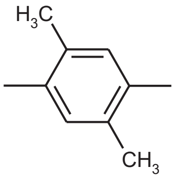
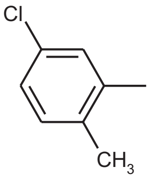
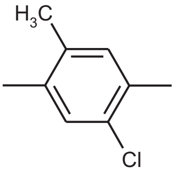
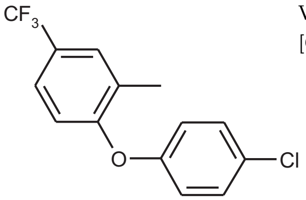
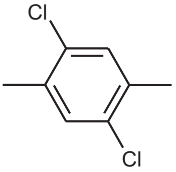
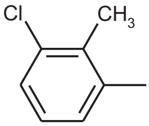


Table 13–1: Yellow disazo condensation pigments.

Pigment ***Constitution No.*** ***CA Reg. No.***	***A*** ***(condensation base)***	***B*** ***(diazo base)***	***Remarks***
Yellow 93 20710 5580–57–4			Mid shade [5]
Yellow 94 20038 5580–57–5			Greenish [5]
Yellow 95 20034 5580–80–8			Reddish [5]
Yellow 128 20037 79953–85–8			Very greenish [6]
Yellow 166 20035 76223–82–4			Mid shade [5]

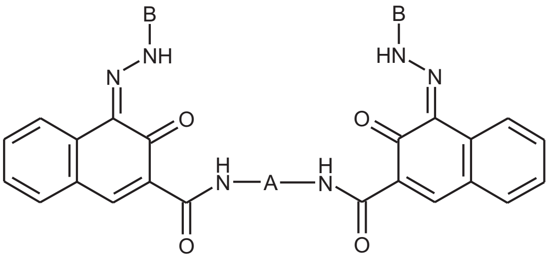


Table 13–2: Orange, red and brown disazo condensation pigments.

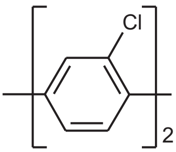
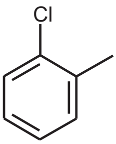
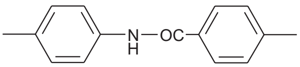
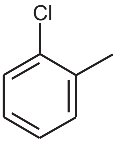
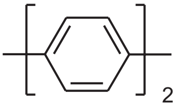
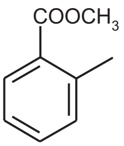
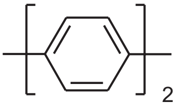
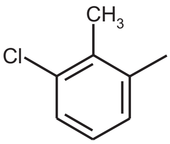
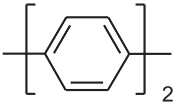
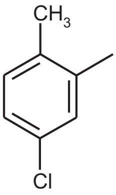
Pigment ***Constitution No.*** ***CA Reg. No.***	***A*** ***(condensation base)***	***B*** ***(diazo base)***	***Remarks***
Orange 31 20050 1344–38–3			[7] *)
Orange 55 [304891-88-1]			[8] *)
Red 139 [12262-44-1]			[9] *)
Red 140			Scarlet [7] *)
Red 141 20044 [3864-06-0]			[7] *)

Table 12–2: Continued

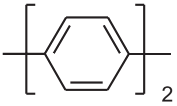
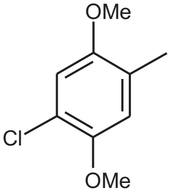
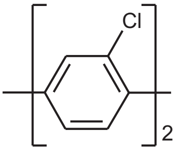
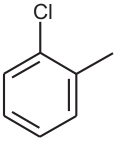
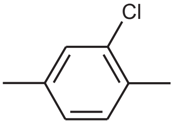
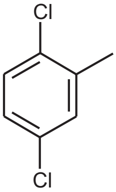
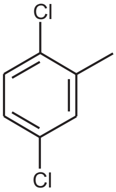
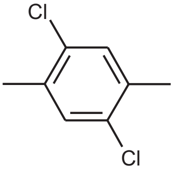
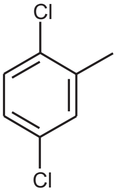
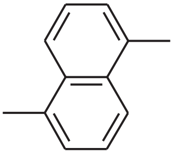
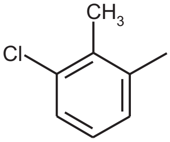
Pigment ***Constitution No.*** ***CA Reg. No.***	***A*** ***(condensation base)***	***B*** ***(diazo base)***	***Remarks***
Red 142 [109944-97-0] [6166-65-0]			[7] *)
Red 143 [122286-63-4]			Yellowish [7] *)
Red 144 20735 5280-78-4			Bluish [7, 10]
Red 166 20730 3905-19-9			Yellowish [7]
Red 214 2000660 82643-43-4 40618-31-3			Bluish [7, 10, 15]
Red 217 [56358-42-0]			[11] *)

Table 12–2: Continued

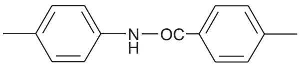
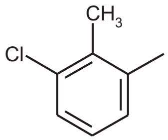
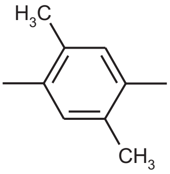
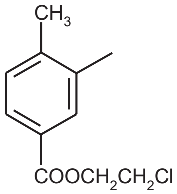
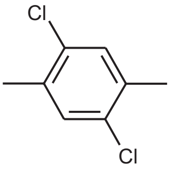
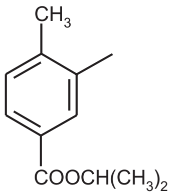
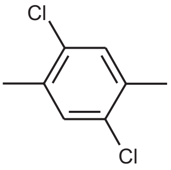
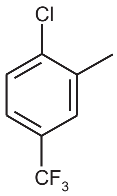
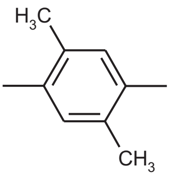
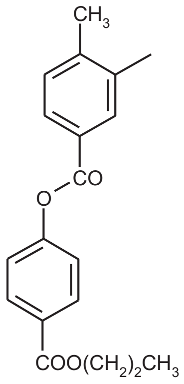
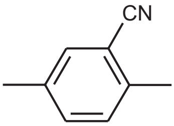
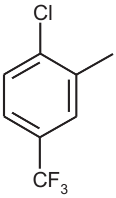
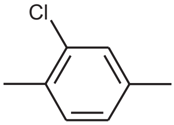
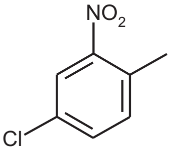
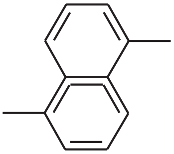
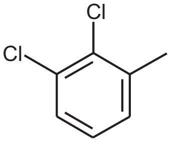
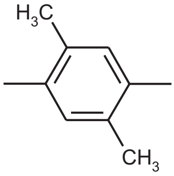
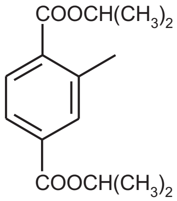
Pigment Constitution No. CA Reg. No.	*A (condensation base)*	*B (diazo base)*	*Remarks*
Red 218 [56418-72-5]			[8] *)
Red 220 20055 68259-05-2			Bluish [12, 13]
Red 221 20065 61815-09-6 71566-54-6			Bluish [13] [12]
Red 242 20057 52238-92-3			Scarlet [14–15]
Red 248 [211502-18-0]			Bluish [13] *)

Table 12–2: Continued

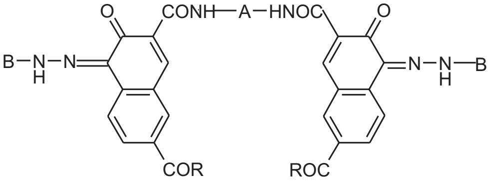
Pigment* *Constitution No.* *CA Reg. No.	***A* *(condensation base)***	***B* *(diazo base)***	***Remarks***
Red 262 [211502-19-1]			[16–17]
Brown 23 20060 35869-64-8			[17–18]
Brown 41 [211502-16-8]			[19]
Brown 42 80648-38-4			[20] *)

*) no longer commercially available

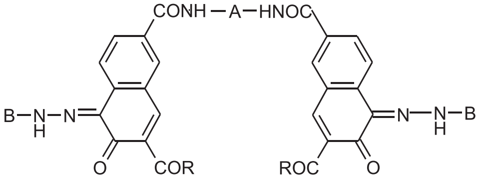
13.3.2
Recent Developments

While most of the synthetic research was done during the three decades following their initial discovery, novel disazocondensation pigments still continue to be reported. New pigments such as Pigment Red 262 or Pigment Brown 41 were registered within the last two decades. More recent work includes the use of novel bridging diamines such as ethylenediamine[21] or p-piperazides[22] for type II Yellows. 6,8-Diamino-2,4-dioxotetrahydroquinazoline was described as a novel condensation base for brilliant red pigments, particularly after aftertreatment in organic solvent. Dark colored camouflage tetrakisazo pigments were made by coupling a substituted amino-azobenzene onto 2-hydroxynaphthoic acid[23]. However, none of these structures appears to have been commercialized, and the chemistry of disazocondensation pigments seems to have come to maturity.

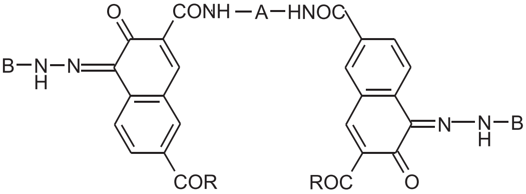
The availability of pure and economical 2-hydroxynaphthalene-3,6-dicarboxylic acid[24] has recently led to a very interesting development not only in the field of disazocondensation pigments[25] but for naphthol azo pigments in general[26]. *Cis* and *trans* symmetrical disazocondensation pigments can thus be obtained, as depicted in **4**, **5** and **6**.



(4)



(5)



(6)

The resulting highly insoluble pigments are said to show very high durability. However, at the time of writing, none of these new structures has actually appeared on the market.

Structural variations to improve in-use properties of pigments such as dispersibility or rheological behavior are a constant area of interest in pigments research. To that end, long chain or cyclic aliphatic groups were built into the condensation base of Yellow type I pigments. Such materials are claimed to have much improved dispersibility in polyvinyl chloride or polyolefins[27–29]. The same improvements are also claimed for mixed yellow systems where the condensation base is partly replaced by aliphatic ester groups formed by conducting the final condensation step in an alcohol[30]. Other recent work on disazocondensation pigments concerns the use of pigment derivatives for viscosity control in paints. Pigment derivatives carrying sulfonic acid or dialkylamino groups are well recognized as very effective viscosity reducing additives for a variety of pigments such as copper phthalocyanines, quinacridones or diketopyrrolopyrroles. Such derivatives were also reported for Pigment Red 242[31] and claimed to improve flow and gloss of corresponding paints.

As is well known, addition of (small amounts of) chemically similar compounds during synthesis or conditioning can have a strong influence on the growth of pigment particles, leading to enhanced pigmentary properties such as strength and transparency. A number of such mixed systems have been published in the case of disazocondensation pigments. Pugin et al.[32] describe the preparation of mixed systems comprising two monoazonaphthoic acid chlorides condensed with one aromatic diamine. Similarly, two different diazotized amines can be coupled onto a bis-naphthol unit bridged via an aromatic diamine. The specific binary system Pigment Red 214 / Pigment Red 166 (i.e. condensation of the corresponding azo carbonic acid chloride with a mixture of *p*-phenylenediamine and di-Cl-*p*-phenylenediamine) has been described as a mixture of the two components[33]. Later on, mono-Cl-*p*-phenylenediamine was included in the investigations, and binaries as well as ternaries in the system Pigment Reds 144 / 166 / 214 were described as solid solutions[34]. In all cases, the high chroma and strength obtained are put forward as a commercial advantage. The same principles were also applied to type I Yellows[35].

Efforts to improve the durability of pigments, or rather the color appearance of the pigmented system, are a constant topic in pigment technology. While specific formulations of disazocondensation pigment with HALS stabilizers were proposed[36], attempts were also made to chemically link such segments to the pigment molecule[37]. The actual efficiency as well as the underlying mechanisms of stabilization with regard to actual reduction of chromophore degradation remain unclear and need to be investigated in more detail.

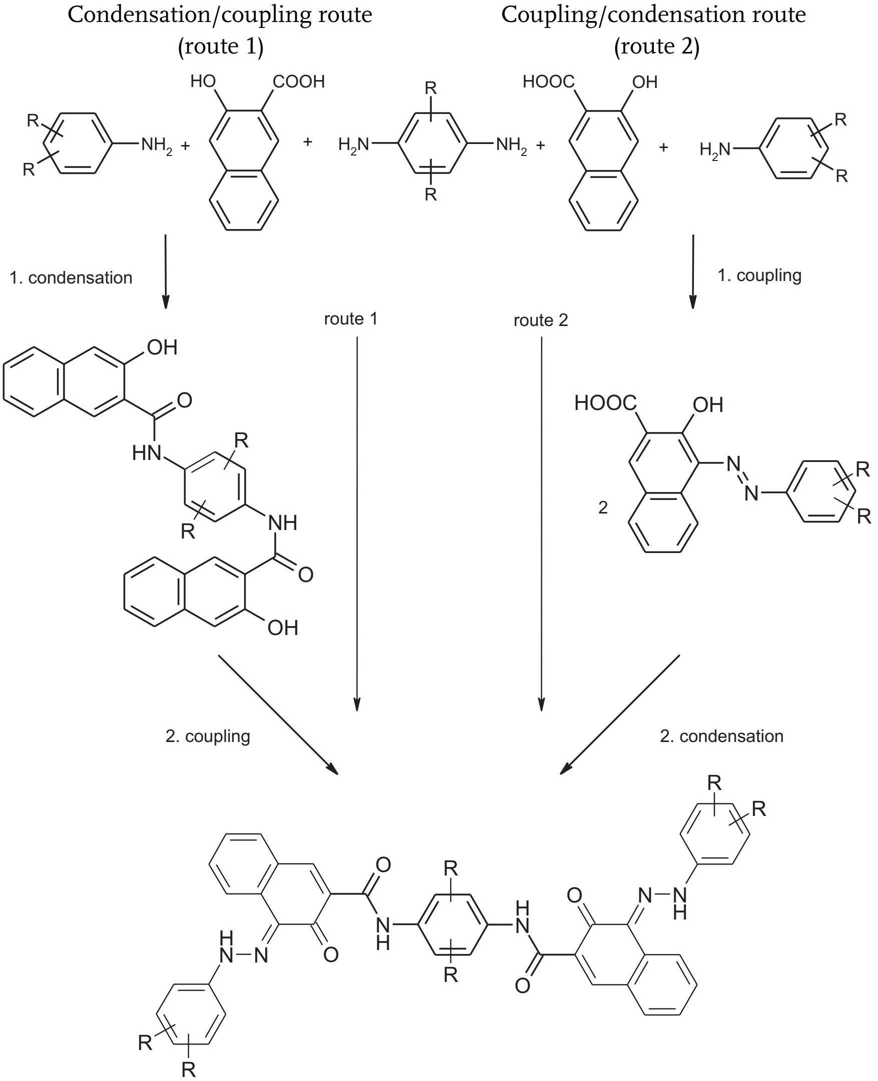
Pigments can be chemically transformed into materials with much higher solubility by replacing the hydrogens of the carbonamide functions with sterically hindering groups, thus making the formation of a hydrogen bond network impossible. This can be achieved e.g. by reacting the carbonamide functions with an oxycarbonate such as *t*-butoxy carbonate (*t*-BOC). From such derivatives, the original pigment can easily be regenerated, e.g., by the application of heat or light. Such pigments are therefore called "latent pigments"[38]. This principle has also been successfully applied to disazocondensation pigments[39].

13.4
Synthesis and Manufacture

The build-up of such large, complex and highly insoluble pigment structures was quite a challenge for the chemists in the early 1950s. By analogy with the synthesis of Naphthol AS pigments, the traditional route to azo reds would consist of coupling a diazotized amine onto the corresponding bisfunctional coupling component obtained after condensation of 2-hydroxynaphthoic acid with a diamine (route 1 in Scheme 13–1). However, this reaction is difficult to run to completion as the intermediate monoazo compound is quite insoluble and does not readily react further, leading to impure materials not showing the properties needed for pigmentary applications. Several approaches were taken to try to obviate these, but possibilities were limited because of the delicate nature of diazonium salts, which do not permit "harsh" reaction conditions.

The breakthrough was achieved by M. Schmid[1] by reversing the reaction sequence to coupling followed by condensation (route 2 in Scheme 13–1). In this route, the diazotized amine is first coupled onto 2-hydroxynaphthoic acid. After conversion to the corresponding acid chloride, double condensation with a diamine is easily achieved, with appropriate reaction media and conditions now possible to run the reaction to completion.

The same reaction sequence is also adopted in the synthesis of yellow disazocondensation pigments. Type I pigments follow the synthetic pathway of bisacetoacetarylide disazo pigments with an aminobenzoic acid as diazobase. Conversion to the acid chloride followed by condensation with two equivalents of an arylamine finally yields the desired pigments. In Type II pigments, a monoazo unit is first built up by coupling a diazotized aminobenzoic acid onto an acetoacetarylide. Two such units are linked, again via conversion to the acid chloride, followed by condensation with an aromatic diamine.



Scheme 13–1: Synthesis of disazocondensation reds.

The intermediate azo carbonic acid can be prepared under typical aqueous diazotisation and coupling conditions and can be readily isolated. However, because of the absence of solubilizing groups on the amine and the coupling component, preparation of the diazonium salt and subsequent coupling can be difficult. Therefore these reactions are preferably carried out in organic solvents such as *o*-dichlorobenzene or nitrobenzene, using alkyl nitrites as diazotizing agents[40]. The dried acid is then converted to the acid chloride in the usual way using a phosphorus halogenide or thionyl chloride, and dimethyl formamide as catalyst, to afford the desired product, which can be isolated and is surprisingly stable under ambient conditions. The final condensation step with the diamine is again carried out in an organic solvent, preferably in the presence of some organic base. An optional heat treatment step to form the final pigment particles, separation in a closed filtering apparatus, washing, drying and grinding conclude the manufacturing process. More economically, these reactions can be carried out in a one-pot synthesis encompassing diazotisation, coupling, acid chloride formation as well as condensation without any intermediate isolation[41]. Several newer publications report the use of new non-chlorinated organic solvents[42–43] for this synthesis.

Pigment finishing or conditioning plays only a minor role for disazocondensation pigments. Very often, the materials obtained after synthesis, especially after a thermal treatment step, are already in pigmentary form. Conventional particle comminution technologies such as milling or kneading are nevertheless employed to prepare special forms (see also Sec. 13.5.2).

13.5
Characterization, Properties, Application

13.5.1
Physical Characterization

Little is known about the crystal structure of disazo condensation pigments. Some powder X-ray diffraction diagrams have, however, been published, in particular for Pigment Yellow 94[44], Orange 31[45], Red 166 and 242[44] and Brown 23[46]. No single crystal structure determination is available, probably because of the difficulty in obtaining suitable single crystals of these highly insoluble materials, which in addition show a distinct tendency to grow as long needles. Modern methods using powder X-ray data for the elucidation of three-dimensional crystal structures probably are not feasible because of the very unfavorable ratio of parameters/observables for these large molecules.

13.5.2
Available Grades

Disazocondensation pigments are available in many commercial forms. Most of the pigments are sold as pure dry powders. Particle sizes are fairly large, providing more or less opaque forms with excellent fastness properties. Some electron micrographs of common pigments are shown below. However, some specially conditioned products such as superfine forms prepared by proprietary milling or kneading processes are available as well, e.g. for Pigment Reds 144, 166 and 221. Such forms are especially suited for thin plastic films or printing inks, where the highest transparency, strength and gloss are required. Electron micrographs of some examples are shown in Figures 13–1 to 13–4. Quite often, the very fine grades are resinated for improved dispersibility. It should also be noted that some particle comminution can occur during incorporation of the pigment powder into masterbatches or millbases.

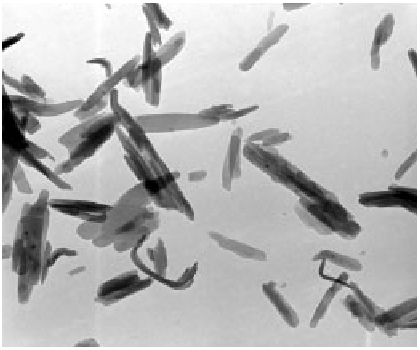


Figure 13–1: Pigment Red 144, normal powder form

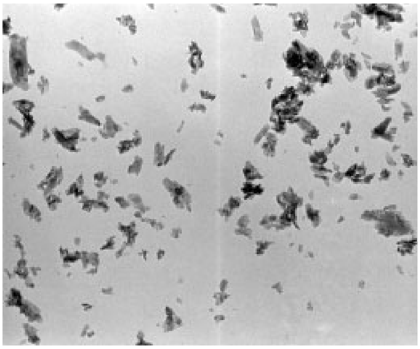


Figure 13–2: Pigment Red 144, micronized form

Figure 13–3: Pigment red 166, normal powder form

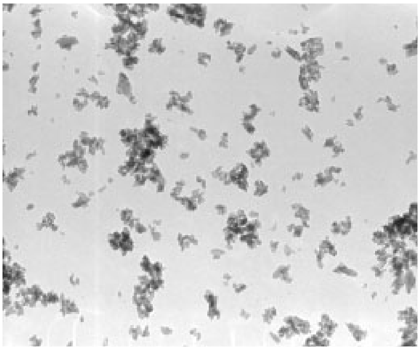


Figure 13–4: Pigment Red 160, micronized form

Many disazocondensation pigments are used in application-specific predispersed forms such as pigment preparations, chips, concentrates or masterbatches from dispersion houses. Such sales forms are mainly useful where extreme fineness of particle size and complete wetting out of the pigment surface must be obtained, so as to secure top strength, gloss and transparency combined with constancy of color and ease of use. Such requirements are typical, for example, of packaging inks, spin coloration of synthetic fibers and high quality calandered films.

13.5.3
Properties and Applications

Disazocondensation pigments span quite a range of application properties, the details of which obviously depend on the specific chemical constitution. All draw some general characteristics from their highly insoluble nature (due to their high molecular weight) and the presence of carbonamide functions. As a general rule they therefore show very good resistance to organic solvents, are largely migration resistant, do not bloom and are fast to overpainting. They are fast to alkalis as well as acids. They posses excellent lightfastness and in some cases are also sufficiently durable to exterior exposure. Their high heat stability makes them well suited for application in plastics (PVC, polyolefins) and synthetic polyolefin fibers. The second major field of application is printing inks, where they are mainly used in high grade packaging and vinyl printing inks. Some use is also found in paints (mainly Pigment Yellow 128).

Pigment Yellows 93 and 95 are important pigments for the coloration of polyvinyl chloride for interior and selected exterior applications. Their excellent heat stability also renders them particularly suited for polyolefins, where they show no warping in injection molding applications. Both are used in polypropylene fibers, where Pigment Yellow 93 represents the industry standard for greenish yellow coloration. Significant use in inks is also reported for Pigment Yellow 93.

Because of its outstanding fastness properties, Pigment Yellow 128 is mainly used in coatings, especially high grade industrial and architectural paints. It also finds some use in packaging inks and polyvinyl chloride as a more lightfast alternative to Pigment Yellow 93.

Pigment Reds 166, 144 and 214 represent the “workhorse” for scarlet to bluish red high grade coloration of flexible polyvinyl chloride and polyolefins, especially polypropylene fibers. All show very good heat stability at low concentrations and have excellent end use properties. However, because of their warping characteristics, they are of limited interest for HDPE injection molding. The pigments are also used in packaging inks, where Pigment Red 166 has replaced Lake Red C. Pigment Red 220 distinguishes itself from other disazocondensation red pigments as it is suitable for HDPE injection molding, where it affords attractive coloration with high dimensional stability and is reported to be suitable for the coloration of polyamide fibers.

Pigment Red 221 is available in a highly transparent form and is used mostly in flexible PVC. It is a key component to achieve brilliant mid to bluish red shades in combination with orange and red inorganic pigments.

Pigment Red 242 is used in a broad variety of plastics and fiber applications, where it provides scarlet coloration with excellent fastness properties. Warping, however, makes it unsuitable for high density polyethylene injection molding. It finds application in inks and to some extent in industrial paints. The relatively new Pigment Red 262 is recommended mainly for rigid PVC, polyolefins, and fibers, where it affords a strong bluish red.

Pigment Brown 23 and 41 are mainly used in interior and exterior PVC applications (for example in window frames).

Apart from such conventional applications, there are more and more so-called high-tech applications being claimed, for which pigments have to be transformed into special forms. Examples include use as electrophotographic toners of Pigment Red 144[47], Pigment Yellow 93 or Pigment Yellow 95[48, 49], as red pigment[50] or as a yellow shading component[51] in color filters, as well as in ink jet applications[52].

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9 US 2'774'755 Ciba (1956)
10 DE 2'500'005 Ciba (1975)
11 US 4'100'156 Ciba (1978)
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28 EP 358'604 Ciba-Geigy (1990)
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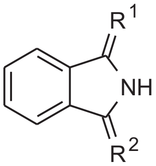
14
Isoindoline Pigments

Volker Radtke, Peter Erk, and Benno Sens

14.1
Introduction

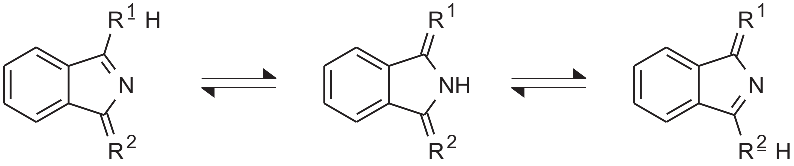
The characteristic feature of this class of pigments is the isoindoline ring system **1.**



1

Figure 14–1: General structure of isoindoline pigments.

The tautomeric forms of this structure are illustrated below with the substituents R^1 and R^2 in the positions 1 and 3, respectively (see structure **2**).



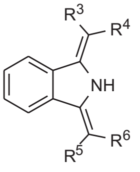
1a **1** **1b**

Figure 14–2: Tautomeric forms of isoindoline pigments.

In the pigment molecules, the substituents are attached to the isoindoline ring either through a carbon bond (methine type) or through a nitrogen bond (azomethine type).

None of the many mono- or bisazomethine pigments described in the literature, e.g.[1, 2], have gained commercial importance, mainly because of their insufficient resistance to solvents and migration, low colour strength or for economic reasons.

Only symmetrical and asymmetrical bismethine compounds of the general structure **2** have made their way into the market.

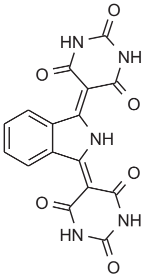
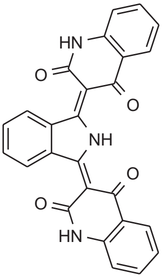


2

Figure 14–3: General chemical structure of commercially available isoindoline pigments.

R^3 through R^6 represent CN, CONH-alkyl or CONH-aryl. R^3 / R^4 and R^5 / R^6 can also be members of a heterocyclic ring system. Six of them are listed in the Colour Index[3] and are or were commercially available.

Figure 14–4 shows the structural formulae of these six isoindoline constitutions listed in the Colour Index. The pigments cover the range from greenish yellow (P.Y. 185), to reddish yellow (P.Y. 139), to orange (P.O. 66 and 69), red (P.R. 260) and brown (P.Br. 38).

	Structure	***Generic name***	***Ref.***
3		P.Y. 139	[5, 6, 10]
4		P.Br. 38	[5, 6]

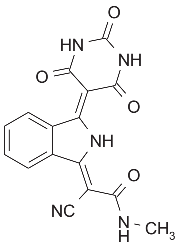
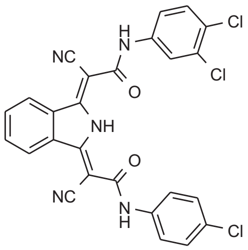
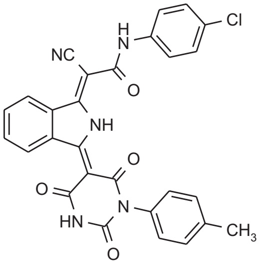
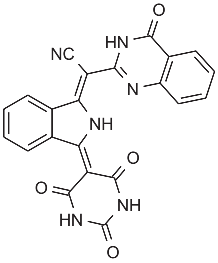
	Structure	*Generic name*	*Ref.*
5		P.Y. 185	[12]
6		P.O. 66	[9]
7		P.O. 69	[14]
8		P.R. 260	[15]

Figure 14–4: Isoindoline pigments listed in the Colour Index.

Table 14–1: Summary of Colour Index data, CAS and EINECS numbers of the above six isoindoline pigments.

C.I. name	*C.I. constitution*	*CAS No.*	*EINECS No.*	*CAS name/chemical formula*
P.Y. 139	56298	36888-99-0	253-256-0	2,4,6(1H,3H,5H)-Pyrimidinetrione, 5,5′-(1H-isoindole-1,3(2H)-diylidene)-bis- / $C_{16}H_9N_5O_6$
P.Y. 185	56280	76199-85-4	278-388-8	Acetamide, 2-cyano-2-[2,3-dihydro-3-(tetrahydro-2,4,6-trioxo-5(2H)-pyrimidinylidene)-1H-isoindol-1-ylidene]-N-methyl- / $C_{16}H_{11}N_5O_4$
P.O. 66	48210	68808-69-5	272-330-5	Acetamide, 2-[3-[2-[(4-chlorophenyl) amino]-1-cyano-2-oxoethylidene]-2,3-dihydro-1H-isoindol-1-ylidene]-2-cyano-N-(3,4-dichlorophenyl)- / $C_{26}H_{14}C_{l3}N_5O_2$
P.O. 69	56292	85959-60-0	289-065-1	Acetamide, N-(4-chlorophenyl)-2-cyano-2-[2,3-dihydro-3-[tetrahydro-1-(4-methylphenyl)-2,4,6-trioxo-5(2H)-pyrimidinylidene]-1H-isoindol-1-ylidene]- $C_{28}H_{18}ClN_5O_4$
P.R. 260	56295	71552-60-8	275-616-8	2-Quinazolineacetonitrile, α-[2,3-dihydro-3-(tetrahydro-2,4,6-trioxo-5(2H)-pyrimidinylidene)-1H-isoindol-1-ylidene]-1,4-dihydro-4-oxo- / $C_{22}H_{12}N_6O_4$
P.Br. 38	–	85223-06-9	286-359-6	2,4(1H,3H)-Quinolinedione, 3,3′-(1H-isoindole-1,3(2H)-diylidene)bis- / $C_{26}H_{15}N_3O_4$

14.2
Historical Background

The history of isoindoline pigments is closely related to phthalocyanine chemistry. An important starting material for both pigment groups is diiminoisoindoline (**10a**) or its tautomeric form aminoiminoisoindoline (**10b**), which can be produced from phthalic anhydride and urea or by addition of ammonia to *o*-phthalodinitrile (**9**).

The stepwise exchange of the imino groups with primary amines has been known since the end of the 1940s[4a]. Monocondensation products of **10** with active methylene compounds were described during the early 1950s[5]. They could be used as textile dyes. The first 1,3-disubstituted isoindoline colorants, synthesized by reaction of *o*-phthalodinitrile and acidic –CH or –NH compounds were published shortly afterwards[6], among them the first pigments. At that time, however, these products did not gain any industrial significance.

Only after *o*-phthalodinitrile became available in high purity on an industrial scale from BASF the importance of these pigments was recognized. By improving the methods of synthesis and finishing it became possible to produce pigments with brilliant hues and better fastness properties. In 1973 BASF released the first isoindoline pigment into the market: Lithol® Fast Yellow 1840 (P.Y. 139). At the same time several other companies (Bayer, Ciba, Dainippon Ink) published novel isoindoline structures[8– 11].

New entries to the market were opaque P.Y. 139 grades
from BASF (Paliotol® Yellow L 2140 HD)
and Bayer (Fanchon® Fast Yellow Y-5700),
P.O. 66 from Ciba (Irgazin® Orange 3GL)
and P.Y. 185 (Paliotol Yellow D 1155)
and P.Br. 38 (Paliogen® Brown K 2683)
from BASF.[12]

The status of isoindoline pigments up to the mid 1980s is summarized in[13].

In the late 1980s two novel structures **14** and **15** were launched as regular sales products by BASF, namely P.O. 69 (Paliogen Orange L 3180 HD) and P.R. 260 (Paliogen Red L 3585 HD).

Both were opaque grades for high performance paints with high chroma and gloss, good rheological properties and outdoor durability.

At the beginning of the new millennium the situation became clearer: P.O. 66, P.O. 69, P.R. 260 and P.Br. 38 all disappeared from the market for technical and economic reasons. Only P.Y. 139 and P.Y. 185 are commercially available today, from several pigment suppliers (Table 14–2).

Table 14–2: Known pigment brands and manufacturers of isoindoline pigments[3].

Colour index/ commercial name	*Manufacturer*	*Application*	*Physical form*
P.Y. 139			
Paliotol® Yellow K 1819	BASF	Printing inks	Powder
Paliotol Yellow K 1841	BASF	Plastic	Powder
Paliotol Yellow L 1820	BASF	Paint	Powder
Paliotol Yellow L 1970	BASF	Paint	Powder
Paliotol Yellow L 2140 HD	BASF	Paint	Powder
Fanchon® Fast Yellow Y-5700	Bayer	Paint, plastic, printing inks	Powder
Fanchon Fast Yellow Y-5740	Bayer	Paint	Powder
Cromophtal® Yellow 2RF	Ciba S.C.	Plastic	Powder
Novoperm® Yellow M2R70	Clariant	Paint	Powder
Graphtol® Yellow H2R	Clariant	Plastic	Powder
Eupolen® Yellow 18–4101	BASF	Plastic	Powder
P.Y. 185			
Paliotol Yellow D 1155	BASF	Printing inks	Powder
Paliotol Yellow L 1155	BASF	Paint	Powder
Eupolen Yellow 11–5501	BASF	Plastic	Powder

14.3
Methods of Manufacture

The preferred starting material for the industrial synthesis of isoindoline pigments is diiminoisoindoline (**10a**) or its tautomeric form aminoiminoisoindoline (**10b**), which can be produced from *o*-phthalodinitrile (**9**) and gaseous ammonia in ethylene glycol or other suitable solvents[4a]. Suitable starting materials further include 1,1-dialkoxy-3-iminoisoindolines, synthesized from **9** and C_1–C_4 alcohols[4b].

10 easily condenses with appropriate active methylene compounds like cyanoacetamides or heterocyclic cyanomethyl compounds to give a monocondensation product **11** which can be used as starting material for the synthesis of asymmetrical isoindolines. The second condensation is carried out at elevated temperature, with the addition of acids.

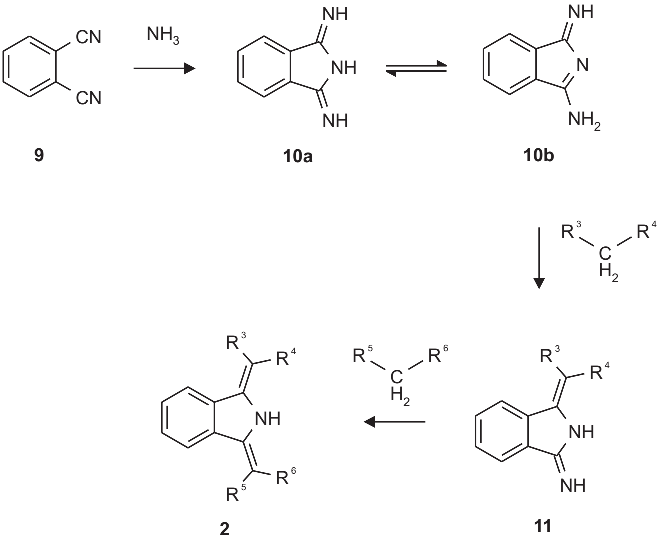


Figure 14–5: Synthesis of bismethine isoindoline pigments.

In the case of barbituric acid and its derivatives it is not possible under standard conditions to isolate a monocondensation product. Because of the high reactivity of barbituric acid, even at a 1 : 1 ratio, the bismethine (P.Y. 139) and unreacted **10** are isolated. So whenever an asymmetrical pigment contains a barbituric acid moiety this building block is incorporated in the second step.

An elegant and economical one-step synthesis of P.Y. 139 is described in[16]. As initially obtained, the pigment is in an unsatisfactory physical, or "crude" form. It is crystallized therefore in aqueous suspension in a finishing process to develop the required physical properties such as crystal shape and size, crystal phase and particle size distribution. This determines important application properties like hue, color strength, rheological behavior, hiding power, transparency and light and weather fastness.

In the case of P.Y. 139, the temperature, surfactant level and other parameters may be varied to obtain fine (Paliotol Yellow L 1820), medium size (Paliotol Yellow L 1970) and coarse products (Paliotol Yellow L 2140 HD) by selectively adjusting advanced finishing procedures and conditions.

State-of-the-art physical methods are used today to control both synthesis and finishing in order to obtain the desired pigment properties[17]. This ensures minimal waste-water pollution and a crude product tailored to the finishing step (Figure 14–6):

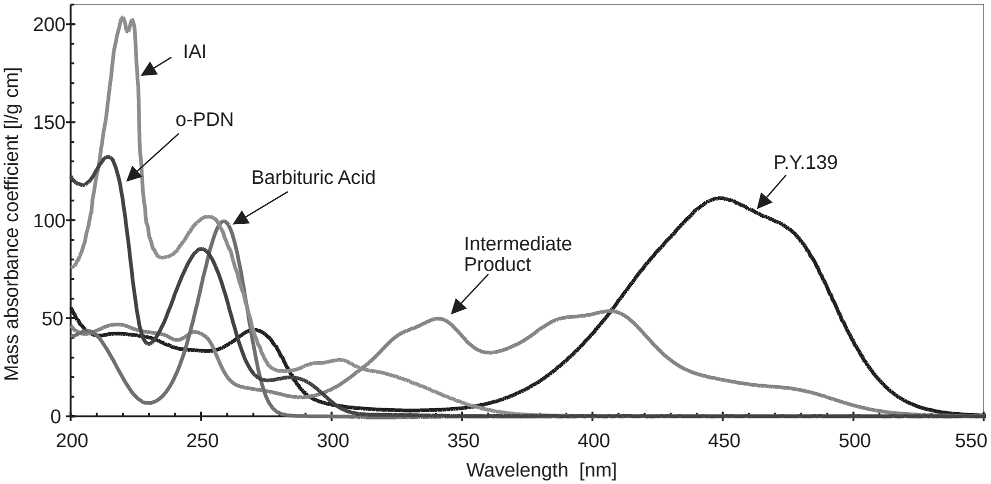
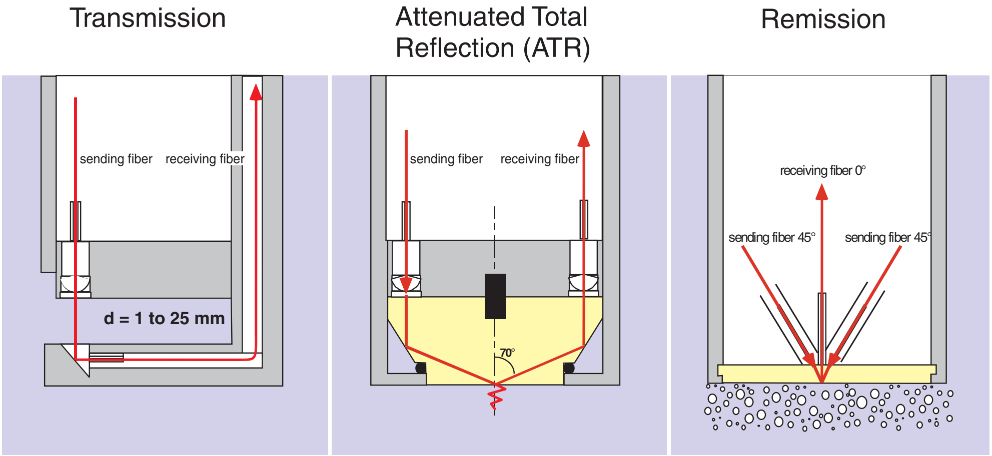


Figure 14–6: Synthesis monitoring of P.Y. 139 by UV/VIS-spectroscopy.

A complete set of such calibration spectra allows precise chemical characterization of the product. Back-coupling allows the synthesis parameters and further processing to be optimized. Subsequent finishing results in a significant change in the particle size.

The color strength, being a function of the pigment's particle size, is determined by this process. The pigment's scattering properties and thus its hiding power increase at the same time. The scattering properties of finished-pigment slurries are significantly affected by the diameter of the particles.

A set of fiber-optic sensors may be used to monitor quality-relevant parameters in real time (Figure 14–7):



weakly absorbing medium, free of particles

strongly absorbing medium, penetration depth approx. 100 nm

highly concentrated suspension, penetration depth few µm

Figure 14–7: Fiber-optic probes for process spectroscopy

The reflectance probe is an excellent device for measure scattering in real time and can be used to monitor and control particle growth:

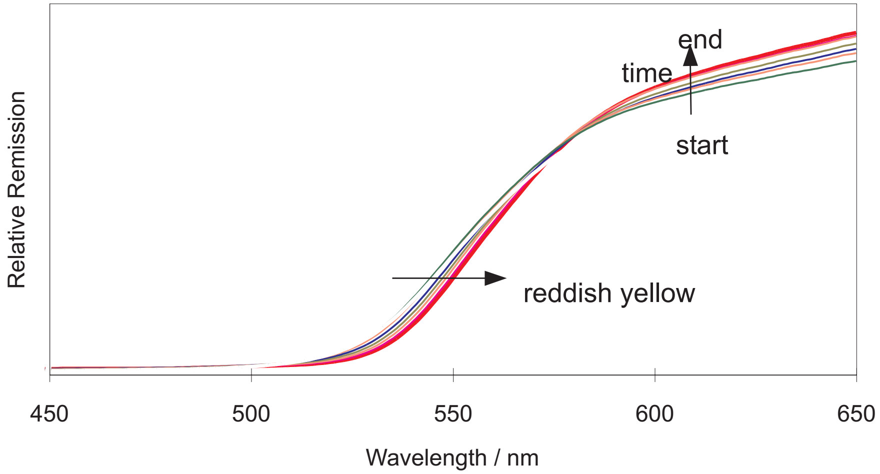


Figure 14–8: Paliotol® Yellow L 2140 HD – finishing real-time monitoring using remission probe.

Figure 14–8 shows the reflectance spectra recorded during finishing. The reflectance capacity of the suspension in the yellow-red region increases with time. At the same time, a bathochromic shift in the reflectance curve is observed. On the basis of this dynamic fingerprint behaviour the precise finishing end-point can be controlled, which is crucial for the specific colour properties.

P.Y. 185 can also be produced in a one-step process in a water / solvent mixture starting with the formation of **10** in an organic solvent, followed by the addition of *N*-methylcyanoacetamide, and carrying out the final condensation with barbituric acid. The very specific crystal size required for ink application of the pigment can be formed directly by appropriate choice of temperature and dispersant without isolation of the crude pigment.

In contrast to the synthesis of P.Y. 139 and 185, the synthesis of P.O. 69 and P.R. 260 pigments is not possible in aqueous media. The monocondensation products of *p*-chlorocyanoacetanilide and cyanomethylquinazolone are synthesized instead in organic solvents because of the insolubility of the starting materials. The final step has also to be carried out in an organic solvent for the same reason.

In the case of P.O. 69, the second condensation step and the finishing can be combined in one step to give coarse crystals required for high hiding power, excellent chroma and good rheological properties. In the case of P.R. 260, the crude pigment form is isolated and recrystallized in an additional finishing step.

14.4
Typical Properties and Major Reasons for Use

The properties of isoindoline pigments depend strongly on their chemical structure as well as on particle size and shape. The influence of the physical properties of the pigments on the color behavior is more pronounced for isoindoline pigments than for other pigment groups, e.g. copper phthalocyanines.

Figure 14–4 summarizes the relationship between chemical constitution and hue. The pigments listed cover the range from greenish yellow to reddish yellow to orange, red and brown.

Depending on particle size, brilliant opaque grades with lower color strength and transparent types with higher color strength can be produced.

Light fastness varies from that required for ink applications and indoor coating levels (D/L 1155 and D 1819) to the level of other polycyclic high performance pigments for outdoor and other long-term applications like industrial and automotive paints (L 2140 HD, P.O. 66, P.Br. 38).

14.5
Crystal Structures of Isoindoline Pigments

14.5.1
Structure Determination

The crystal structures of P.Y. 185 and P.R. 260 have been determined from single crystals by X-ray structure analysis (Table 14–2)[18]. Because of the extremely low solubility of P.Y. 139, single crystals could not be obtained. Therefore, the crystal structure of P.Y. 139 has been determined from diffraction data from a highly crystalline powder sample (Table 14–3)[18]. Indexing of the diffraction pattern gave access to the unit cell, and systematic absences pointed to space group *A bac*. The unit cell and the symmetry restraints of the space group allow for only one position of the molecule. First, this model has been improved by minimization of intra- and intermolecular energy using force field methods[19]. Subsequently, the structure has been refined in space group *C mca* by a combined Rietveld and energy minimization approach[20].

Table 14-3. Crystallographic data, packing coefficient PKC, calculated packing energy PE and specific packing energy SPE (PE/molecular mass) of isoindoline pigments..

	PY139	***PY185***	***PR260***
Formula Mass [a.u.]	$C_{16}H_9N_5O_6$ 367.3	$C_{16}H_{11}N_5O_4$ 337.3	$C_{22}H_{12}N_6O_4$ 424.4
Space group	*C mca*	$P\bar{1}$	$P\bar{1}$
Z	8	2	4
Z′	1	1	2
a [Å]	21.198(4)	8.158(2)	9.147(2)
b [Å]	6.847(1)	9.827(2)	10.302(2)
c [Å]	19.292(4)	9.942(2)	21.410(6)
α [°]	90.0	96.94(2)	97.97(2)
β	90.0	103.28(2)	97.47(2)
γ	90.0	110.15(2)	111.52(2)
V [Å^3]	2800.2	710.6	1822.6
ρ [g/cm^3]	1.742	1.576	1.547
PKC [%]	80.0	78.2	76.5
PE [kcal/mol]	–86.4	–62.0	–70.2
SPE [kcal/a.u.]	0.235	0.184	0.165
vdW	–30.7	–29.9	–37.9
Cb	–42.0	–23.7	–23.8
H-bond	–13.7	–8.4	–8.5

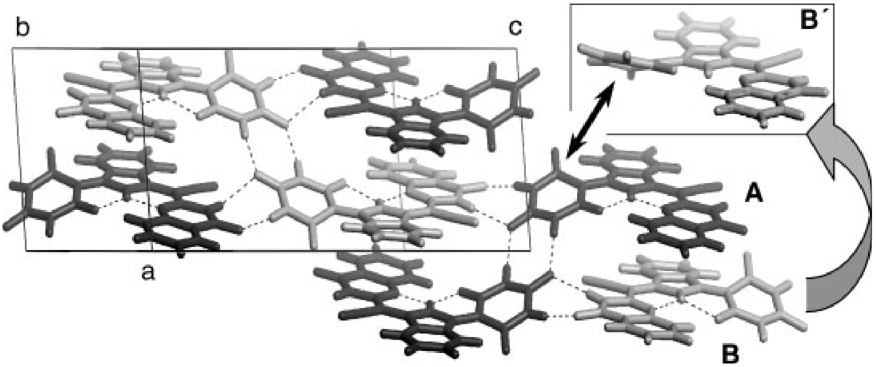


Figure 14–9: Packing diagram of P.R. 260. A (dark molecules) and B (light gray molecules) depict different conformations, as indicated by the arrow. For comparison, B has rotated by 180° to B'. The selection of molecules belongs to one sheet. Dashed lines represent intra- and intermolecular hydrogen bonds.

P.R. 260 P.R. 260 crystallizes in the triclinic space group $P\bar{1}$ with 2 molecules in the asymmetric unit. The 2 molecular units (A and B) differ mainly in the conformation of the barbituric acid groups, which are skewed toward opposite sides of the molecular plane (Figure 14–9), while the isoindoline and the cyanomethylquinazolone unit are nearly planar. The combination of these two molecular conformations allows the maximum number of hydrogen bonds to form in the packing.

The resulting hydrogen bond network propagates in sheets of the P.R. 260 molecules parallel to the crystallographic [011] plane. In these sheets the molecules are stacked in an ABAB arrangement along the a-axis. The stacks are linked by hydrogen bonds. Each barbituric acid group forms two hydrogen bonds with the barbituric acid group of an identically configured molecule and two hydrogen bonds with the quinazolone moiety of the differently configured molecule. It should be noted that two hydrogen bond acceptors are not involved in this network. One carbonyl group of the barbituric acid substituent and the cyano group point toward carbon-attached hydrogens in the adjacent sheet.

P.Y. 185 P.Y. 185 forms a simple layer structure in space group $P\bar{1}$. The molecular unit is entirely planar. The layers are perpendicular to the b-axis and repeat in an ABCABC like sequence. Accordingly, the averaged interlayer distance is as short as b/3 = 3.276 Å. The molecules in one layer are linked by pairs of symmetry-based

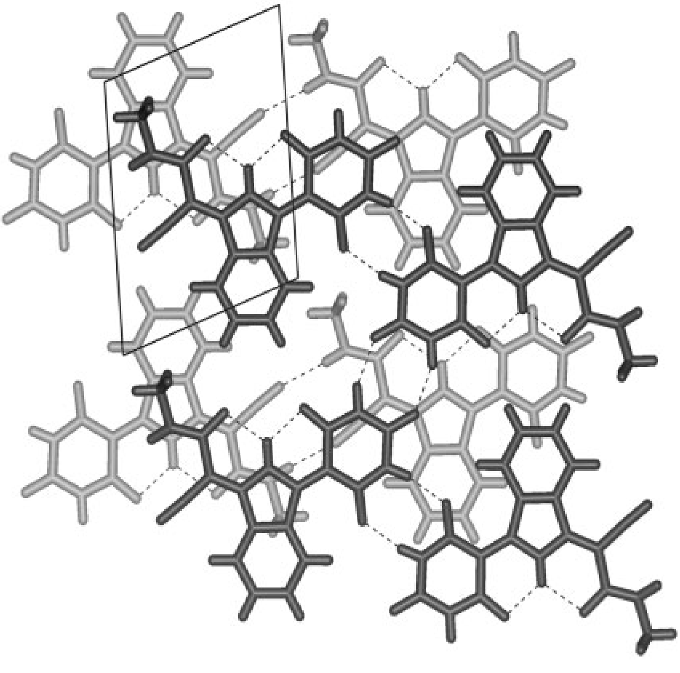


Figure 14–10: Projection of P.Y. 185 along the b-axis showing two adjacent layers of molecules. Dashed lines represent intra- and intermolecular hydrogen bonds.

hydrogen bonds (Figure 14–10). One of these pairs is formed by the cyano group and the amide hydrogen. Two other cyclic hydrogen bond motifs, formed by the barbituric acid substituents, interlink the molecules in "zipper" fashion. All hydrogen bond donors and all acceptors are involved in the resulting 2-dimensional hydrogen bond network.

P.Y.139 P.Y. 139 was found to crystallize in the highly symmetrical space group *C mca*. The molecule has mirror symmetry *(Cs)* and the barbituric acid fragments are tilted by an angle of ca. 20° with respect to the isoindole ring system (Figure 14–11). As for P.Y. 185, all hydrogen bond acceptors and all donors participate in hydrogen bonds, forming a 2-dimensional network. The layers are nearly perpendicular to the b-axis and are separated by an average distance of 3.424 Å. They form an ABAB sequence, and, as a consequence, molecules in neighboring layers are oriented in opposite directions with respect to the c-axis. Molecules in the same row (parallel to the c-axis) are arranged head-to-tail and the intermolecular distance between the carbonyl oxygen and the β-hydrogens is only 2.51 Å, pointing to a considerable C–H···O-interaction.

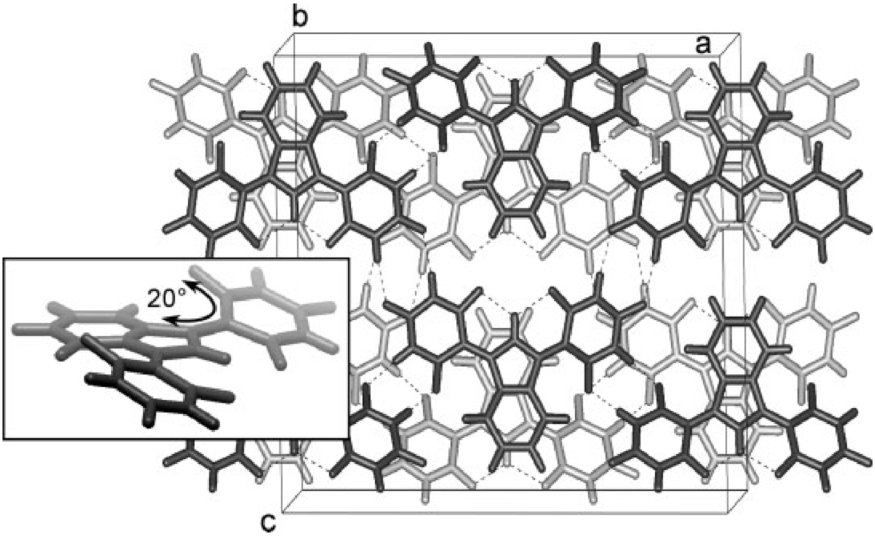


Figure 14–11: Molecular structure and packing diagram of P.Y. 139. Dashed lines represent intra- and intermolecular hydrogen bonds.

5.2
Discussion

The packing coefficients (PKCs) of organic molecular crystals range from 0.65 to ca. 0.80 (0.74 is the PKC of identical spheres)[21]. The packing coefficients of the investigated isoindoline pigments exceed this value (Table 14–3). Close packing is related to strong intermolecular interactions and must also be supported by the molecular shape.

Hydrogen bonding plays a major part in all isoindoline structures. As a result, the molecules form 2-dimensional hydrogen bond networks. The structure of these networks reflects the hydrogen bond-forming capabilities of each species and their interplay with the respective molecular shape. As an example, in the structure of P.R. 260, three intermolecular hydrogen bond donors are facing four hydrogen bond acceptors, one of which binds two donors. As a consequence, the molecule must adopt two conformations, which are packed in a complex stacking mode. On the other hand, the respective numbers of hydrogen bond donors and acceptors in P.Y. 139 and in P.Y. 185 match, and, especially in the case of P.Y. 139, the shape and symmetry of the molecule perfectly support the formation of tight packing. Accordingly, P.R. 260 has a comparatively low and P.Y.139 a very high packing coefficient, which is indicative of strong intermolecular attractive forces.

The trend found for the packing coefficients is confirmed by the packing energies (PEs) of the pigments, which have been calculated using the Dreiding 2.21 force field[19, 22] in combination with atomic point charges (Table 14–3)[19, 23]. The packing energy of a molecular crystal may also be estimated from well established empirical correlations with, for example, the molecular surface or the number of electrons[24].

For comparison, a specific packing energy SPE = PE / mol. mass has been defined. The SPE values of the investigated isoindoline differs significantly. The specific packing energy of P.Y. 139 exceeds the corresponding value of P.R. 260 by 42 %, and thus marks P.Y. 139 as the intrinsically more stable solid.

In conclusion, the analysis of the packing coefficients and the specific packing energies suggests a stability order P.R. 260 < P.Y. 185 < P.Y. 139. This sequence is reflected in the properties of the pigments, e.g. thermal stability, overpaint and weather fastness. In view of this relation, isoindoline pigments may be seen as a class of intuitively "crystal engineered" pigments[25].

14.5.3
ESA Data

In their surface characteristics determined by ESA (Electrokinetic Sonic Amplitude) measurements (4 : 1 water / ethanol, Matec MBS 8000), Paliotol Yellow L 1155 and the three P.Y. 139 grades show similar behavior. All carry a small to negligible negative charge, only L 2140 HD being slightly more highly charged. Their isoelectric points are in the range pH 2 to pH 4.

In the stabilization of L 1155, L 1820 and L 1970 in liquid media, electrostatic forces will play only a negligible role; only in the case of L 2140 HD do these forces seem to be of some significance (Table 14–4).

Table 14–4: ESA data of isoindoline pigments.

	Initial ESA signal [μPa/V/m]	*Isoelectric point [pH]*
L-1155	–17	1.68
L-1820	–27	2.43
L-1970	–40	4.02
L-2140 HD	–163	1.63

A weak point of isoindoline pigments is their sensitivity to alkali. In aqueous printing inks and paints, products with fine primary particles are not stable in storage. Plastics containing alkaline additives may undergo discoloration.

Only coarsely crystalline pigments like Paliotol® Yellow L 2140 HD are stable up to pH 8.5–9 and can be used in waterborne automotive paints. A patent[19] describes the addition of acidic buffers to overcome the negative effects of alkaline additives in plastics.

Table 14–5 lists typical properties of commercially available isoindoline pigments.

Table 14–5: Typical properties of isoindoline pigments.

	P.Y. 139 (L 1820)	*P.Y. 139 (L 1970)*	*P.Y. 139 (L 2140 HD)*	*P.Y. 185 (D 1155)*
Density (g/cm^3)	1.74	1.74	1.74	1.49
Bulk volume (l/kg)	5.0	3.3	5.0	4.0
Specific surface (m^2/g)	55	22	25	36
Particle size distribution (median) (nm)	154	216	339	130
Oil absorption (g/100 g)	65	35	50	52
Hue angle at 1/3 SD [1]	78	71	66	95
Reduction ratio at 1/3 SD [2]	13.7	8.0	3.9	11.9
Light fastness [3]				
full shade	8	8	8	7
1/3 SD	7	7	8	6
Fastness to weathering [4]				-
full shade	3–4	4	4	-
1/3 SD	2–3	3–4	4	–
Heat resistance [5]	200 °C	200 °C	200 °C	180 °C
Fastness to overspray [6]	5	5	5	-
Chemical resistance [7]				
2 % HCl	5	5	5	5
2 % NaOH	4–5	4–5	5	3

Table 14–5: Continued

	P.Y. 139 (L 1820)	P.Y. 139 (L 1970)	P.Y. 139 (L 2140 HD)	P.Y. 185 (D 1155)
Fastness to solvents [8]				
water	5	5	5	5
ethanol	5	5	5	4–
butylacetate	5	4–5	5	4–5
MEK	5	5	5	4
xylene	4–5	4	5	5
mineral spirit	5	4	5	5
Solvenon PM	4–5	4–5	5	3–4

1) Hue angle at 1/3 SD in an alkyd/melamine system according to CIE-LAB system (DIN 6174)

2) Parts of TiO_2 required to reduce 1 part of pigment to 1/3 SD

Lightfastness was tested in an alkyd/melamine system. Assessment was made using the 8-step blue scale according to DIN EN ISO 105-B01 (formerly DIN 54 003)

4) Weatherfastness results are based on two-year exposures in Florida in an alkyd/melamin system. Changes in color were assessed using the gray scale according to DIN EN 20105-AO2 (formerly DIN 54 001).

5) Heat resistance for pigments for coatings was tested in an alkyd/melamine system below 200 °C, in a silicone resin above 200 °C. Pigments for plastic application were tested in PE-HD at a pigment: TiO_2 ratio of 1 : 10

6) Fastness to overspray: An alkyd/melamine paint film baked at 140 °C for 30 min is coated with a white paint of the same composition and then rebaked at 160 °C for 30 min. Discoloration of the white coat is assessed using the gray scale according to DIN EN 20105-AO2 (formerly DIN 54 001)

7) Chemical resistance: The cured paint film (alkyd/melamine system, 10% pigmented) is exposed to solutions of 2% hydrochloric acid and 2% sodium hydroxide for 24 hours. The gray scale according to DIN EN 20105-AO2 (formerly DIN 54 001) was used to access color changes

8) Fastness to solvents: The test is carried out on the pigment powder. A closed filter bag containing 0.5 g of the pigment is immersed in 20 ml of the test solvent for 24 hours. The colour change of the solvent is compared against a standard colour sclae according to DIN EN 20105-AO3 (formerly DIN 54 002)

14.5
Pigment Grades; Discussion of Individual Pigments

Isoindoline pigments are primarily marketed in the form of powders, but are also available as predispersed pigments (Table 14–2).

The main applications for P.Y. 139 are all types of paints including automotive finishes, plastics like polyolefin fibers and PVC and packaging inks. P.Y. 185 is mainly used for the coloration of plastics and in packaging inks.

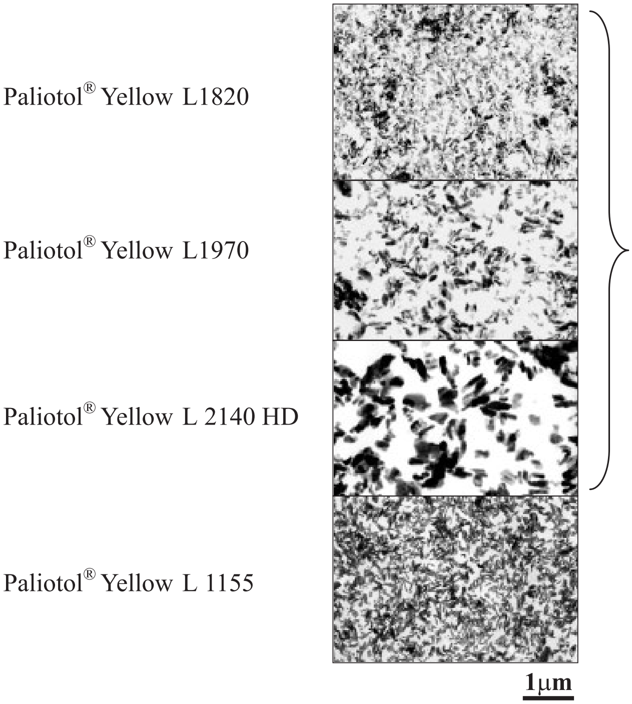


Figure 14–12: Electron micrographs of isoindoline.

Electron micrographs of the commercially available grades of two chemical structures are shown in Figure 14–12. The first three photographs of P.Y. 139 clearly show the influence of the finishing conditions on particle growth. The fine particles of Paliotol Yellow L 1820 offer a maximum of transparency and color strength, the coarse crystals of L 2140 HD an optimum of hiding power, chroma in full shade and durability at the expense of reduced color strength. L 1970 lies half-way between these extremes.

P.Y. 185 (D 1155) has fine particles very similar to those of L 1820, characteristic of a pigment with high transparency.

The hydrodynamic diameters of the three P.Y. 139 grades determined by quasi-elastic light scattering (Microtac UPA 150) for L 1820, L 1970 and L 2140 HD are 145 nm, 243 nm and 344 nm, and agree well with the electron micrographs. Whereas L 1820 has a significant share of particles below 100 nm this proportion is very small in L 1970 and nearly negligible in L 2140 HD, in accordance with the good exterior durability and good rheological properties of this pigment.

Optical properties and spectral reflection curves of P.Y. 185 and P.Y. 139 in an alkyd / melamine system at a constant pigment / TiO_2 ratio of 1 : 10 are shown in Figure 14–13:

Obviously P.Y. 185 only absorbs violet and blue light. The reflectance edge in white reduction lies in the 500 nm region. Therefore it looks a very greenish yellow.

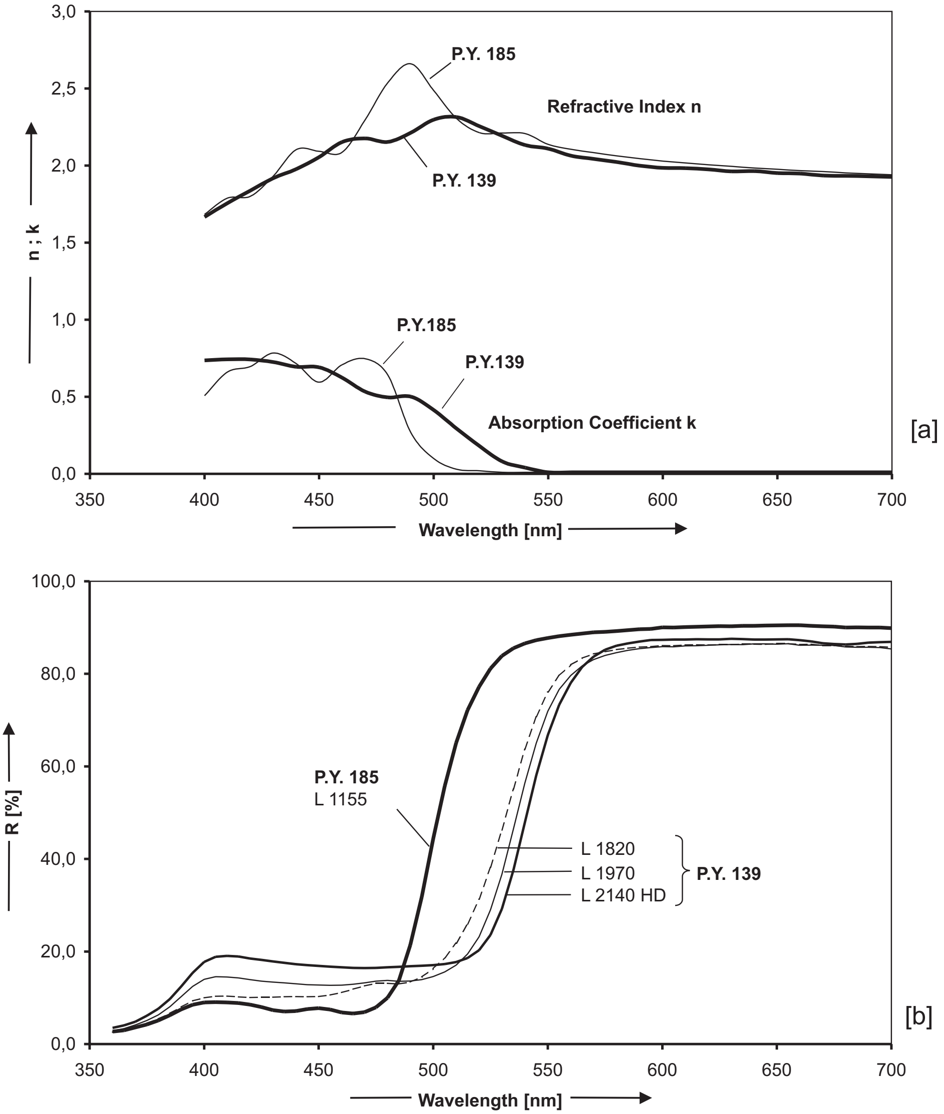


Figure 14–13: Optical constants [a] and remission spectra (1 : 10 TiO_2) [b] of P.Y. 139 and P.Y. 185.

On the other hand P.Y. 139 still shows some absorption in the bluish green region, which shifts the reflectance significantly to longer wavelengths. As a result all P.Y. 139 species look a reddish yellow.

The higher reflectance of L 2140 HD compared to L 1970 and L 1820 (λ = 400–500 nm) corresponds to the lower color strength of this pigment. Also the shift to a more reddish shade in comparison to the fine particles of L 1820 is clearly to be seen (λ range 520–560 nm).

The understanding of the interaction of pigments and the media into which they are incorporated has made enormous progress during the last decades. From these findings it is obvious that pigments cannot be characterized by fixed physical data and a chemical structure. Pigments should be regarded as materials with individual properties which make them suitable for potential applications. Bearing this in mind, a short overview of commercially available isoindoline pigments is given below.

P.Y.139 – transparent forms The three BASF grades Paliotol® Yellow D 1819, L 1820, K 1841 differ only slightly in the size of the primary particles. The final milling process, however, is directed toward the final field of application.

Paliotol Yellow D 1819 is mainly used in NC-packaging inks. Its main merit in this field is good transparency, high colour strength and good rheological properties.

Paliotol Yellow L 1820 is mainly used in industrial paints. Its high colour strength can be combined with the good hiding power of suitable inorganic extenders to reduce pigmentation cost.

Paliotol Yellow K 1841 is mainly used for colouring polyolefins (LDPE, HDPE and PP). It also performs well in SPVC and EPVC. However, the pigment's chemical structure makes it sensitive to alkali. Positive properties are high transparency, colour strength, good light fastness and relatively good heat stability. Consequently, its main application is in colouring polyolefin films, tapes and fibers as the pigment of choice to replace diarylide yellows and lead chromates. For engineering plastics containing alkaline additives, its thermal stability is not sufficient.

Graphtol® Yellow H2R (Clariant) is recommended for PVC, cable sheathing compounds, PO and PP spin-dying. Colouristically it is very close to Paliotol Yellow K 1841.

Cromophtal® Yellow RF (Ciba S.C.) has its major use in PP fibers and PVC and is slightly weaker and duller than K 1841.

Bayplast® Yellow R (Bayer) is recommended for the same fields of application as the above-mentioned products. Compared to K 1841 it is distinctly weaker, redder and duller.

P.Y.139 – semiopaque form **Paliotol Yellow L 1970** offers a very good compromise between colour strength, hiding power, weather fastness and rheological behaviour. It has its main application in lead-free solvent-borne paints, where it offers economic incentives compared to yellow pigments of different chemical structures.

P.Y.139 – opaque forms **Paliotol Yellow L 2140 HD** offers the optimum in terms of hiding power, brilliancy in full shade, outdoor durability and rheological properties, unfortunately at the expense of reduced colour strength. The pigment is the product of choice for lead-free high grade industrial and automotive OEM and refinish reddish yellow paints. It is stable even in automotive waterborne systems. On fresh concrete and similar applications, however, it cannot be used.

The old Bayer pigment Fanchon® Fast Yellow Y-5700 has slightly higher colour strength than L 2140 HD, but is inferior in terms of hiding power and brilliance. In their overall performance the recently introduced products Fanchon Fast Yellow Y-5740 (Bayer) and Novoperm® Yellow M2R70 (Clariant) are very similar to L 2140 HD.

P.Y. 185 Paliotol Yellow D 1155 has its main application in solvent-borne packaging inks because of its high colour strength, good transparency and excellent rheological properties.

Eupolen® Yellow 11–5501 For application in plastics, the predispersed form instead of the powder pigment is recommended. Compared to the powder grade, the predispersed pigment offers absence of dust and considerable advantages in terms of colour strength and ease of processing.

14.6
Pigment Manufacturers; Economics

The first isoindoline pigment appeared on the German market in 1973: Lithol® Fast Yellow 1840 (P.Y. 139), manufactured by BASF.

Nowadays several finishing forms of the same chemical structure are on offer from other companies, among them Bayer, Ciba S.C. and Clariant. Table 14–4 lists the current producers of isoindoline pigments.

Only P.Y. 139 and P.Y. 185 grades are on the market today. Products of different chemical structures were withdrawn for technical and economic reasons. The commercially most important product is P.Y. 139.

Among the isoindoline suppliers, BASF is No. 1. This company has the advantage of being the most experienced producer of the important starting material *o*-phthalodinitrile. By the beginning of 2000, BASF has dedicated a 1200 tons/y plant to PY. 139. For the production of this pigment, BASF employs an integrated, flexible process concept. The use of state-of-the-art technology and a high degree of automation helps to ensure a high and constant quality level and sustained competitiveness.

The capacity of the other suppliers Bayer, Ciba S.C. and Clariant is not known, because in most cases they are using multipurpose equipment.

BASF is so far the sole supplier of P.Y.185.

14.7
Toxicology and Ecology

Isoindoline pigments do not exhibit acute toxicity in animal tests by oral and inhalative administration. Tests have shown that they do not cause irritation of the skin or mucous membranes. The Ames test for mutagenicity gave negative results, and the test for genotoxicity shows no clastogenic effects.

A 4-week feeding trial to test for chronic toxicity in rats, involving the administration of up to 1.000 mg per kg of body weight, did not reveal any adverse effects (C.I. Pigment Yellow 185). The pigments are therefore believed to be neither toxic nor bioavailable.

Isoindoline pigments are sparingly soluble in water. They exhibit practically no toxicity to fish. The pigments are not biodegradable, but since they are also not bioavailable either, they do not accumulate in living organisms. This was shown by bioaccumulation tests in fish.

Acknowledgements

We should like to thank Mr. D. Müller of Bayer, Mr. H. Liebig of Ciba S.C. and Dr. R. Jung of Clariant for providing technical literature and our colleagues Dr. T. Clemens, Dr. H. Endriss, Dr. V. Koch, Dr. W. Lotsch and Dr. J. Schröder for their cooperation.

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15
Isoindolinone Pigments

Abul Iqbal, F. Herren, and O. Wallquist

15.1
Introduction

From the viewpoint of basic chromophore structures, organic pigments of commercial significance today may be classified into four major groups, namely

1. Azo pigments
2. Phthalocyanine pigments
3. Carbocyclic quinoid pigments
4. Heterocyclic pigments.

Featuring appropriate chromophore moieties embedded in a heterocyclic structural frame, the last group of products represents a very special class of colorant. Although only accounting for less than a quarter by weight of the world potential of organic pigments, heterocyclic pigments generally combine high value with high performance. The most important classes of commercially available heterocyclic pigments comprise quinacridones, diketopyrrolopyrroles, isoindolines, isoindolinones, dioxazines, and, to a lesser extent, thioindigo and quinophthalones.

With the exception of dioxazines, which are characterized by the “aza quinoid” chromophore unit, the heterocyclic ring system in the above pigments almost invariably incorporates one or more chemical functional groups from among NH, S, O, C=O, and double bonds. The relative positioning of the double bonds, the carbonyl C=O and the heteroatom groups to each other is frequently such that they may be formally viewed as comprising (cross-conjugated) vinylogous α-diketones or hydrazines, enamines or amidines, and vinylogous carboxamides or carboxylic esters. More importantly, when the hetero atom is nitrogen, the specific juxtapostion of the carbonyl C=O and amine NH groups afford strong inter- and intramolecular hydrogen bond formation in such pigments, thus accounting, directly or indirectly, for their high insolubility and heat stability.

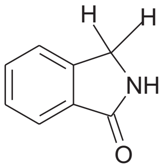
Again, in certain heterocyclic pigment molecules, the nature and spatial arrangement of the donor hetero atoms may be such as to make them ideally suitable as multidentate ligands, allowing the formation of very insoluble and heat stable transition metal complex pigments featuring five and six membered chelate rings.

The present chapter describes one such member of this group of heterocyclic pigments, namely isoindolinone pigments, chemically featuring an aromatic semicyclic amidine or enamine chromophore structure and affording primarily yellow to orange shades. Certain metal complex pigments based on isoindolinone molecules are also briefly included in the description. The chapter will highlight, in particular, the chemistry, physico-chemical properties, and applications of colorants incorporating the isoindolinone structure.

15.2
Chemistry

15.2.1
Azomethine-Type Isoindolinones

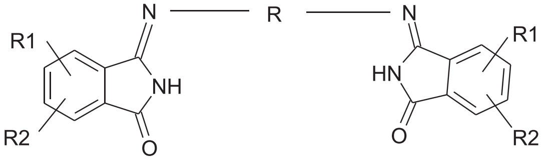
All isoindolinone pigments are characterized by the presence of the isoindolinone ring structure **1**.



1

Formal replacement of the two hydrogen atoms at the 3-position by a substituted nitrogen atom yields an azomethine (>C=N–) linkage at this position – the ensuing product being conveniently referred to as an azomethine-type isoindolinone derivative. If, however, the two hydrogen atoms are replaced by an appropriately substituted carbon atom to yield a C=C double bond, the resulting semicyclic amidine derivative is classed as a methine-type isoindolinone.

ICI in 1946 was the first to take out a patent on isoindolinone type dyes and pigments[1], protecting products of the general formula **2**, where each of the isoindolinone benzene rings contain up to two substituents (R_1, R_2), while R is derived from an aromatic or heterocyclic diamine.

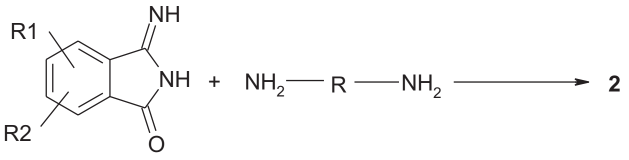


2

R = aromatic and heterocyclic rings

In the following years, Elvidge and Linstead reported on the preparation of additional compounds represented by the general formula **2** [2, 3]. The use of heterocyclic diamines has also been reported to yield yellow dyes[3, 4].

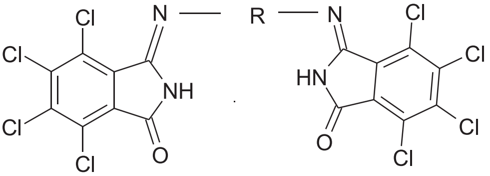
Although the initial products at ICI were mainly made from unsubstituted phthalimide, the majority of their compounds were prepared by the condensation of a primary diamine with the corresponding 3-iminoisoindolinone derivative **3**, affording in general yellow or orange pigments.



3

Even as late as the 1970s, Bitterli and Kehrer[5] reported the preparation of yellow isoindolinone pigments starting with unsubstituted (R^1, R^2 = H) and dichloro (R^1, R^2 = Cl) derivatives of 3-iminoisoindolinone (**3**). However, because of their poor color strength and fastness properties, such products have gained no commercial significance.

In the late 1950s, however, Pugin et al. at Geigy discovered that, surprisingly, both color strength and fastness properties could be significantly improved in such pigments through perchlorination of the isoindolinone benzene rings, thus making them commercially viable. Pertinent patents were filed claiming the use of tetrachlorophthalimide as starting material to make azomethine-type isoindolinone pigments of the general structure **4**.



4

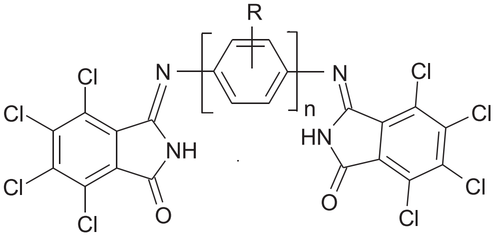
R = aromatic, heterocyclic ring

This represented a major breakthrough in the area of isoindolinone pigments, much of the work done on tetrachloroisoindolinones at Geigy being covered in an excellent comprehensive paper published by Pugin et al.[6].

From a chemical standpoint, the azomethine-type isoindolinones **2** and **4** are derivatives of phthalimide, and may also be viewed as acylated exocyclic amidines with the acylamino group forming a part of the heterocycle.

The two tetrachloroisoindolinone moieties in compounds **4** are connected with each other via condensation with an appropriate aromatic or heterocyclic diamine. It is interesting to note that the aromatic substitution pattern of the bridging diamine has a strong influence on the color of the ensuing pigment.

Commercially significant tetrachloroisoindolinone pigments may be depicted by the general structure **5**, where the bridging amine moiety is represented by an aromatic diamine.

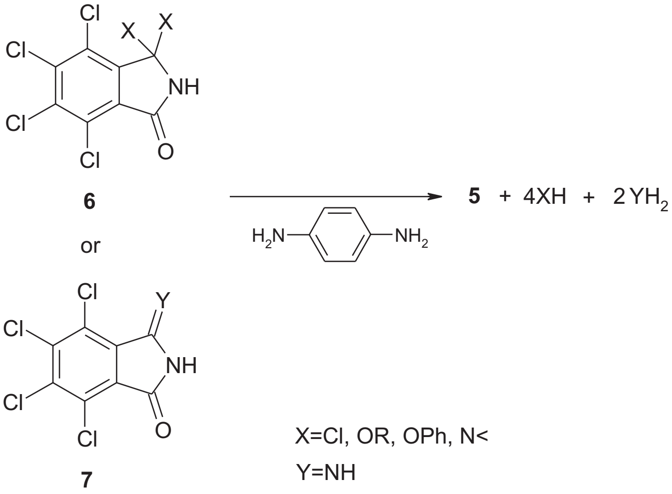


5

R = H, CH_3, OCH_3, Cl

n = 1,2

The synthesis of pigments **5** generally involves the condensation of an aromatic diamine with two equivalents of an activated tetrachloroisoindolinone intermediate, e.g., one represented by the general structure **6** or **7**.

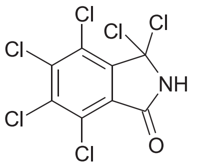


X=Cl, OR, OPh, N<

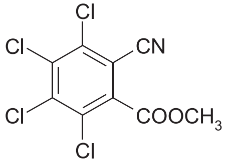
Y=NH

Such starting materials are characterized by the presence of good leaving groups in the 3-position, facilitating the nucleophilic condensation of primary amine groups to afford the azomethine linkage. Thus, reactant **6** carries in the 3-position two sp^3 bonded monovalent substituents (X) such as a chlorine atom, alkoxy group or secondary amine, while in reactant **7**, Y represents an sp^2 bonded divalent substituent such as an NH, N-alkyl, or N-aryl group.

As opposed to the previously disclosed iminoisoindolinone intermediate **3**, two other key precursors of tetrachloroisoindolinone, namely **8** and **9**, are employed in the commercial production of the corresponding pigments.

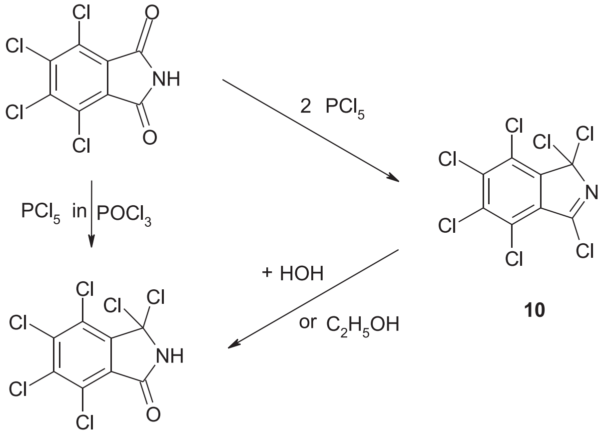


8



9

Intermediate **8** reacts smoothly with a primary diamine to afford the desired pigment directly. It may, however, be also converted first with an alcoholate, phenolate, amine, or sodium sulfide into the corresponding **6**-type intermediate, which in turn can undergo facile reaction with primary aromatic diamines to yield the corresponding pigment **5**.

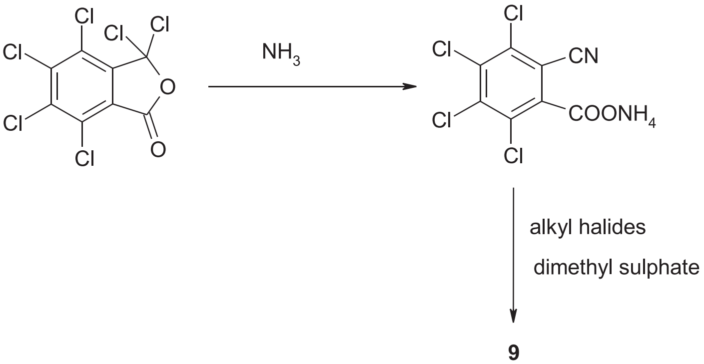


8

As for intermediate **8**, two routes are available for its synthesis. According to one route, tetrachlorophthalimide may be chlorinated with one equivalent of phosphorus pentachloride in phosphorus oxychloride to yield the desired product in one step.

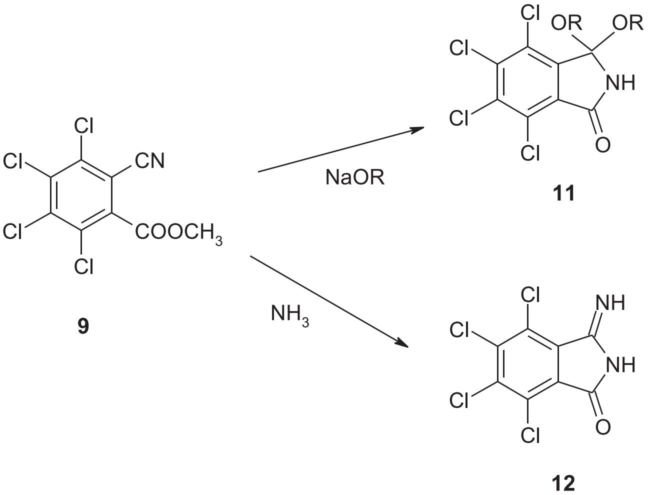
Alternatively, tetrachlorophthalimide may be reacted with two equivalents of phosphorus pentachloride, affording 1,3,3,4,5,6,7-heptachloroisoindolenine (**10**) as an intermediate, which can be subsequently transformed with one equivalent of water or alcohol into **8**.

Intermediate **9**, on the other hand, can be prepared by treatment of 3,3,4,5,6,7-hexachlorophthalic anhydride with ammonia to yield the ammonium salt of 2-cyanotetrachlorobenzoic acid, which is subsequently converted into the corresponding metal (Ag, Ba, Ca, or Na) salt, before being finally reacted with an alkyl halide or dialkyl sulfate to yield **9**.



The direct condensation of diamines with intermediate **9** generally does not lead selectively to the desired product. The latter is therefore first cyclized to a reactive tetrachloroisoindolinone precursor of type **6** or **7** by reacting with such reagents as alcoholates, amines or sodium sulfide, before being subjected to facile condensation with a diamine.

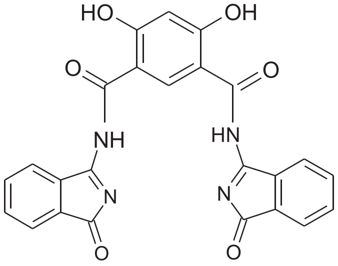
Thus, reaction with alkali alcoholate or ammonia leads to the formation of the activated compounds **11** or **12.** Simple heating of **12** with a primary aromatic amine in an organic solvent in the presence of acetic acid now allows facile replacement of the imino group in the 3-position by the corresponding arylimino substituent.



Intermediate **12** can also be obtained by reaction of tetrachlorophthalonitrile with an alkali metal hydroxide[7], or by a single step reaction of tetrachlorophthalic anhydride with ammonia or urea in a solvent under pressure[8].

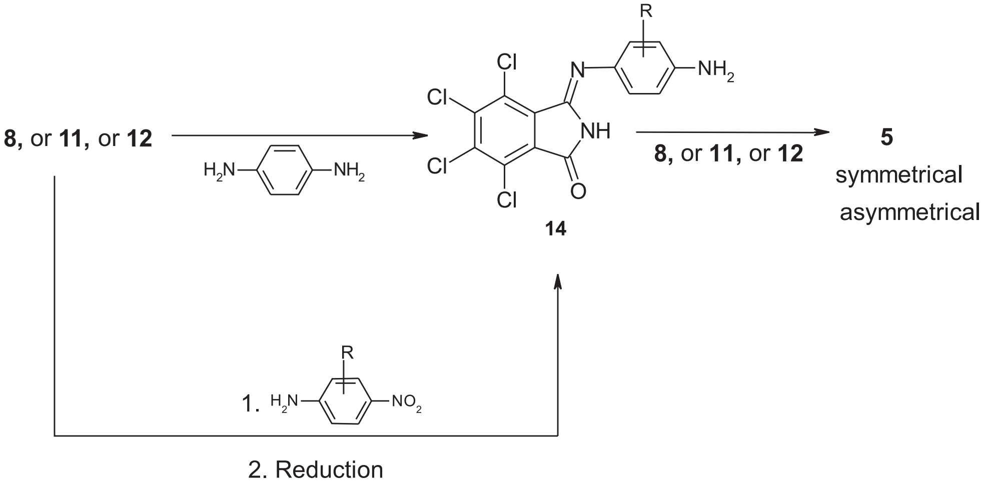
The various reactive tetrachloroisoindolinone intermediates described above all react more or less smoothly with diamines under conditions determined (among others) by the nature of the substituent at the 3-position of tetrachloroisoindolinone, their reactivity sequence being **8** > **11** > **12**. But the nature of the diamine has also an influence on the reaction rate, and hence on the condensation parameters. Obviously, substituents creating greater steric hindrance or reducing nucleophilic reactivity of the primary amine group can impede the condensation reaction. Thus, for example, higher temperatures are required for the reaction with aromatic diamines carrying an ortho substituent, such as *o*-dianisidine, or *o*-toluidine.

The non-chlorinated analog of iminoisoindolinone **12** can also be reacted with appropriate phthaloyl chlorides to yield, e.g., yellow isophthalamide pigments **13** [9].



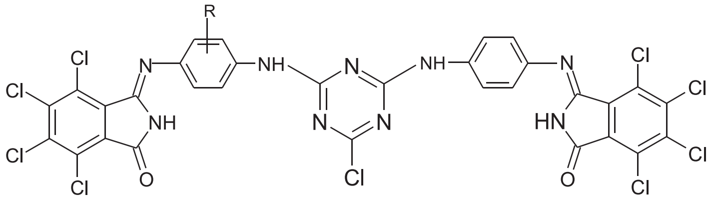
13

Pugin and von der Crone[6] also reported the following synthetic variations for tetrachloroisoindolinone pigments **5.**



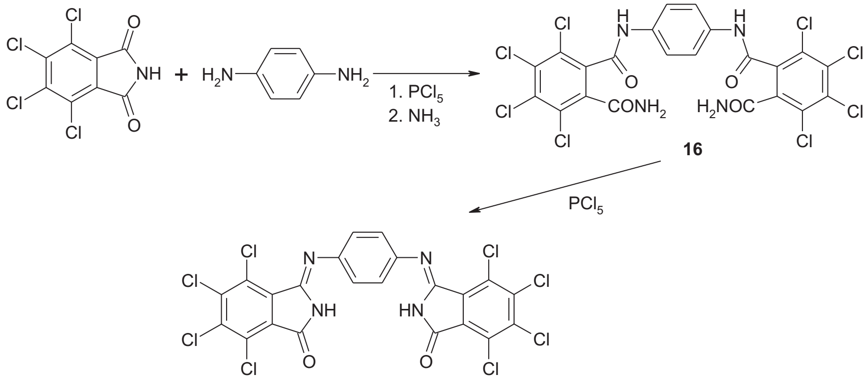
Starting material **8** or **11** or **12** is reacted with an excess of a diamine to form, in a one-step reaction, the intermediate **14**, or it is reacted with a nitro-aromatic amine followed by reduction of the nitro group to yield, in a two-step reaction, the same condensation product. Intermediate **14** features a free amino group, which can now be condensed with a second molecule of the same reactive tetrachloroisoindolinone as above, or with a differently substituted isoindolinone derivative. In the latter case, of course, pigments with asymmetric structures are obtained.

It is interesting to note that monocondensed derivatives of type **14**, in an attempt to prepare lightfast pigments, have also been reacted with cyanuric chloride to yield yellow to red isoindolinone derivatives **15** [10].

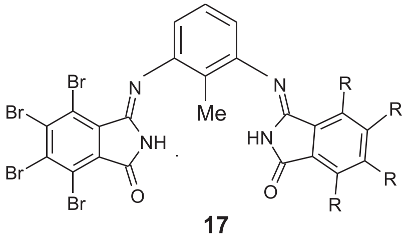


15

Dainippon Ink, in 1976, published a patent[11] claiming yet another one-pot synthetic approach to tetrachloroisoindolinone pigments **5**. In their process, easily available tetrachlorophthalic anhydride is reacted with an appropriate aromatic diamine at a 2:1 molecular ratio in the presence of ammonia and phosphorus pentachloride to first yield the corresponding bisacylated *p*-phenylene diamine derivative **16.** Subsequent ring closure to the desired tetrachloroisoindolinone pigment is effected with additional phosphorus pentachloride in a high boiling solvent such as trichlorobenzene.



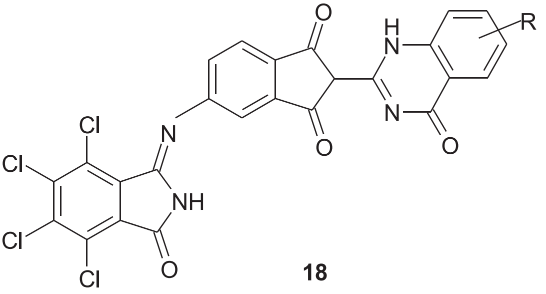
Perbrominated isoindolinones of structure **17** were prepared by reacting appropriate diamines with the tetrabromo analog of **6**, which in turn was obtained from the perbromo analog of **9** [12].



17

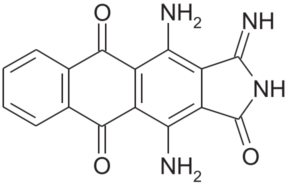
R = Br, Cl

Depending on in situ and post-synthetic treatment procedures, azomethine-type tetrachloroisoindolinone pigments may result in several crystal modifications, e.g., in α, β, and δ types[13]. Mono and disazomethine pigments featuring heterocyclic ring systems have also been claimed by several companies[14]. The heterocyclic structure **18** even features two pigment chromophores, namely the quinophthalone and the isoindolinone moieties[15].



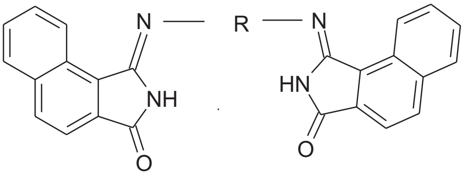
18

Another example of a bichromophoric system incorporating isoindolinone and the anthraquinone moities is shown by structure **19**. Such products are conveniently synthesized from the corresponding anthraquinone-2,3-dinitrile derivatives, and have been claimed as greenish blue polyester dyes[16].



19

Yet another type of polycyclic azomethine isoindolinones, where the isoindolinone benzene ring is either linearly or angularly fused with other benzene rings, have also been reported. Yellow to orange bisazomethine pigments of structure **20** were synthesized from the corresponding naphthalene dicarboxylic acids and diamines in the presence of phosphorous pentachloride[17].

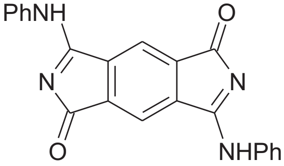


20

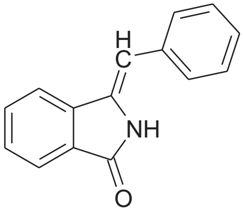
R = aromatic, heterocyclic ring

Mono condensation products such as **14** have also been used as a diazo component[18], or as a coupling component[19] after acetoacetylation with diketene, to prepare a variety of monoazo and disazo pigments.

Monomeric and polymeric phenylene-bridged azomethine-type isoindolinone pigments have been prepared, e.g., by the reaction of intermediates such as **21** and **22** with appropriate aromatic mono and diamines[20].



21



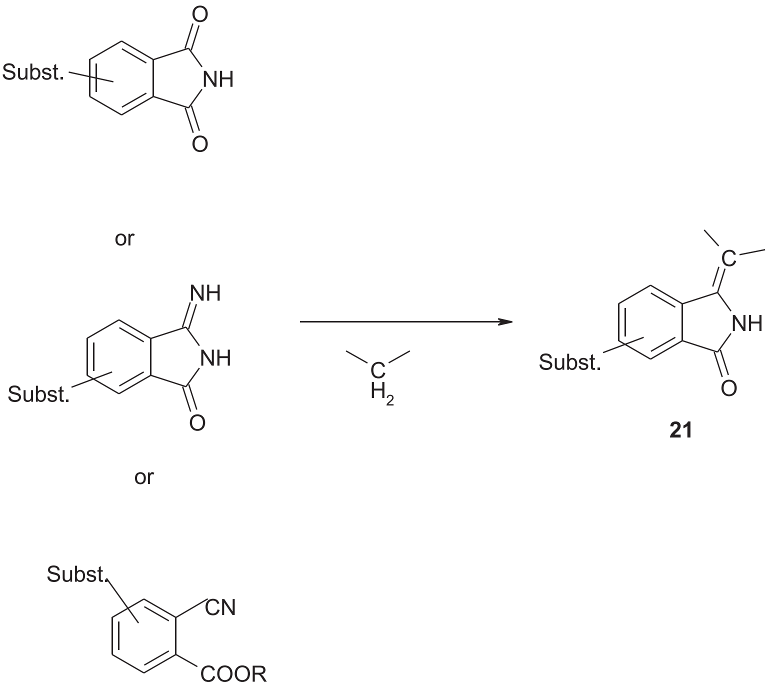
22

15.2.2
Methine-Type Isoindolinones

In comparison with their azomethine analogs described above, methine-type isoindolinones have gained little significance as pigments, although bismethine isoindoline pigments constitute commercially important yellow to red products[21].

Methine isoindolinones of generic structure **23** can be prepared by the reaction of active methylene compounds with either phthalimides [e.g., 22], or iminoisoindolinones [e.g., 23], or α-cyanobenzoates by analogy with the methods described above for azomethine type isoindolinones.

Methine isoindolinones have also been prepared by treatment of the corresponding phthalides with ammonia [e.g., 24].



21

15.2.3
Metal Complexes Based on Isoindolinones

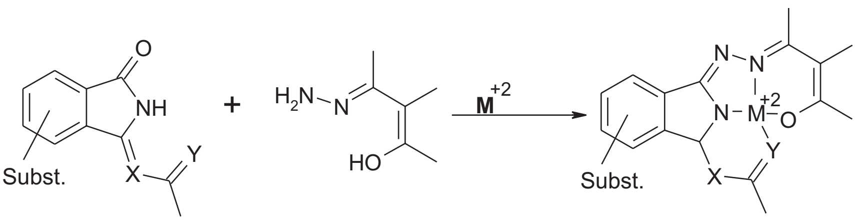
Although both azomethine and methine-type monocondensed isoindolinone products, in their own right, are of little or no importance as pigments, certain derivatives belonging to this class of compounds may serve as bidentate ligands for complexing with appropriate transition metals, yielding useful metal complex pigments.

For example, *meso*-tetraaryltetrabenzoporphyrin zinc complex results from heat treatment of the corresponding 3-benzylidenisoindolinone with zinc benzoate[25].

Appropriately substituted methine and azomethine isoindolinones featuring substructure **24** were also converted into stable metal chelate pigments of general structure **26** via a metal template reaction with aromatic and heterocyclic α-hydroxy aldehyde or ketone hydrazone derivatives incorporating the structural element **25**[26].

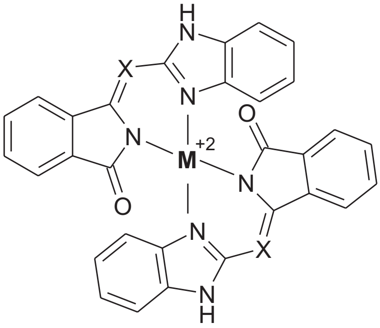
In such reactions, the pre-coordination of the reactant ligands with metal significantly facilitates the reaction between the amide carbonyl group of the isoindolinone ring and the amino group of hydrazone to ultimately yield metal chelate complexes of multidentate methine – azomethine type isoindoline ligands. Such products range in shade from yellow to blue-red and feature high pigment fastness properties when their chemical structures are appropriately designed.

Further, stable 2:1 transition metal complex pigments **27** (C.I. Pigment Yellow 177) and **28** (C.I. Pigment Yellow 179), featuring six-ring chelates, have been prepared from methine and azomethine type isoindolinones[27].



24 **25** **26**

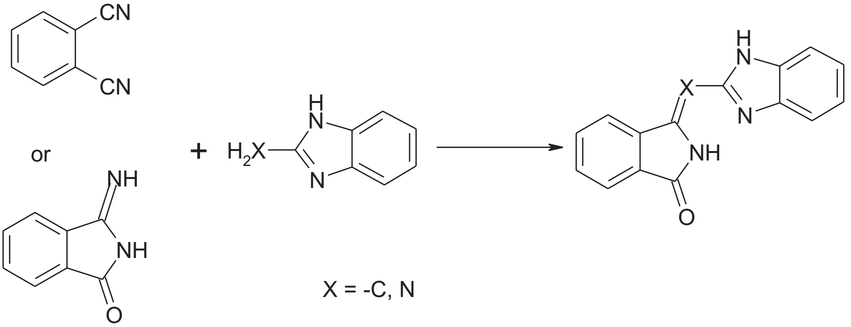
X= -C, N ; Y= O, S, N
M = Ni, Zn, Cu, Pd



27: X = C-CN; M = Ni, Co, Zn

28: X = N; M = Ni, Co, Zn

The corresponding ligands may be produced via condensation of phthalonitrile or iminoisoindolinone with appropriate N- and C-nucleophiles, namely 2-aminobenzimidazole and 2-cyanomethylene benzimidazole.



X = -C, N

It is worth mentioning here that metal template reaction of hydrazones **25** with such insoluble pigments as **27** and **28**, in particular when M=Ni, also affords the corresponding chelate pigments **26** in a smooth reaction.

Analogs of metal complex pigments **27** and **28** featuring other heterocyclic amines and methine compounds have also been reported in the literature[28].

15.3
Physico-Chemical Properties

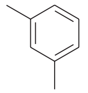
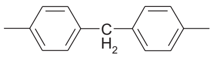
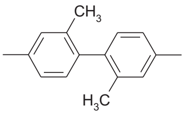
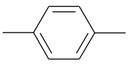
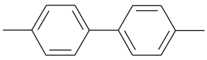
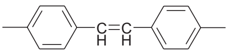
Azomethine-type tetrachloroisoindolinone pigments **4** are thermally very stable, decomposing at around 400 °C without melting. They are practically insoluble in most organic solvents at room temperature. As structural analogs of phthalimide, tetetrachloroisoindolinone pigments feature a fairly acidic hydrogen residing at the ring nitrogen atom. Such pigments are thus capable of forming more or less soluble alkali salts in a number of protic and aprotic polar solvents. Moreover, they can be methylated with dimethyl sulfate to yield the corresponding *N*-methyl isoindolinone derivatives.

In contrast, the exocyclic azomethine linkage (>C=N–) is remarkably stable in both alkaline and even acidic conditions. However, as soon as the isoindolinone pigments are dissolved in concentrated sulfuric acid under harsh conditions of temperature and solvent, they are hydrolytically cleaved into the corresponding diamine and phthalimide derivative.

Pugin and von der Crone[6] have carried out a detailed study of the structure-property relationship of tetrachloroisoindolinone pigments **4** in solution.

Table 15–1 shows the maximum wavelength of light absorption and molecular extinction coefficient for a series of tetrachloroisoindolinone pigments of the general formula **4**, in which the diamine component is varied.

Table 15–1: Influence of the bridging diamine component on the light absorption and color properties of tetrachloroisoindolinone pigments 4

R in compound 4	*λ_{max} [µm] (in DMF)*	*log ε_{max} (in DMF)*	*Solid state color*
	385	3.945	greenish yellow
	391	4.143	greenish yellow
	397	4.150	yellow
	425	4.000	reddish yellow
	420	4.27	orange
	436	3.934	red

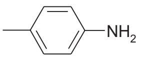
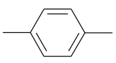
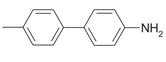
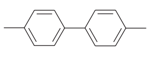
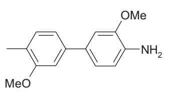
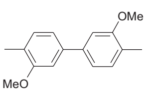
The selected isoindolinone pigments depicted in Table 15–1 all show a strong absorption between 380 and 435 nm. The nature of the diamine bridge does have an effect, albeit not so strongly pronounced, on the light absorption properties of the pigments. Thus, diamines with interrupted conjugation of the double bonds between them, as well as diamines that are sterically forced out of coplanarity, cause a hypsochromic shift of maximum wavelength of absorption, as opposed to their conjugated and planar analogs. Upon prolongation of the double bond conjugation, or upon substitution by an auxochromic group, however, a bathochromic shift results.

As with many dyes, such pigments, in the dissolved state, also exhibit a relatively broad absorption spectrum with a single maximum. Moreover, as one would expect, the spectrum of the monocondensed product **14** containing only one tetrachloroisoindolinone moiety shows a very similar spectrum to that of pigment **4** containing two tetrachloroisoindolinone moieties.

As a matter of fact, monocondensation products **14b** with a free amino group absorb at even higher wavelengths, in comparison to the dicondensed analog (compare Table 15–2).

Since replacement of the free amino group in moncondensation product **14** by the second tetrachloro isoindolinone moiety, yielding the dicondensation product **4** , causes a hypsochromic shift in comparison to the free amino (–NH_2) group of the mono condensation product, it is conjectured that the tetrachloroisoindolinone substructure is not in conjugation with the remainder of the pigment molecule[6]. Most probably, the aromatic ring of the diamine is coplanar with one of the tetrachloroisoindolinone units, while the second tetrachloroisoindolinone moiety is twisted out of this plane. No concrete evidence, however, has yet been advanced for such conformational asymmetry.

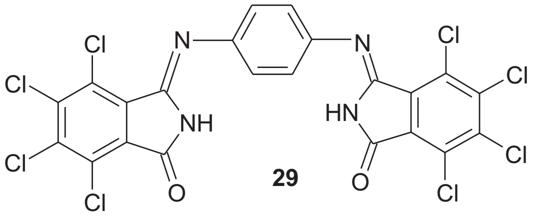
Table 15–2: Comparison of the light absorption properties of mono- and dicondensed tetrachloroisoindolinone pigments (measured in DMF).

R =	*Compound 14*		*Compound 4*	
	λ_{max} μm	*ε_{max}*	*λ_{max} μm*	*ε_{max}*
 	454	4.02	425	4.0
 	436	4.05	420	4.27
 	440	3.816	425	4.126

Monocondensed methine and azomethine isoindolinone analogs of **14** and **23** are much more soluble and much less stable than their dicondensed counterparts in terms of fastness properties, and hence of little commercial significance as pigments.

15.4
Commercial Products and Applications

Depending on the substitution pattern, the diamine azomethine-type tetrachloroisoindolinone pigments **4** are available in shades ranging from yellow (**29**, C.I. Pigment Yellow 109, and **30**, C.I. Pigment Yellow 110) via orange (**31**, C.I. Pigment Orange 61) to red (**32**) and brown. However, the commercially significant members are primarily reddish yellow (**29**) to greenish yellow (**30**).



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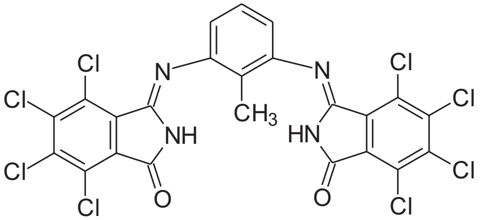

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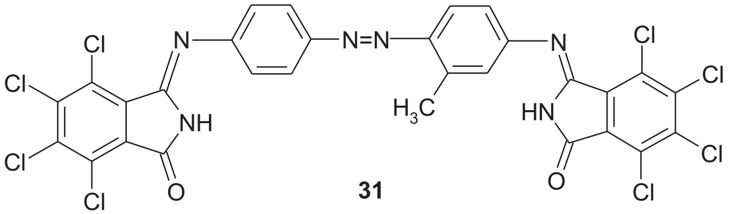

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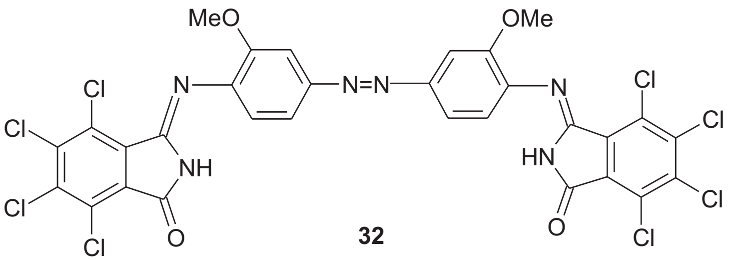

32

They are sparingly soluble in most solvents and resistant to acids and bases, as well as to reducing and oxidizing agents. They are further characterized by excellent heat, light, and weather stability, and exhibit a high melting point (400 °C).

By virtue of their high performance properties, azomethine-type tetrachloroisoindolinone pigments **5** find extensive application in general and high grade industrial paints including original automobile and automotive refinishes. They are also used in plastics and in spin dyeing, as well as in high performance printing inks, especially for metal deco and laminated plastic sheets, and in printing inks for banknotes and securities.

Non-metalated azomethine-type isoindolinone pigments have been patented as both toners[29] and as charge generating materials[30] for electrophotographic imaging and non-impact printing. The use of simple, low molecular weight azomethine isoindolinones for dyeing of keratin fibers and compositions containing them has also been reported[31]. Azomethine-type tetrahalogenated isoindolinone pigments featuring aromatic azo bridges have been claimed as near-IR reflecting pigments[32]. Azomethine isoindolinones have been prepared which are claimed to be useful as antimicrobial agents, being lipoxygenase inhibitors[33].

Monocondensed methine isoindolinones are generally too soluble and are not light fast enough to find application as coloring pigments. However, as mentioned earlier, they may serve as ligands or intermediates for insoluble metal complex pigments. As with azomethine isoindolinones, methine isoindolinones have also been used as charge generating materials in electrophotography[34].

Several patents claim the use of methine isoindolinone dyes derived from methyl quinoline as fluorescent and electroluminescent materials[35]. Fluorescence in such compounds has also been used to detect leaks in oil-filled devices[36] or as chromophores for electrooptical devices[37] and information storage[38]. While specific alkylideneisoindolinone derivatives have been tested as vasodilators[39], several patents have been taken out on specific biological activities (e.g., for agricultural use) of miscellaneous monomethine, in particular, benzylidene isoindolinones[40].

Methine isoindolinone metal complex pigments, in general, have so far met with very limited commercial success. This is primarily due to their dull and weak shades, as well as low fastness properties.

In the case of the pigment **27** (C.I. Pigment Yellow 177), replacement of the central metal ion, cobalt, by zinc yields a much more brilliant shade, albeit of poorer light fastness. Mixed cobalt/zinc complexes balancing color esthetics and pigment performance have been recommended for spin dyeing of polypropylene and polyamide fibres. The yellow pigment **28** (C.I. Pigment Yellow 179) is recommended for use in paints, especially in automotive finishes, because of its high light and weather fastness.

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16

Perylene Pigments

Michael Greene

16.1

Definition of Perylene Pigments

The name perylene pigments refers to a class of high performance pigments made up of *N*,*N*'-disubstituted perylene-3,4,9,10-tetracarboxylic acid imides or perylene-3,4,9,10-tetracarboxylic acid dianhydride.

16.1.1

History

Following their discovery in 1913 and subsequent use as vat dyes, the development and commercial use of these substances as pigments was not realized until the late 1950s. Today, perylenes are recognized as an important class of commercially available high performance pigments, although there are still more perylene vat dyes than perylene pigments. Perylene pigments are primarily used in the coloration of automotive paint and in the mass coloration of synthetic fiber and engineering resins. Characteristics include high color strength, weatherfastness and heat stability.

Excellent sources of information on perylene pigments are “Industrial Organic Pigments” by Herbst and Hunger[1], and the contribution by F. Graser in Vol.1 of the “Pigment Handbook”[2].

16.1.2

Colour Index and Identity

Table 16.1 summarizes the commercially available perylene pigments[3], with the general formula (**1**).

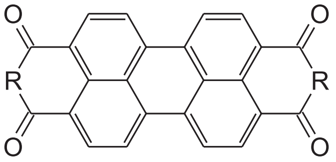

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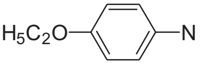
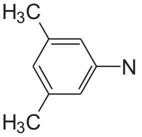
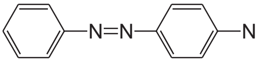
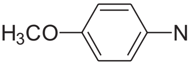
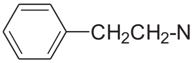
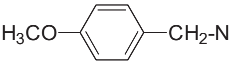
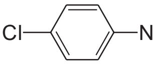
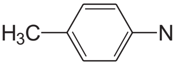
Table 16.1: Commercially available perylene pigments.

CI Pigment name	*Constitution No.*	*CAS No.*	*R*	*Shade*
Red 123	71145	24108-89-2		Scarlet-red
Red 149	71137	4948-15-6		Yellowish red
Red 178	71155	3049-71-6		Red
Red 179	71130	5521-31-3	H_3C–N	Red-maroon
Red 190	71140	6424-77-7		Bluishred
Red 224	71127	128-69-8	O	Bluish red
Violet 29	71129	81-33-4	H–N	Red-bordeaux
Black 31	71132	67075-37-0		Black
Black 32	71133	83524-75-8		Black

While CI Pigments Black 31 and 32 are commercially available, they are used only for niche camouflage coating applications.

Two red perylene pigments, shown in Table 16.2, are also to be found in older versions of the Colour Index, and in other literature, but are no longer made in commerce.

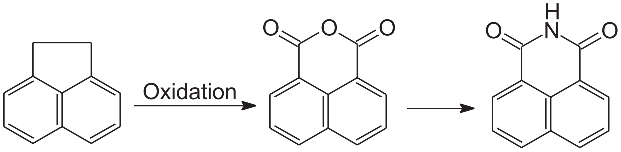
Table 16.2: Formerly manufactured perylene pigments.

CI Pigment name	*Constitution No.*	*R*
Red 189	71135	
Red 228		

16.2
Synthesis of Perylenes

16.2.1
Conversion of Perylenes: Acenaphthene to Perylene Tetracarboxylic Acid Diimide (PTCI, Pigment Violet 29)

The process to manufacture the perylene chromophore is basically unchanged since its discovery in the early 1900s. The reaction sequence begins with catalyzed air oxidation of a coal tar extract, acenaphthene (**2**), to produce naphthalic acid anhydride (**3**). There are several catalysts, such as V_2O_5, that are used Commercially in this oxidation reaction. Naphthalic acid anhydride is available from several global suppliers in a range of purities.

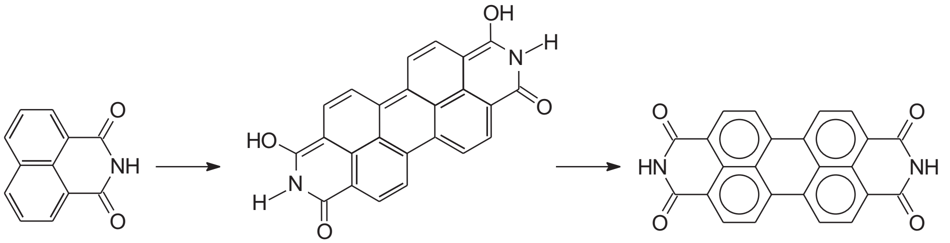


2 **3** **4**

In the second stage of the process, (**3**) is condensed with aqueous ammonia to yield naphthalimide (**4**). The reaction is quantitative and the purity is high[4].

The imide can also be prepared by use of ammonium sulfate.

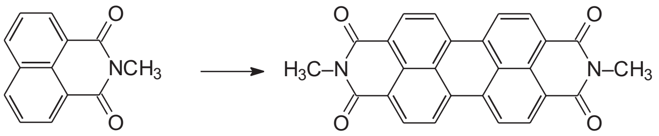
The third reaction stage is the most important and complex in the sequence, and is an alkaline fusion reaction. This is the synthesis stage in which the perylene chromophore is chemically formed, as well as the step in which many of the important physical properties of perylene tetracarboxylic acid diimide (PTCI) are determined. In the fusion reaction, (**4**) is fused with itself via a bimolecular nucleophilic substitution in the presence of molten alkali at temperatures in excess of 200 °C. The resulting alkaline mass is then precipitated by slowly mixing into water. The subsequent slurry contains perylene in its reduced (leuco) form or salt. One of the several possible isomers of the lenco form is represented with the general formula (**5**).



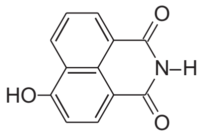
4 **5** **6**

The leuco compound is next oxidized with air or peroxide, optionally with surfactants, to give PTCI (**6**) or its imide salt as a slurry, which is finally acidified prior to filtration. The yield of the fusion sequence of reactions is typically greater than 85 %[5].

Several reports in the patent literature claim the direct fusion of *N*-methylnaphthalimide (**7**) to CI Pigment Red 179 (**8**) (the *N*,*N*'-dimethylimide of PTCI)[5].



7 **8**



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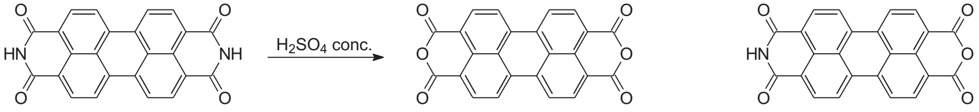
Practical experience, however, using conditions common to those for the fusion of naphthalimide, indicates that this reaction gives Pigment Red 179 (**8**) in less than 50 % yield, thus proving that it is not an acceptable route to this important perylene pigment. A fusion mechanism based on isolation of a small amount of *N*-hydroxynaphthalimide (**9**) from the fusion reaction has been implied[6]. More recent model studies on alkali fusion reactions provides additional insight into this important but experimentally challenging reaction[7]. In an alternative fusion reaction recently reported by Japanese workers[8], naphthalimide was oxidatively coupled using diazabicyclononene (DBN) and alkoxide in diglyme at 130–170 °C. Yields of PTCI (**6**) greater than 95 %, with purity of 99 %, were reported. The Fusion is also claimed to work afficiently with a wide variety of substituted imides (including methyl naphthalimide) (**7**). However, the high cost of DBN renders this approach unlikely for commercial use.

New processing techniques allow for more precise control of the fusion reaction and also the precipitation and oxidation stages. These include the continuous manufacture of PTCI (**6**)[9], and fusion of naphthalimide (**4**) under vacuum or in the absence of oxygen[10]. Such advances are important for better understanding and control of the performance properties of perylene pigments.

16.2.2
Synthesis of Perylene Tetracarboxylic Acid Dianhydride (PTCA) by Hydrolysis of PTCI to PTCA, and PTCA as a Pigment (Pigment Red 224)

PTCA (**10**) is synthesized from PTCI (**6**) by hydrolysis in concentrated sulfuric acid at temperatures in excess of 200 °C. A number of by-products are typically present, including sulfonated perylenes and the half imide, half anhydride (**11**).



6 **10** **11**

By adjusting the processing conditions and using special purification techniques, high purity PTCA (**10**) can be obtained, although the yield is not high[11]. Amination of PTCA to perylene diimides is readily carried out, but because of the relatively low yield of PTCA (**10**) from the hydrolysis reaction, this route to diimide pigments is more expensive than the alkylation process (detailed below) but remains the only commercial route to ultra-high purity perylenes.

PTCA (**10**) is not only important as a perylene pigment intermediate, but also possesses attractive tinctorial and fastness properties as Pigment Red 224. It shows strong and brilliant color, and exhibits excellent fastness and thermal stability[12].

A major disadvantage with this pigment is that while it performs excellently in organic solvent-based coatings, it readily hydrolyzes under aqueous alkaline conditions to form an intense yellow-green fluorescent dyestuff, and is therefore unsuitable for most water-based coatings applications.

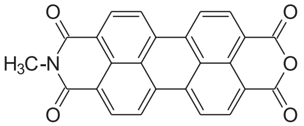
16.2.3
Alkylation of PTCI to Pigment Red 179 and other Perylene Pigments

While Pigment Red 179 (**8**) can be produced by condensation of PTCA (**10**) with methylamine, it is more commonly manufactured by methylation of PTCI (**6**). The alkylation is not easy to carry out, and the efficiency of the reaction is an important factor in the color of the subsequent pigment. Half-methylated or unreacted PTCI are both bluer than Pigment Red 179 and such impurities can markedly influence the color of the final product. Common alkylating agents used include methyl chloride, for example with the aid of a buffer[13] or surfactant[15] or inorganic base and dipolar aprotic solvent[16], dimethyl sulfate, for example with glycol and caustic soda in a double arm mixer[14], and dimethyl carbonate[17]. Use of dialkyl carbonates is an interesting modern technology because these alkylating agents are relatively nonhazardous.

16.2.4
Synthesis of Perylene Pigments and Mixed Crystals by Condensation of PTCA with Amines

Whenever the imide substituent in a perylene diimide pigment is greater than C1, the preferred route to the pigment is by condensation of PTCA with a primary amine. Provided the amine is sufficiently soluble, condensation can readily be carried out in water, whereas less soluble or reactive amines require high boiling solvents such as quinoline or imidazole for completion of the reaction. In some instances the amine can be used as its own solvent. Pigment Red 179 (**8**) produced from PTCA (**10**) can be made very pure, with unreacted dianhydride or by-product monomethylimide monoanhydride (**11**) removable by alkaline extraction, to give a significantly yellower and more chromatic pigment, sometimes called Perylene Red, rather than Perylene Maroon. It is common practice to optimize the pigment properties of products made by this route by means of subsequent milling and solvent treatment[18–21].

Somewhat more difficult is the production of highly chromatic and transparent Pigment Red 179 (**8**) for automotive coatings applications. The introduction of non-pigmentary additives during the condensation of PTCA (**10**) with methylamine is one technique that has been reported to be effective[22,23]



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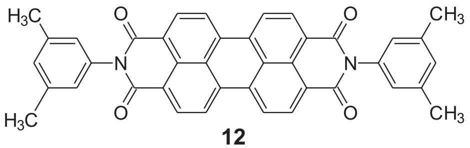


12

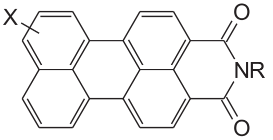
In the manufacture of the most important pigment for plastics systems, Pigment Red 149 (**12**), by condensation of PTCA with 3,5-xylidine, for example, it is possible to upgrade the working properties in engineering resins of the alpha phase pigment by introduction of some phenetidine with the xylidine in the condensation, thus effecting a mixed crystal condensation[24]. See also Section 16.4. Other mixed crystal pigments based upon halogenated perylene diimides have also been reported[25].

16.2.5
Half Imide, Half Anhydrides of PTCA (10)

Although not commercially available as pigments, the half imide/half anhydrides of PTCA (**10**), for example (**11**), are beginning to find academic and commercial interest, since they can be used to produce both unsymmetrical perylene diimides and perylene mono-imides (through decarboxylation)[26–27].

16.2.6
Derivatives of Perylene as Performance Enhancers

In recent years, perylene derivatives have been reported as performance enhancers in upgrading the coloristic and working properties of established perylene pigments. As with derivatives of the majority of other high performance pigments, perylene derivatives can effect particle size control and give enhanced rheology in specific automotive paint formulations, especially high solids solvent – based coatings. Mono-decarboxylated half-imides of perylene (**13**) are reported as effective dispersants and performance enhancers for perylene-based paint formulations, with upgraded coloristic and rheological properties[28–30]. The perylene derivatives may be added during the synthesis or conditioning of the perylene, or as a post-mix. Similarly, specific perylene diimides have also been reported as performance enhancers[31–39].



13

16.3
The Conditioning of Perylene Diimide Pigments

The product(s) of condensations and alkylations of perylenes are typically non-pigmentary in their behavior, and are often termed “crudes”, because of their need for upgrading in tinctorial and working properties rather than only in chemical purity. Conditioning of the crude pigment is usually necessary to achieve the full extent of color and working properties possible with perylene pigments. Such treatment(s) typically involve adjustment of particle size and size distribution, chemical purity, surface electrical charge on the pigment, morphology, desired crystal phase, as particle wettability and stability.

As with other high performance pigments, perylene pigment conditioning can be carried out by such common methods as wet or dry milling, salt grinding, acid pasting and swelling, vatting and bleaching, and solvent/heat treatments. Such conditioning is tailored to produce pigments with enhanced physical, coloristic and application – specific properties. Manipulation of particle size, size distribution, and particle surface characteristics is a primary goal.

Acid pasting is a pigmentation process in which perylene “crude” is dissolved in concentrated (>90 %) sulfuric acid, and then reconstituted by precipitation under precisely controlled conditions, to produce a pigment with the desired physical characteristics. Acid swelling is a similar process, except that 75–85 % sulfuric acid is used to partially solubilize the crude and give an equilibration between the smallest and largest particles of the mass; this is followed by precipitation under controlled conditions.

Vatting is a process where the perylene crude is reduced in an aqueous alkaline dithionite solution to a (colorless) leuco form, then filtered and washed to remove impurities. It is then oxidized by air or peroxide to give purified and recrystallized perylene pigment[40]. Since this type of processing purifies the pigment, higher chroma and specific hue shifts can often be obtained as a result.

Since perylene pigments are only sparingly soluble in common solvents, the solvent conditioning of crudes is commonly done under “harsh” conditions. For example, a common method to adjust the particle size and morphology of a perylene diimide crude is by acid pasting in concentrated sulfuric acid, followed by a series of solvent aftertreatments, to give a pigment with high transparency and purity[41–43]. Numerous types and methods of surface treatment of perylene pigments are found in the literature. These are summarized by Merkle and Schafer in Vol. 3 of the Pigment Handbook[44]. Common treatment agents include abietic acid and its salts, alkyl fatty acids[45] and amines, and a wide range of surfactants including anionics, cationics, and nonionics.

16.4
Mixed Crystals and Solid Solutions of Perylene Diimide Pigments

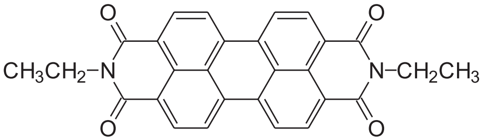
While perylene pigments are not considered to readily form solid solutions, such products have been reportedly prepared from common perylenes coprecipitated from concentrated sulfuric acid[46]. There have been, however, many references to mixed crystals, for example as already noted (see Section 16.2.4) from condensation of PTCA with mixtures of primary amines, or by coprecipitation of perylene with a second perylene or separate organic pigment[47]. As may be appreciated, the formation of mixed crystal pigments is a technique which allows for manipulation of the end color or specific performance properties of the pigment. Such mixed crystal pigments are prepared when higher levels of brilliance or difference in hue are required, but cannot be realized by changes in chemical purity or particle size or size distribution.

16.5
Drying of Perylene Pigments

Since the majority of perylene pigments are marketed in the form of powders, the pigment products must first be dried. Conventional methods of drying perylenes include oven/tray drying, spin-flash drying, spray drying and freeze drying. As might be expected, the specific method used for drying can have a significant effect on the physical properties of the final pigment, especially in its degree of agglomeration and aggregation. This effect is carried over to the dispersibility and coloristic properties of the dry pigment.

16.6
Physical Chemistry and Color Physics of Perylene Pigments

The solution spectra of perylene pigments are all very similar. However, the color of the solid pigments can vary widely, from black to red, depending on the imide substituent. Bulky, sterically hindered substituted perylene diimides cause significant differences in the typical packing of the molecules in the pigment crystal, and this is at least partly responsible for some dramatic color shifts. Such dependence of color on crystal packing is a phenomenon known as crystallochromy. Haedicke and Graser completed a study of more than twenty perylenes by single-crystal X-ray diffraction, and concluded that the color of a crystalline perylene pigment is related to both the area of overlap and the distance between adjacent perylene molecules in the crystal[48–52]. All perylene diimide pigments studied show shifts in either transverse (lateral) or longitudinal directions along the perylene pi systems. One exception is the *N,N′*-diethyl perylene diimide (**14**). For this red perylene, the molecules exhibit slight twisting. Perylenes are not so well understood that complete correlation of structure with color property relationships is yet possible. The best treatment of this topic however is found in a recent review paper on the effect of crystal structure on the color application properties of organic pigments[53]. A number of computer simulations and theoretical studies on the crystal packing of perylene pigments have also been published[54–55].



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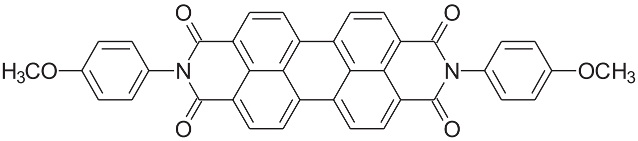
For the majority of perylene pigments, both color and stability properties derive from electronic pi-pi interactions. However, for Pigment Violet 29 (**6**), the unsubstituted diimide, hydrogen bonding between the imide hydrogens and the carbonyl groups is also possible, and is undoubtedly the reason for the added stability of this perylene pigment.

As with most high performance organic pigments, perylene pigment properties are dependent on the particle size and size distribution, crystal morphology, surface character and degree of crystallinity[56–57]. These are dealt with in an excellent review paper on the development of organic pigments with particular reference to physical form and consequent behavior in use[58].

Particle size and size distribution are key performance indicators for perylene pigments. In general, perylenes become yellower as particle size decreases. Again, transparency increases as particle size decreases. Weatherfastness, however, decreases as particle size decreases, but is still excellent in comparison to that of other pigment types, particularly with Pigment Violet 29 (**6**) and Pigment Red 179 (**8**) in coatings. Care has to be taken, however, spin dyeing and other mass coloration techniques with engineering resins and other resins are concerned, as here the normally insoluble perylene pigment may show some modest solubility in solvent or molten resin. In such applications, the method of dispersing the pigment in the resin, as well as the type of resin or other additives used, can have a major effect on the weatherfastness of the final pigmented article.

The morphology of perylene pigments is typically acicular (needle shaped). The method of manufacture, and especially the conditioning, can however effect minor changes in the morphology, particularly where milling, grinding and reprecipitation processes are employed. Polymorphism is possible, and has been reported for Pigment Red 149 (**12**) and Pigment Red 190 (**15**), but not for Pigment Red 179 (**8**); although theoretical polymorphs have been predicted[59], perylene pigments are hydrophobic in nature. This factor is significant in understanding and manipulating their surface characteristics for optimal dispersion in water and solvent-borne coatings[60].



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16.7
Perylene Pigments and their Applications

Perylenes are most often used in conjunction with other pigments in their end product application. For example, in automotive coating formulations it is common for limited amounts of quinacridone pigments to be added to improve specific coloristic properties or provide a particular color nuance. In this example the perylene pigment is considered the base pigment, because of its high color strength, while the less color-intense quinacridones are added to the formulation as tinting agents. It is also common for perylene pigments to be added to formulations to improve the overall film performance, but with less regard to the color influence of the perylene pigment.

The most important perylene for use in the coatings industry is Pigment Red 179 (**8**), which is a maroon to red in color. It is the perylene pigment that most often appears in the patent literature for formulation into OEM coatings. The pigment is available with a wide variety of surface treatments and other physical characteristics. In addition to its use with other high performance pigments, it is often formulated with metal flake, mica and other special effect pigments. A typical US automotive formulation containing Pigment Red 179 is called Toreador Red, in which the perylene pigment imparts a rich deep color, high transparency and brilliancy, as well as outstanding weatherfastness.

In addition to the use of Pigment Red 179 (**8**) in plastics and engineering resins, a most important perylene for this application is Pigment Red 149 (**12**). This is a clean, slightly bluish red pigment, which exhibits outstanding heat stability, (greater than quinacridone) coupled with high color strength and lightfastness. It finds use in the high temperature coloration of polystyrene and ABS, in the casting of methacrylic acid methyl ester resins, in polycarbonate, and in the spin dyeing of polyacrylonitrile and polypropylene[61–63]. To be avoided are hindered amine light stabilizers (HALS), which may promote partial reduction of the perylene molecule, and produce a dull brownish color as well as diminished light fastness. In addition to coatings, synthetic resins and synthetic fibers, perylene pigments are also used in textile printing.

16.8
Perylenes as Functional Colorants

A comparison of perylene patents and review articles over the last twenty years clearly indicates the importance and potential for perylene-based pigments, dyestuffs and their derivatives in non-traditional applications such as electrophotographic photoconductors, laser dyes, and fluorescent probes[64–70].

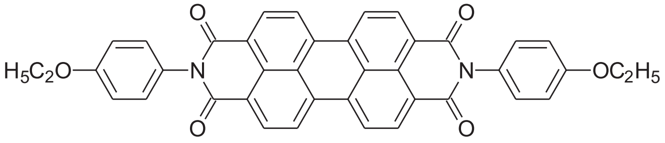
The full potential for perylene colorants in such "functional" applications is still emerging, and is clearly beyond the scope of this book. Of growing importance to perylene pigments are waterborne coatings[71]. Here, the surface of the perylene pigment must be modified to effect wetting in the water-based system, and aid dispersion. This is very important as more automotive paint lines convert over to water-based systems. The greatest challenge for the perylene pigment producer is to make the water dispersible version of the pigment closely match the coloristic and working properties of the solvent dispersible version. To further complicate performance matters, the perylene pigment is also expected by the user to perform at a consistent and high level in resin systems and formulations that are constantly being updated by the automotive coatings producer!

The ability of the perylene pigment producer to meet such challenges, render its pigments more dispersible, and meet specific tinctorial specifications such as briliancy in various resin systems ensures a continuing market for this pigment type in old and new fields of applications.

16.9
Current Producers

The global capacity for perylenes is today estimated at approximately 1500 tonnes. Bayer and BASF are the largest suppliers of high performance perylene pigments. Bayer (Perrindo®, Indofast Brilliant®) Products are strongest in the US market, while BASF (Paliogen® and Paliotol®) products are strongest in Europe. Other suppliers of perylene pigments are Clariant (Hostaperm®) and Sun Chemical (Sunfast®). Both Bayer and Sun Chemical have US production facilities for perylenes and their intermediates, while BASF and Clariant have production facilities in Germany.

In recent years, Chinese producers of perylene intermediates have manufactured perylene crudes and entered the market with finished pigments such as Pigment Red 123 (**16**) for textile coloration. Competition from Asia for the traditional US and German perylene pigment market is expected to intensify in future years, and some consolidation of the present producers is likely.



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16.10
Pricing Trends and Economics of Use

Pricing for perylene pigments ranges from $18–50/lb, in the US, with the median price being over $30/lb. Currently, however, perylene prices are falling as good quality products from China are beginning to enter the US and European market, and today's decreased demands for automobiles with blue-shade red paint containing Pigment Red 179 (**8**) are currently decreasing. There are some signs, however, that price and red car color popularity stabilization may be occurring.

16.11
Health, Safety and Environmental Considerations

Because of their general inertness, high degree of stability, and low acute oral toxicities[53], perylene pigments, in common with other high performance pigments, are essentially non-toxic, with little or no threat to human health or the environment, and are not considered in the US to be hazardous under OSHA's Hazard Communication Standard. Normal standards for good industrial hygiene should be in place, however, when handling these pigments, to avoid potential irritation of the respiratory tract and eyes and skin, by pigment dust.

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17

Phthalocyanines – High Performance Pigments with New Applications

Masao Tanaka

17.1

Introduction

In recent years, several excellent treatises on copper phthalocyanine pigments have been written, focusing on the synthesis, properties and traditional applications of this remarkable family of truly high performance pigments. In no way is the objective in this chapter to replicate such stand-alone works; rather it is to expand the reader's horizon to include several of the more "high performance" and non-traditional application areas which continue to extend the creative possibilities for this class of product.

Copper phthalocyanine blue (C.I. Pigment Blue 15) is without exception the most significant of any synthetic organic pigment produced today, with its excellent color strength and durability. It has a high molar absorption coefficient (ca. 10^5), and its light fastness and weather fastness are superior to all other organic pigments. Additionally, its synthesis is readily performed from lower cost materials (phthalic anhydride, urea and copper salts), making production of this complex molecule both facile and economic. In 1999, approximately 80 000 tonnes were produced worldwide.

Phthalocyanine blue is known to exist in several crystal modifications, with its three more important crystal forms, alpha, beta and epsilon, all industrially available. The beta form is greenish blue, and the important epsilon form is the most reddish shade of blue. Its halogenated derivatives are also used as important green pigments.

Recently, a series of chemical substances called "functional dyes" have attracted considerable attention. Because such "dyes" have long conjugated pi-electron systems and in many cases possess intramolecular charge transfer structures, "functional dyes" are expected to show interesting optical and electronic properties. Among functional dyes, phthalocyanine compounds have been extensively investigated because of their excellent physical, chemical and coloristic properties, as mentioned above[1]. For example, about 1000 related US patents, published from 1990 onwards, are retrievable from the World Patent Index data base of Derwent, and more than 30 % of these are classified in such non-colorant applications as electrophotography, catalysis, and infrared radiation absorption.

Phthalocyanine compounds contain macrocyclic conjugated pi-electron systems and metal ions in the central void. These phthalocyanine structures are very similar to porphyrins, one of the most important compounds in biochemistry. Accordingly, phthalocyanine compounds are expected to facilitate interesting catalysis and multi-electron processes. Almost all metal and semi-metal ions can be incorporated in the central void of the phthalocyanine molecule, and the characteristics of such phthalocyanine compounds can be modified by the metal ions. About seventy metals are known to incorporate in the phthalocyanine molecule.

The molecular shapes of phthalocyanine compounds are very simple. They are rigid cruciforms, basically dish-like with no configurations. But, in the crystal, the molecules of phthalocyanine compounds can be stacked in different arrangments, and show the various crystals forms recognized by X-ray diffraction spectra. The differences in stacking are called polymorphism. Polymorphism leads to the differing intermolecular interactions and, therefore, differing electron structures for each molecule in the crystals. When phthalocyanine compounds are designed as functional materials, it is very important to consider the molecular structure, including metal ions and substituents, as well as the crystal structures.

17.2
Application of Optical Properties

17.2.1
Color Filters for Liquid Crystal Display Devices

Copper phthalocyanine blue pigments have been widely used in the subtractive color process, e.g., in offset printing inks. The three primary colors of this process are cyan, yellow and magenta. Beta-form phthalocyanine blue is the pigment of choice for the cyan colorant.

Recently, requirements for pigments have been made in the additive color process, in which the three primary colors are blue, green and yellow. A good example is the color filter used in liquid crystal displays. In this field of applications, dyes are being replaced with pigments to improve the light fastness.

The epsilon form of copper phthalocyanine blue (C.I. Pigment Blue 15:6) and brominated copper phthalocyanine green (C.I. Pigment Green 36) are used respectively as the basic colorants for blue and green pixels in color filters. But these two pigments are not satisfactory as the primary colors in the system.

Figure 17–1 shows the absorption spectra of C.I. Pigment Blue 15:6 and C.I. Pigment Green 36, compared with the light emission spectrum of the three-band fluorescent light, which is used as the light source of liquid crystal display devices. The absorption of C.I. Pigment Green 36 in the region between 450 nm and 500 nm is too small to cut the hindrance emissions of fluorescent light, and C.I. Pigment Green 36 is usually toned with yellow pigment to supplement the absorption of this region. Similarly, the absorption profile of C.I. Pigment Blue 15:6 is insufficient in the region between 500 nm and 550 nm, and so C.I. Pigment Blue

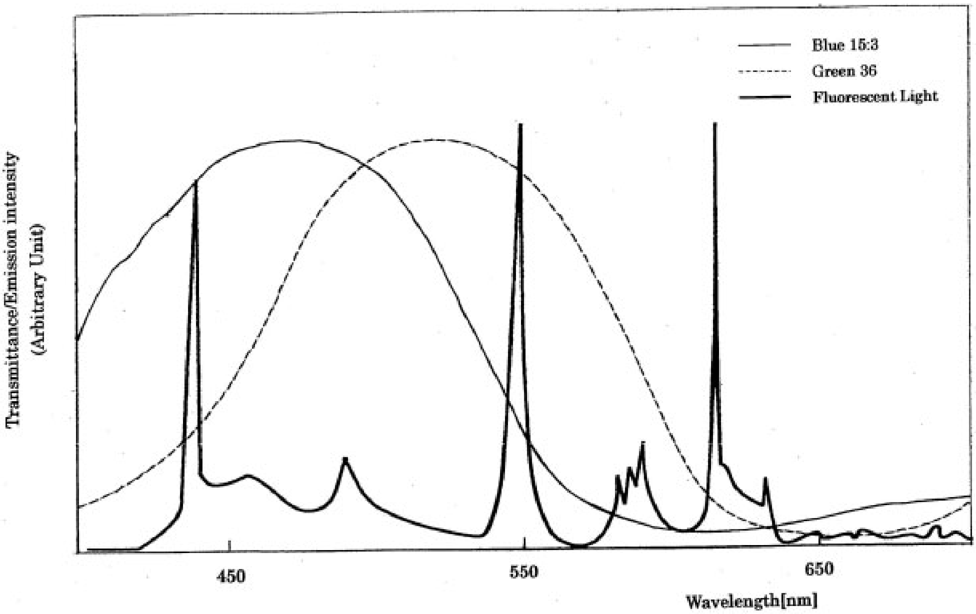


Figure 17–1: Absorption spectra of C.I. Pigment Blue 15:6 and Green 36, and emission spectrum of three band fluorescent light.

15:6 is usually toned with violet pigment. As is well known, the mixing of two colors reduces the purity of the blend, so more reddish blue pigments and yellowish green pigments, which can be used for blue and green pixels in a single colorant, are necessary to improve the image quality of liquid crystal display.

It may be not so easy to develop such pigments, but blue pigments with a more reddish shade may be affected by consideration of crystal forms, substituents, and central metal ions. It has been found that copper phthalocyanine, synthesized from a mixture of phthalic anhydride and a small portion of trimellitic anhydride and pyromellitic anhydride in sulfolane as solvent under pressure, exhibits the pi form, with a more reddish shade than that of epsilon copper phthalocyanine[2].

17.2.2
Ink Jet Inks

Although acid dyes have been typically used for the coloration of ink jet inks, phthalocyanine pigments are now replacing these dyes, especially in industrial applications such as signs, advertisements and textiles, to improve the water resistance and light fastness. For cyan inks, C.I. Pigment Blue 15:3 and 15:4 have been used.

Recently, Kodak has put new inks on the market. Aluminum phthalocyanine (Figure 17–2, CAS Reg. No. 81422-13-1) is employed as cyan colorant in this ink system. This new cyan ink exhibits a very yellowish shade of blue, almost turquoise.

The absorption spectrum is demonstrated in Figure 17–3 and compared with that of C.I. Pigment Blue 15:3. Apparently, the absorption around 550 nm is reduced compared with that of C.I. Pigment Blue 15:3. One of the characteristics of this ink system may be good reproducibility of cathode ray tube images with little adjustment of colors. From a chemical perspective, this colorant is particularly interesting. The ligands on the third coordination site of aluminum phthalocyanines are usually very reactive, and are readily exchanged by other ligands or nucleophiles. For example, the well-known chloroaluminum phthalocyanine is in equilibrium with two species, hydroxyaluminum phthalocyanine and a mu-oxo dimer, in the basic aqueous media as shown below.

$$\mathrm{AlPc{-}Cl} \underset{\mathrm{Cl^-}}{\overset{\mathrm{OH^-}}{\longleftrightarrow}} \mathrm{AlPc{-}OH} \underset{\mathrm{+H_2O}}{\overset{\mathrm{-H_2O}}{\longleftrightarrow}} \mathrm{AlPc{-}O{-}AlPc}$$

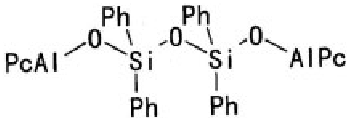


Figure 17–2: Aluminum phthalocyanine used in Kodak's ink jet ink.

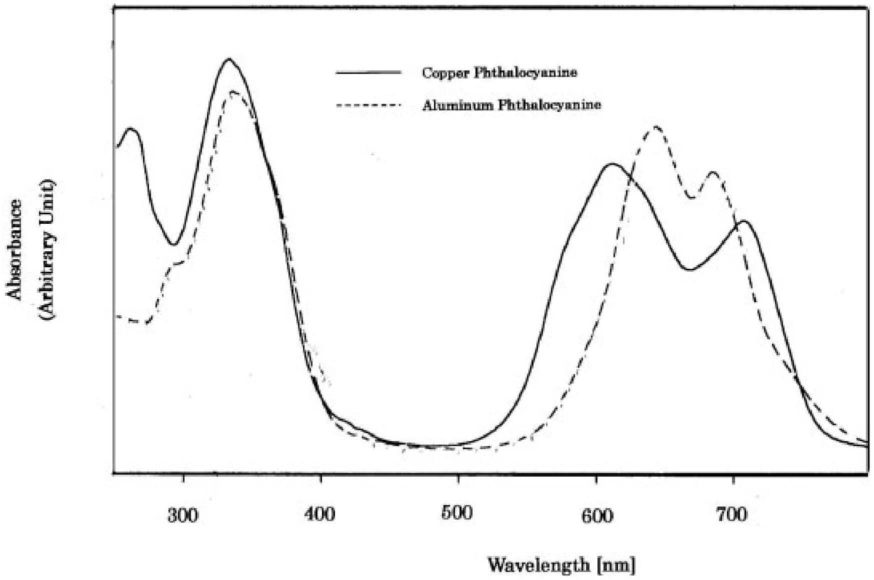


Figure 17–3: Absorption spectra of Kodak's aluminum phthalocyanine and copper phthalocyanine (Blue 15:3).

Kodak's aluminum phthalocyanine is formed as the dimer structure by using a bidentate ligand, bis(diphenylsiloxy) dianion, as the third ligand. This bulky and hydrophobic ligand may prevent exchange reactions of the ligand in aqueous ink systems.

Today's requirements for dispersibility and dispersion stability of pigment-based ink jet inks require an extremely high level of performance. Dainippon Ink and Chemicals has developed new micro-encapsulation technologies for the solution of such problems[3]. Their micro-encapsulated pigments exhibit concentrated polymer layers on the pigment surfaces. The encapsulation polymers used are basically (meth)acrylic acid-(meth)acrylate ester copolymers.

Water-borne dispersions of such micro-encapsulated pigments show excellent dispersibility and dispersion stability. Table 17–1 shows the changes of physical and coloristic properties of the dispersions of micro-encapsulated C.I. Pigment Blue 15:3 after one year's storage under ambient conditions[4]. These dispersions contain about 13.3 % pigment by weight, and the ratio of micro-encapsulation polymer to pigment is 0.5. The median diameter in the dispersion is less than 100 nm and is storage stable. Rheological properties, viscosity and surface tension are also stable. Because of this, no aggregation occurs during storage. As a result, little change of coloristic properties is observed. In addition, micro-encapsulation treatments add excellent resistance toward water-soluble organic solvents in pigment dispersions compared with dispersions employing commercially available polymeric dispersants, e.g., styrene-maleic anhydride co-polymers.

Table 17–1: The changes of physical and colorimetric properties of the dispersions of B-15:3.

	As prepared	*After one year*
Median diameter	95 nm	89 nm
Viscosity	4.1 mPa s	4.1 mPa s
Surface tension	36.7 mN/m	36.4 mN/m
L*	31.1	31.6
a*	7.9	7.1
b*	33.6	34.8

17.2.3
Infrared Radiation Absorbents

Phthalocyanines typically exhibit absorption in the red region of the spectrum. It is therefore relatively easy to make phthalocyanine compounds absorb near infrared radiation by molecular modification. For example, the introduction of electron-donating substituents, such as alkyloxy and alkylthio groups, to the phthalocyanine moiety is a convenient way to shift the absorption maximum toward longer wavelengths ("red shift"). At the same time, the introduction of such groups, especially in the 3- and 6-positions, increases the solubility of phthalocyanine compounds to organic solvents by reducing the molecular interaction in the stacking columns of phthalocyanine crystals.

Such soluble phthalocyanine compounds can be dissolved in polymer films and used as near infrared radiation absorbents of sunlight. Two interesting application fields have been proposed: as a shield from heat radiation[5] and as a controller of plant growth in agriculture[6].

Heat radiation can be absorbed by films containing phthalocyanine compounds and transformed into an excited state. When the excitation energy is relaxed by non-radiative transitions in a vibration-relaxation process, the excitation energy is used to raise the temperature of the phthalocyanine compounds, and the heat is then diffused into the surrounding air through the films. Such materials can thus be applied to the windows of buildings and automobiles. About 90 % of the heat in the automobile is estimated to come in from the windows. The absorbent materials are believed to cut off about 50 % of the heat radiation.

In plant growth, the quality of light, its power distribution by wavelength, etc., impacts upon the morphology of the plant, i.e. its differentiation, development, and elongation. This phenomenon is known as photomorphogenesis. Thus, selective absorption of radiation of a particular wavelength in the red and near infrared region can significantly affect plant growth. Such effects of films, containing phthalocyanine compounds, have been confirmed for mini-tomatoes, spinach, poinsettia, and so on.

Phthalocyanine compounds which absorb near-infrared radiation are available from Yamamoto Chemicals, a subsidiary of Mitsui Chemicals. Figure 17–4 shows the absorption spectra of a series of their products. Currently, they have 23 near infrared radiation-absorbing phthalocyanine compounds and eight absorbents composed of other materials. The absorption maxima of such phthalocyanine near-infrared radiation absorbents are between 670 nm and 1000 nm. They may cost between one thousand and ten thousand dollars a kilogram! Films of poly(vinyl chloride) and polyolefins containing phthalocyanine near-infrared absorbents are also commercially available.

Similar products and films are also available from Nippon Shokubai.

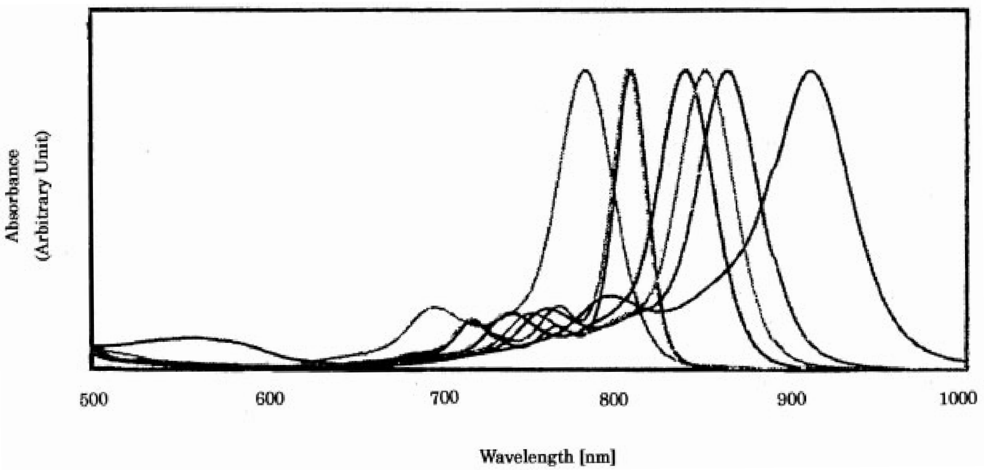


Figure 17–4: Absorption spectra of commercially available near-infrared absorbing phthalocyanines (copyright: Yamamoto Chemicals)

17.2.4
CD-R

The most successful application of near infrared radiation-absorbing phthalocyanine compounds is in the recording material CD-R. According to the international standard specification, the recording materials of CD-R must have an absorption maximum around 780 nm, which wavelength permits both recording and read-out. The thickness, refractive index, and extinction coefficient of the recording material are all optimized to maximize the reflectance of the recording layer.

Mitsui Chemicals and Ricoh employ such phthalocyanine compounds for their CD-R products. Compared with cyanine dyes (usually pentacyanine dyes), phthalocyanine compounds are excellent with respect to light fastness and performance for high rate recording, but are much more expensive. Evaluation results of commercially available CD-R are available to consumers from the Internet web sites. In order to increase the demand for phthalocyanine compounds in CD-R recording materials, cost reduction may be the most significant hurdle to overcome.

Phthalocyanine compounds used for CD-R are soluble in organic solvents, and are applied by spin coating. The absorption spectra of the coated films are relatively sharp compared with those of films with pigments dispersed in polymers. Mitsui Chemicals uses a mixture of many isomers of phthalocyanine compounds to utilize the shoulder of the absorption spectra. Figure 17–5 shows examples of such mixtures of phthalocyanine compounds[7].

To increase the recording density, DVD-R materials are being energetically developed. The recording materials for DVD-R should absorb at shorter wavelengths: 635 nm or 650 nm in current specifications. But such soluble phthalocyanine compounds as used for CD-R are considered to be difficult to apply in DVD-R, because the absorption of these materials in the region between 630 nm and 650 nm is too intense. To utilize the absorption at these wavelengths as shoulder, phthalocyanine compounds must be electronically similar to the original state with no substituents, and such phthalocyanine compounds may be difficult to make in thin and uniform films for recording layers.

Matsushita Electric Industry has investigated evaporation techniques for films of such sublimable phthalocyanine compounds as dichlorotin phthalocyanine and dichlorosilicon phthalocyanine for the recording layer of DVD-R[8]. Using evaporation films of 100 nm thickness, they achieved a reflectance of 60 % at 650 nm, and an 11T-signal output of 0.4 in the ratio to output of commercially available CD.

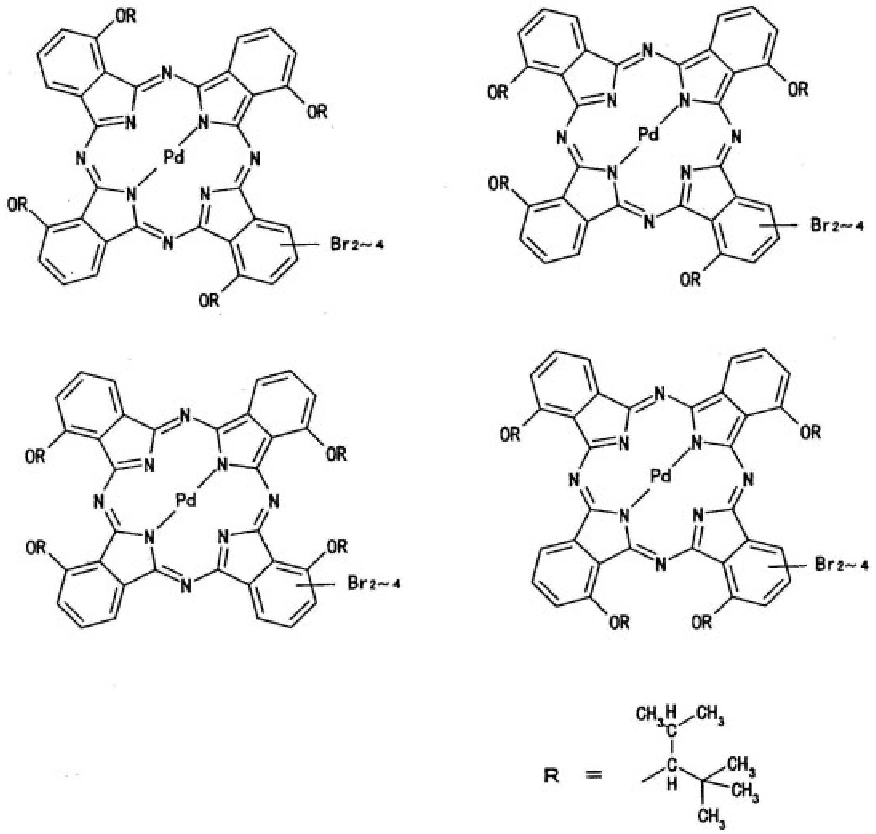


Figure 17–5: Mixture of phthalocyanines compounds used for CD-R (refer to patent examples).

17.3
Application of Optoelectronic Properties

17.3.1
Electrophotographic Photoreceptor

Electrophotography is today's leading process for duplication and printing, and is one of the most successful applications of phthalocyanine compounds in non-colorant fields.

Amorphous selenium metal was originally used as the photoconductor (photo charge carrier generator) of the Carlson process in electrophotographic reprography. Because of its toxicity and difficulty of fabrication, selenium was then replaced by organic photoconductor materials (OPC).

In the early stages of this replacement, azo compounds were predominantly used as charge carrier generating materials, since design of their required molecular characteristics was relatively easy. As a result, they were more photosensitive compared with early phthalocyanine OPC compounds. Disazo compounds were used for analog duplicators in which halogen lamps or fluorescent lights were installed as light sources, and trisazo compounds, with sensitivity to near infrared radiation, were used for laser beam printers and digital duplicators in which laser diodes were the light sources.

In the ten years that followed after the expiration of the basic application patent of Xerox[9], very photosensitive phthalocyanine compounds were developed and phthalocyanine OPCs became the leading materials for this application.

Originally, well-known phthalocyanine compounds were developed with a strong absorption in the red region (660–670 nm), with a molar absorption coefficient of 10^5, and the possibility of modifying to the near infrared radiation. A large number of phthalocyanine compounds were investigated, and currently titanyl (oxotitanium) phthalocyanines are considered overwhelmingly superior to others in the market. Many patents have been published for photoconductive phthalocyanine compounds based upon this technology.

In 1998, about 70 million OPC photoreceptors were produced, compared to 800 000 and 500 000 selenium and amorphous silicon photoreceptors, respectively. Of these 70 million OPC photoreceptors, 45 million were by Canon, 10 million by Mitsubishi Chemicals, 4 million by Fuji Electric, 3 million each by Yamanashi Electronics and Dainippon Ink and Chemicals, and 5 million by others. The largest fraction of these OPC photoreceptors were based upon titanyl phthalocyanines.

Although titanyl phthalocyanine is known to have two crystal forms (alpha and beta), in the course of OPC investigations over the past fifteen years, many new crystal modifications were discovered, exhibiting different patterns of X-ray diffraction spectra.

The shape of the titanyl phthalocyanine molecule is not planar but pyramidal, where the titanium atom is out of the plane of the phthalocyanine macrocycle and the symmetry of the molecule is reduced from D_{4h} to C_{4h}. Accordingly, titanyl phthalocyanines can have more crystal modifications than such planar molecules as copper phthalocyanine or metal-free phthalocyanine. General procedures used in the development of new crystal modifications involve solvent treatment of amorphous titanyl phthalocyanines obtained by acid pasting or milling procedures.

Among a variety of titanyl phthalocyanines, the Y-form, developed by Konica, is said to be the most sensitive[10]. The quantum efficiency of Y-form titanyl phthalocyanine for photo carrier generation is reported to be almost 1. Y-form titanyl phthalocyanine is also reported to incorporate one water molecule to one titanyl phthalocyanine molecule in the crystal. The location of these water molecules in the crystal is as yet not clear, but they are considered to play an important role in the high sensitivity of the Y-form[11]. On the other hand, the incorporated water molecules are reversibly desorbed, and the sensitivity changes according to the quantity of water in the crystals. Because of such instability in sensitivity, photoreceptors with the Y-form of titanyl phthalocyanine have not yet been commercialized.

During an investigation to improve the stability of the sensitivity of Y-form titanyl phthalocyanine, 1+1 adduct compounds of titanyl phthalocyanine and gem-diols were found. Their photosensitivity is comparable to that of the Y-form[12].

Recently, Fuji Xerox announced a new series of printers, with hydroxygallium phthalocyanine as the charge generating material. Hydroxygallium phthalocyanine is reported to have several crystal forms, with the V form as the most photosensitive. The photosensitivity of the V form hydroxygallium phthalocyanine is comparable to that of Y form titanyl phthalocyanine, but is independent of the humidity[13].

Photoconductive phthalocyanine compounds are usually prepared by the photoreceptor makers and their subsidiaries, and are not commercially available. For titanyl phthalocyanine, only crude material, which requires appropriate treatment to fine tune the desirable photosensitivity, is available from Sanyo Color Works, Orient Chemicals, and Toyo Ink Manufacturing. Such products may also cost several thousand dollars a kilogram.

Dainippon Ink and Chemicals markets its photoconductive X-form metal-free phthalocyanines as the Fastogen Blue 8120 series. Products include materials for printers and material for plate-making. X-form metal-free phthalocyanine is less

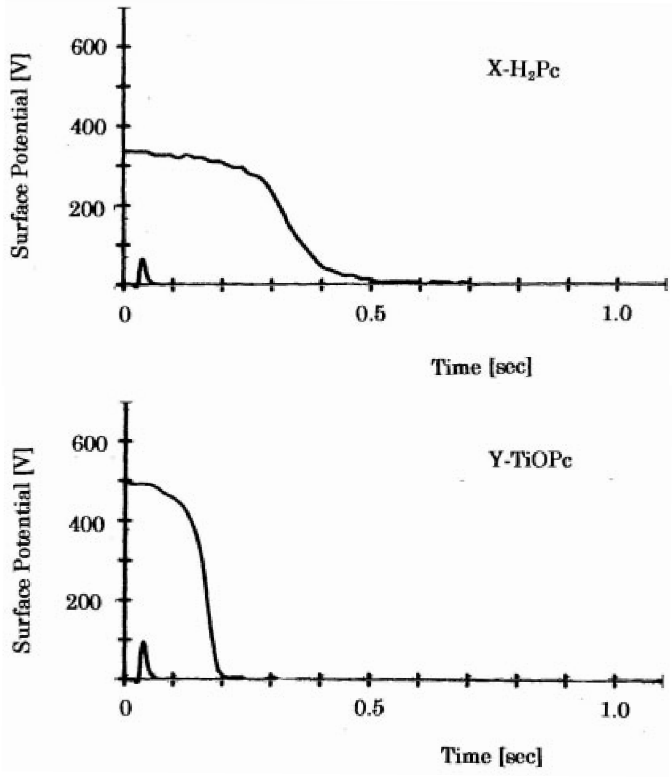


Figure 17–6: Transient decay curve of single-layer photoreceptors with X-form metal-free phthalocyanine and Y-form titanyl phthalocyanine.

sensitive than titanyl phthalocyanine, but is considerably lower in price. The cost is "only" two to five thousand dollars a kilogram. Figure 17–6 shows a comparison of the transient decay curve of the surface potential of single-layer photoreceptors with X-form metal-free phthalocyanine and Y-form titanyl phthalocyanine. The cause of lower photosensitivity in the X-form of metal free phthalocyanine seems to be the long induction period and the low decay rate. This may be related to the fact that X-form metal-free phthalocyanine needs some impurity to achieve practical levels of photosensitivity. Similar behavior is recognized in the electrical conductivity of metal-free phthalocyanine[14].

Recently, Orient Chemicals put new types of photoconductive phthalocyanine compounds on the market, such as the mu-oxo dimers of aluminum phthalocyanine and gallium phthalocyanine. The trade name of these products is OPTRON. Figure 17–7 shows the typical spectral response of the photosensitivity of layered type photoreceptors based on these products. Gallium phthalocyanine dimer is a little less sensitive than Y-form titanyl phthalocyanine below 820 nm, but has excellent photosensitivity in the longer wavelength region around 850 nm. Aluminum phthalocyanine dimer is specifically photosensitive between 600 nm and 650 nm, and may be advantageous to a light source with shorter wavelengths, which can improve the resolution of images. Again, these materials currently cost more than ten thousand dollars a kilogram.

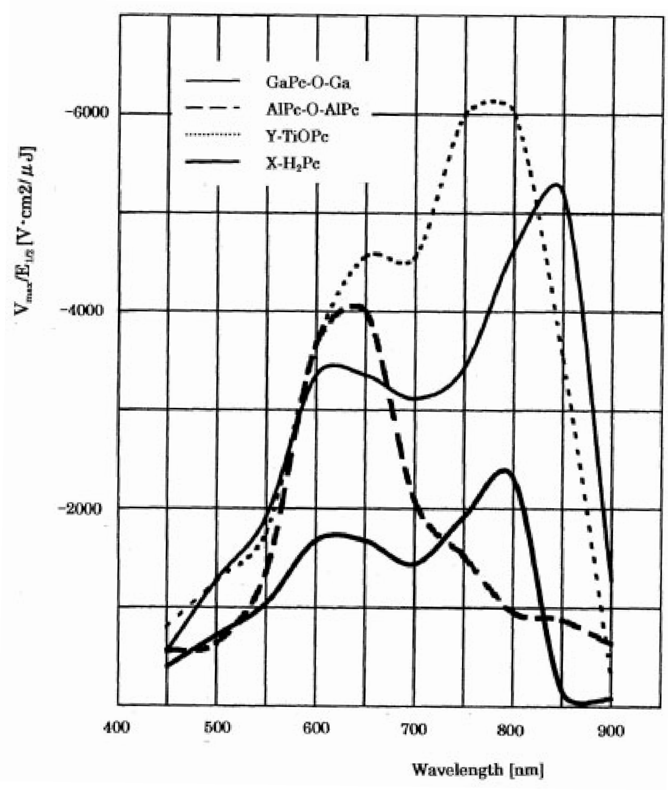


Figure 17–7: Spectral Response on the Photosensitivity of Dual Layer Photoreceptors with Dimer Phthalocyanine Photoconductors (copylight: Orient Chemicals).

The research groups of Xerox and Fuji Xerox have been investigating the relationship of electrophotographic sensitivity of phthalocyanine compounds and their crystal structures by Rietvelt analysis techniques[15]. They have emphasized the importance of the relationship between the direction of molecular overlapping and the direction of transition moment existing in the molecular plane. Although the Rietvelt analysis technique is an approximation based on whole pattern fitting of powder X-ray diffraction spectra, it is very useful to consider the relation between photosensitivities and crystal structures of phthalocyanine compounds obtained by this technique. Because it is difficult to obtain phthalocyanine compounds with new morphology as single crystals for strict structure analysis, in most cases only powder X-ray diffraction spectra are obtained, and are used for identification purposes.

Generally, pi-pi interaction between stacked molecules is considered to cause the absorption of phthalocyanine compounds in the near infrared region. Mizuguchi et al. have investigated the origin of the absorption of phthalocyanine compounds in the infrared region, and proposed a different mode of interpretation. In addition to pi-pi interaction, they propose consideration of the molecular distortion for titanyl phthalocyanines[16] and molecular distortion and exciton coupling for beta-form metal-free phthalocyanine[17].

17.3.2
Nonlinear Optical Devices

Development of nonlinear optics is expected to provide the breakthrough in overcoming the theoretical limitation of electronic computers. Organic nonlinear optical materials are expected to achieve a much quicker response than that of inorganic materials. Because the optical nonlinearity of organic materials originates from pi electrons, it responds much more quickly to change in electric fields than the optical nonlinearity of inorganic materials, which is based on lattice electrons.

Phthalocyanine compounds usually exhibit centrosymmetry, either in their molecular structure or in the higher structure of their crystals. Phthalocyanine compounds are thus suitable for third order optical nonlinearity. In addition, phthalocyanine compounds are expected to exhibit large nonlinearity originating from two-dimensionally delocalized pi-electrons in the highly conjugated macrocyclic moiety. The Optical Kerr effect, which is the phenomenon that the refractive index changes in relation to the intensity of incident light, is one of the most important third order optical nonlinearities applicable to optical processing.

Evaporated films of chlorogallium phthalocyanine and fluoroaluminum phthalocyanine have been reported to have high third order nonlinear susceptibility[18]. Since that time, phthalocyanine compounds have been extensively investigated in the form of evaporated films, Langmuir-Blodgett films, and spin-coated films. Evaporated films of vanadyl phthalocyanine and titanyl phthalocyanine were also found to have a higher third order nonlinear susceptibility[19].

At present, in the development of nonlinear optical devices, although semiconductor quantum structure devices are still predominant, devices with phthalocyanine compounds are gaining significant ground. Hitachi have fabricated an all-optical switching device using evaporated films of dichlorotin phthalocyanine and have confirmed the utility of such devices[20].

Phthalocyanine compounds are thermally very stable, and are the most suitable organic materials for evaporation. The evaluation of evaporated thin films at the molecular level is progressing remarkably by means of probe microscopy techniques[21]. When the relationship between nonlinear optical performance and molecular orientation of evaporated films of phthalocyanine compounds is optimized, it may be possible to develop practical nonlinear optical devices using phthalocyanine compounds for optical processing.

17.4
Application of Catalysis

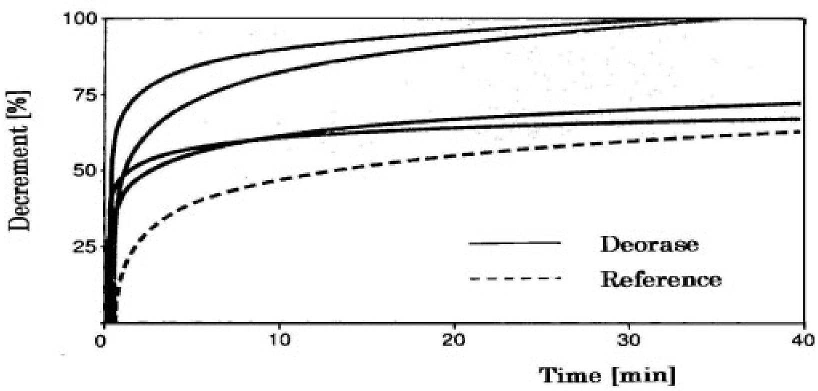
17.4.1
Deodorizers

Phthalocyanine compounds can be incorporated with many kind of metals coordinated in the molecules, and show a variety of catalysis effects corresponding to the metals used[22]. Typical examples are oxidase-like oxidation reactions and catalase-like reduction reactions with iron phthalocyanines and cobalt phthalocyanines. In oxidase-like processes, organic compounds with activated hydrogen are dehydrogenated by molecular oxygen to yield the desired oxidized products and hydrogen peroxide. In the catalase-like process, hydrogen peroxide is decomposed into water and molecular oxygen.

Within this field, many basic investigations and proposals for practical application have been made by Shirai et al.[23]. They have investigated tetra- and octa-carboxylic acid derivatives of iron phthalocyanine and cobalt phthalocyanine, and found that catalytic activity is affected by the states of electron spins of metal ions and inactivated by formation of the mu-oxo dimer. Iron and cobalt ion in high spin states are more reactive than that in low spin states. High spin states of metal ions are achieved by modification of ligands. Shirai et al. have applied these materials as fiber deodorizers for such odors as ammonia, trimethylamine, hydrogen sulfide, and methanethiol, in which the phthalocyanine compounds are supported on fibers of cotton, wool, rayon, and artificial fibers.

Orient Chemicals market iron phthalocyanine derivatives and cobalt phthalocyanine derivatives as deodorizers under the trade name of DEORASE. These materials were developed in collaboration with Shirai et al. Figure 17–8 shows the deodorizing effects of the products supported on textiles on ammonia and hydrogen sulfide.

Ammonia



Hydrogen Sulfide

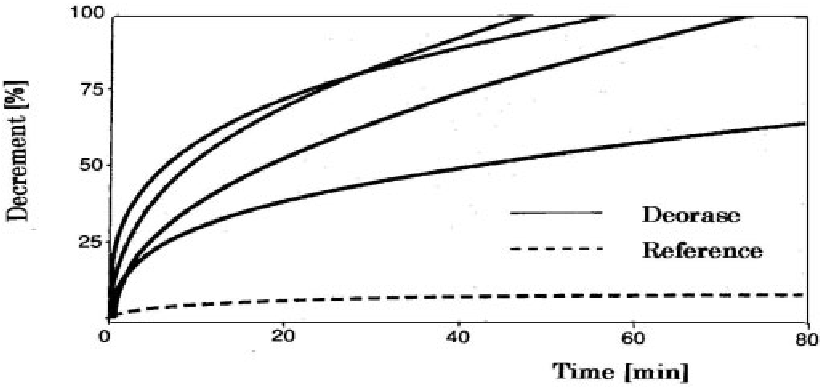


Figure 17–8: Deodorizing effects of phthalcyanine compounds supported on textiles (copyright: Orient Chemicals).

17.4.2
Photodyamic Therapy

Photodynamic action, in which photochemical reactions are used to destroy microorganisms and affected tissues by a combination of photosensitizers, oxygen, and visible or near infrared light has been well known for more than one hundred years, and is currently being explored in the development of anti-tumor agents[24].

In the early stage of investigation with porphyrin compounds, haematoporphyrins were used as photosensitizers[25]. These compounds exhibit absorption maxima in the region of 590–680 nm. To improve their penetration depth in tissues, analogous compounds with longer absorption wavelength have been researched. Radiation with a wavelength of 700 nm penetrates twice as deeply into developed tissues than radiation of wavelength 650 nm and ten times as deeply as radiation of wavelength 600 nm.

Photosensitizers used for photodynamic therapy must of course be non-toxic to tissue so as to absorb light with a wavelength longer than 630 nm, must accumulate selectively in the affected tissues, and must generate singlet oxygen with high efficiency.

Phthalocyanine compounds could be extremely promising materials for this application[26]. Sulfonic acid derivatives of chloroaluminum phthalocyanine and zinc phthalocyanine have been investigated in detail. Sulfonic acid substituents appear to exhibit optimum value. For zinc phthalocyanine, the disulfonic acid is the most effective. In most cases, these materials are reported to be highly selective in tissue accumulation and more sensitive than porphyrin compounds.

17.5
Conclusion

Phthalocyanine compounds exhibit many kinds of electronic, optical, magnetic, and optoelectronic characteristics. To hyperbolize, “phthalocyanine compounds can do anything.” But, viewed in practical terms, phthalocyanine compounds stand up to the competitive materials in the market in respect of every characteristic. I refer principally to those application fields where phthalocyanine compounds have superiority over competition.

Consequently, electroconductivity (including the many papers of Hanack[27]) and photovoltaic characteristics are not mentioned. The development of new phthalocyanine compounds with expanded pi-electron systems, such as two-dimensionally polymerized phthalocyanine compounds[28] and dendritic structures[29], are also outside the scope of this subject matter.

Further investigation must surely increase even further the superiority of phthalocyanine compounds over other high performance materials.

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18

Quinacridone Pigments

Edward E. Jaffe

18.1

Introduction

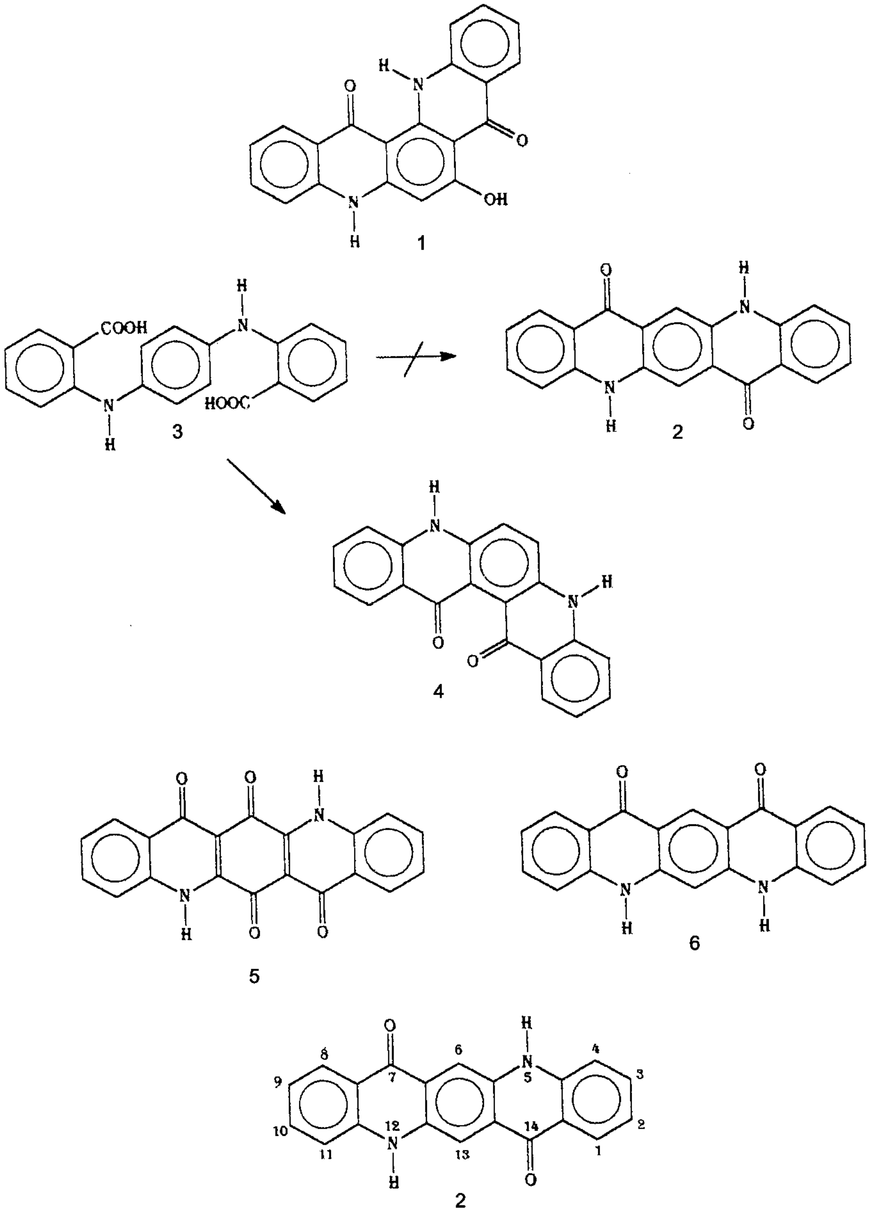
Many studies, including the original study at DuPont's Pigments Laboratory in Newark, New Jersey, have yielded a large fund of basic knowledge about quinacridone, its polymorphism, substituted derivatives, solid solutions and isomers, and about other related compounds. These studies contributed significantly to commercialization of this family of pigments, ranging in color from golden yellow to scarlet, maroon, red, magenta and violet. They are useful pigments because of their outstanding chemical and photochemical stability, extremely low solubility, and attractive colors. They are widely used where color retention on outdoor exposure is very important. The work at DuPont has stimulated studies in pigment laboratories throughout the world, leading to manufacturing facilities in the USA, Europe and Japan. Now, the base of manufacturing is broadening to other industrially expanding countries, including India and China.

18.2

Historical Background

The name quinacridone was first coined by S. Niementowski[1] in 1896 and was attributed to the compound **1**, obtained by reacting phloroglucinol with anthranilic acid. Although a linear isomer of **1** was also thought to have been formed, it was subsequently shown[2] that the presumed mixture consisted entirely of the angular isomer **1**. In 1906 it was erroneously claimed[3] that linear quinacridone (**2**) in the form of yellow crystals resulted from cyclization of 1,4-bis(*o*-carboxyanilino) benzene (**3**) in concentrated sulfuric acid. Many years later the product was proven to be the angular isomer **4** (Scheme 18–1)[4]. The first authentic example of the linear quinacridone ring system was described by V.V. Sharvinin 1915[5], when quinacridonequinone (**5**) was synthesized. Other claims to the synthesis of linear *trans*-quinacridone (**2**) were either shown or presumed to be erroneous.

The isomeric linear *cis*-quinacridone, or isoquinacridone (**6**), was first described in 1921[6], and the linear *trans*-quinacridone **2**, quino (3,2-b) acridine-5, 12-dihydro-7, 14-dione, was synthesized by an unambiguous route by H. Liebermann and coworkers[7] in Berlin in 1935.

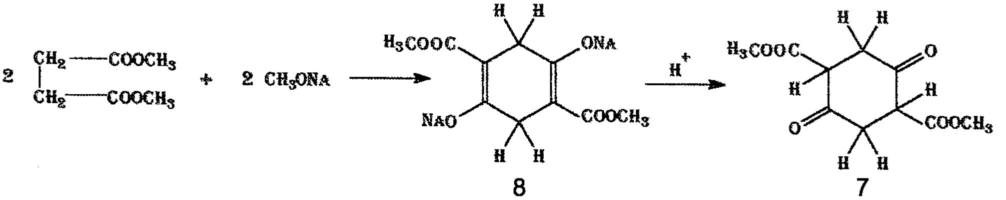


Scheme 18–1.

The red-violet compound attracted no particular attention until 1955, when DuPont chemists discovered two attractive syntheses, demonstrated its photochemical stability, and identified three polymorphic forms, each with distinct structural characteristics. In addition, methods were developed for the preparation of quinacridone in useful pigmentary forms. The first pigments were commercialized in 1958.

18.3
Quinacridone Syntheses

Today two commercial synthetic routes are available for the manufacture of quinacridone pigments and some substituted derivatives. The key starting material in either synthesis is dialkyl succinoylsuccinate (7), which is synthesized from dialkyl succinate in the presence of a sodium alkoxide catalyst, usually sodium methoxide. The first step is a Claisen condensation, and this is followed by a Dieckman cyclization, yielding the disodium salt 8, which upon acidification yields 7 (Scheme 18–2)[8].

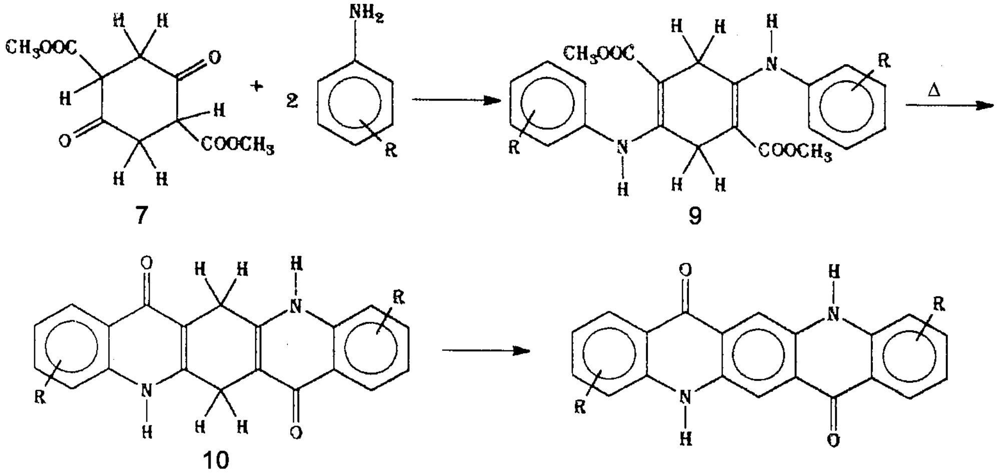


Scheme 18–2.

An alternative but commercially unimportant synthesis[9] of 7 starts with diketene, which is chlorinated to form 4-chloroacetoacetyl chloride, and the latter is reacted with alcohol to form alkyl 4-chloroacetoacetate. The ester undergoes an alkoxide-catalyzed intermolecular displacement of chlorine to form 7, after acidification.

The dibeta-keto ester 7 readily undergoes acid-catalyzed reactions with aniline and other aromatic amines to form 2,5-diarylamino-3,6-dihydroterephthalates 9 in excellent yields[10]. The structure of 9 was established on the basis of its elemental analysis, chemical behavior, and IR and NMR spectra[11].

In the so called “solvent process” (Scheme18–3), the intermediates 7 and 9 are synthesized in a high boiling inert solvent such as diphenyl ether or the eutectic mixture of diphenyl ether and biphenyl[8, 10] or sulfolane, etc. The chosen solvent also serves as the medium for the following cyclization reaction. Ring closure of the diarylamino ester 9 takes place under Conrad-Limpach reaction conditions. Since the discovery of the uncatalyzed thermal cyclization of β-anilinoacylates to 4-quinolones by Conrad and Limpach[12], this reaction has been widely applied for the synthesis of various quinolones. In this case[13], as is typical, the double cyclization is accomplished by heating the ester 9 in a high boiling inert solvent while allowing co-product alcohol to distill out. High dilution favors the monomolecular reaction. Since the β-anilinoacrylate structure is required for this cyclization, the reaction is

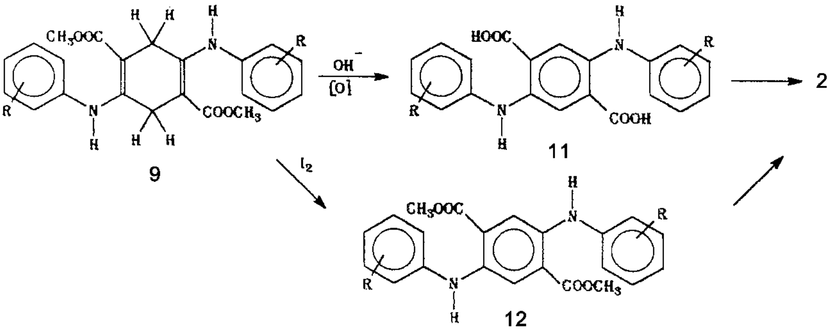


Scheme 18–3. Synthesis of quinacridones via 6,13-dihydroquinacridone.

carried out in an inert atmosphere to avoid aromatization of the center cyclohexadiene ring. Under proper experimental conditions, a very high yield of the nearly colorless 6,13-dihydroquinacridone (**10**) is obtained. The mechanism of this reaction is not known with certainty, but is believed to involve the elimination of alcohol to form an intermediate ketene, which undergoes rapid cyclization and prototropic shifts to form the quinolone moieties. The insoluble **10** is isolated by filtration.

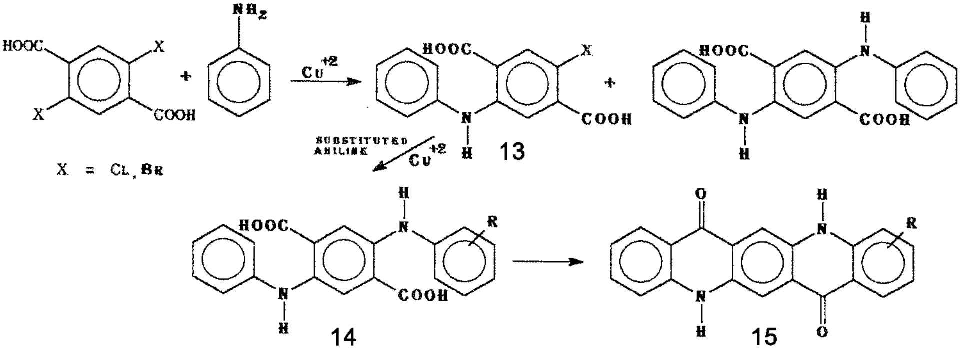
The oxidation of **10** to quinacridone can be accomplished in many ways, including oxidation with aromatic nitro compounds in aqueous alcoholic base[13] or by the use of air[14] or hydrogen peroxide[15]. Dehydrogenation can also be accomplished with various quinones like anthraquinone-2-sulfonic acid[16] or palladium on charcoal[17]. The key to successful oxidation is the production of not only chemically but also crystallographically pure quinacridone.

An alternative commercial process for the manufacture of quinacridone, the polyphosphoric acid (PPA) process (Scheme 18–4), also starts with **7** which is converted to **9**, usually by the acid-catalyzed reaction with aromatic amines in alcohol as a solvent. Without ester isolation, it is subjected to oxidation with some of the same oxidizing agents mentioned earlier for the oxidation of **10**, and hydrolyzed in the alcoholic aqueous base to produce the water soluble disodium salt of 2,5-diarylaminoterephthalic acid, which upon acidification produces excellent yields of 2,5-diarylaminoterephthalic acids (**11**). All reactions can be carried out in the same vessel[18]. Under these conditions oxidation precedes hydrolysis, since 2,5-dianilino-3,6-dihydroterephthalic acid has never been isolated. Alternatively, **9** can be oxidized to the ester **12**, with a variety of oxidizing agents, including iodine[19]. Either acid **11** or the corresponding ester **12** can be cyclized in hot PPA[20] of about 83–85 % P_2O_5 content to produce excellent yields of quinacridone or its substituted derivatives. Although PPA is the preferred cyclizing acid, other agents like benzoyl chloride in nitrobenzene, other acid chlorides like PCl_5, $POCl_3$, $AlCl_3$, $SiCl_4$, or hydrofluoric acid have been successfully used in this cyclization reaction.



Scheme 18–4. Synthesis of quinacridones via 2,5-diarylaminoterephthalic acids (PPA process).

Still another synthesis, which yields moderate yields of **11**, is based on the Ullmann reaction of 2,5-dibromo- or 2,5-dichloroterephthalic acids or esters with aromatic amines (Scheme 18–5)[21]. This approach is suitable for the preparation of unsymmetrically or monosubstituted quinacridones by a two-step reaction sequence which allows the isolation of 2-halo-5-aryl-aminoterephthalic acid (**13**) for subsequent reaction with a different amine. Although the yields are moderate the resulting terephthalic acids (**14**) can be cyclized by the same methods described earlier. For a short period, 2-methylquinacridone (**15**, R=2-methyl) was commercialized by Sandoz.



Scheme 18–5. Synthesis of quinacridones via ulmann reaction.

Using one or more of the three methods, and others which are more complicated (see below), about 150 differently substituted quinacridones have been reported in an extensive list of patents and other publications in the last 40 years.

18.4
Structural Data and Spectra

Despite its relatively low molecular weight (312), quinacridone, which is a microcrystalline powder, does not melt or decompose up to 400 °C and is very sparingly soluble in organic solvents. The low solubility may be attributed to strong intermolecular hydrogen bonding between the carbonyl oxygens and the N–H hydrogen atoms, which are favorably situated for strong bonding. Thus, *N*, *N'*-dimethylquinacridone is an alcohol-soluble compound[22] because it no longer possesses the required structural features for intermolecular hydrogen bonding. By contrast, 2,9-dimethylquinacridone, with the same molecular weight, is even less soluble than the parent compound. Other support for intermolecular bonding in the solid state comes from a comparison of visible spectra in the solid state with a solution in hexamethylphosphoramide. The visible absorption spectrum of quinacridone is characterized by three bands increasing in intensity with increasing wavelengths (Figure 18–1). The spectrum in the solid state (of the red gamma phase) is similar to that in solution but is not as well resolved and shows a strong bathochromic shift which for the major absorption is 41 nm. A shift of this magnitude can be attributed to intermolecular bonding. This is further supported by the position of the N–H and C=O stretching frequencies in the IR spectrum. The most important confirmation comes from the symmetry requirements and dimensions of the unit cells of several forms of quinacridone.

In considering the chemical properties of quinacridone it is helpful to look at the chemical behavior of pyridones. These compounds behave neither as secondary amines nor as unsaturated ketones even though the upper center structure **16** appears to make a more important contribution to the resonance in the ground state than the other two (Scheme 18–6). However, to the extent that the others contribute to the resonance of the system, the N–H hydrogens are more acidic and the carbonyl oxygens more basic than the center structure would suggest. The IR spectrum of quinacridone in the solid state shows that it does not exist in the enolic form **17**, but tells us relatively little about the degree of contribution of the zwitterionic form **18.** X-ray structural determinations of peptides and related substances have shown that on average the zwitterionic form contributes about 40 % to the structure of an amide group[23]. Since quinacridone is a divinylogous diamide, contribution by zwitterionic forms must play a significant role. It is noteworthy that the spectrum of quinacridone in concentrated sulfuric acid shows

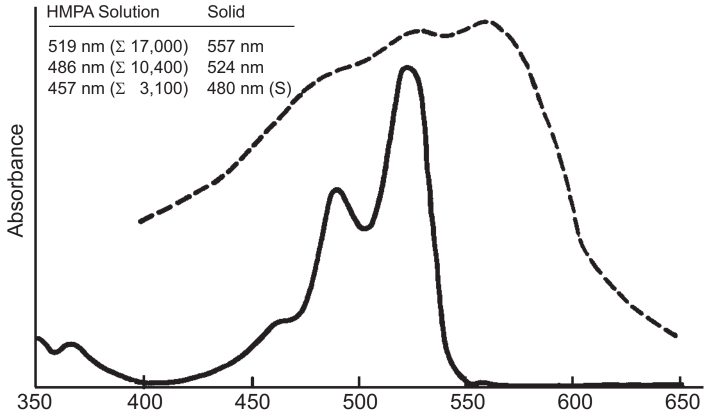
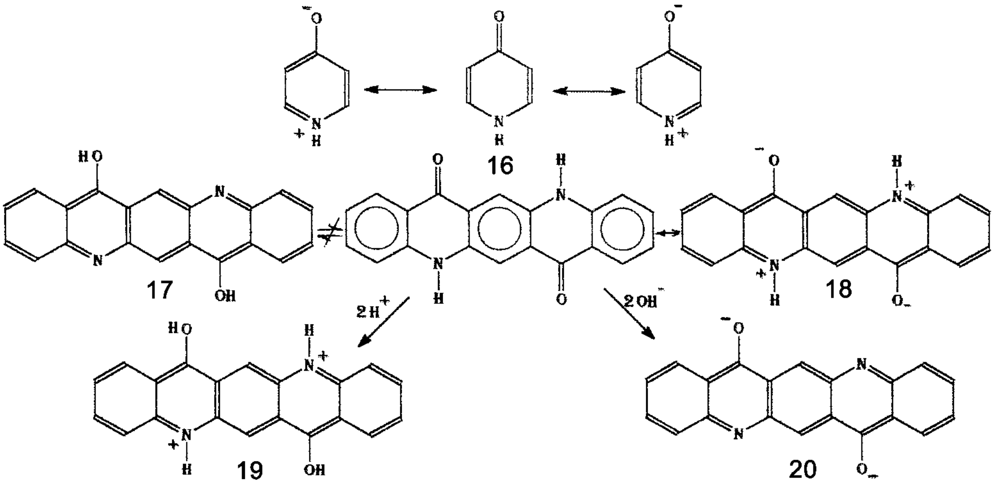


Figure 18–1: Visible spectra of quinacridone; — absorption spectrum of quinacridone in hexamethylphosphoramide solution; – – – reflectance spectrum of gamma quinacridone in an acrylic resin film.



Scheme 18–6. Structure of quinacridone and its conjugate acid and base.

remarkable similarity to the visible spectrum of pentacene in trichlorobenzene solution but shows a strong bathochromic shift relative to the visible spectrum of quinacridone in *N*,*N*′-dimethylformamide (DMF) solution (Figure 18–2). This is to be expected if the degree of aromatic character of the molecule is increased on protonation. The spectrum is best interpreted on the basis of the di-cation **19**, where protonation has taken place on the oxygens rather than the nitrogen atoms. This is in agreement with the work by Katritzky and Jones[24], who showed by an NMR study that protonation of pyridones and quinolones takes place on oxygen atoms. Likewise, the spectrum of quinacridone in basified methanol shows great similarity to the spectrum of the diprotonated species,

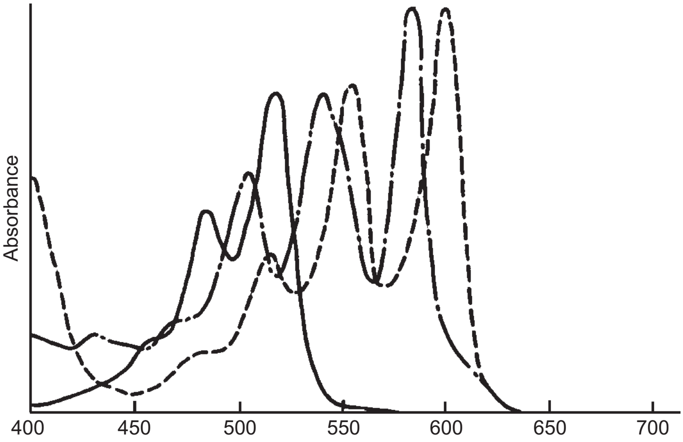


Figure 18–2: Spectra of
— quinacridone in dimethylformamide solution;
– – – in concentrated sulfuric acid solution;
– · – pentacene in trichlorobenzene solution.

but the former shows a bathochromic shift. This suggests that the visible spectra of both species are due to the same chromophore. The spectrum in basic solution is, therefore; also indicative of an aromatic structure which is best formulated as the dianion **20.**

18.5
Polymorphism

Quinacridone, like many of its substituted derivatives, was found to be polymorphic in nature. Three distinct polymorphic modifications were recognized early in the development study, each with its characteristic X-ray diffraction pattern (Figure 18–3). The red gamma[25c] polymorph's molecular arrangement shows that each molecule is bonded to four neighboring molecules[26], as shown in Figure 18–4, and the violet beta[25b] form to two adjacent molecules[27] depicted in Figure 18–5. The latter molecular arrangement leads to a minimum overlap in stacking orientation and reinforcement of transition dipoles along the stacking axis with consequent light absorption in the solid state at longer wavelengths. The red alpha polymorph is the least stable, actually metastable, form and is, therefore, commercially unimportant[25a,28]. The beta and gamma forms (P.V. 19, CAS 1047–16–1) are both important commercial pigments produced in opaque and transparent varieties. They show similar stabilities, the gamma being more stable in polar systems and the beta in less polar environments. Each can be converted to the other when treated with specific solvents in their nascent crystalline state. It has also

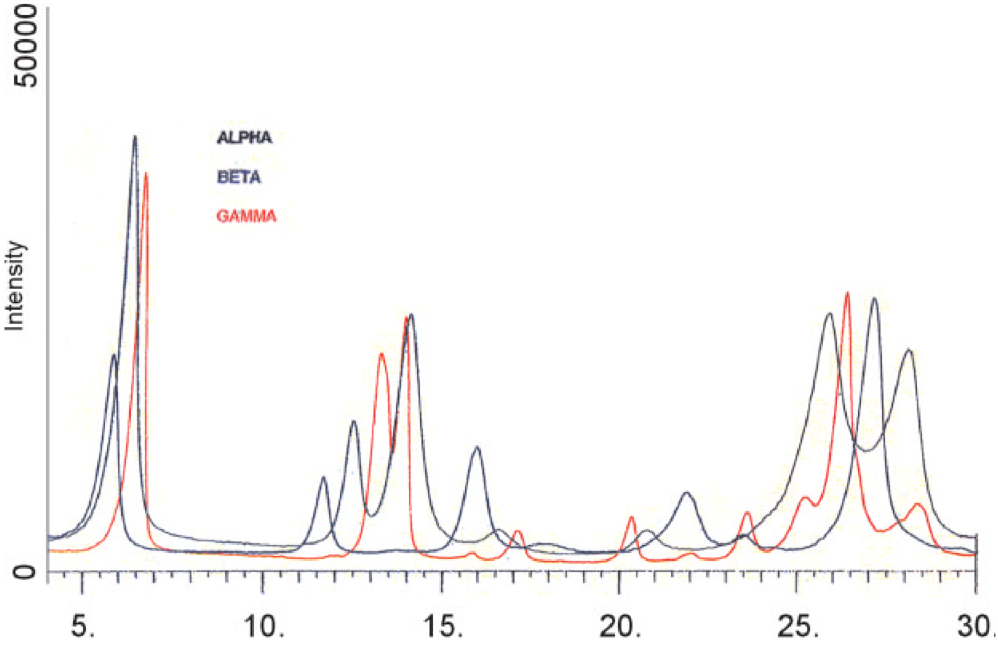


Figure 18–3: Powder X-ray diffraction patterns of three polymorphic forms of quinacridone.

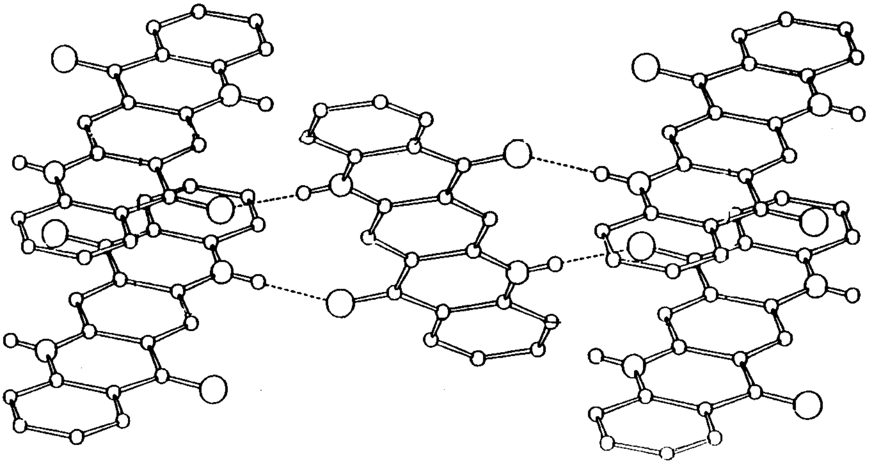


Figure 18–4: Projection of gamma quinacridone crystal.

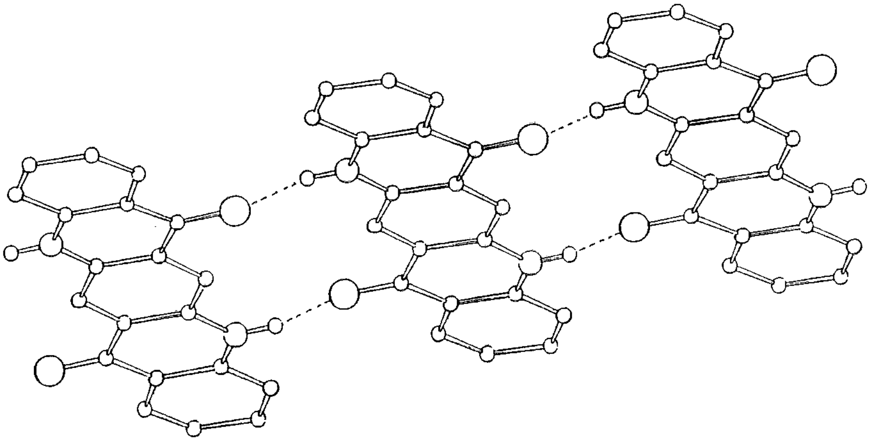


Figure 18–5: Projection of beta quinacridone crystal.

been recognized that the gamma form exists in three polytypes γ', γ'' and γ''', differing somewhat in color and X-ray diffraction patterns. Newer forms[29, 30] are fairly yellow shade reds as relatively large particle size opaque pigments. Opaque gamma quinacridone having particle sizes of about 0.2–0.5 μm (shown in the photomicrograph in Figure 18–6) is produced directly in that form[25c] or deliberately grown to the desired particle sizes[31]. The corresponding semitransparent particle size-reduced counterparts (Figure 18–7) are obtained either by salt milling in the presence of a phase-directing solvent[32] or by drowning a quinacridone solution in strong acid into an appropriate medium[20, 33] with subsequent treatment under specific conditions. The same is true for the beta polymorph, except that different solvents are employed for drowning the acid solution or treating the initially generated alpha phase[20]. When milling large particle size beta pigment a phase directing solvent also has to be employed, otherwise the ultimate product is bound to contain the alpha, higher energy form.

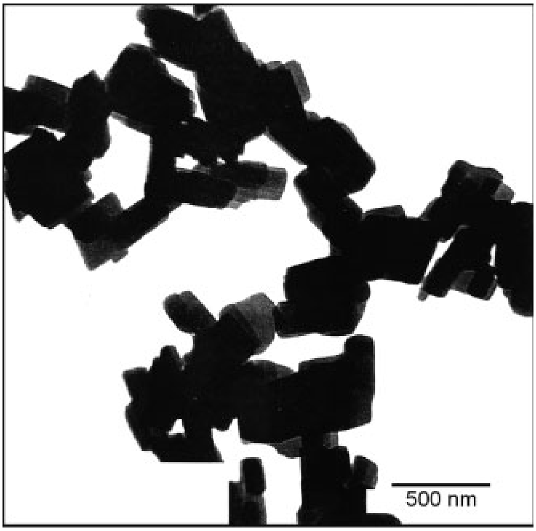


Figure 18–6: Electron photomicrograph (40 000 ×) of opaque gamma quinacridone.

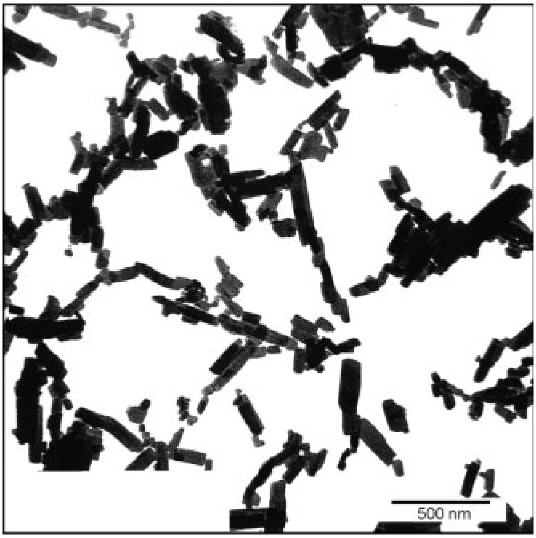


Figure 18–7: Electron photomicrograph (40 000 ×) of semitransparent gamma quinacridone.

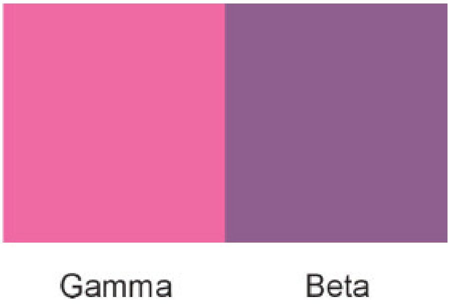


Figure 18–8: Two quinacridone polymorphs extended with TiO_2.

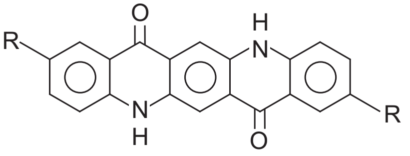
Figure 18–8 demonstrates TiO_2 extensions (10 parts pigment and 90 parts TiO_2) of gamma and beta quinacridone polymorphs. These forms, as well as the red alpha polymorph, are chemically identical but have different arrangements of the molecules in their crystal lattices. The red gamma phase has become an article of commerce, while the thermodynamically less stable alpha phase, with similar color attributes, has not.

A large particle size opaque beta polytype has also been recently commercialized[34]. Claims have also been made in the patent literature[35] to several other forms of quinacridone.

18.6
Substituted Quinacridones

Quinacridone substituted in the peripheral rings can be prepared by the synthetic methods described earlier using appropriately substituted aniline. *Para*- and *ortho*-substituted amines give rise to 2,9- and 4,11-disubstituted quinacridones, respectively. *Meta*-substituted anilines, on the other hand, by virtue of the availability of two different cyclization positions, give rise to three possible isomeric compounds, 3,10-, 1,8- and 1,10-disubstituted derivatives, the first being the predominant compound. In some instances, the three isomers can be separated. The individual compounds can also be distinguished by NMR[36]. Like the parent compound, many of the substituted derivatives, including 6,13-dihydroquinacridone[37], are polymorphic in nature. For example, 4,11-dichloroquinacridone exists in three polymorphic forms[38], as does 2,9-dichloroquinacridone[39]. Several forms of 2,9-dimethylquinacridone have also been described[40]. The same is true for a variety of other substituted derivatives. Since different polymorphic modifications of the same compound have different colors (Figure 18–8), it is difficult to correlate the substituent effect, for example in the 2,9-positions, with the color of the pigments in the solid state. This, of course, is not the case in solution, where all polymorphs of the same compound, having lost their solid structure, absorb identically. In general, 2,9-disubstituted quinacridones, some of which are commercially important, range in color from red to magenta to bluish-violet. On the other hand, substituents in the 4,11-positions cause a hypsochromic shift relative to the parent compound. Compounds such as 4,11-dimethoxy, 4,11-dimethyl, and 4,11-difluoroquinacridone range in color from reddish scarlet to orange. Even in DMF or concentrated sulfuric acid solutions, the longest wavelength absorptions of 2,9-disubstituted quinacridones show only an approximate correlation with either σ or σ+ substituent functions. In Table 18–1 are recorded the longest wavelength absorptions of several disubstituted quinacridones in DMF and in concentrated sulfuric acid solutions. It is noteworthy that electron-releasing substituents like OCH_3 or CH_3 shift absorptions to longer wavelengths, as expected. However, the same is observed with 2,9-dichloro and 2,9-difluoro derivatives. This is interpreted as a function of the predominating halogen mesomeric effect over the inductive electronic effect, in view of the partial positive charge residing on the N–H moieties. The CF_3 group, which withdraws electrons inductively only, shows the expected hypsochromic shift relative to the parent compound. The most stable polymorphs of 2,9-dimethyl (P.R. 122, CAS 980-26-7), 2,9-dichloro (P.R. 202 CAS 3089-17-6) and 2,9-difluoro derivatives are all various magenta colors, the first two being important commercial pigments.

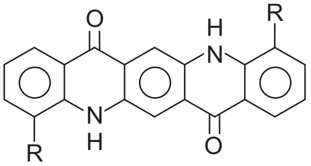
Table 18-1. Spectral Date for Quinacridone and some 2,9-disubstituted derivatives.



R	*In DMF*	*In Conc. H_2SO_4*
OCH_3	542	612
CH_3	527	606
H	519	597
F	526	604
Cl	527	609
CF_3	508	587

The color of 4,11-disubstituted quinacridones, unlike the 2,9-disubstituted counterparts, are dominated by steric rather than electronic effects. As is shown in Table 18–2, the solubility of these compounds (in boiling α-chloronaphthalene, b.p. 264 °C) increases with increasing bulk of the substituents, and correspondingly the photochemical stability in the solid state decreases. This observation reinforces the belief that the outstanding outdoor durability of some quinacridones is associated with strong intermolecular hydrogen bonding. In the 4,11-disubstituted compounds, increasing bulk of substituents appears to cause weakening of the intermolecular hydrogen bonds and consequently greater solubility and reduced photochemical stability. In fact, 4,11-dichloroquinacridone, an attractive scarlet compound readily accessible from *o*-chloroaniline, does not show the acceptable outdoor durability required for high performance pigments. By moving the chlorine substituents from the 4,11- to the 3,10-positions (P.R. 209, CAS 3573-01–1), where the inductive effect is predominating and steric interference to hydrogen bonding is absent, one observes a hypsochromic shift relative to the parent compound and acceptable outdoor durability. This pigment is commercially available.

Table 18-2. Relative solubility and photochemical stability of Quinacridone and some 4,11-disubstituted derivatives.



R	*Solubility*	*Photochemical stability in solid state*
H	|	↑
F		
Cl	Increasing	Increasing
CH_3	↓	|
CF_3		

18.7
Photostability and a Suggested Mechanism

Quinacridone and most 2,9-disubstituted derivatives show excellent outdoor durability. This has been demonstrated by exposing these pigments in appropriate coatings in Florida for at least two years as either opaque or transparent pigments in combination with TiO_2, aluminum flakes or various nacreous pigments, frequently used in automotive coatings. The opaque, large particle size (0.2–0.5 μm), low surface area (20–30 m^2/g) pigments show outstanding weatherfastness. However, very transparent, small particle size (0.02–0.05 μm or 20–50 nm), high surface area (70–80 m^2/g) pigments like 2,9-dichloroquinacridone also qualify as high performance pigments from a weatherfastness point of view. Similar performance has been observed in other less demanding systems.

As in most compounds, the photostability is governed by competition between rates of chemical reaction in the excited state and rates of deactivation to the ground state. The high degree of photostability of opaque gamma quinacridone is demonstrated[41] by its quantum yield of 1.8×10^{-8} (defined as the ratio of number of molecules degraded to the number of quanta of light absorbed) when dispersed in an acrylic polymer and exposed, under highly controlled conditions, to a xenon-arc lamp modified to simulate ordinary sunlight. The quantum yield decreases with increasing wavelength of exposure and, of course, increases with an increase in incident ultraviolet light. Thus, the total rate of the exceedingly slow chemical reaction is about 8 orders of magnitude slower than the deactivation process. In many systems, particularly in solution, deactivation of excited states occurs via fluorescence. But solid state quinacridone exhibits no fluorescence at all. This observation suggests that in this family of compounds radiationless deactivation takes place which is closely linked with effective intermolecular hydrogen bonding. 4,11-Dichloroquinacridone, which is not sufficiently lightfast (it is actually poor on outdoor exposure), shows a definite light emission (fluorescence) at 600 nm wavelength (Figure 18–9). Apparently radiationless deactivation is ineffective in this case, presumably because of significantly less effective intermolecular hydrogen bonding inferred from 6.5 times greater solubility (in boiling α-chloronaphthalene) and 3.5 times higher quantum yield[41] relative to quinacridone. The degree of interference with intermolecular hydrogen bonding by the bulky chlorine groups is demonstrated in the three-dimensional structures in Figure 18–10. Whereas quinacridone is the most photostable, least soluble, non-light-emitting substance, 4,11-dichloroquinacridone in this series is the least photostable, most soluble, light-emitting compound. 4,11-Difluoroquinacridone falls in the middle on all counts. Thus, a key requirement for acceptable weatherfastness is the absence of sterically interfering groups in the immediate vicinity of the intermolecularly hydrogen-binding atoms. The ability of intramolecular hydrogen bonds to aid in the deactivation of excited states has been unequivocally established[42]. Movement of a hydrogen between bonding centers is believed to catalyze the crossing of molecules from the excited state to an upper vibrational level of the ground state. Facile vibration deactivation completes the molecular electronic decay. Complete hydrogen transfer has also been

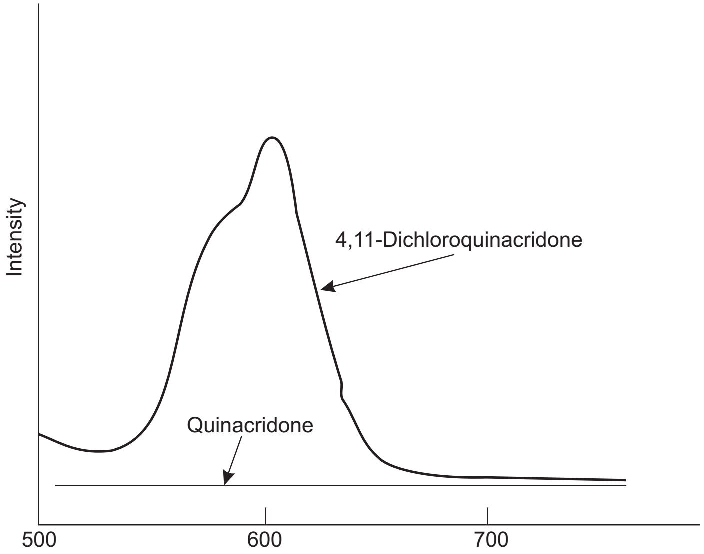


Figure 18–9: Emission spectra of solid state quinacridones under 400nm radiation excitation.

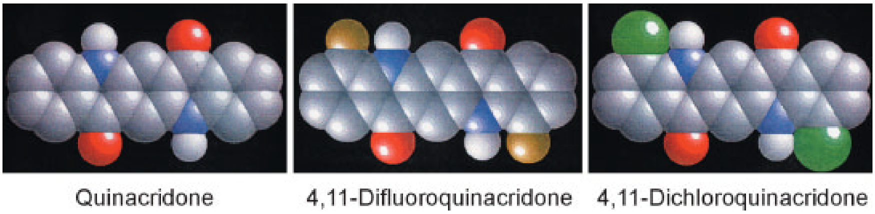
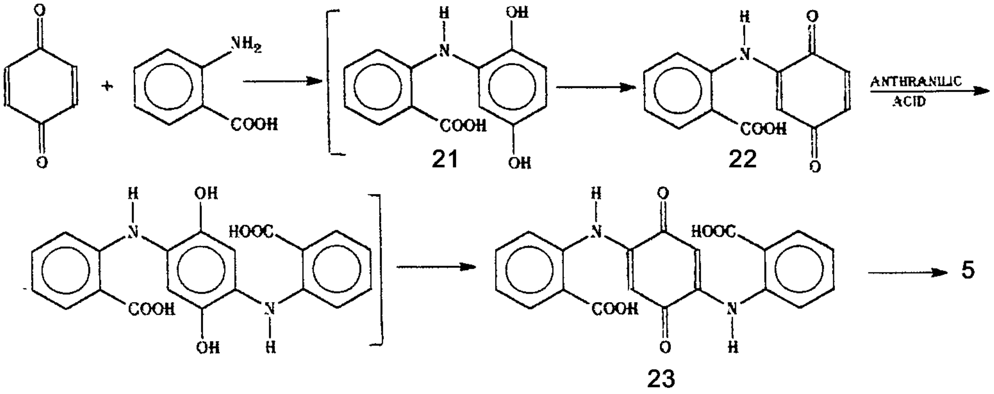


Figure 18–10: Three dimensional structures (white: hydrogen; red: oxygen; yellow: fluorine; green: chlorine).

demonstrated[43] in the excited state, and return of the hydrogen atom upon deactivation to the ground state in intramolecularly hydrogen bonded molecules. However, a complete hydrogen transfer does not have to take place to catalyze the deactivation process, particularly in intermolecularly bonded systems, of which quinacridone is one example.

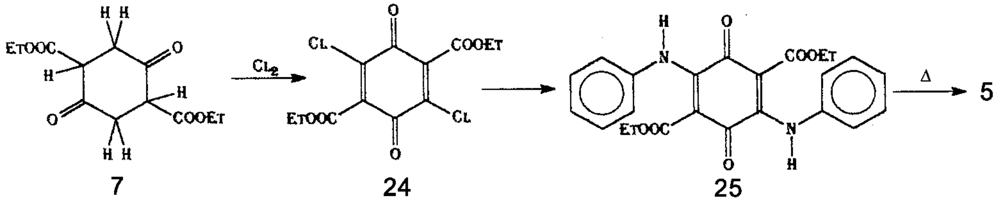
18.8
Quinacridonequinone

Thus far, we have considered substitution in the peripheral benzene rings only. Quinacridonequinone can be considered, in a general sense, as a 6,13-derivative. In fact, this quinone was the first compound ever synthesized with the true linear quinacridone ring system[5]. The method employed for its synthesis was the addition of anthranilic acid to *p*-benzoquinone, followed by the cyclization of the resultant 2,5-bis(*o*-carboxyanilino)-1,4-benzoquinone (**23**) in concentrated sulfuric acid (Scheme 18–7). The yield of the intermediate **23** was fair, but the cyclization reaction took place in very good yield. Many years later it was recognized, based on the mechanism of 1,4-amine additions to quinones, that benzoquinone served as a reactant as well as an oxidizing agent to convert the intermediate substituted hydroquinone **21** to the intermediate quinone **22**, and the process is repeated again upon the addition of the second anthranilic acid molecule. By the simple expedient of adding an oxidizing agent ($NaClO_3$) and a catalyst (V_2O_5), a very good yield of the intermediate dicarboxylic acid **23** was obtained[44]. In addition, under essentially the same reaction conditions the starting material *p*-benzoquinone can be replaced by the less expensive hydroquinone, provided sufficient oxidizing agent is available to generate the quinone in situ. Today, several other methods are available for the manufacture of quinacridonequinone, which is an important ingredient in several commercial high performance pigments.

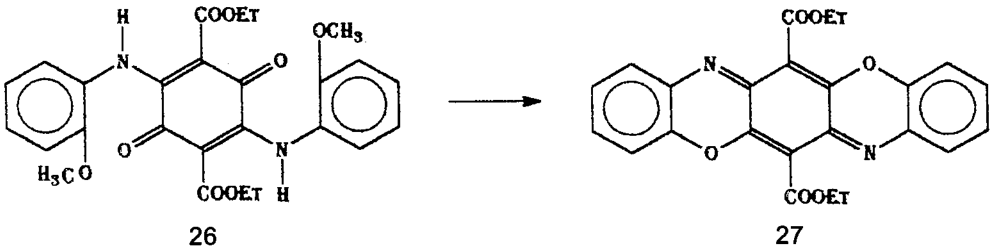


Scheme 18–7. Synthesis of quinacridonequinone (mechanistic implications).

Easily accessible routes are simple oxidation of quinacridone or 6,13-dihydroquinacridone with sodium dichromate in strong acid[45] or oxidation of the latter with $NaClO_3$ catalyzed with V_2O_5[46]. Conversely, quinacridonequinone can be reduced to quinacridone by means of finely divided metals under a variety of conditions. A good yield of quinacridone is obtained by reducing quinacridonequinone with zinc powder in 70 % sulfuric acid or in a eutectic mixture of $AlCl_3$ and NaCl[47]. Still another very versatile synthesis[48] for various substituted quinacridonequinones starts with dialkyl succinoylsuccinate (Scheme 18–8). Chlorination of the dibeta-keto ethyl ester **7** yields 2,5-dichloro-3,6-diethoxycarbonyl-1,4-benzoquinone (**24**), presumably by chlorination followed by dehydrochlorination. The dichloro ester is very reactive with respect to nucleophiles. Aniline and many substituted aromatic amines, whether weak or strong bases, react with **24** to displace the halogen atoms, and in the presence of an HCl scavenger produce excellent yields of 2,5-diarylamino-3,6-diethoxycarbonyl-1,4-benzoquinones (**25**). The resulting esters undergo a Conrad-Limpach reaction by cyclization in high boiling inert solvents to produce quantitive yields of quinacridonequinone or its substituted derivatives. The synthetic method is quite general, possessing the advantage of readily available starting materials. There is one important exception[48]. Diarylamino compounds having an active hydrogen or other similar function in the *ortho* position undergo an alternative cyclization reaction to yield substituted triphenodioxazines (Scheme 18–9). Thus, the diarylamino ester **26** derived from *o*-anisidine gives rise to 6,13-diethoxycarbonyl triphendioxazine (**27**) at a lower cyclization temperature than is required by the ordinarily expected cyclization to a substituted quinacridonequinone.



Scheme 18–8. Synthesis of quinacridonequinone via 2,5-dichloro-3,6-diethoxycarbonyl-1,4-benzoquinone.

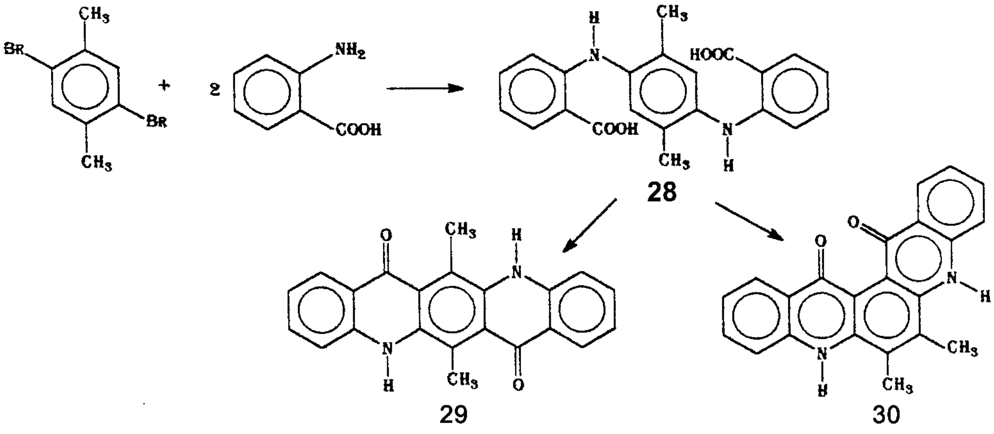


Scheme 18–9. Generation of 9,10-dicarbethoxycarbonyl triphendioxazine.

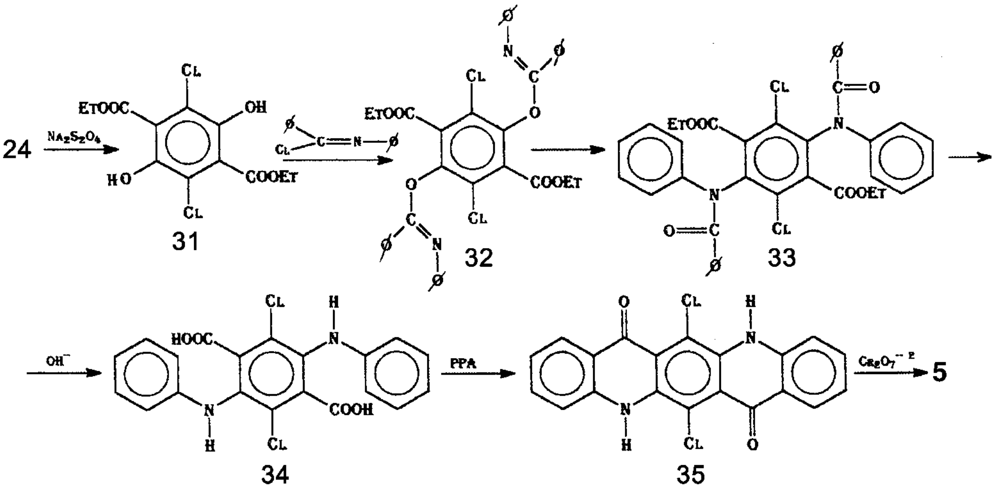
18.9
Other 6,13-disubstituted Quinacridones

There is only one 6,13-disubstituted quinacridone, namely 6,13-dimethylquinacridone (**29**), described in the literature by Lesnianski and Czerski[49] in 1926, aside from the reduction product of quinacridonequinone, which is 6,13-dihydroxyquinacridone. However, there is considerable doubt, based on the reported properties of the isolated yellow compound and the properties of the unequivocally synthesized 6,13-dichloroquinacridone, whether the structure is that of the linear compound **29** or the isomeric angular compound **30** (Scheme 18–10). Although not absolutely proven, it is quite conceivable that the acid-catalyzed cyclization of the dicarboxylic acid **28** was preceded by a Jacobson rearrangement which shifted a methyl group from a *para* to an *ortho* position with respect to the second methyl group.

The choice to synthesize 6,13-dichloroquinacridone[50], in an attempt to resolve this point[11], was based on the availability of an appropriate starting material (Scheme 18–11). The previously described 2,5-dichloro-3,6-diethoxycarbonyl-1,4-



Scheme 18–10. Reported synthesis of 6,13-dimethylquinacridone.



Scheme 18–11. Synthesis of 6,13-dichloroquinacridone.

benzoquinone (**24**) was reduced to the corresponding hydroquinone **31**, and its disodium salt was reacted with *N*-phenylbenzimidoyl chloride to yield the dibenzimidate ester **32**. The latter compound was subjected to the Chapman rearrangement. The thermal rearrangement of benzimidate esters to N-aroyl diphenylamines was discovered by A.W. Chapman[51] in the late 1920s, and the mechanism of the reaction was elucidated by K.B. Wiberg and B.I. Rowland[52] in the mid 1950s. The dibenzimidate ester **32** is particularly suitable for this rearrangement, giving an excellent yield of the diamide diester **33**. Vigorous hydrolysis of this compound leads to 2,5-dianilino-3,6-dichloroterephthalic acid (**34**). It is noteworthy that, unlike the colored 2,5-dianilinoterephthalic acid (ε_{max} 435nm), the dichloro derivative is a colorless (ε_{max} 295 nm) compound. Clearly, the hexasubstituted center benzene ring of **34** precludes coplanar arrangement and consequently effective electronic interaction between the anilino and carboxy groups. Cyclization of the dicarboxylic acid in PPA provides an excellent yield of 6,13-dichloroquinacridone (**35**) . Oxidation of this compound with sodium dichromate in aqueous acid yields quinacridonequinone, thus fixing the position of the chloro substituents. The spectrum of **35** in DMF is very similar to that of quinacridone itself in solution, both in terms of position and intensity of absorptions. Based on these results, it is believed that 6,13-dimethylquinacridone, referred to earlier, can also be expected to be a red rather than yellow substance.

The Chapman rearrangement has also been applied to the synthesis of the parent compound as well as other derivatives not easily accessible by other means. However, this synthesis is mostly of theoretical interest and at present has no manufacturing applications.

18.10
Solid Solutions

The phenomenon of solid solution formation has been known for some time in the copper phthalocyanine series of pigments. For example, partially chlorinated copper phthalocyanine is in effect a solid solution of the parent compound and small amounts of chlorinated derivatives, thereby stabilizing the crystal structure of the pigment. In the quinacridone series this phenomenon was discovered early and exploited to a greater extent from a theoretical and commercial point of view. There are fundamentally two types of solid solutions in this series of pigments. One, the predominant type, consists of a “host” compound and one or more “guest” compounds, the combination retaining the structure and X-ray diffraction pattern of the “host” compound. The second type, sometimes referred to as mixed crystals (also as solid compounds), can consist of two or more related compounds, the combination of which acquires a new structure and an X-ray diffraction pattern totally different from the X-ray patterns of the component parts. The first solid solution prepared[53] in the quinacridone series was obtained inadvertently when 6,13-dihydroquinacridone was oxidized under conditions which led to a mixture of quinacridone and quinacridonequinone in an approximate two to one molar ratio. Upon particle size reduction of the crude product, a transparent brown pigment was obtained. Incorporation of the pigment in a metallic automotive finish showed it to be an attractive maroon (P.R. 206, CAS 71819-76[54]) with outstanding long term outdoor durability. The solid solution has the X-ray diffraction pattern of quinacridonequinone despite the presence of more than 60 % quinacridone, and differs radically from a mixture of the two ingredients in the same weight ratio (Figure 18–11). Once the threshold of saturation is exceeded, excess quinacridone bands show up in the X-ray diffraction pattern.

Quinacridonequinone itself is a yellow compound deficient in lightfastness, but by virtue of solid solution formation the resulting maroon pigment shows outstanding photochemical stability. Clearly, energy of excited quinacridonequinone molecules is transferred to quinacridone, which is adept at returning the system to the ground state

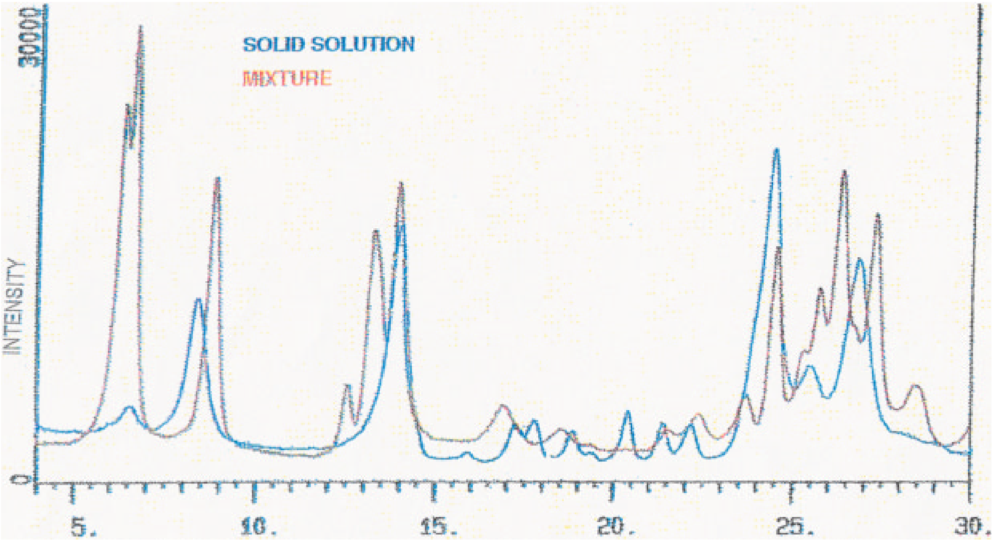


Figure18–11: Powder X-ray diffraction patterns of quinacridone and quinacridonequinone solid solution, and physical mixture of the same ingredients.

by dissipating energy as heat. To stabilize quinacridonequinone with quinacridone does not require saturation of the "host" molecule – as little as 30 % or less of quinacridone is sufficient to stabilize the system[55]. In fact, such a product is a transparent, strongly red-shade yellow commercial pigment (P.O. 48, CAS 71819-74-4[54]).

Later, it was shown that the phenomenon of solid solution formation is widespread in this family of pigments. The previously discussed scarlet pigment 4,11-dichloroquinacridone was greatly improved in weatherfastness by solid solution formation (P.R. 207, CAS 71819–77–7[54]) with the parent compound. In this case the approximate composition is also two moles of quinacridone and one mole of the substituted counterpart, retaining largely the scarlet color of the latter and the photochemical stability of the former. The X-ray diffraction pattern of the solid solution is different from that of a mixture of the two ingredients (Figure 18–12) or those of the individual components. As in most cases, while the X-ray diffraction pattern of a mixture is simply additive and predictable, the solid solution shows a non-additive diffraction pattern and an unpredictable color effect.

Similarly, quinacridone forms solid solutions with 2,9-dimethyl or 2,9-dichloroquinacridone at about a ratio of two moles of unsubstituted to one mole of the substituted compound, the X-ray diffraction patterns of which are virtually identical and are different from those of mixtures of the individual ingredients (Figure 18–13). One blue-shade red is an article of commerce (P.V. 42, CAS 71819–79–9[54]. In fact, using quinacridone and three 2,9-disubstituted derivatives, a series of binary and ternary solid solutions are formed, as depicted in Figure 18–14[38]. The large triangle is subdivided into four smaller triangles and the areas where binary and ternary solutions are possible are shown. It is obvious that solid formation is unpredictable and requires numerous experimental determinations to delineate areas of solid solution formation.

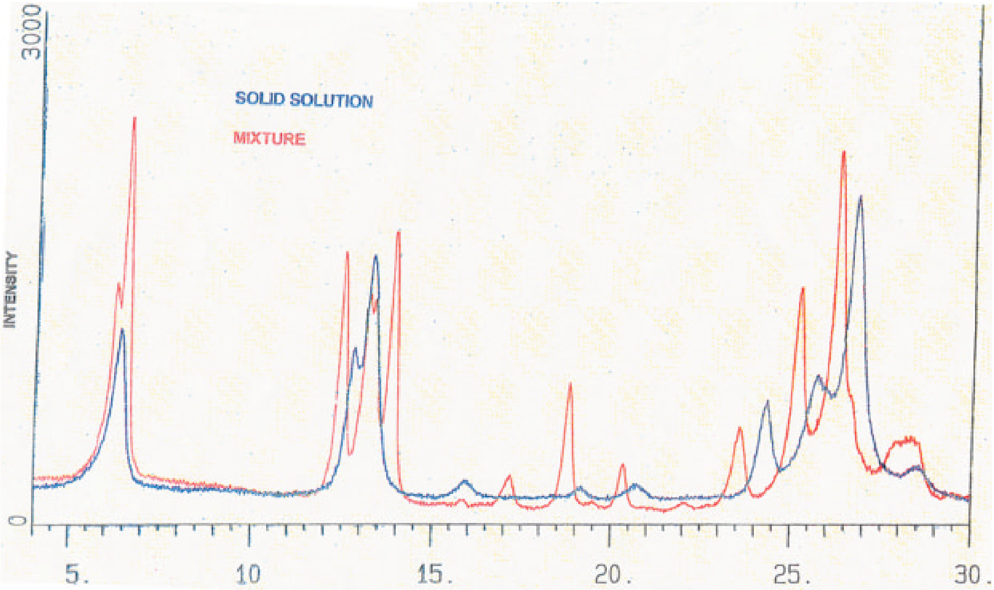


Figure 18–12: Powder X-ray diffraction patterns of quinacridone and 4,11-dichloroquinacridone solid solution, and physical mixture of the same ingredients.

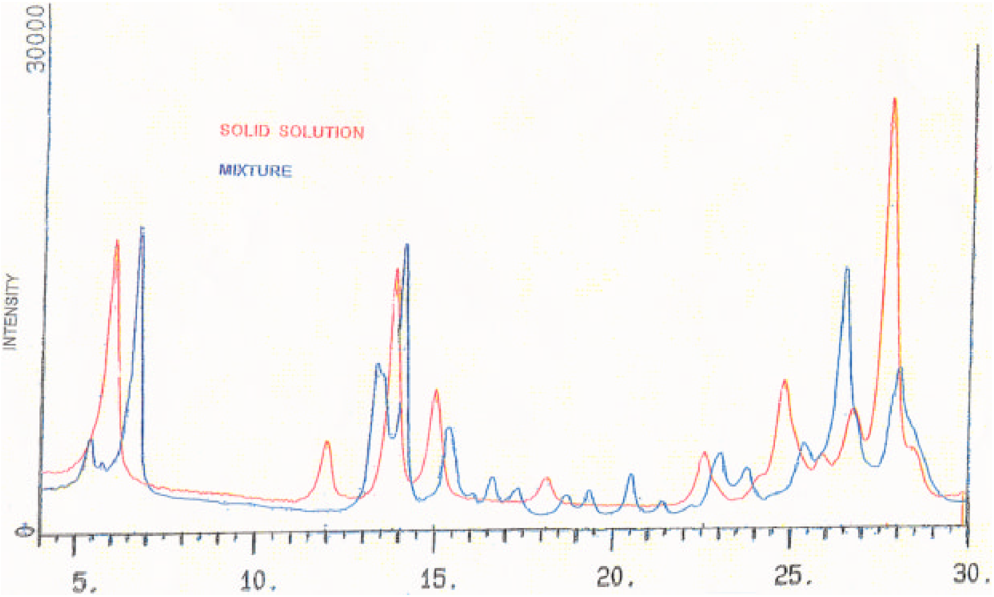


Figure 18–13: Powder X-ray diffraction patterns of quinacridone and 2,9-dichloroquinacridone solid solution, and physical mixture of the same ingredients.

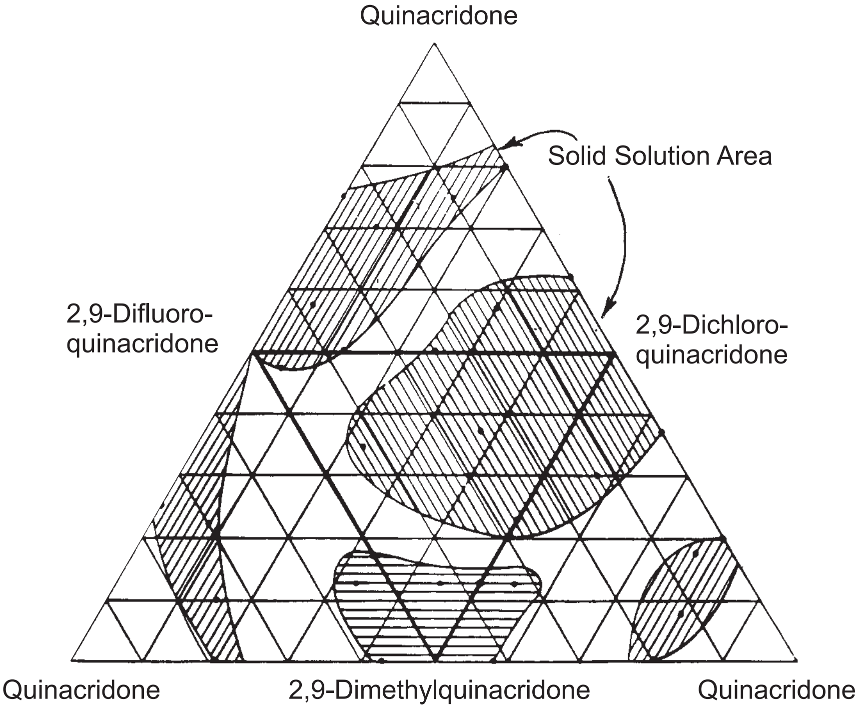
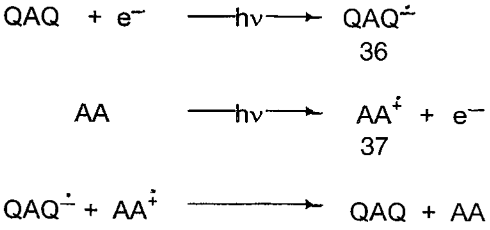


Figure 18–14: Phase diagram of solid solutions formation between quinacridone, 2,9-dimethylquinacridone, 2,9-dichloroquinacridone, and 2,9-difluoroquinacridone.

An interesting quaternary orange solid solution[56] consisting of quinacridone, 4,11-dichloroquinacridone, quinacridonequinone, and 6,13-dihydroquinacridone has been prepared, in which the last component has a positive effect on the photochemical stability of the system.

There are many methods of solid solution preparation[38, 57]. The essential step is to reduce the size of the component particles by the usual methods (milling, drowning strong acid solutions of quinacridones, etc.) and then ripening the resultant smaller or amorphous pigment particles, if necessary in the presence of organic solvents, to afford the opportunity for incorporation of one substance into another. Since most solid solutions are thermodynamically stable combinations, they tend to form under reasonably favorable conditions.

So far we have dealt with solid solutions, which invariably incorporate one or more photochemically stable ingredients. A question frequently posed is whether this is an essential prerequisite for high performance pigment durability. The answer is that it is not, in certain systems. Quinacridonequinone is an attractive, transparent, golden yellow pigment of poor weatherfastness. Incorporation of quinacridone or related pigments inevitably changes the color. In order to preserve the color of quinacridonequinone itself, the stabilizer would have to be colorless or yel-



$$\mathrm{QAQ} + e^- \xrightarrow{h\nu} \underset{36}{\mathrm{QAQ}^{\bullet -}}$$

$$\mathrm{AA} \xrightarrow{h\nu} \underset{37}{\mathrm{AA}^{\bullet +}} + e^-$$

$$\mathrm{QAQ}^{\bullet -} + \mathrm{AA}^{\bullet +} \longrightarrow \mathrm{QAQ} + \mathrm{AA}$$

Scheme 18–12. Suggested quinacridonequinone photostabilization mechanism.

low. It was discovered that certain colorless compounds, which have a structural relationship to quinacridone, enter the quinacridonequinone lattice to a limited extent. Such a colorless compound is *N,N′*-diphenyl-*p*-phenylene diamine, which saturates the quinacridonequinone lattice at about 15 % content. Even though the diamine readily undergoes oxidation to the violet *N,N′*-diphenylquinone-1,4,-diimine when incorporated into solid solution at about 10 % concentration[58], it provides significant photochemical stabilization of quinacridonequinone. A more powerful yellow stabilizer was later discovered.

This is 2-anilinoacridone or AA[59], which at a similar concentration in solid solution with quinacridonequinone imparts excellent durability to the system. The resultant pigment, PO 49 (CAS 71819–75–5), is an article of commerce[54].

In this case, two components, which are by themselves not photochemically stable, form a durable solid solution. The mechanism for this stabilization is not known. It is, however, certain that these stabilizers, and certain others which were similarly tested, were all amines, which under the influence of light, are subject to loss of a p-electron. If this were the key to such stabilization, a free radical cation (**37**) would be generated. On the other hand, it has been demonstrated that quinacridonequinone itself initially undergoes rapid photoreduction in conventional binders. Thus, it is extremely likely that the quinacridonequinone (QAQ) molecule abstracts an electron from the binder in its initial process of reduction to generate the intermediate free radical anion **36** (Scheme 18–12).

These two types of free radicals are assumed to react with each other by means of an electron shift, which returns the system to its original state. For such a process to proceed, solid solution formation is essential. With the addition of a gold colored pigment, the color range of the quinacridone pigment family has been significantly expanded, as shown in Figure 18–15, where each panel represents a coating pigmented with 10 % of a quinacridone or quinacridone solid solutions and 90 % of titanium dioxide.

Figure 18–15: Color range of quinacridone pigments (TiO_2 extension).

18.11
Conditioning and Surface Treatment of Quinacridones.

While some production processes for quinacridones deliver fully pigmentary products, others require particle size reduction before sale in commerce. Generally, relatively large particle size pigments, which are more effective at light scattering, are opaque and relatively weak, after extension with white pigments like titanium dioxide. After particle size reduction, however, such pigments are much more transparent and correspondingly much stronger relative to their opaque counterparts. A variety of methods are in use for particle size reduction, including dry[32] and liquid[60] milling, and also precipitation (sometimes called acid pasting) from strong acid solutions such as concentrated sulfuric acid[61], polyphosphoric acid[20], monomethylsulfuric acid[62], etc. In all cases, the "ripening" of the resultant particles is of critical importance. The greatest problems are encountered with the very small nanosized particles required for highly transparent pigments, which produce attractive metallic finishes. Such particles must be small and have well defined crystallinity to provide the required outdoor durability. To avoid light scattering, it is important not only to achieve the required small particle sizes, but also to prevent the tendency of small particles to flocculate after dispersion has been achieved at considerable cost. This tendency also leads to poor millbase viscosity and poor paint flow after dispersion. To improve the rheological properties of these pigments and thus help increase pigment concentration during dispersion and in paint formulations, which is in turn closely tied to environmental considerations, a great number of pigment surface treatments have been described in the patent literature. Among them are treatment with various functional derivatives of quinacridone, including the mono and disulfonic acids[63], some of their amides[64], and derivatives such as 2-phthalimidomethyl[65], 2-(3′,5′-dimethyl-pyrazol-1-yl) methyl[66], heterocyclic aromatic acid amides of aminomethyl-quinacridones[67], and many others. The effectiveness of such surface treatments is a function of the specific binders and solvent systems, as well as the presence of polymeric dispersants. An example of an effective surface treatment can be seen by comparing the appearance under an electron microscope of a transparent quinacridone magenta pigment dispersion formulated with untreated pigment (Figure 18–16) with the same dispersion formulated with surface treated pigment (Figure 18–17)[68]. It is apparent that the treated pigment, unlike its untreated counterpart, is deflocculated, shows significantly lower viscosity, and exhibits improved gloss and distinctiveness of image in the resulting finish. Some of the quinacridone derivatives mentioned above also serve as effective particle growth inhibitors.

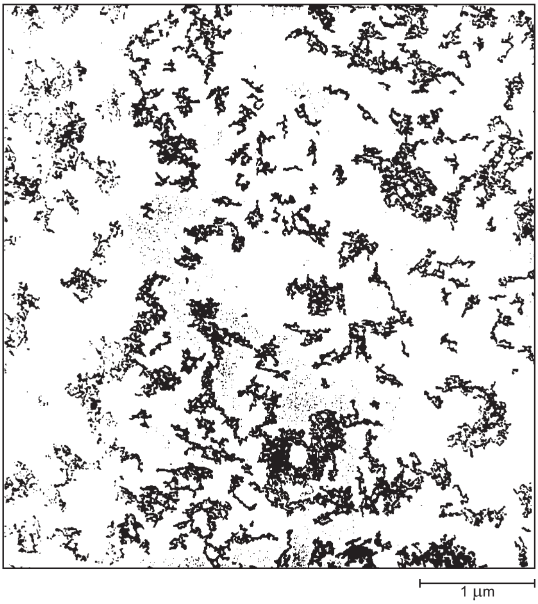


Figure 18–16: Electron photomicrograph (40 000 ×) of surface untreated 2,9-dichloroquinacridone magenta.

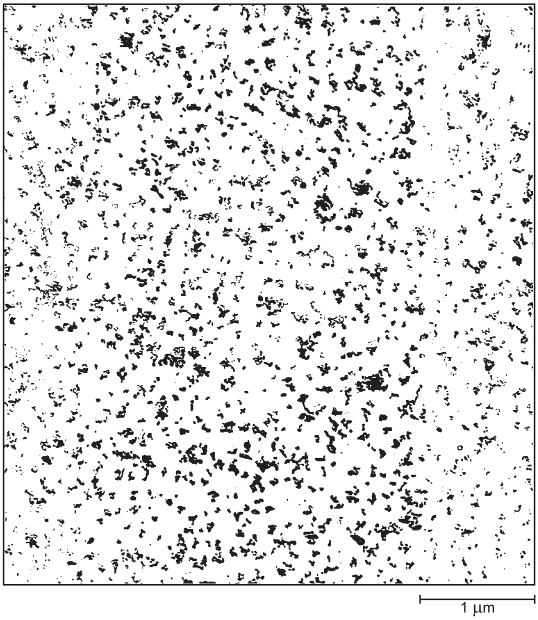


Figure 18–17: Electron photomicrograph (40 000 ×) of surface treated 2,9-dichloroquinacridone magenta.

18.12
Applications

Quinacridone pigments are used primarily for decorative and functional effects. They provide a variety of colors, and contribute to long term durability in a variety of systems.

The coatings industry is a major consumer of quinacridones. They are used in interior finishes, plastics for interiors of automobiles, architectural and industrial paints (whether solvent based or waterborne), powder coatings, and radiation curable finishes. They are also used in demanding printing ink applications, lithographic, sheetfed offset and metal decorating applications, and screen and textile printing. They are also used extensively in coloring various plastics, including polyvinyl chloride, polyethylene, polypropylene, polystyrene, acrylonitrile-butadiene-styrene, and polyethylene terephthalate. The least soluble quinacridones are usable in nylon. Quinacridones are also used for pigmentation of textile fibers such as polypropylene, polyester, and even (in some cases) nylon fibers.

Artists' colors utilize quinacridones because of the demand for specific colors with long lasting properties. More detailed information regarding applications of specific quinacridones can be found in many commercial publications, as well as in books devoted to pigment technology[69].

In addition, some quinacridones have found unusual applications. For example, both quinacridone and its 2,9-dimethyl derivative have been found to exhibit desirable photovoltaic characteristics[70], and show relatively high power conversion efficiencies in solar cell fabrication. Some quinacridones have also been found to be reasonably good photoconductors[71], and 2,9-dichloroquinacridone has been shown to be a photoreceptor in electrophotography[72]. A variety of other atypical applications have also been claimed in the patent literature.

18.13
Health and Safety Factors

Because of their high degree of insolubility in most organic solvents and water, quinacridone pigments are essentially not bioavailable, and are therefore practically not absorbed or metabolized in the body. Quinacridone shows low oral and dermal acute toxicity in the rat, with LD50 >10 g/kg and >2 g/kg respectively. It is also non-irritating to eye and skin[73]. Such figures demonstrate a low degree of acute toxicity. While long term health effect data for quinacridones is limited, in vitro mutagenicity testing for beta and gamma phase quinacridones gave negative results. Both pigments have been accepted for food contact application by the US Food and Drug Administration[74].

18.14
Business Aspects

In 1958, production of both beta and gamma polymorphs of quinacridone began in the USA at Newport, Delaware, with an annual capacity of 115 tons. Today, approximately 40 years later, annual worldwide sales are estimated at 3400 tons, a 30-fold increase! Major producers are Ciba SC, whose quinacridones are marketed as “Monastral” in North America and “Cinquasia” elsewhere. Clariant markets its products as “Hostaperm”, Sun Chemical as “Sunfast”, Bayer as “Quindo”, and Dainippon as “Fastogen”. Ciba, Clariant and Sun account for about 80 % of all sales. The remainder is shared by Bayer, Dainippon and other smaller producers, including Sudarshan in India. Estimated worldwide geographical distribution of quinacridone sales is as follows:

NAFTA Countries	42 %
Europe	30 %
Pacific Rim/Asia	24 %
Rest of World	4 %

In terms of volume, beta (violet) and gamma (red) quinacridones are still the most important pigments, followed by 2,9-dimethyl- and 2,9-dichloroquinacridone, and also various solid solutions. An increase in consumption of quinacridones usually follows the growth in various national economies. As with the rest of the organic pigment business, competition for the quinacridone market is usually intense, and prices have recently shown a downward tendency, particularly as capacity has been expanding. Additionally, most producers have been effecting better process improvement, including use of improved starting materials and better solvent utilization, driven by economic and regulatory requirements. In today’s competitive environment, such process economies and improved product performance are essential to enable producers to compete effectively.

Such product and process innovation is an ongoing aim in today’s pigments industry. There is always a need for improved saturation (brightness) of the various colors in the paint area, and for improved dispersibility, rheology, and resistance to flocculation, particularly in the transparent pigment grades, and also for compatibility with new coatings systems. In plastics systems, upgrades in dispersibility and in heat and dimensional stability (warpage) are always welcomed in the marketplace.

As a result of the overall excellence of the properties of quinacridone pigments, their broad color palette, availability, and reasonable pricing, quinacridones are today contributing to a more colorful world, and are making a positive contribution to the aesthetic side of human experience.

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19

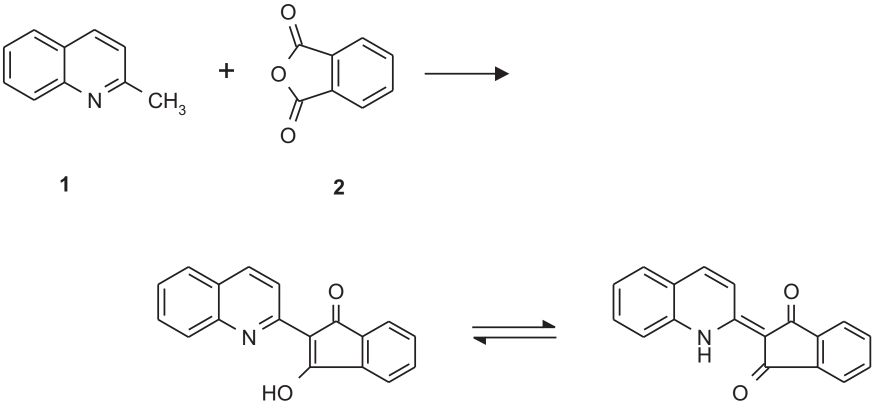
Quinophthalone Pigments

Volker Radtke

19.1

Introduction

Quinophthalone pigments are polycyclic compounds that derive their name from the parent compound quinophthalone (**3**), which was first synthesized by Jacobsen in 1882 by reacting quinaldine (**1**) with fused phthalic anhydride (**2**) (see Figure 19–1)[1].



1 **2**

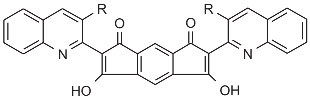
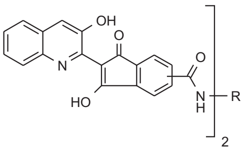
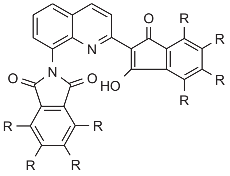
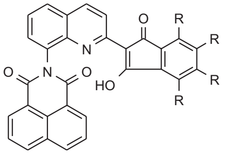
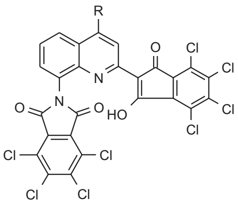
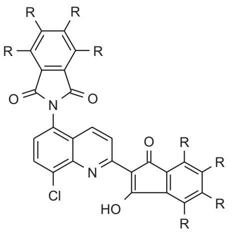
3a **3b**

Figure 19–1: Synthesis of quinophthalone.

Quinophthalone colorants have a long history as dyes, especially as disperse dyes, acid dyes and paper dyes[2].

The first quinophthalone pigments were described in the 1960s. Table 19–1 shows the chemical composition of quinophthalone pigments known from the patent literature, the shades of the products and the dates of the relevant patent applications.

Table 19–1: Quinophthalone pigments known from the patent literature.

Structure	*R*	*Shade*	*ref.*	*year*
4 	H OH	red yellowish brown	[4]	1965
5 	Arylene	yellow orange	[5]	1964
6 	Cl Br	greenish yellow	[6]	1968
7 	Cl	yellow	[7]	1975
8 	Alkyl Phenyl	yellow	[8]	1975
9 	H Halogen	yellow	[9]	1976

19.2 Historical Background

Quinophthalone (**3**) and its derivatives are normally products with good solubility in organic media. Neutral compounds like 3-hydroxyquinophthalone and its brominated derivatives are often used as disperse dyes for the coloration of polyester fibres[3] and styrenics. Sulfonated derivatives represent suitable anionic dyes for the coloration of wool, silk, paper and food. Products carrying basic side chains with quaternary nitrogen atoms are used for coloring paper[4].

Simple quinophthalone molecules are not suitable as pigments under standard application conditions in plastics and paints. In order to improve their resistance to solvents and migration several routes were followed:

1. Doubling the molecule by replacing phthalic anhydride with pyromellitic dianhydride[5],
2. Increasing the molecular weight by means of diamide bridges built from trimellitic acid and aromatic diamines[6],
3. Introducing suitable substituents, especially halogen atoms and imide groups[7–10].

The pigments produced following these routes are yellow, orange and brown, with remarkable lightfastness, good resistance to solvents and migration, and satisfactory heat stability.

Only one of them was launched as a regular commercial grade by BASF in 1973: Lithol® Fast Yellow 1090, the reaction product of 8-aminoquinaldine (**10**) with 2 equivalents of tetrachlorophthalic anhydride (**11**).

This pigment is listed in the Colour Index[11] as Pigment Yellow 138. Table 19–2 summarizes its C.I. constitution number, CAS and EINICS numbers.

During the 1980s and 1990s no new quinophthalone structures were published; only process applications were filed[12].

Table 19–2: Quinophthalone and other high performance yellow pigments.

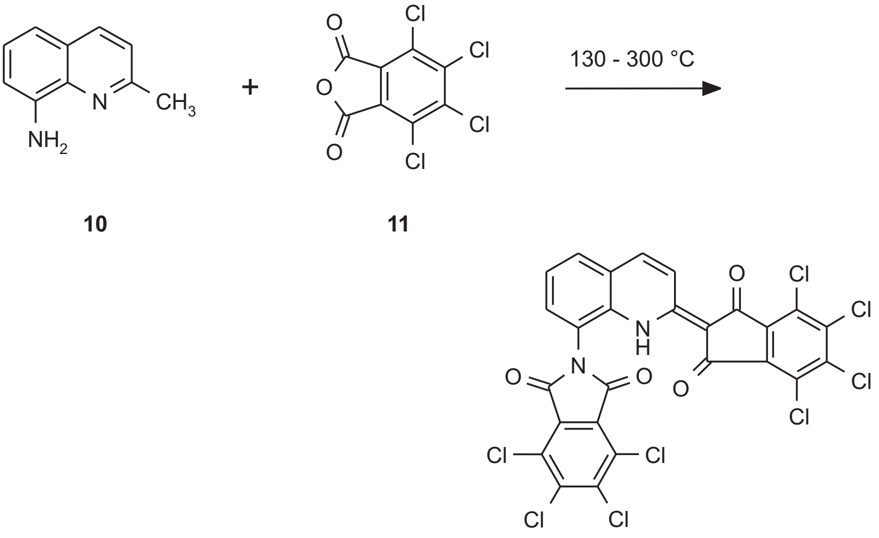
C.I. name	*C.I. constitution*	*CAS no.*	*EINECS no.*	*CAS name/ chemical formula*
P.Y. 138	56300	30125-47-4	250-063-5	1H-Isoindole-1,3(2H)-dione, 4,5,6,7-tetrachloro-2-[2-(4,5,6,7-tetrachloro-2,3-dihydro-1,3-dioxo-1H-inden-2-yl)-8-quinolinyl]-
P.Y.139		36888-99-0	253-256-2	2,4,6(1H,3H,5H)-Pyrimidinetrione, 5,5′-(1H-isoindole-1,3(2H)-diylidene)bis-
P.Y. 185		76199-85-4	278-388-8	Acetamide, 2-cyano-2-[2,3-dihydro-3-(tetrahydro-2,4,6-trioxo-5(2H)-pyrimidinylidene)-1H-isoindol-1-ylidene]-N-methyl-

19.3
Methods of Manufacture

The basic patent[7] describes the synthesis of PY 138 by reaction of 1 molecule of 8-aminoquinaldine (**10**) with twice the stoichiometric amount of tetrachlorophthalic anhydride (**11**) in an inert solvent in the presence of zinc chloride (Figure 19–2). Suitable solvents include halogenated hydrocarbons, diphenyl, diphenylether or mixtures of these substances, high boiling alcohols, *N*-alkylpyrrolidone, dimethylformamide, dimethylacetamide or benzoic acid[13].

The product "crude" isolated after dilution of the reaction mixture does not have pigmentary properties. It crystallizes as large irregular particles which have low color strength. It is finished to the required particle size by standard procedures, e.g. by wet milling in aqueous media[14] or by dry milling followed by solvent treatment at elevated temperatures[15]. Suitable solvents are alcohols, ketones, carboxylic acids, aliphatic carbonamides, esters, cyclic hydrocarbons, aromatic chloro- or nitrohydrocarbons or mixtures of these substances.

The formation of the imide ring in PY 138 by reaction of the primary amino group with one mol of tetrachlorophthalic anhydride is faster than the formation of the phthalone ring. It is therefore possible to isolate 1 : 1 condensation products, which can be used as starting materials for asymmetrical quinophthalone pigments. So far products of this type have not been commercialized.



6

Figure 19–2: Synthesis of P. Y. 138.

19.4
Typical Properties and Major Reasons for Use

PY 138 is a greenish yellow pigment with good heat stability and resistance to solvents and migration. It offers good light and weathering fastness and is stable to acid and alkali. The pigment has its main fields of application in high performance plastics and coatings.

Hiding power and tinting strength depend largely on the shape and size of the primary particles. Grades with low specific surface areas of 15 m^2/g provide the maximum of hiding power and very good rheological properties in paints even at high pigment concentrations. These products lend themselves to use in solid shades. Products with higher specific surface areas are more transparent and exhibit higher color strength, at the expense, however, of inferior light and weathering fastness and reduced rheological properties. These grades are also suitable for coloring plastics.

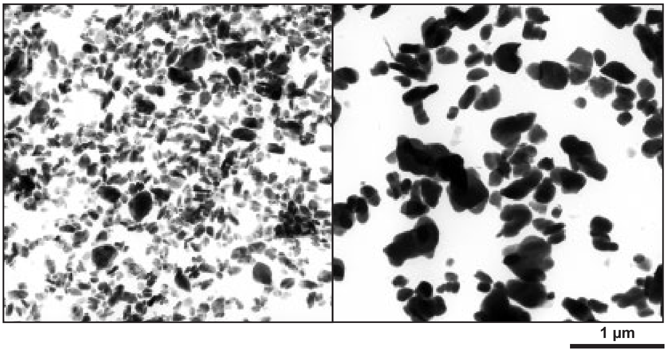
Table 19–3 summarizes typical properties of PY 138 grades.

Table 19–3: Typical properties of quinophthalone pigments.

	Paliotol® Yellow		
	L 0960 HD	***L 0962 HD***	***K 0961 HD***
density (g/cm^3)	1,82	1,82	1,82
bulk volume (l/kg)	2,5	3,8	4,5
specific surface (m^2/g)	24	15	25
particle size distribution (mean) [nm]	220	390	220
oil absorption (g/100 g)	40	30	40
hue angle at 1/3 SD[1)]	97	95	97
reduction ratio at 1/3 SD[2)]	6,5	4,3	6,2
light fastness[3)]			
full shade	8	8	8
1/3 SD	7	7	7
fastness to weathering[4)]			
full shade	4–5	4–5	4–5
1/3 SD	3–4	4	3–4
heat resistance (°C)[5)]	250	250	260
fastness to overspray[6)]	5	5	
chemical resistance[7)]			
2 % HCl	5	5	5
2 % NaOH	5	5	5
fastness to solvents[8)]			
water	5	5	5
Ethanol	5	5	5
Butylacetate	5	5	5
MEK	4	4	4
Xylene	4	4	4
mineral spirit	5	5	5
Solvenon PM	4–5	4–5	4–5

19.5
Pigment Grades and Discussion of Individual Pigments

The properties described above qualify quinophthalone pigments for applications including high quality industrial finishes, coloring of plastics and metal deco inks. Commercial products are supplied as powders, pigment preparations and liquid dispersions.



Paliotol® Yellow L 0960 HD **Paliotol® Yellow L 0962 HD**

Figure 19–3: Electron micrographs of two commercially available P.Y. 138 grades.

The influence of the finishing conditions on the size of the primary particles is obvious (Figure 19–3). Paliotol® Yellow L 0960 HD being recrystallized at lower temperatures has smaller and less uniform particles than Paliotol® Yellow L 0962 HD, which is finished at higher temperatures. The plastic grade K 0961 HD is similar to L 0960 HD in primary particle size, but differs in size of the agglomerates because of its different final milling process.

The remission spectra (Figure 19–4) can be elegantly interpreted by means of the optical constants, on the basis of Mie's theory. Small remission values for blue light, due to the solid-state absorption band (40–460 nm) are followed by a steep incline at 500 nm. At longer wavelengths the optical window is open to green and red light, which can be scattered effectively by the TiO_2 particles of the white reduction.

The remission edge of L 0962 is shifted to longer wavelengths. As a result, L 0962 HD appears more reddish than L 0960 HD.

Electrokinetic sonic amplitude (ESA) measurements (water / ethanol 4:1, Matec MBS 8000) show a very similar picture for the two quinophthalone pigments. They carry a very small negative charge and their isoelectric points are close to pH 3. Both pigments can be used in aqueous and solvent-borne systems. From the ESA-data (Table 19–4) it can be concluded that electrostatic forces play only a minor role in the stabilization of these systems.

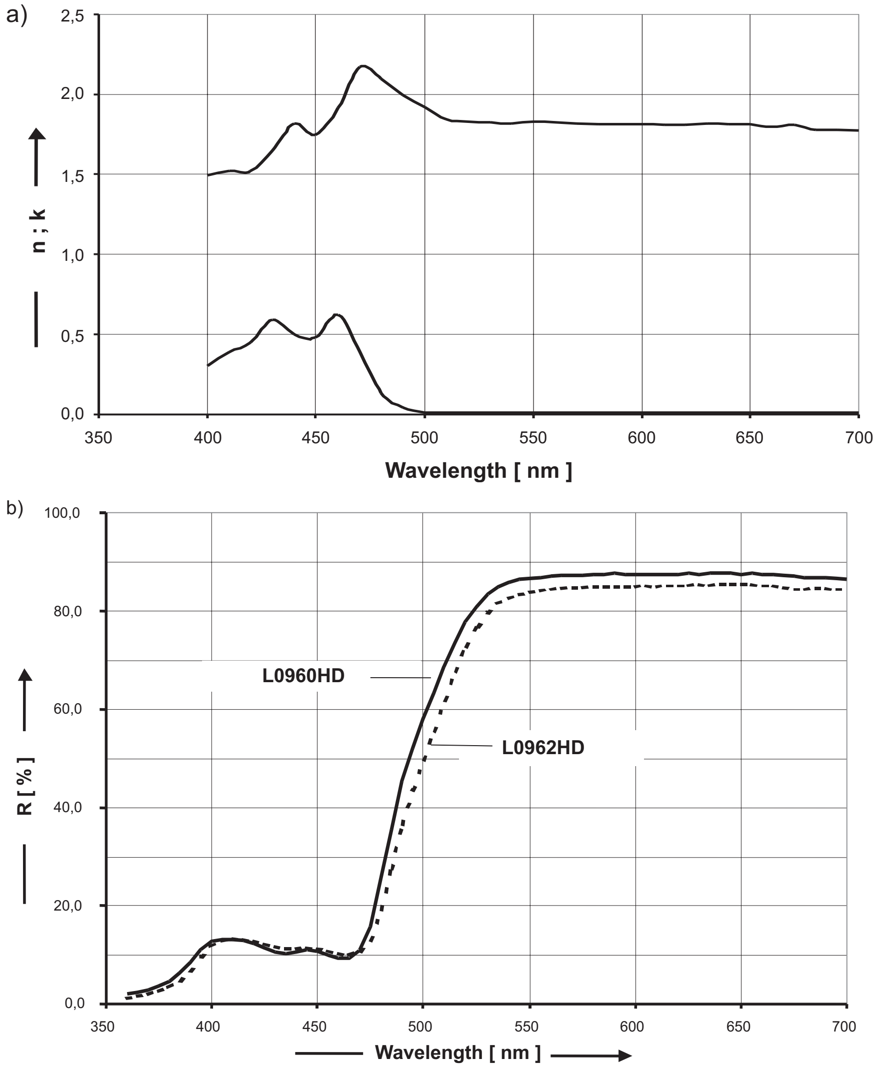


Figure 19–4: Optical constants (a) and remission spectra (1:10 TiO_2) (b) of P.Y. 138.

Table 19–4: ESA data of quinophthalone pigments.

	Initial ESA signal [µPa/V/m]	*isoelectric point [pH]*
L 0960 HD	–52	2,70
L 0962 HD	–56	2,80

19.5.1
Discussion of Individual Pigments

Paliotol® Yellow D 0960 is specifically used in metal deco and screen printing inks, where its very good light- and weather fastness is required.

The good temperature stability in HDPE and the very good light fastness in full shade and white reductions qualify **Paliotol Yellow K 0961 HD** for its use in plastics. Additional merits of the pigment are its high tinting strength and chroma. K 0961 HD is suitable for PVC as well as for polyolefins and engineering plastics, except polyamide. Significant applications include HDPE gas pipes, exterior automotive body parts and Lego building systems.

The pigment is also available as several pigment preparations: Eupolen® Yellow 09–6101 (for masterbatches) and Luprofil Yellow 09–6105 (for PP fibers and yarns). These predispersed pigments offer technical advantages in terms of processability and color strength.

For paints, two grades are offered, differing in the size of the primary particles. Paliotol Yellow L 0960 HD has a mean particle size of ~ 220 nm and a specific surface area of 24.0 m^2/g, while L 0962 HD has particles of ~ 390 nm and a specific surface area of 15 m^2/g.

Paliotol Yellow L 0960 HD offers a fair compromise between tinting strength and chroma on the one hand and hiding power, durability and rheological behavior on the other. Although the pigment is stable to acid and alkali in oven-cured systems, it exhibits some sensitivity to fresh concrete. The pigment shows excellent weather fastness in deep shades, but fades rapidly in tints. For durability and economic considerations, it is best combined with opaque inorganic pigments such as nickel titanate or bismuth vanadate. Paliotol Yellow L 0960 HD is mainly used in industrial paints. It is also available in the form of a liquid dispersion in an aldehyde resin with wide compatibility for solvent based paints: Sicoflush® P Yellow 0960.

The coarsely crystallized **Paliotol Yellow L 0962 HD** offers better weathering fastness, improved hiding power and good rheological properties at the expense of reduced color strength. Paints for commercial transport and automotive OEM and refinish fulfill durability requirements with a pigment:TiO_2 ratio of up to 1:4. L 0962 HD can also be used in waterborne paints of pH 8.5 – 9.0. A co-finished pigment of L 0962 HD with bismuth vanadate (Paliotan® Yellow L 1145) offers appreciable economic and technical advantages.

19.6
Pigment Manufacturers: Economics

The first quinophthalone pigment appeared on the German market in 1973: Lithol Fast Yellow 1090, produced by BASF.

This grade was replaced with Paliotol Yellow L 0960 HD, D 0960 and K 0961 HD a few years later. In 1982, a pigment with lower specific surface, better hiding power and outdoor durability was launched as Paliotol Yellow L 0962 HD.

BASF is still the sole producer of PY 138. The company is backward integrated in the synthesis of the key intermediate 8-aminoquinaldine, which is part of the BASF "Verbund". Excellent technical properties and a competitive cost / performance ratio have formed the basis for the success of PY 138 since its introduction. A new 1000 tonnes/year plant came on stream in Ludwigshafen in 1999. The unit, which consists of two closed production lines connected in series, replaces an older line of lower capacity. It is managed by modern process control equipment and produces no effluent. This investment will help to satisfy the demand for PY 138 grades, sales of which achieved double-digit growth rates in the field of high performance paints and the coloration of plastics in recent years.

Quinophthalone colorants, which are now available in the form of powders, granules, predispersed pigments and liquid dispersions, are listed in Table 19–5.

Table 19–5: Known pigment brands and manufacturers of quinophthalone pigments[1].

P.Y. 138	*Manufacturer*	*Main application*	*Physical form*
Paliotol Yellow D 0960	BASF	Printing ink	Powder
Paliotol Yellow K 0961 HD	BASF	Plastic	Powder
Paliotol Yellow L 0960 HD	BASF	Paint	Powder
Paliotol Yellow L 0962 HD	BASF	Paint	Powder
Sicoflush P Yellow 0960	BASF	Paint	Liquid dispersion
Eupolen Yellow 09-6101	BASF	Plastic	Powder
Luprofil Yellow 09-6105	BASF	Plastic	Powder

19.7
Toxicology and Ecology

Quinophthalone pigments do not exhibit acute toxicity in animal tests by oral, dermal and inhalative application. Other tests have shown that they do not cause irritation of the skin or mucous membranes. The Ames test for mutagenicity gave negative results, while genotoxic testing shows no clastogenic effects.

Quinophthalone pigments are poorly soluble in water. They exhibit practically no toxicity to fish and daphnia, as values determined for fish (orfe, acute, 48 h, $EC_{50} >$ 100 mg/L; daphnia, $EC_{50} >$ 100 mg/L) indicate.

Acknowledgements

I should like to thank my colleagues Dr. Th. Clemens, Dr. H. Endriss, Dr. P. Erk, Dr. W. Lotsch and Dr. B. Sens for their cooperation.

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2 Ullmann, Encyclopedia of Industrial Chemistry, 5th edn., 1993, Vol. A 16, p. 525
3 B.K. Menukian and A. Mangini, Chimie 24 (1970) 328
4 DP 33 29 340 to BASF
5 CH-PS 463 667 to Sandoz
6 DP 12 79 258 to Ciba
7 DP 17 70 960 to BASF
8 DE-OS 26 26 271 to Teijin
9 DE-OS 26 38 528 to Teijin
10 DE-OS 27 06 872 to Teijin
11 Colour Index International, Pigment & Solvent Dyes, Society of Dyers and Colourists: 2nd edn. Issue on CD-Rom, 1997, 3rd edn. Issue on CD-Rom, 1999
12 DE-OS 196 63 880 to Bayer
13 DP 40 20 423 to BASF
14 DP 27 46 164 to BASF
15 DP 23 57 077 to BASF

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20

Thiazines, Oxazines and Other Novel High-Performance Pigments

B. L. Kaul

20.1
Introduction[1]

In modern society, pigments are widely used for decorative and even functional purposes in plastics, fibers, printing and writing inks, coatings and cosmetics, to name only a few selected applications.

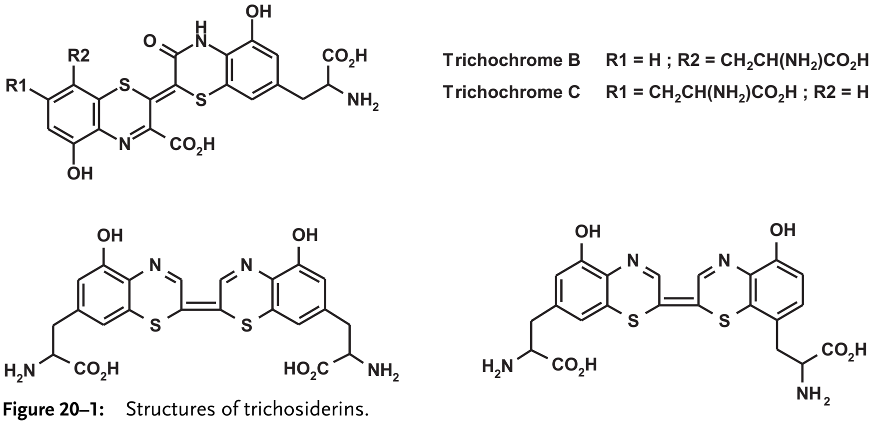
However, as modern industry becomes more sophisticated and successful in developing better performing and more durable products, requirements for higher value-in-use pigments and colorants are becoming acute. Moreover, the constant increase in ecological and environmental conscientiousness and the frequent regulatory constraints regarding the fate of products from cradle to grave, have given a new impetus to the development of novel π-electron systems as organic pigments.

Novel thiazines, oxazines and other novel high-performance pigments are an outcome of the research effort at Clariant to meet these newer requirements.

20.2
Thiazine (THI) Pigments[2,3]

The THI chromophore has been borrowed from nature. THI pigments structurally belong to the biochrome family of so-called “trichosiderins”, as shown in Figure 20–1, which are found in natural keratinoid materials such as red human and animal hair, as well as bird and chicken feathers. Biologically they are derived from sulfur and aromatic ring-containing amino acids such as tyrosine.

In Figure 20–2, the basic structure and chromophoric system of THI pigments is depicted. It consists of two thiazine residues conjugated to each other by a double bond. As we will see later on, the two delta-lactam groups are not only responsible for their color but particularly for their functionalities, like gamma lactam groups in the case of diketopyrrolopyrroles, which are also shown in Figure 20–2. Furthermore, careful inspection of the inherent intramolecular chromophore of THI (shown in bold) indicates a close analogy to the core DPP chromophore.



Trichochrome B R1 = H ; R2 = $CH_2CH(NH_2)CO_2H$

Trichochrome C R1 = $CH_2CH(NH_2)CO_2H$; R2 = H

Figure 20–1: Structures of trichosiderins.

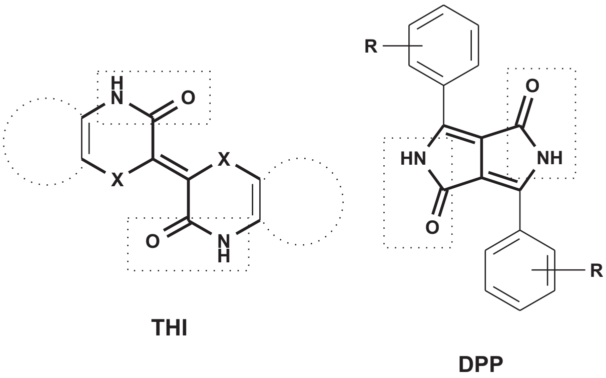


Figure 20–2: THI core chromophore versus DPP core chromophore.

20.3 Synthesis

The THI chromophore is readily synthesized by the interaction of two moles of an *o*-aminothiophenol (or its salts) with one mole of a 2,3-dihalo-maleic or fumaric acid or their derivatives, as shown in Figure 20–3. The classical indigo synthetic approach is also described.

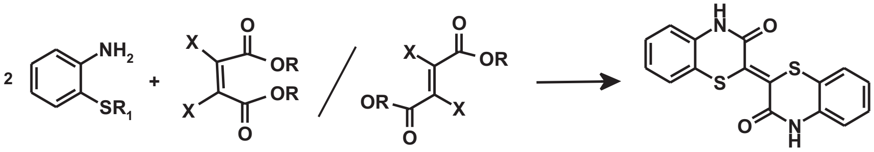


Figure 20–3: Synthesis of THI pigments.

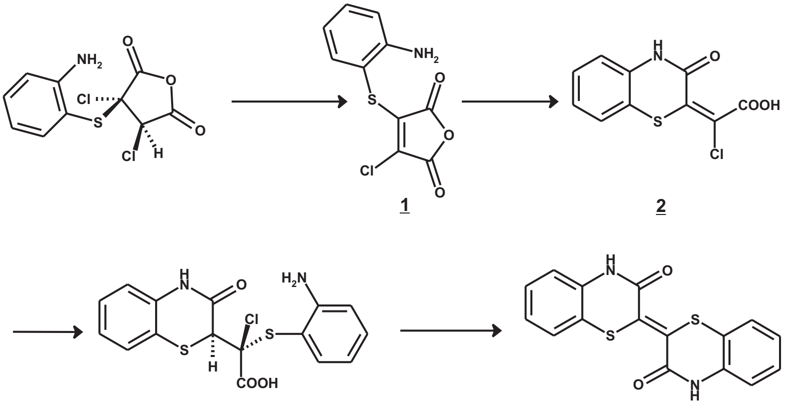


Figure 20–4: Mechanism of the formation of THI pigments.

The synthesis has been shown to occur stepwise (Figure 20–4), in which one mole of an *o*-aminothiophenol reacts initially with one mole of a dihalo-maleic or -fumaric acid derivative to lead first to the monocondensed structure **1**, and then to the monocyclized product **2**. The intermediate **2** then reacts with a second mole of an *o*-aminothiophenol to lead to *cis* or *trans* THI, depending upon the temperature and the reaction conditions employed. Thus it is possible to readily obtain asymmetrical THI systems not obtainable using the classical indigo synthesis.

Because of their cyclic carbonamide groups, THI pigments can readily undergo copigmentation and formation of organic alloys / solid solutions with chemically related pigments such as diketopyrrolopyrroles (DPP), quinacridones, isoindolinones and benzimidazolone pigments, thereby enabling variations of shades and fastness properties according to various value-in-use requirements. However, from consideration of the size, shape and other molecular characteristics, and especially their highly saturated colors, THI pigments seem to be particularly compatible with DPP pigments, thereby readily providing supramolecules such as shown in Figures 20–5 and 20–6.

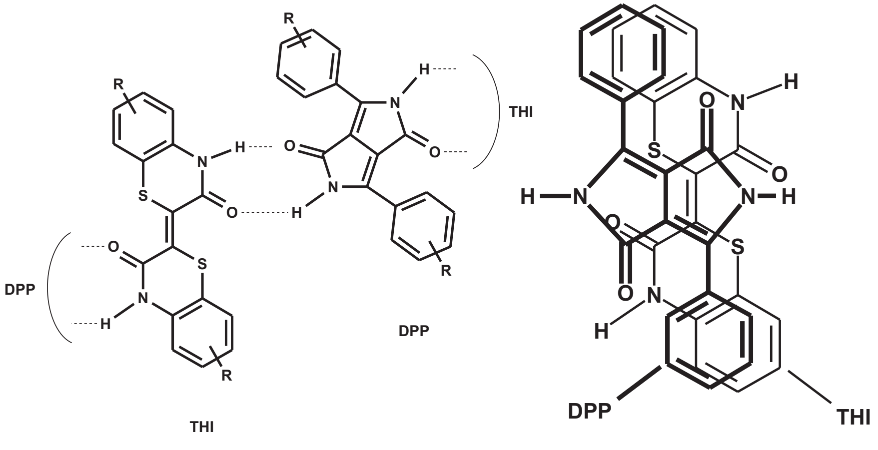


Figure 20–5: Supramolecularly conjugated THI-DPP chromophores.

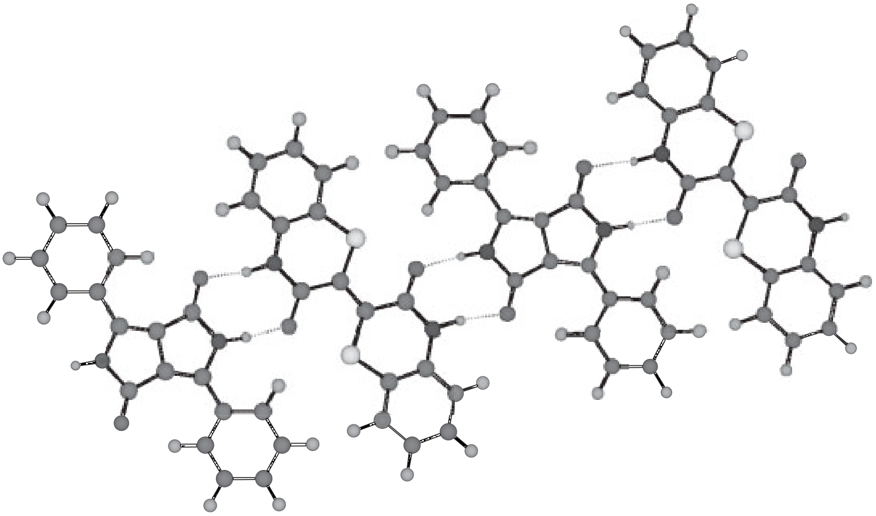


Figure 20–6: Supramolecularly conjugated THI-DPP chromophores

Since the individual molecules are of the same size and shape, with similar polarities and other electronic configurations, their ideal intermolecular bondings and formation of co-pigments can lead to a synergistic effect, resulting in better performance than from the corresponding individual molecules.

20.4
Crystal Structure[6,7]

Figure 20–7 shows the crystal structure of a THI-pigment confirming its *trans* linearity and planar structure.

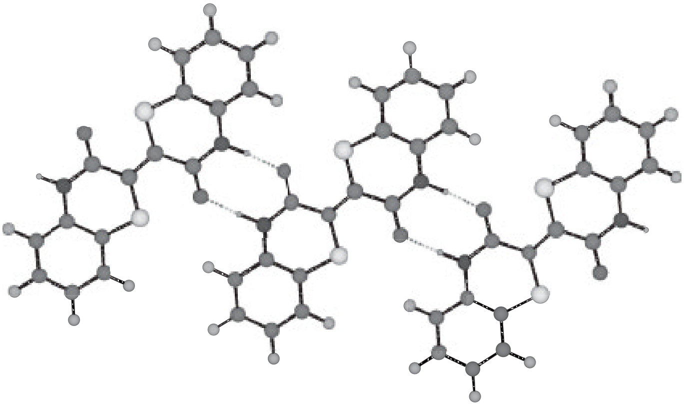
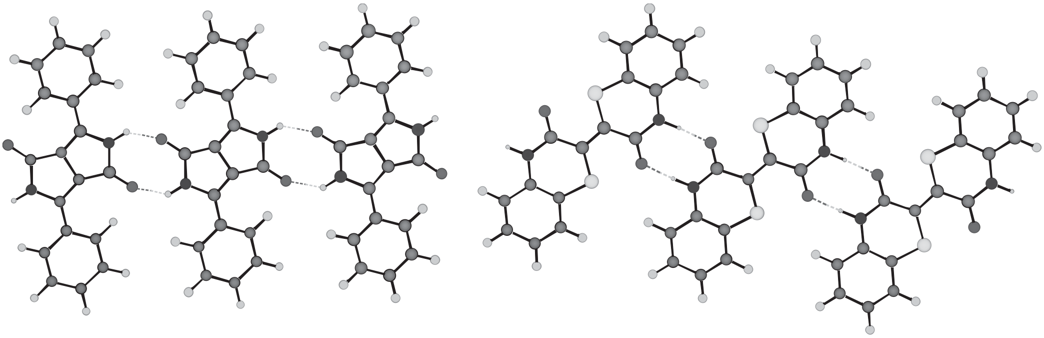


Figure 20–7: Crystal structure of a THI pigment.

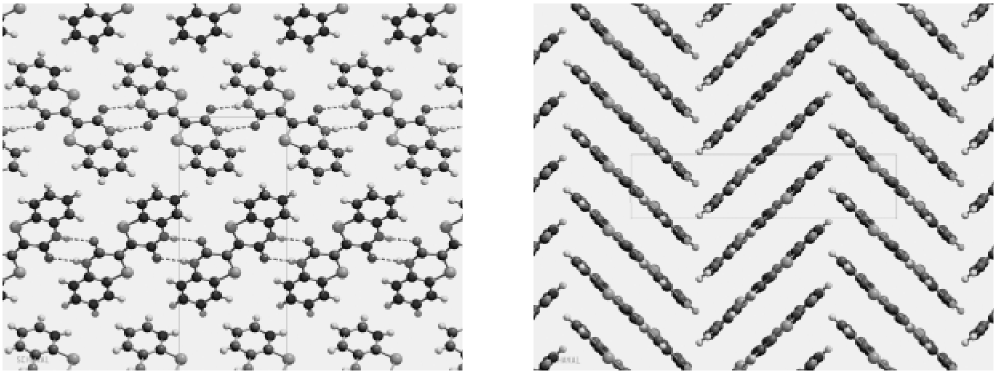


DPP molecule **THI molecule**

Figure 20–8: Structure of THI versus DPP pigments.

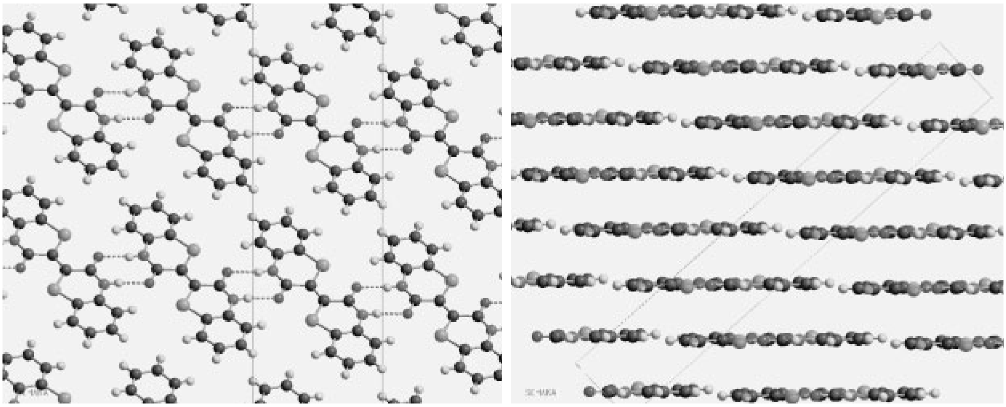
Figure 20–8 shows the crystal structure of a thiazine indigo compared to a diketopyrrolopyrrole with very similar molecular size, shape and particularly intermolecular hydrogen bondings, which are mainly responsible for their pigmentary character such as insolubility, heat stability and exposure durability.

Like many of the high-performance pigments such as quinacridones, DPPs and phthalocyanine pigments, THI pigments can exist in more than one crystal form. So far, three different crystal modifications with different crystal packings have been identified.



View along the x axis View along the z axis

Figure 20–9: Crystal structure of the α modification of a THI pigment.



View along the x axis

View along the y axis

Figure 20–10: Crystal structure of the β modification of a THI pigment.

Whereas the α-phase illustrated in Figure 20–9 shows a “head-to-tail” ladder-like packing of its molecules, in the β-phase shown in Figure 20–10, molecular chains are formed parallel to each other, analagous to the packing found in β-quinacridone or DPP Red BO molecules.

20.5
Color and Constitution

THI pigments owe their color and functionality to their so-called “supramolecular conjugation” rather than to their inherent intramolecular indigo H-chromophore. Thus, although THI pigments provide only yellow solutions when dissolved, their shades vary between yellow and red in the solid state as pigments. Absorption spectra in solution and in the solid state as dispersions in plasticized PVC usually show a difference of almost 90 nm, confirming supramolecular conjugation similar to that of quinacridones and DPP pigments.

20.6
Economy of Use

Here, of particular importance is their very high opacity coupled with highly chromatic colors, which in turn contribute towards even further opacity by enabling combinations with opacifying but less chromatic inorganic pigments. THI pigments are thus preferred for mass-tone applications in most areas.

20.7
Application Properties and Value-in-Use

THI pigments are suitable for almost all applications of organic pigments except engineering polymers, where they tend to go into solution. In low concentrations they provide high value-in-use as a result of:

- their heat stability in polyolefins up to 290–300 °C
- enabling warpage- / deformation-free HDPE moldings
- high opacity coupled with very high color saturation
- ease of incorporation (dispersion, flow, etc.)
- chemical inertness
- high insolubility in almost all solvents
- high performance in the intended applications (processability and durability)
- ability to form supramolecules with synergistic values
- relationship to nature and thus potential environmental compatibility
- economies of use

For paints, their very high opacity, excellent gloss and high durability, particularly in combination with other organic and inorganic pigments in mass tone, are their main outstanding characteristics. Their exceptionally high opacity also enables the production of coatings with less pigmentation levels and thereby not only less cost of coloration but also fewer of the technical problems usually encountered in the coatings field, where pigment loading is always a critical factor. Also, the productivity of the coating application process itself is increased because of the reduced demand for paint to achieve the required hiding and therefore a reduced time required to dry and/or cure the paint.

For plastics, of particular interest is the finding that these pigments do not cause warpage of HDPE moldings, thereby enabling use, for example, in bottle crates and other high-precision HDPE moldings of “stable” forms.

Because of their color saturation, opacity, non-toxicity and insolubility, THI pigments would also be potentially suitable as cosmetic colors.

Because of their high opacity, THI pigments do not provide any advantage over azo condensation or perylene pigments for fiber applications.

THI pigments also do not offer any advantage over state-of-the-art pigments in white reductions for paint applications.

For printing ink application, however, their very high opacity could be of interest in certain specialty applications.

20.8
Pigment grades

Yellow to red THI pigments will be made available in plastics and coatings grades.

20.9
Pigment Specifications and Manufacturers

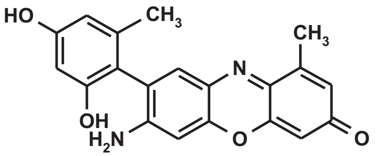
THI pigments are proprietary pigments from Clariant, and are not yet commercially available. A typical electron photomicrograph of a THI Red is shown in Figure 20–11.

Figure 20–11: Electron photomicrograph of a THI pigment

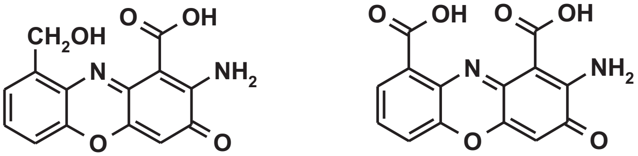
20.10
Oxazine Pigments[4,5]

The oxazine chromophore has also been found in nature (Figure 20–12). The corresponding orange-red dioxazine, triphenodioxazine has long been known as a synthetic chromogen. It is too soluble in organic solvents and/or polymers and resins, however, to be used as an organic pigment. Annellation of the outer rings, for example with *N*-alkylindole, as is the case with Pigment Violet 23, more commonly known as carbazole dioxazine violet, leads not only to a bathochromic shift due to the extension of its conjugating π-electron system, but also to increased insolubility and hence pigmentary functionality. The sparing solubility of C.I. Pigment Violet 23 is not simply due to its higher molecular weight but is also apparently due to stronger π-π interactions as a result of its extended and enriched electron system.

CI Pigment Violet 23 is now believed to possess an angular structure rather than the linear form indicated in textbooks (Figure 20–13). CI Pigment Violet 23 is reddish-violet in color and is characterized by an exceptionally high tinting strength and unique vividness of shade, very good light fastness and very good heat stability in almost all plastics except nylon. Although used to tint phthalocyanine blues to



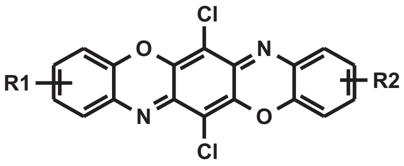
Aminoorceine



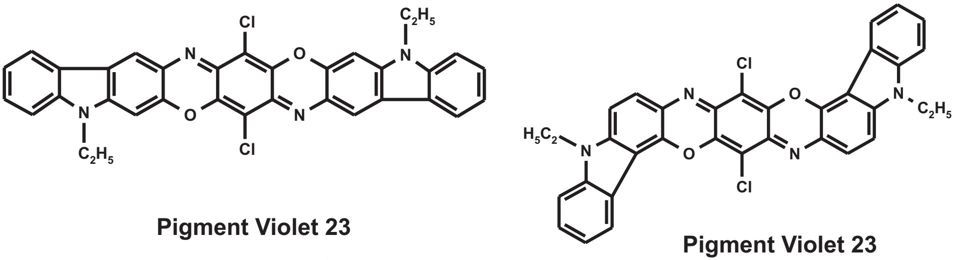
Cinnabarine

Cinnabaric acid

Figure 20–12: Oxazine chromophore as found in nature.



(orange - red)



Pigment Violet 23
(old structure)

Pigment Violet 23
(new structure)

Figure 20–13: Tripheno-dioxazine pigments.

produce reddish-blue shades, it tends to dissolve in polymers and resins, particularly polar systems, when used in low concentrations.

As part of a general program to improve performance characteristics of the traditional carbazole dioxazine pigment in such areas as bleed resistance, solvent fastness and heat stability, and at the same time to extend the range of shades beyond violet, a new class of dioxazine pigment bearing quinoxalinedione and benzimidazolone moieties in place of carbazole residue has been developed at Clariant (Figure 20–14). By simple manipulation of the substituents on the heterocyclic

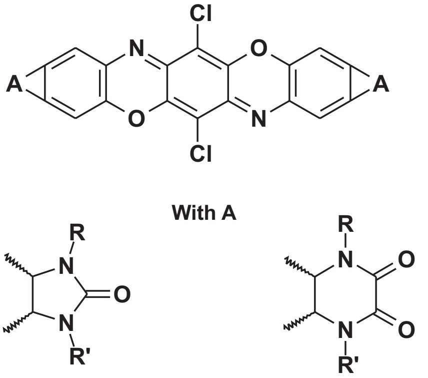


Figure 20–14: Novel quinoxalindione- and benzimidazolone-dioxazine pigments.

nitrogen atoms to influence the supramolecular conjugation and crystal packing, it has been possible to produce pigments varying in shade from bordeaux via red violet to reddish blue.

20.11
Chemistry

Preparation of the benzimidazolone-dioxazine pigments usually involves a multistep synthesis followed by finishing. A typical reaction scheme depicting the synthesis of the unsubstituted derivative, but which can be generalized for all other substituents, is shown in Figure 20–15.

Nucleophilic aromatic substitution of one chlorine atom in 1,3-dichloro-4,6-dinitrobenzene with ammonia yields 2,4-dinitro-5-chloroaniline. Nucleophilic aromatic substitution of the remaining chlorine by methoxide leads to 5-methoxy-2,4-dinitroaniline. Subsequent reaction of the amine function with chlorosulfonyl isocyanate followed by hydrolysis gives 5-methoxy-2,4-dinitro-phenylurea. Following reduction of the two nitro-groups and ring closure, 6-methoxy-5-amino-benzimidazolone (**2**) is obtained. Reaction with chloranil followed by ring closure results in the crude pigment, which is then finished in a final step.

Of special note is the linear structure of the resulting molecules (Figure 20–16), unlike the angular structure of Pigment Violet 23, as confirmed by NMR. This is perhaps due to the known higher reactivities of the 5 and 6 positions of the benzimidazolone molecule.

Figure 20–17 shows the crystal structure of the *N*,*N*-diethyl[7] derivative, further confirming the linearity of the molecule as well as the intermolecular hydrogen bondings responsible for the high insolubility, heat stability and exposure durability.

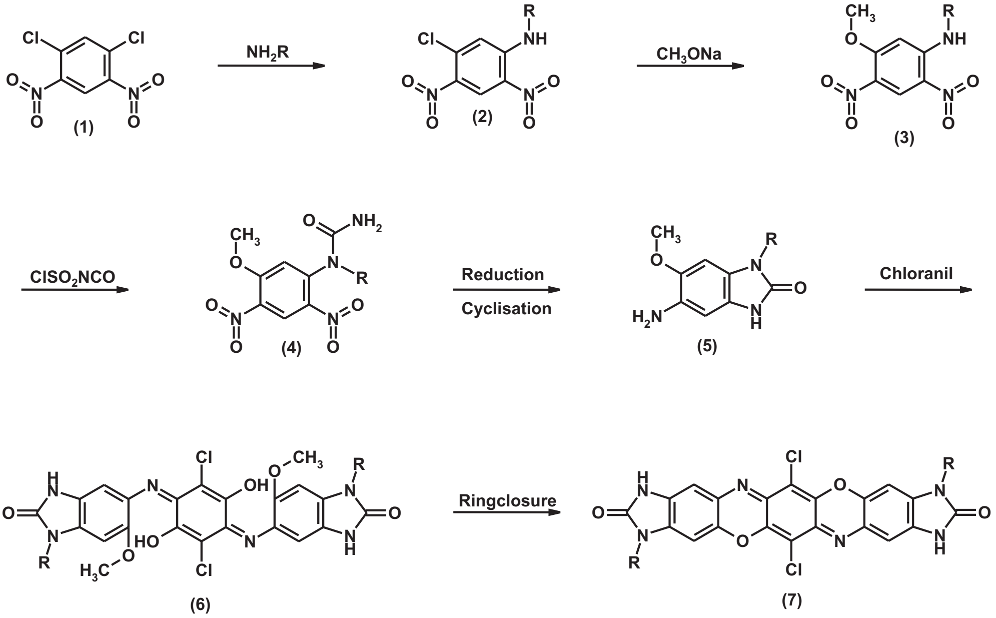


Figure 20–15: Typical synthesis of benzimidazolone-dioxazine pigments.

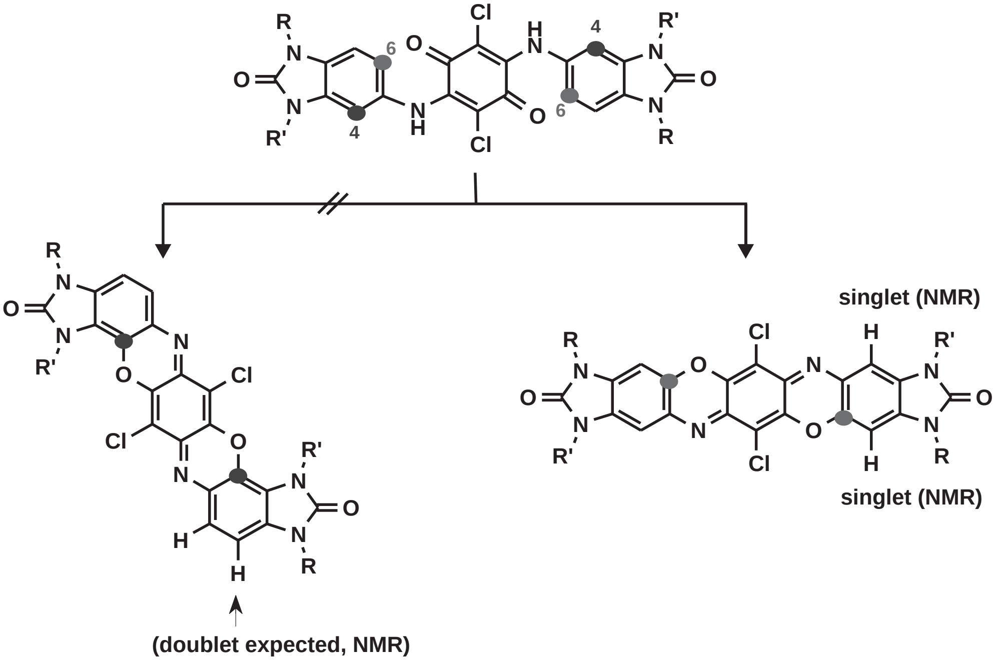


Figure 20–16: Cyclization and structure of benzimidazolone-dioxazine pigments.

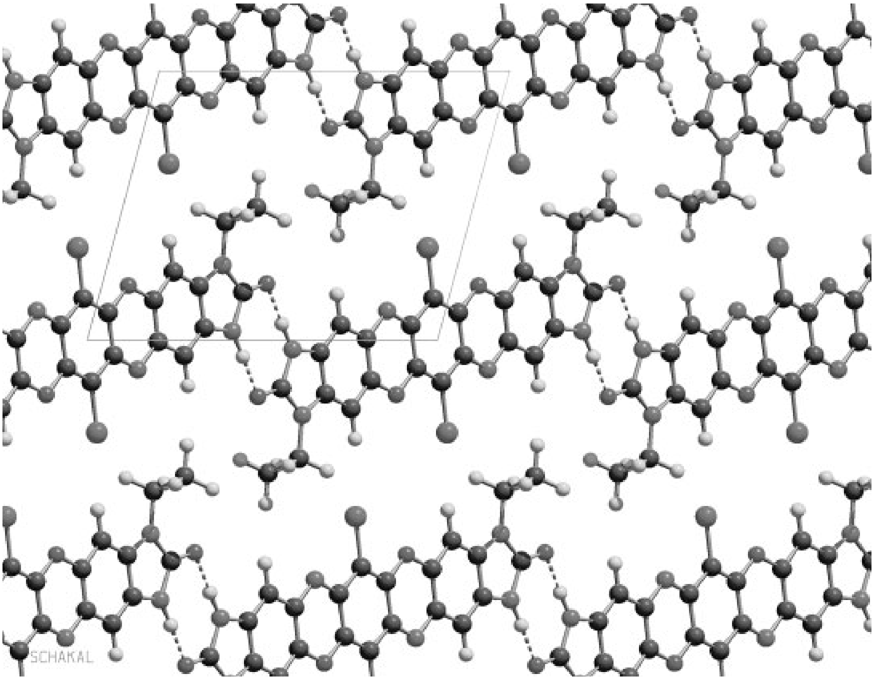


Figure 20–17: Crystal structure of benzimidazolone-dioxazine pigments.

20.12
Color and Constitution

As has been demonstrated, the annellated imidazolone rings do indeed contribute toward the color appearance and the functionality of the resulting benzimidazolone-dioxazines, and the substituents on the nitrogen atoms play an important role in imparting color to the resulting systems. It is believed that, as in the case of THI pigments, supramolecular conjugation and not simple π-π interactions or intermolecularly hydrogen bonded stacking of molecules is responsible for the color and the functionality of this new class of pigments.

The proof of this hypothesis, and particularly of the role of supramolecular conjugation in explaining the relationship between color and constitution of organic molecules, is provided by the absorption spectra of the carbazole-dioxazine pigment and the three benzimidazolone-dioxazine pigments shown in Figure 20–18.

Of particular importance is the marked difference between the absorption spectra of the *N*-methyl and those of *N*-ethyl derivatives. None of the prevailing theories of color and chemical constitution can explain or predict these distinct differences.

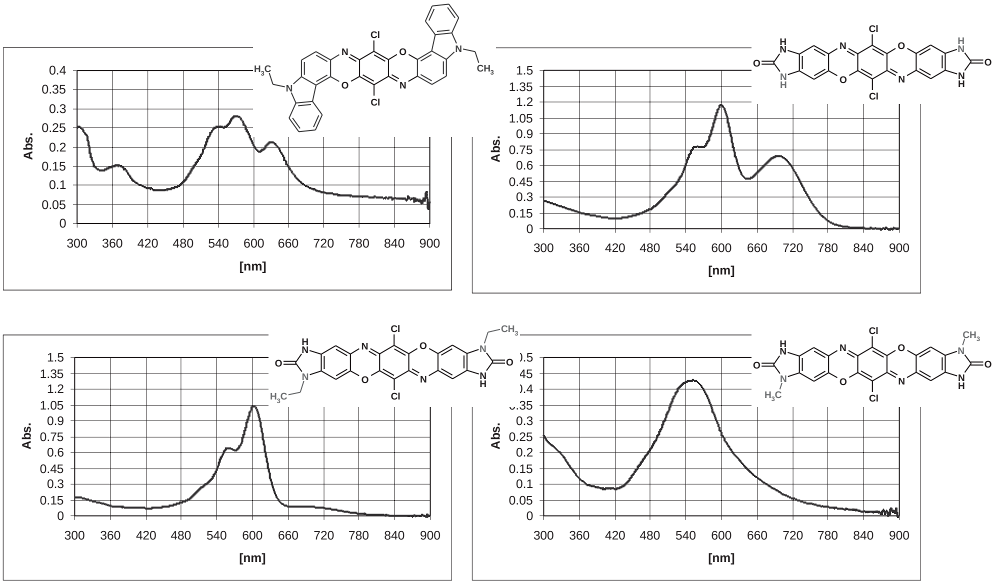


Figure 20–18: Absorption spectra (DMSO) of benzimidazolone-dioxazine pigment versus carbazole-dioxazine pigments.

20.13 Economy and Value-in-Use

Like most high-performance pigments, benzimidazolone-dioxazines are expected to be more highly priced than classical pigments. However, their outstanding tinctorial strength should reflect their overall value within reasonable limits, in line with the following:

- hyper color strength, up to 3 times that of quinacridones, indanthrone blue or thioindigo
- much higher insolubility than carbazole-dioxazine violet
- higher performance (heat / durability, etc.) than any of the state-of-the-art pigments (quinacridones)
- highly favorable application properties at equal coloration value.

20.14 Application Properties

Benzimidazolone-dioxazine pigments are characterized by high heat stability, solvent resistance and excellent durability. Of particular importance is their very high tinting strength, which is up to three times that of Pigment Red 88 and twice that of Pigment Violet 19 and Pigment Blue 60, with even better shade and fastness properties.

After two years of Florida exposure in acrylic melamine formaldehyde (A/MF) lacquers, the parent, unsubstituted benzimidazolone-dioxazine shows at least similar durability to Pigment Violet 23.

Benzimidazolone-dioxazine pigments identified for commercialization thus far are red-violet to reddish-blue in shade. They are characterized by an exceptionally high tinting strength, and their heat stability and resistance to aggressive solvents and plasticizers is much superior to that of carbazole dioxazine pigments.

Test results conducted thus far suggest that benzimidazolone-dioxazine pigments should be suitable for almost all applications for the highest performance requirements expected of a high-performance organic pigment.

20.15
Pigment Grades

Benzimidazolone-dioxazine pigments are expected to become available in all typical color delivery forms of organic pigments.

20.16
Pigment Specifications and Manufacturers

There are no standard specifications yet for benzimidazolone-dioxazine pigments.

Benzimidazolone-dioxazine pigments are proprietary pigments from Clariant.

Acknowledgements

I am particularly indebted to Dr. B. Piastra, Dr. P. Kempter, Dr. P. Boeglin and Dr. M. Schmidt for their contributions.

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21

Chemical and Physical Characterization of High Performance Organic Pigments

C. Nicolaou

21.1

Introduction

The term High Performance Pigment has been defined in different ways over the years. What was considered a High Performance Organic Pigment (HPOP) in the early 1900s may not so be today. For example when Red Lake C (PR 53:1) was discovered in 1902 it exhibited high color strength, good solvent fastness and good heat stability compared to other colorants. Today such pigments, although still widely used, are no longer classified as HPOPs. Thus at any given time period the term HPOP refers to the best current performing pigments. What is now, at the beginning of the 21st century, considered a high performance pigment may not be in the years ahead.

Despite the many recent advances in pigment technology, there are still few pigments that meet most of the requirements for excellence of performance in most given systems. Not many pigments are totally insoluble in the medium in which they are dispersed or remain completely inert over their intended service life.

The main criteria that are used to classify pigments as HPOPs are heat stability, lightfastness, weather fastness, durability, solvent resistance, migration resistance, color strength, dispersibility and value in use. Improvements in some of these areas are still required for many HPOPs.

Since pigments are highly insoluble in the media in which they are dispersed, they exist mainly as crystalline solids. Thus, their performance is dependent not only on their chemical structure, but also, to a large extent, on their morphological features such as particle size and size distribution, particle morphology, crystal modification, crystallite size and degree of crystallinity. These physical features have a large effect on tinctorial strength, dispersibility, dispersion stability, rheological properties, heat stability, lightfastness and migration resistance[1–5]. Today's HPOPs are designed to meet these performance criteria in specific applications and are not meant to be used universally.

Thus, for assessment of pigment performance, both chemical and physical characterization are often required. There are various reasons for the need to characterize pigments and pigment compositions. These include chemical structure confirmation as well as physical characterization for competitive product identification, for solving production problems, for completion of patent applications, for addressing customer complaints or requests, for optimizing research and development processes, for regulatory requirements, and for responding to environmental concerns.

In this chapter, the application of various spectroscopic, chromatographic, X-ray and microscopic techniques to the analysis and characterization of HPOPs will be presented. In so doing, however, it must be stressed that because of sheer space limitations it would be impractical to cover all aspects of the methods currently used to analyze, identify and characterize today's pigment products and related materials. Mention should therefore be made of the following fourteen techniques, which are not discussed in detail here but are all in use today in pigments laboratories and are worthy of further study.

1. Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma (ICP), for determination and quantitation of metals present in products and impurities.
2. Atomic Force Microscopy (AFM), for surface measurement and two-dimensional particle size analysis.
3. Contact Angle measurement, for determination of wetting properties of powders and thin films.
4. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA), for monitoring reaction sequences, e.g. in calcination of inorganic pigments, and for determining decomposition temperatures of pigments and water of crystallization in pigments.
5. Diffuse Reflectance Spectroscopy, for monitoring of inorganic pigment production.
6. Electron Diffraction Analysis, for structural identification of microcrystals and crystallites.
7. Electron Spectroscopy (ESCA), for surface characterization.
8. Electron Paramagnetic Resonance Spectroscopy (EPR), or Electron Spin Resonance (ESR), for studying paramagnetic properties of crystals, including metal ions, free radicals, and organometallics.
9. Electrokinetic Sonic Amplitude (ESA), for measurement of surface charges on pigments.
10. Helium Pycnometry, for determination of specific gravities of pigments.
11. Near Infra Red Spectroscopy (NIR), for process monitoring of inorganic pigments.
12. Nitrogen Adsorption, for determination of pigment surface areas and porosity of powders.
13. Nuclear Magnetic Resonance Spectroscopy (NMR), for identification of pigments and related materials.
14. X-Ray Fluorescence Spectroscopy (XRF), for identification and quantitation of elements.

21.2
Visible Spectrophotometry

Since electronic transitions occur in the UV and Visible range of the electromagnetic spectrum (200–700 nm), the color of molecules is associated with electronic excitation due to absorption of incident light[6–9]. The selective absorption of visible light by the organo-chromophores (e.g. conjugated double bonds) is primarily responsible for the hue of a substance. The tinctorial strength of a pigment composition is highly dependent on the amount of pigment present, the crystal packing and particle size distribution of the colorant. Electronic spectroscopy has been used extensively for the analysis and measurement of colorants. The pigment content or extinction coefficient (in the case of a pure colorant) can be determined by visible spectrophotometry. X-ray diffraction and electron microscopy are used to determine crystallite size and particle size.

Traditionally, UV-Visible spectra have been obtained in solution. Quantitative analysis is obtained based on the Beer-Lambert law. For quantitative analysis by solution spectrophotometry the colorant must be completely dissolved and other components in the sample must not interfere with the determination. In addition, purified standards containing known amounts of the pigment being determined are required. Since HPOPs are highly insoluble, strong organic solvents or concentrated sulfuric acid are usually employed in order to effect complete dissolution of the pigment.

21.2.1
Visible Spectroscopy of Copper Phthalocyanines

Copper phthalocyanine blue pigments are soluble in concentrated sulfuric acid. The solutions are quite stable at room temperature for several hours. The sample preparation for this analysis is quite simple. The pigment sample (3–5 mg) is weighed on a microbalance and then dissolved in concentrated sulfuric acid by stirring and/or sonication. After complete dissolution the sample is diluted to a known volume and the Visible to Near IR spectrum is scanned from 400 to 900 nm. Based on the absorbance and weight concentration of the sample and that of the reference pure standard at the wavelength of maximum absorption (λ_{max}), the amount of pigment in the sample is determined.

DMSO, 1-chloro-naphthalene and 1-methyl-naphthalene can also be used for dissolution of copper phthalocyanine blue. This is particularly useful for plastic matrices where sulfuric acid is not recommended. The solubility in these solvents is limited to about 2 mg/L. The use of a microbalance is necessary for weighing low mg amounts of sample.

Because of the fairly high extinction coefficient (3.36538×10^5), very small amounts of copper phthalocyanine blue pigments can be detected and measured. Figure 21–1 shows the visible spectrum of Copper Phthalocyanine Blue at a concentration of 62 μg/L in 1-methyl-naphthalene (λ_{max} 677nm).

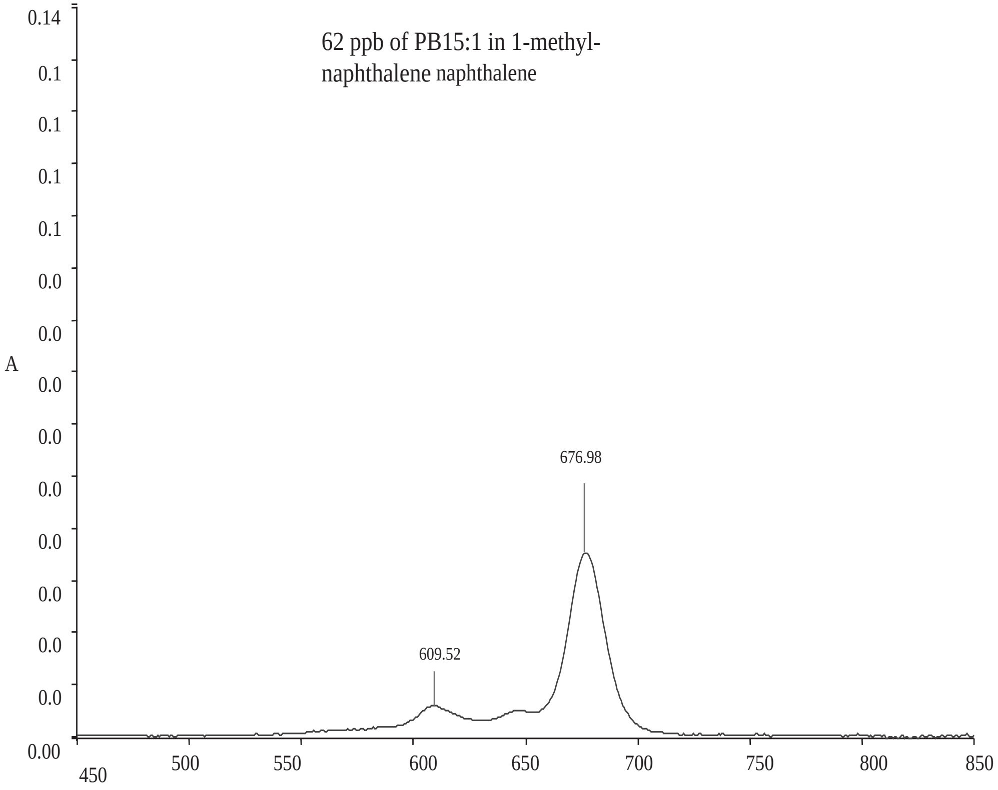


Figure 21–1: Visible spectrum of Copper Phthalocyanine Blue in DMSO.

This technique has been employed not only for measuring toner content but also for the determination of trace amounts of phthalocyanine blue contaminating other pigments such as Diarylide Yellows or Naphthol Red pigments. Small amounts (ppm levels) of phthalocyanine blue may be present as a contaminant or as a shading agent. Figure 21–2 illustrates the application of visible spectrophotometry to the determination of low ppm levels of copper phthalocyanine in PY 17. For this analysis 10 mg of sample are dissolved in 1-methyl-naphthalene and the visible spectrum of the resulting solution is scanned from 500 to 990 nm. The same approach has been used to determine low percent levels of copper phthalocyanine blue in PR 170. Another important application is the determination of color migration of copper phthalocyanine blue, at the 5–10 ppb level, from plastics used for food packaging.

Visible spectrophotometry has also been applied similarly to the analysis of copper phthalocyanine green (PG7). This pigment is even less soluble than the non-chlorinated phthalocyanine blue. For quantitative analysis, extreme care is needed in order to ensure that the sample is in solution. Sulfuric acid is the preferred solvent except in the case of polymeric matrices. Figure 21–3 shows the Visible spectrum of PG 7 at a concentration of 140 µg/L in DMSO (λ_{max} is at 727.5nm).

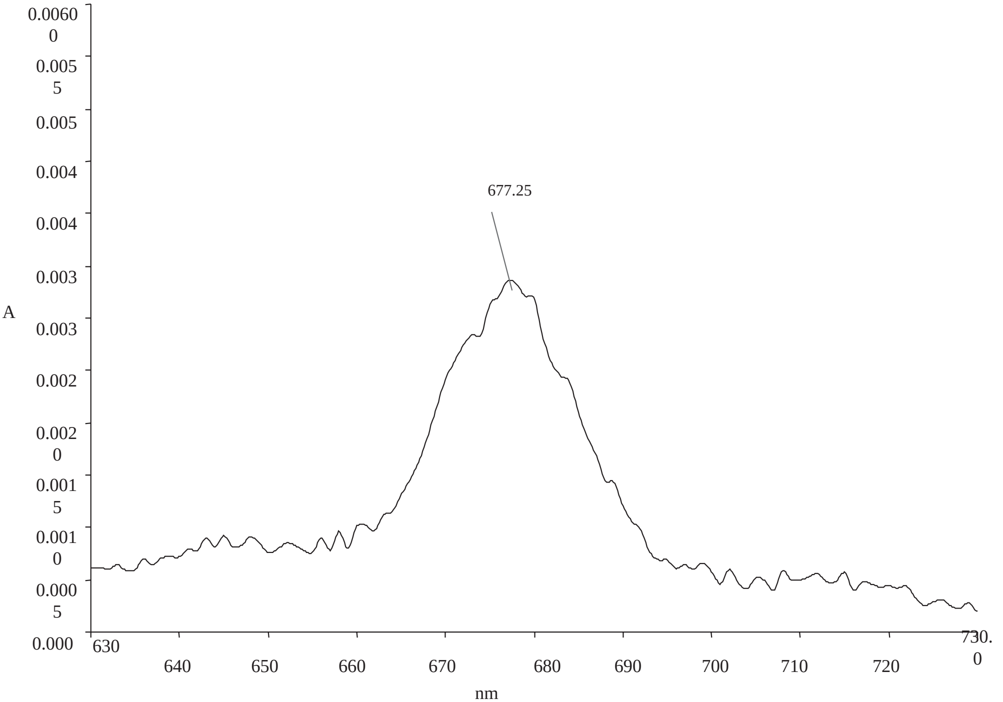


Figure 21–2: Visible spectrum of low ppm PB 15 in PY 17.

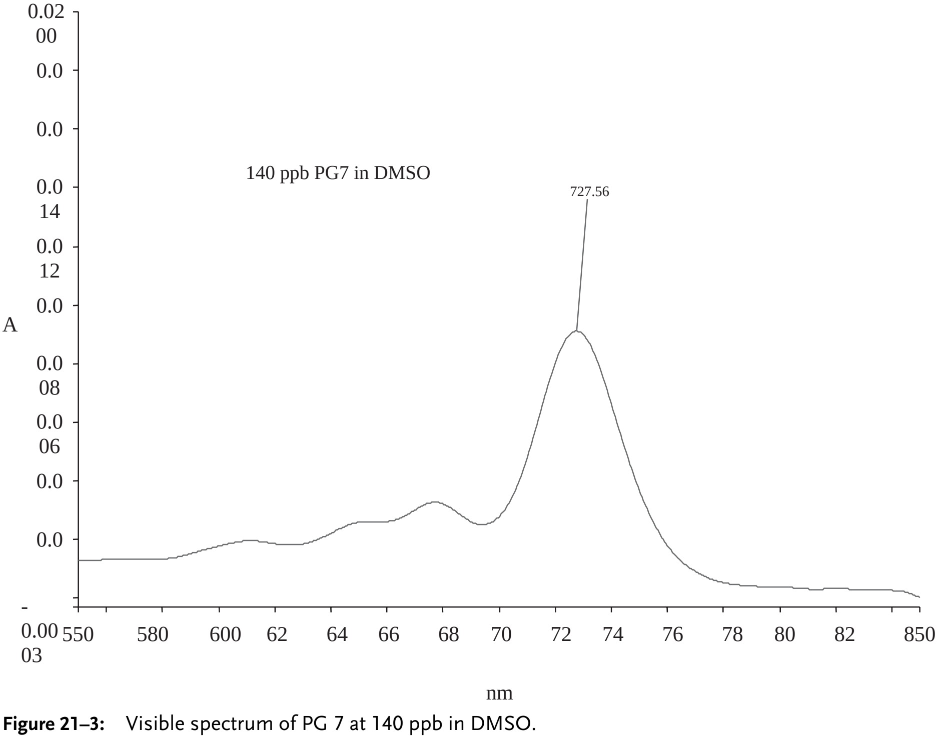


Figure 21–3: Visible spectrum of PG 7 at 140 ppb in DMSO.

21.2.2
Visible Spectroscopy of Colored Thin Films

Electronic absorption spectra of thin films colored with copper phthalocyanines have also been recorded (see Figures 21–4 and 21–5). Compared to the solution spectra, solid state spectra have broader bands, and there is also a shift in the wavelength of maximum absorption. This is attributed to the phenomenon known as crystallochromy. In the solid state, electronic excitation takes place between bands of energy levels formed by the interaction (coupling) of the chromophores in the solid

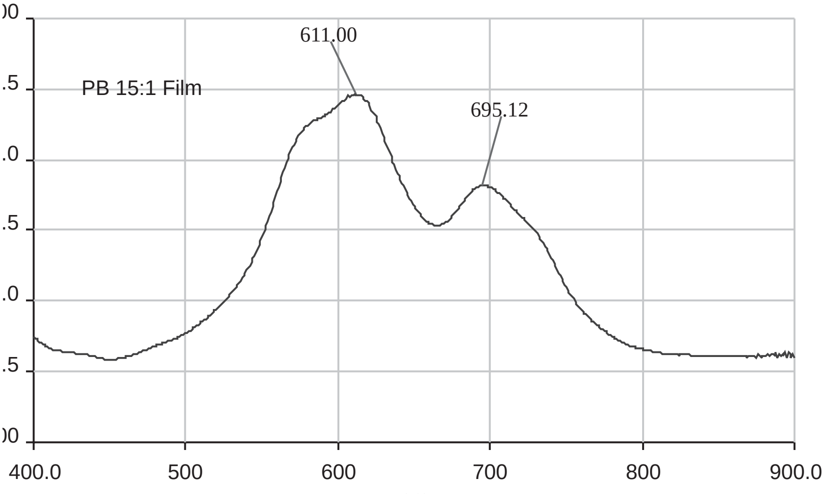


Figure 21–4: Visible spectrum of PB 15:1 in solid state thin film.

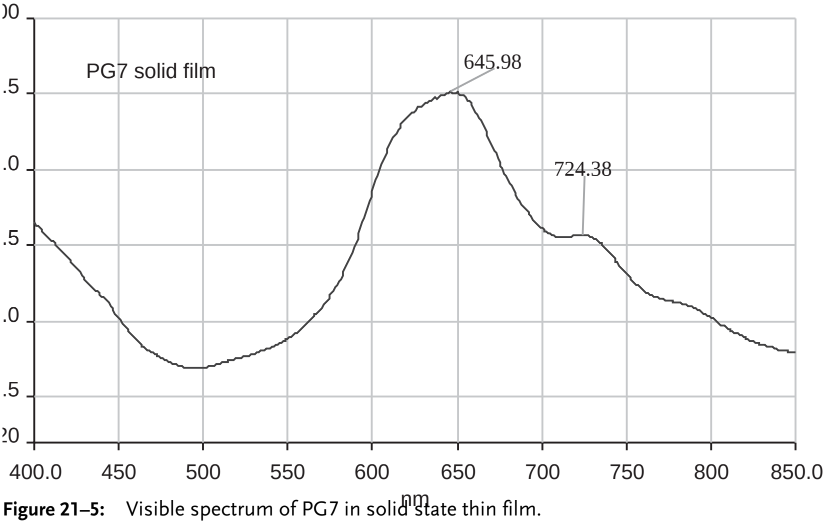


Figure 21–5: Visible spectrum of PG7 in solid state thin film.

state, as opposed to excitation at the molecular level that occurs in solution. Empirical correlations and quantum mechanical calculations have been used to explain chrystallochromy[10–15].

Solid state absorption spectra are useful for evaluating relative tinctorial strength by comparison with reference standards. The absorption at λ_{max}, as well as the absorption sum over the visible range of the spectrum, must be taken in consideration when determining relative strength from absorption spectra. After accounting for tinctorial differences based on the absorption spectra, other color differences are best determined by using the CIELAB system for color measurement.

21.2.3

Visible Spectrophotometry of Other HPOPs

The same technique used for copper pthalocyanines may be applied to other HPOPs using suitable solvents. Examples include quinacridone pigments (PV 19, PR 122, PR 202), perylenes (PR 179, PR 149, PV 29), diketopyrrolopyrroles (PR 254) and dioxazines (PV 23). The extinction coefficients at λ_{max} of several HPOPs are listed in Table 21–1.

Table 21–1: λ_{max} and extinction coefficients of high performance organic pigments.

Pigment type	λ_{max}	*Extinction coefficient Absorbance L mole^{-1}*	*Solvent*
PB15:1	677 nm	3.35417×10^5	1-methylnaphthalene
PG 7	727 nm	7.0200×10^4	DMSO
PR122	532 nm	1.3886×10^4	DMSO
PR144	576 nm	5.3219×10^4	H_2SO_4
PR 179	552 nm	7.9796×10^4	H_2SO_4
PR188	495 nm	2.1309×10^4	*o*-DCB
PR 202	530 nm	2.4539×10^4	DMSO
PR254	516 nm	3.6253×10^4	DMSO
PV19	523 nm	1.3528×10^4	DMSO
PV 23	941 nm	8.8936×10^4	H_2SO_4
PV29	595 nm	7.4958×10^4	H_2SO_4

21.3

FT-IR Spectroscopy

Because of the limited solubility of HPOPs, FT-IR spectroscopy has been used extensively for their analysis and identification since the solid pigments can be analyzed directly using ATR devices or by mixing with non-IR absorbing salts such as KBr. Normally the pigment sample is dried prior to analysis and the FT-IR spectrum is recorded. The sample preparation is minimal, except when quantitative analysis is needed or when the sample matrix is quite complex and the pigment is present at low concentrations.

For identification purposes a reference library of known spectra is essential. Even though there are commercial libraries available they tend to be of limited value since the listings are incomplete and the method used for sample preparation may not be the preferred one. More often, pigment companies build their own libraries using their own techniques.

21.3.1

Sample preparation for FT-IR analysis of pigments

Commercial pigment products such as inks, paints or colored plastics consist of several components, and in many cases the pigment is present at small concentrations. FT-IR analysis of such commercial products requires special analytical methods for separating the pigment from the other components prior to analysis. One way to isolate the pigment is to take advantage of its limited solubility and attempt to extract the other organic matter using selected solvents. The strongest solvent that does not dissolve the pigment is usually selected. Acetone, toluene, chlorinated benzenes, tetrahydrofuran and alcohols are often used. Extraction may be accomplished by dispersing approximately 1 g of sample in a solvent (40 ml) in a Teflon tube for several minutes using ultrasonication and or heating. After that the sample is centrifuged and the supernatant liquid discarded. The extraction is repeated at least twice depending on the sample matrix. After removal of residual solvent, the FT-IR spectrum of the insoluble pigment is recorded. In most cases identification is accomplished especially in conjunction with the visible spectrum of the sample. Often the insoluble part of the sample may contain a mixture of pigments, or it may contain inorganic extenders. In such cases a good match with reference spectra will not be possible, and other methods of characterization must be used. These include solid probe mass spectrometry or X-ray diffraction and X-ray fluorescence (for element identification). Such techniques however are more expensive, and skilled analysts are needed to operate the instruments and interpret the results.

For quantitative analysis of binary pigment mixtures, it is necessary to prepare reference standards at various concentrations to cover the range of interest. Initially the FT-IR spectra of the two pigments of interest are recorded and overlaid on the computer monitor. The spectra are then evaluated for differences. Quantification of one of the pigments in the presence of the other can only be achieved if there is at least one medium or strong intensity band that is not common to both pigments. Once this is confirmed, mixtures of the two pigments are prepared by grinding and mixing on a roller mill. Concentrations from 5 to 90 % are often prepared. The FT-IR spectra of the mixtures are then recorded by ATR or by transmission using KBr pellets. If transmission is used, the amount of KBr and pigment has to be accurately weighed and mixed uniformly. For most cases 1–3 % pigment in KBr are used. After mixing and grinding, ca. 125–130 mg of the mixture are weighed and pressed into a pellet. The FT-IR spectrum is then recorded and the absorbance of the band of interest and that of a reference band from the other pigment component are measured using the computer software. The ratio of the absorbance of the analyte band to that of the reference band is calculated and then plotted as a function of concentration. The equation of the regression line of the calibration curve is used to calculate the amount of pigment in the samples. Samples are prepared in the same way as the standards. The use of peak absorbance ratios eliminates random errors due to sample analysis and errors due to difference in sample thickness. It does not however correct for errors in weighing and mixing the standards used to obtain the calibration curve. Thus, the preparation of the standards is the most important step and every care must be taken to ensure good mixing. Errors due to improper mixing of the standards will give low correlation coefficients for the regression equation.

21.3.2
Application of FT-IR Spectroscopy to the analysis of HPOPs

Quantitative FT-IR methods have been successfully used to analyze binary mixtures of quinacridone and perylene pigments.

Using quantitative FT-IR, PV 19 can be measured down to 5 % concentration in PR 122. The PV 19 bands at 960 cm^{-1}, 849 cm^{-1}, 748 cm^{-1} or 480 cm^{-1} may be used. The reference band of PR 122 at 1205 cm^{-1} is used for obtaining absorbance ratios. The FT-IR spectra of PV 19 at 10 % level in PR 122, of pure PV 19 and of pure PR

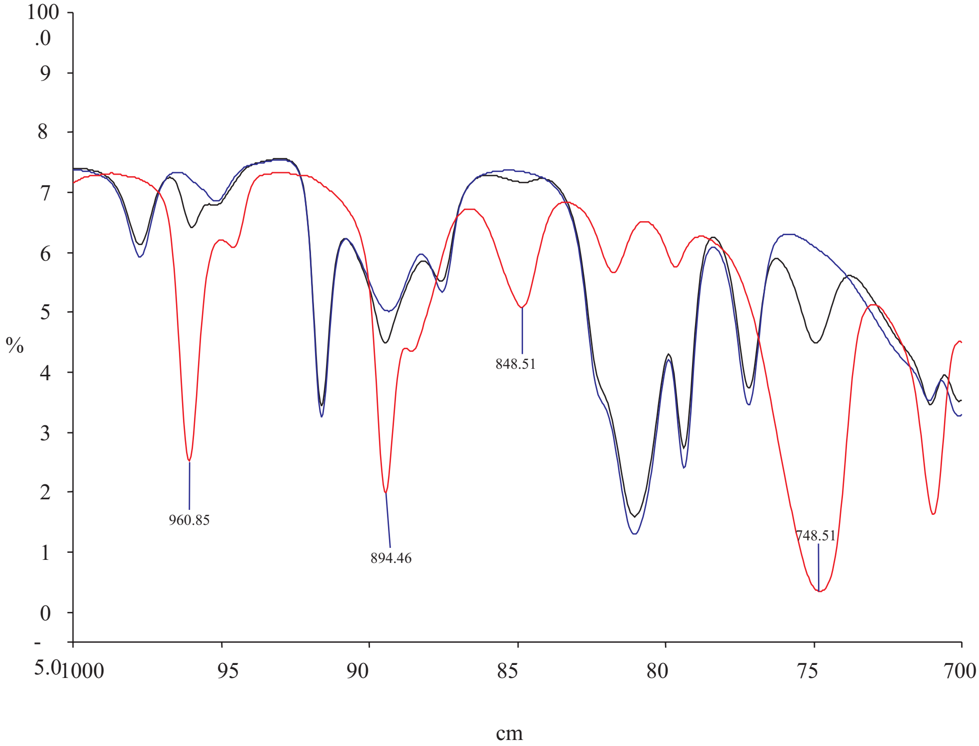


Figure 21–6: FT-IR spectra of PV19 at 10 % level in PR 122, of pure PV 19 and of pure PR 122.

122 are shown in Figure 21–6. The absorption bands of PV19 at 960 cm^{-1}, 849 cm^{-1} and 748 cm^{-1} are easily discernible and can be accurately measured.

Similar work has been carried out with binary mixtures of other quinacridones, as well as sulfonated PV19. For example, PV 19 was measured at a 3.5 % level in PR 202, based on absorbance of the PV 19 band at 752 cm^{-1} and the PR 202 band at 840 cm^{-1}. PR 122 at 5 % concentration in PV 19 can be detected based on the absorbance of the band at 1215 cm^{-1}.

Phthalimido-methyl-quinacridone (PMQ) derivatives have also been determined by FT-IR down to 5 % concentration in PV 19 and in PR 122 based on the absorbance of the carbonyl group near 1710 cm^{-1}. Quinacridone sulfonic acid (QSA) has been measured at 18–75 % concentration in PV 19.

Another notable application of quantitative FT-IR is the determination of phthalimido-methyl derivatives (PM) of copper phthalocyanines. Samples are prepared in a similar manner to that described above for the quinacridones. In this case the carbonyl band near 1720 cm^{-1} was used for calculating the amount of the PM derivative (Figure 21–7).

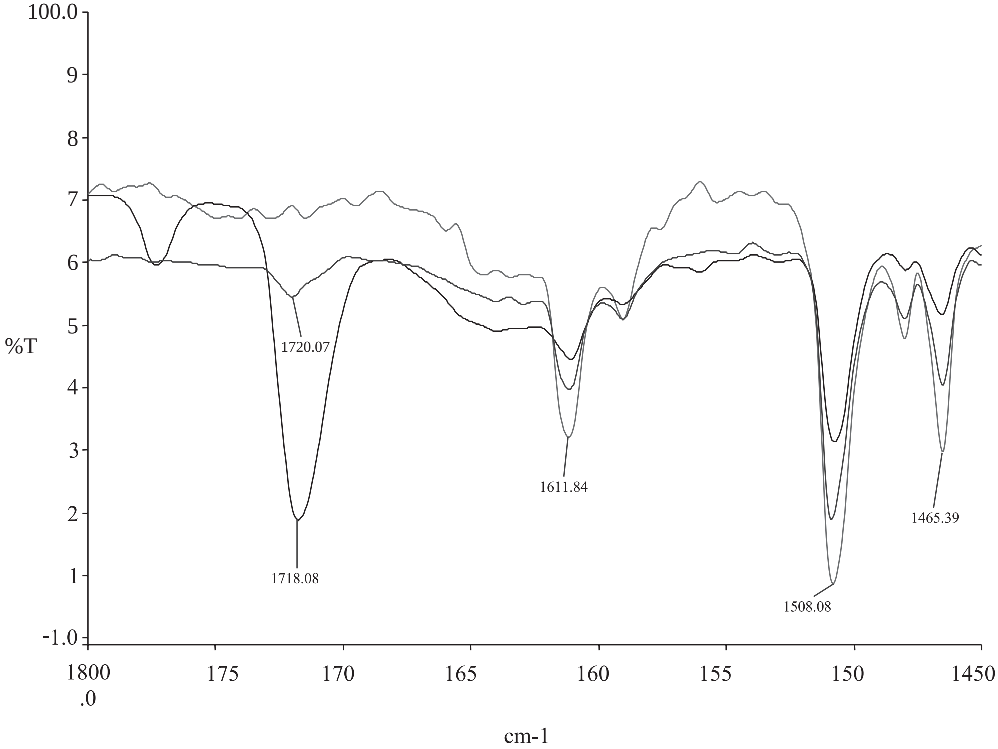


Figure 21–7: FT-IR spectra of PM derivative of Copper Phthalocyanine Blue "as is" and at 5 % level in PB 15, and of pure PB 15.
]

The amount of PV 29 in PR 179 can be measured to below 1 %, using the absorption band of PV 29 at 460 cm^{-1} and the reference absorption band of PR 179 at 515 cm^{-1}. This method is used routinely to monitor the amount of PV 29 in PR 179 at levels below 2.5 %.

21.3.3
FT-IR Microspectroscopy

This technique has been used for the identification of undispersed particles in plastic applications. It is particularly useful for resolving customer complaints as well as process development problems. As a general rule particles 20 microns or larger can be analyzed by FT-IR spectroscopy. The approach is to focus the IR beam onto the particle of interest using the microscope, and then scan the FT-IR spectra several times (100 scans), either in transmission or reflectance mode. The sample is then moved slightly to another position and the microscope is focused on a portion of the sample without a defect. The FT-IR spectrum of this part of the sample is recorded in exactly the same way as that of the defective part. The spectrum of the non-defective part is then subtracted from spectrum of the defective part of the sample. The difference spectrum is then used to identify the "spot" or particle in the defective part. Optical microscopy is often used together with FT-IR microspectroscopy to aid in selecting the area of interest to be analyzed.

21.4
Mass Spectrometry of HPOPs

There have been considerable advances in mass spectrometry over the last 10 years. New techniques such as matrix-assisted laser desorption ionization (MALDI), electrospray ionization (ESI), thermospray ionization, plasma desorption and ion spray have all been widely used to obtain mass spectra of polar and non-polar compounds, up to a mass of several thousand Daltons. New MS-MS techniques can provide structural information based on fragmentation of selected ions and are of great value for both qualitative and quantitative analysis, especially in difficult matrices. There is no one method of ionization that is ideal for all samples. Often the analyst and the pigment chemist must work together to select the best way to analyze a given sample. There have been numerous applications of mass spectrometry for the identification of dyes and pigments[16–19]. In this section, the application of the more traditional and less expensive Electron Impact (E.I.) Ionization Mass Spectrometry technique to the identification of HPOP will be illustrated. The solid sample is analyzed directly using solid probe techniques, whereby the solid pigment or pigment formulation is introduced into the ionization chamber without chromatographic separation. A temperature-controlled solid probe device is used to heat the sample under vacuum at temperatures up to 800 °C. Most HPOPs volatilize under these conditions and are stable enough to produce molecular ions as well as fragmentation ions. By adjusting the temperature program, the more volatile pigments can be volatilized first and can be separated from the less volatile components of the sample.

21.4.1
Application of Solid Probe EI Mass Spectrometry to the analysis of HPOP

The solid probe EI/MS of PB 15 is illustrated in Figure 21–8. The intensity of the molecular ion at 575 is quite strong.

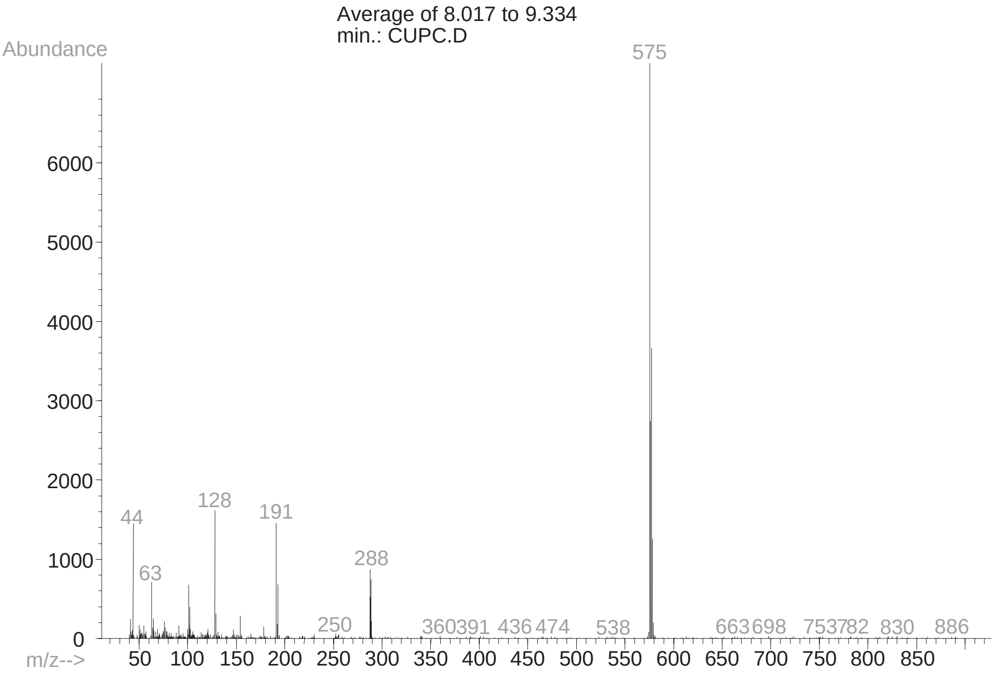


Figure 21–8: Solid probe EI MS spectrum of PB 15.

The solid probe EI/MS of PR 179 is next illustrated in Figure 21–9. Again the molecular ion at 418 is easily observed. The mass ion at 390 may be attributed to PV 29 or could be due to fragmentation of the R179 molecular ion.

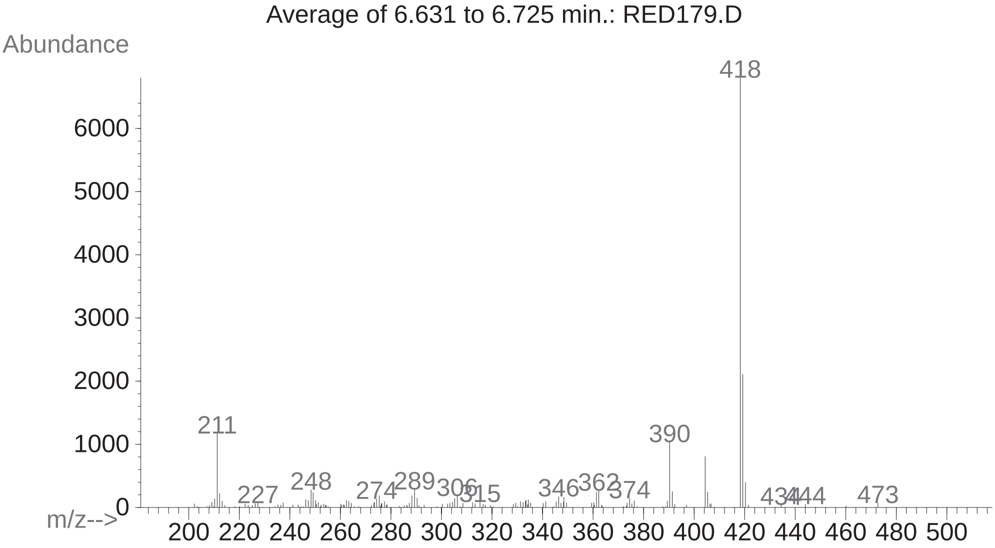


Figure 21–9: Solid probe EI MS spectrum of PR 179.

The solid probe MS of a commercial DPP pigment sample is illustrated in Figure 21–10. It shows the presence of dichlorinated PR 254 (molecular ion 356), mono-chlorinated DPP (molecular ion at 322) and the non-chlorinated analog, PR 255 (molecular ion 288).

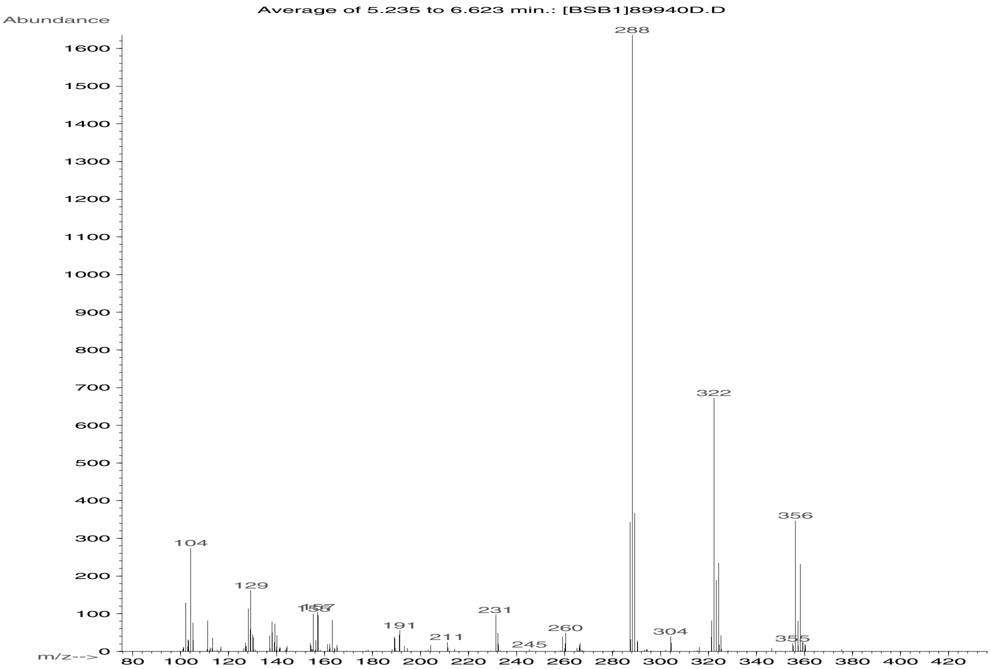


Figure 21–10: Solid probe EI MS spectrum of DPP Pigment.

The technique of solid probe mass spectrometry has been used to explain pigment fading in commercial automotive paint panels. A small amount of the paint is scraped off the faded panel sample and analyzed directly using E.I. mode. The intensities of the molecular ions of interest are measured and their ratio is calculated. A reference sample without fading (before exposure to light) is also analyzed under the same conditions as the faded sample. The ratio of the intensities of the two ions of interest is calculated again. From the ratio of the intensities of the molecular ions in the faded and non-faded panel the degree of pigment degradation can be estimated. Figure 21–11 shows the EI-MS spectrum of a commercial paint containing PR 179 and PR 254. This paint faded in the field and was analyzed and compared to the non-exposed panel of the same paint. The ions at 418 and 440, corresponding respectively to PR 179 and PR 254, were monitored and measured. The intensity ratio of the two ions in the faded (Figure 21–11) and non-exposed paint (Figure 21–12) panels was measured. From this ratio it was established that the amount of DPP pigment in the faded sample was ca. 4 times lower than that in the non-exposed sample. The PR 179 content in the two panels remained unchanged.

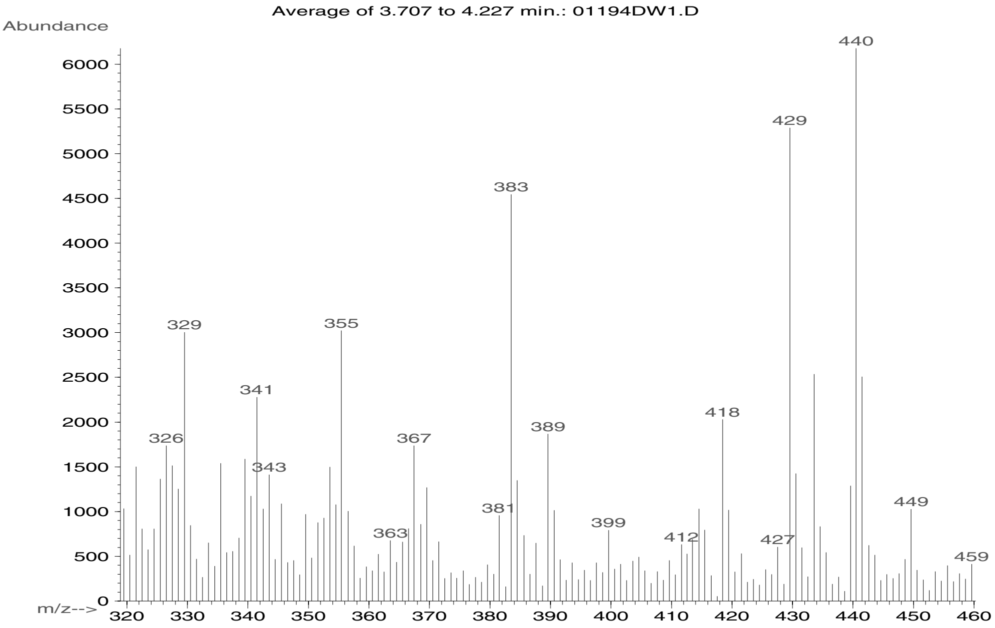


Figure 21–11: Solid probe EI-mass Spectrum of a faded paint panel containing PR254 and PR202.

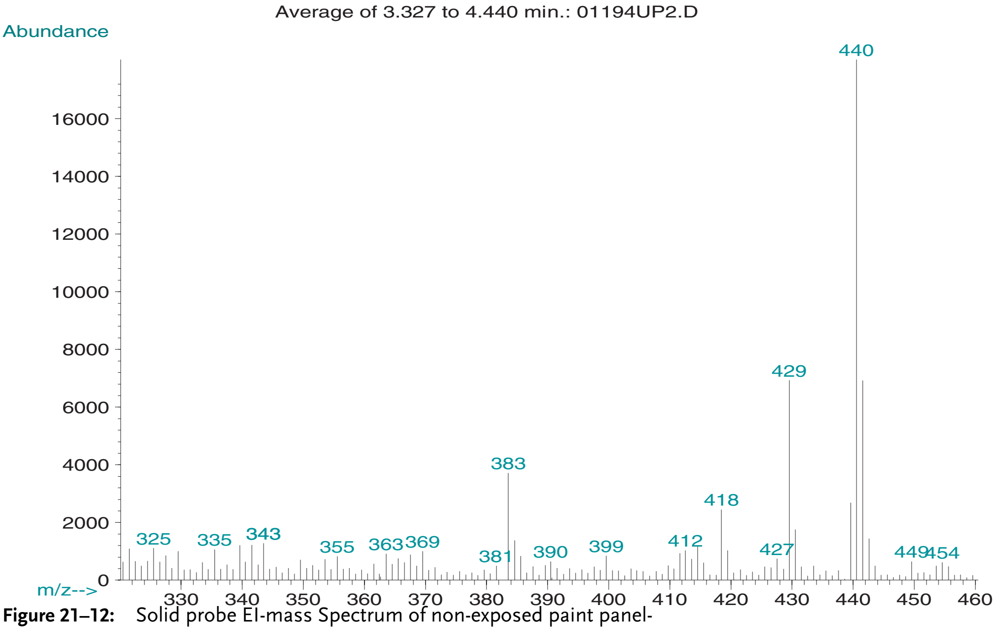


Figure 21–12: Solid probe EI-mass Spectrum of non-exposed paint panel-containing PR254 and PR202.

The solid probe EI-MS spectrum of PV 23 (Figure 21–13) shows the presence of the molecular ions near 588 to 592 as well as the molecular ions of the mono-chlorinated analog (molecular ion at 554) and the non-chlorinated product (molecular ion

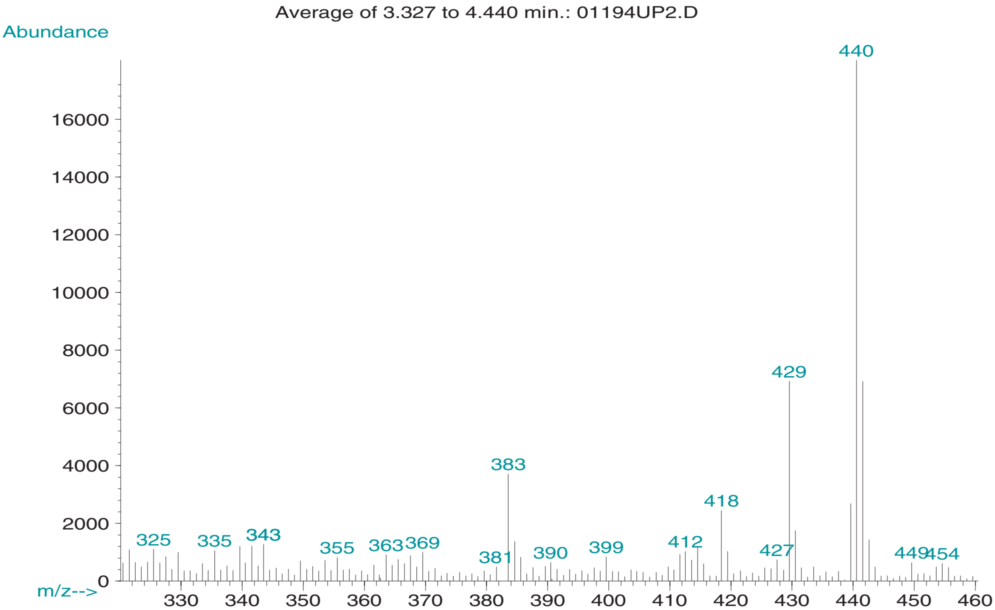


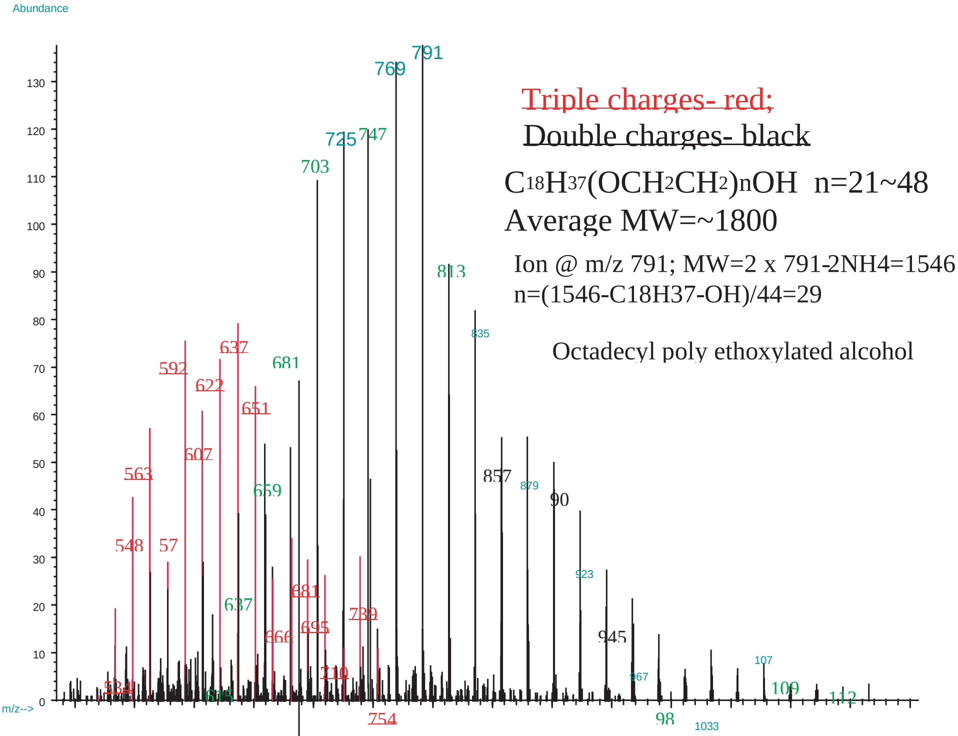
Figure 21–13: Solid probe EI-mass spectrum of PV 23 molecular ions 588–592.

at 520). This MS method has been used to evaluate differences in chemical composition between various batches of PV 23, in order to help explain coloristic differences.

Solid probe EI-MS spectra of other HPOPs such as quinacridones (PV 19, PR 122, and PR 202), PR 170, PR 188, PR 144 have also been obtained.

21.4.2
Applications of Electrospray Ionization for the Analysis of HPOPs

Electrospray ionization mass spectrometry (ESI-MS) has been applied to the analysis of more polar components of pigment compositions such as surfactants, or sulfonated derivatives of pigments. These polar compounds are usually soluble in polar organic solvents and can be easily extracted and analyzed. The extracted material may be analyzed directly by infusion into the electrospray ionization chamber or after separation by reverse-phase HPLC. Since the ESI-MS technique is highly sensitive for ionic or easily ionizable compounds, small amounts of surface treatment agents can be detected readily. This is useful for reverse engineering of unknown competitive samples as well as production problems. Anionic, cationic and nonionic surfactants and their mixtures can be analyzed and identified quite readily. Figure 21–14 illustrates the ESI-MS spectrum of surfactants extracted from an unknown commercial pigment.



Triple charges- red;
Double charges- black

$C_{18}H_{37}(OCH_2CH_2)_nOH$ n=21~48
Average MW=~1800

Ion @ m/z 791; MW=2 x 791-2NH4=1546
n=(1546-C18H37-OH)/44=29

Octadecyl poly ethoxylated alcohol

Figure 21–14: ESI-mass spectrum of surfactants extracted from a commercial HPOP.

Sulfonated copper phthalocyanine derivatives have also been detected by ESI-MS analysis. Species corresponding to tri-, di- and mono-substituted copper phthalocyanine have been identified (see Figure 21–15).

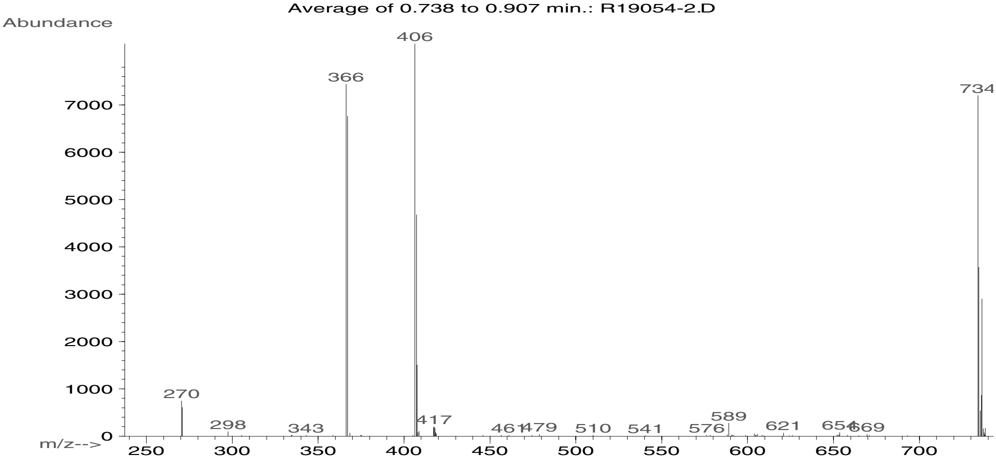


Figure 21–15: ESI-mass spectrum of sulfonated copper phthalocyanine.

Liquid chromatography with ESI-MS has also been used widely to identify impurities and byproducts in HPOPs. This was applied to the analysis of impurities in PR 144 (see Figure 21–16). These are impurities that were extracted from the disazo-conden-

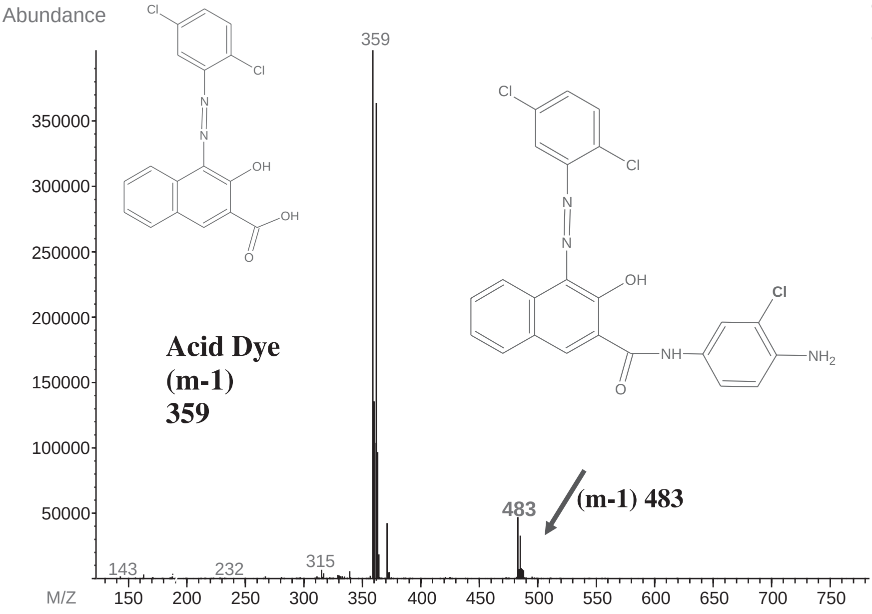


Figure 21–16: HPLC ESI-mass spectrum of impurities extracted from PR 144.

sation pigment PR 144. A mixture of a decomposed product (m–1=483), unreacted acid dye amine intermediate (m–1=359) and unreacted BONA coupler (m–1=187) were all detected and measured.

21.5
Powder X-ray Diffraction Analysis of HPOPs

Powder X-ray diffraction is an excellent analytical tool for identification and physical characterization of crystalline samples. It can be used for chemical identification (by matching unknowns with X-ray patterns of known reference samples), for crystal structure information, and for crystallite size determination. Such information is extremely valuable for pigment characterization. Many pigments exhibit polymorphism and each morph can have dramatically different physical properties (shade, opacity, heat stability, surface area, particle size and shape, melting point). These properties define to a large extent the performance characteristics of the pigment and therefore its applications.

X-ray powder diffraction data of pigments and dyes have been collected and reviewed by A. Whitaker[20]. There is also an extensive review of the X-ray diffraction of synthetic colorants by the same author published in 1995[21].

The theory and practice of X-ray powder diffraction has been published in many books[22–25], and only the principle will be mentioned here.

When X-rays pass through a crystal they may be diffracted and produce beams at specific angles. This occurs because the wavelength of X-rays is of the same order of magnitude as the interatomic distances in molecules (10^{-10} m). The diffraction angles depend on the wavelength of the incident X-rays, the crystal orientation and the crystal structure. The X-rays are predominantly diffracted by electron density, and analysis of the diffraction angles produces an electron density map of the crystal. Diffraction will occur only when the relationship between the angle of the incident rays (θ), the wavelength of the radiation (λ) and the interplanar distance (d) obey Bragg's Law,

$$2d \sin \theta = n\lambda$$

where n is an integer and $n\lambda$ is the path difference between waves scattered from adjacent lattice planes with equivalent indices. This equation does not apply to amorphous materials, since they lack a three-dimensional structure.

The size of the crystallite in a given dimension is determined using the Scherrer equation

$$t = \frac{0.9\lambda}{b_{1/2} \cos \theta}$$

where t is the crystallite size, λ is the wavelength of the incident X-ray beam, $b_{1/2}$ is the peak width at half height and θ is the Bragg angle.

The main advantage of X-ray diffraction is that the combination of interplanar distances and associated intensities is dependent on the crystal structure. As mentioned above, the patterns are unique not only for the chemical structure of the compound but also for the polymorphs (different forms of the same chemical composition).

The most common X-ray tubes use Cu (K_{alpha} line 1.5418 Angstroms) or Mo (K_{alpha} line 0.71073 Angstroms) as target elements. For organic pigments, the 2θ range is usually 4 –35°. For inorganic compounds the range is $2\theta = 4 - 60°$. Modern instruments are computerized and equipped with auto-samplers and therefore many samples can be analyzed automatically without operator intervention. Typical runs are 30–45 min long per sample.

There are numerous references regarding X-ray powder data of HPOP. For information on such data the reader is referred to an excellent review that was published by H. Whitaker in 1995[21].

The purpose of this section is to present some practical information of the application of powder X-ray diffraction (XRD) to the characterization of HPOP.

21.5.1
Sample Preparation for XRD

For dry powders, the sample is simply transferred into the sample holder and leveled carefully using a flat object such as a glass slide. If the sample is in the form of dispersion or paint or ink, the solvent is evaporated at low temperatures (not higher than 80 °C) and then ground by hand before transferring to the sample holder. The solid sample is then placed in the instrument and the X-ray pattern is obtained at a predefined 2θ angle range. For samples that contain low amounts of pigment (less than 5 %), it is often necessary to extract non-pigment components in order to increase the line intensities of the pigment. Identification becomes rather difficult when the line intensities are very weak, or when there is strong interference from other components in the sample.

After recording the XRD pattern, computer software programs are used for measuring the *d* spacings, the corresponding line intensities, and the crystallite size. The X-ray pattern of the sample may be compared to reference samples stored in the computer for identification.

21.5.2
Applications of Powder XRD

Powder XRD has been applied, for example, to the quantitative determination of alpha and beta phase contents of copper phthalocyanines, as well as the beta and gamma forms of Quinacridone Violet and Quinacridone Red, PV 19. For quantitative analysis, pure standards of each phase are mixed at various ratios from 0 to 90 %. For copper phthalocyanine blue alpha and beta phase determination, the 2θ angles used are at 16.1° for the alpha form and 18.1° and 18.5° for the beta form. For quinacridone beta/gamma analysis, the 2θ angles are at 13.8° for the gamma and 15.8° for the beta form.

Once the patterns are obtained, the intensities of the lines at the 2θ angles corresponding to the phase of interest are measured. The ratio of intensities is then calculated at each concentration and plotted against the concentration of the phase to obtain a standard calibration curve. The regression equation of the line is used to calculate the crystal phase content in unknowns.

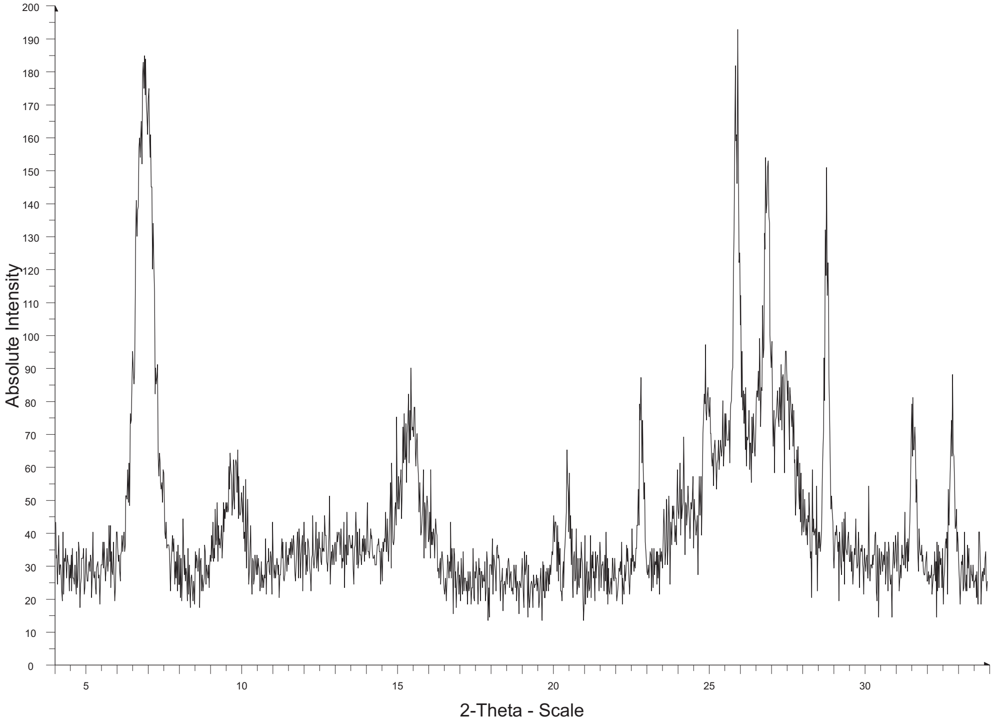


Figure 21–17: X-ray powder diffraction pattern of red shade (alpha phase) PB 15.

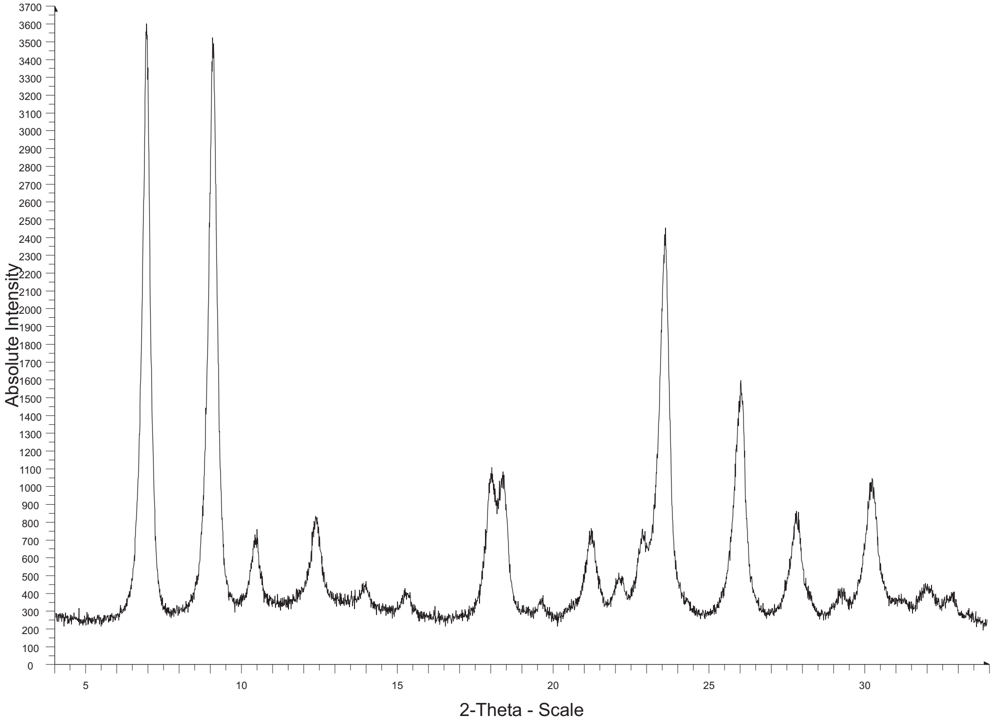


Figure 21–18: X-ray powder diffraction pattern of green shade (beta phase) PB 15:3.

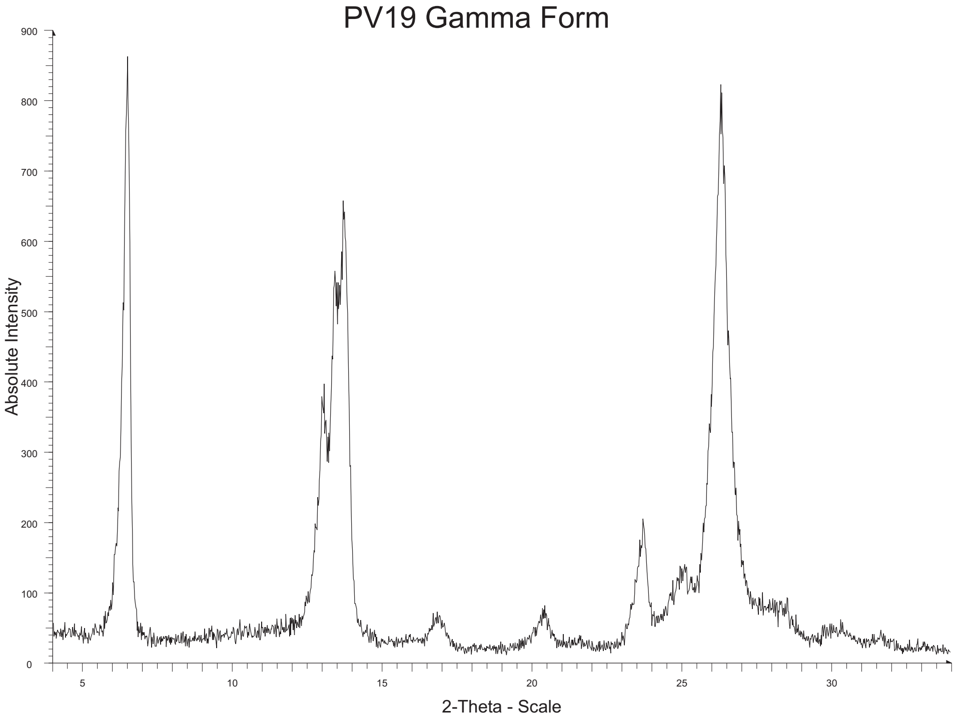


Figure 21–19: X-ray powder diffraction pattern of Quinacridone Red gamma phase PV 19.

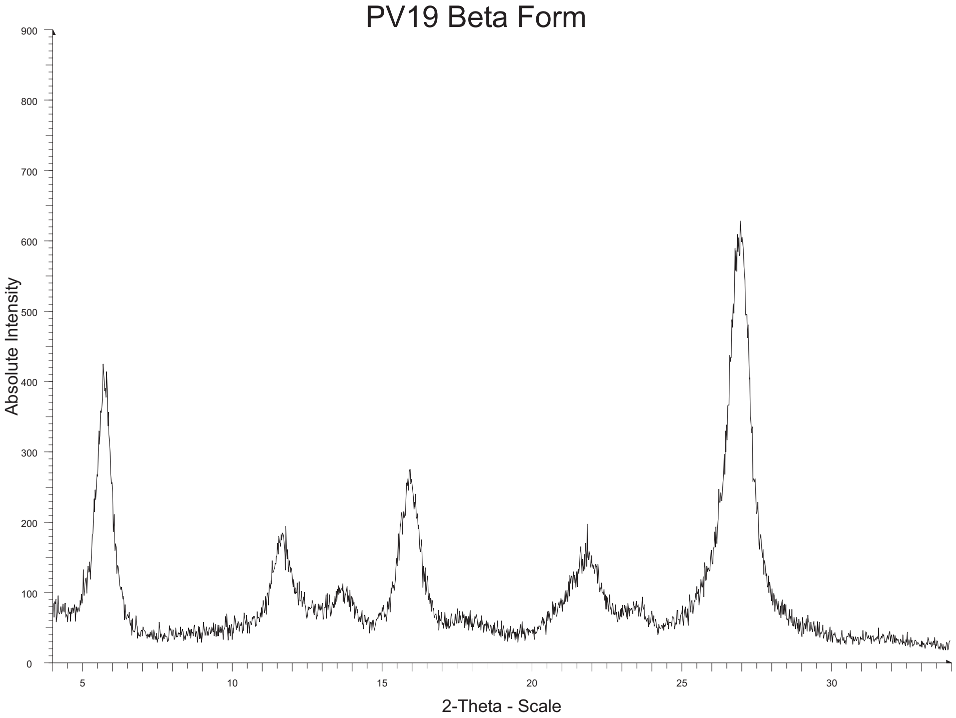


Figure 21–20: X-ray powder diffraction pattern of Quinacridone Violet beta phase PV 19.

Using this approach, quantitative analysis of the beta or alpha form of copper phthalocyanine can be determined at levels below 2 %. Similar detection limits have been obtained for the gamma and beta forms of Quinacridone PV 19.

The XRD patterns of the alpha and beta forms of copper phthalocyanine blue and the gamma and beta forms of Quinacridone PV 19 are shown in Figures 21–17 to 21–20.

Another important parameter that can be measured from the XRD pattern is crystallite size, which can have a significant effect on color strength, opacity, ease of dispersion, flow and rheological behavior of the pigment.

Visual examination of the line broadening in the XRD pattern can provide a quick evaluation of the degree of crystallinity of the pigment particles. Larger crystals have more intense and sharper lines. In cases where the differences in crystallinity between samples are not apparent on visual examination, the crystallite size is measured using the Scherrer equation.

The crystallite size may be plotted versus other physical parameters such as opacity, color strength, or viscosity. It is often used in conjunction with primary particle size data (obtained from electron microscopy) and surface area measurements in order to obtain a more thorough evaluation of the pigment particle morphology. Such investigations are very useful in evaluating production problems, resolving customer complaints, or generating data for evaluating R&D projects.

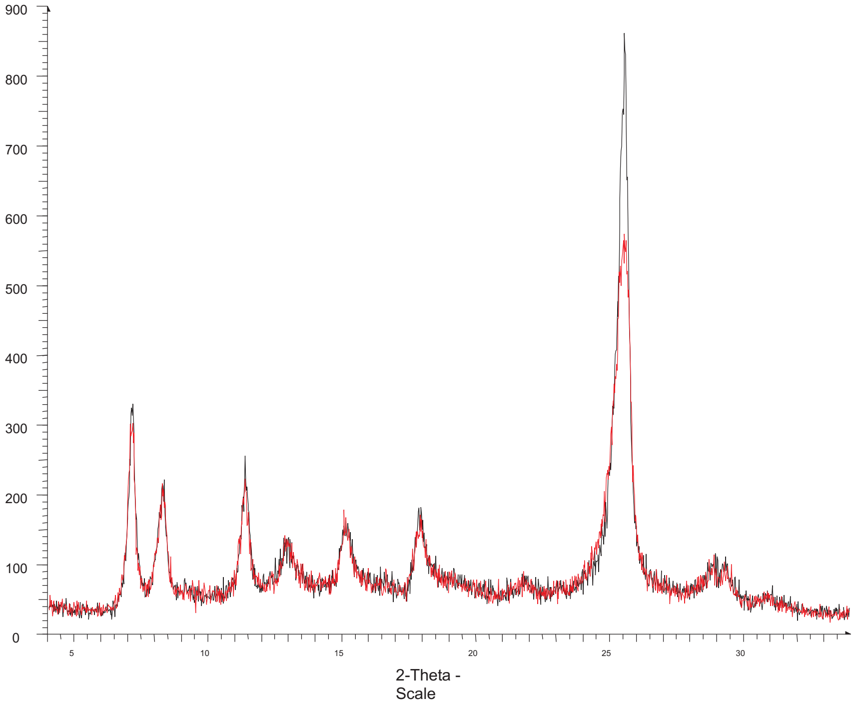


Figure 21–21: X-ray powder diffraction patterns of two samples of PR 170 of different crystallite size.

Figure 21–21 illustrates the superimposed XRD patterns of two samples of PR 170. The bands in one of the samples are broader and less intense, suggesting differences in crystallite size. The crystallite size at $2\theta = 25.5°$ was measured for these samples and found to be 158 for the more intense sharper line and 122 Å for the broader, less intense peaks.

XRD is also used for crystal morphology of solid solutions. These can be prepared by crystallizing together a small amount of a secondary pigment with the main pigment component. This often results in a different crystal form that does not correspond to either pigment when prepared separately. Figure 21–22 shows the XRD pattern of a sample of solid solution pigment obtained using two different quinacridone pigments. The 2θ angles at 5.9°, 13.5°, 15° and 24.7° were not present in the XRD patterns of the two quinacridone pigments prepared separately under the same conditions. In the absence of known XRD patterns, chemical identification of such solid solutions may be provided using solid probe mass spectroscopy.

In addition to organic pigment analysis, XRD is used extensively for the analysis of inorganic crystalline compounds. Thus, inorganic extenders such as clay, barium sulfate, titanium dioxide, and other crystalline salts that could be present in commercial pigments are easily detectable by XRD.

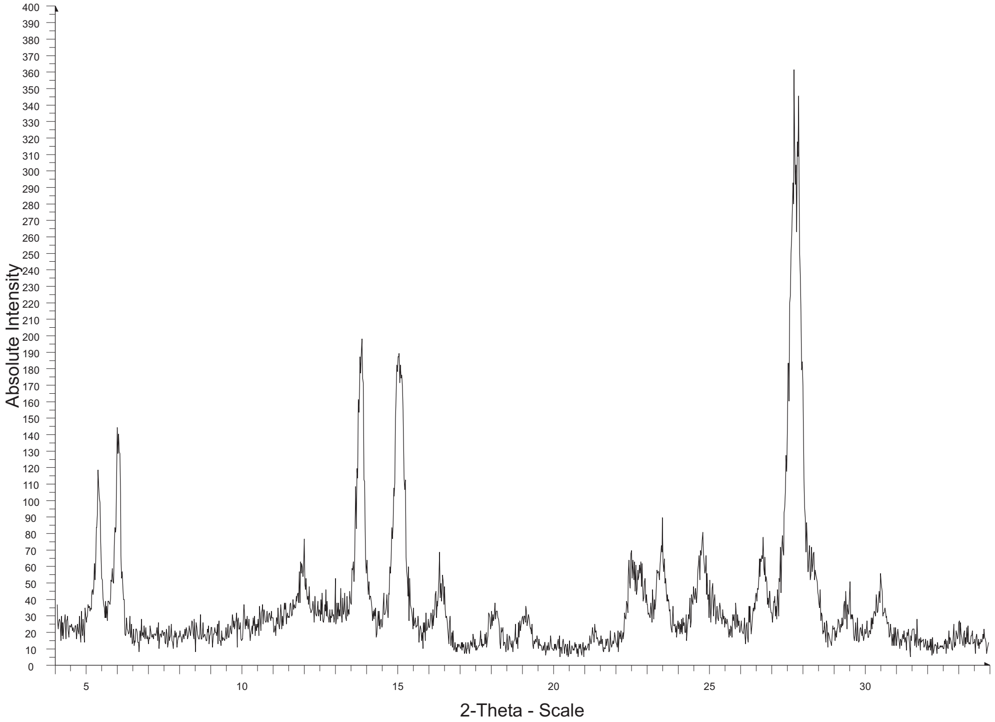


Figure 21–22: X-ray powder diffraction pattern of quinacridone solid solution pigment.

The disadvantage of XRD is that it is impossible to predict the pattern of a phase unless the single crystal data are available and this is rare. Most X-ray powder data published today is in the form of patents that are not abstracted by the International Center for Diffraction Data. Another disadvantage is that XRD requires a relatively large sample size, compared to other methods of analysis and the limit of detection is at best close to low percent levels. Therefore small amounts of co-couplings or shading agents, for example, may not be detected by XRD if present.

Table 21–2 lists the 2θ angles of some common HPOPs obtained using the Cu K alpha line at 1.5418 Å.

Table 21–2: 2-Theta angles of high performance organic pigments (s = strong line, m = medium line, w = weak line).

Pigment	***2-Theta angle (degrees)***							
PB 15:1 alpha	7.5 s	10 w	15.5 w	16.2 w	24 w	26.5 w	27.5 w	
PB 15:3 beta	6.7 s	9.0 s	10. 4 w	17.8 w	18.5 w	23.5 m	26 w	30.2
PB epsilon	7.2 s	9.2 s	4.3 w					
PV 19 beta	5.4 s	11.3 m	15.8 m	21.8 w	22 s			
PV 19 gamma	6.5 s	12.8 w	13.8 s	20 w	26.5 s			
PV 23 alpha	9–10.5 w	21 w	23 w	26 w				
PV 23 beta	5.5 s	10 s	12.9 w	23.2 w	25.6 s			
PV 29	10 w	12 s	19.8 w	25 m	27 s	30.3 w		
PR 122	5.5 s	11.2 w	14 w	15.1 w	24.3 w	25.4 w	27 m	
PR 146	5.4 w	8.1 w	11 w	12.8 w	18 m	20 m	27 s	
PR 149 gamma	5.2 s	7.5 m	10.7 s	12.3 w	115.8 w	21.5 w	24. m	
PR 170 alpha	7.2 w	11.5 w	13.5 w	16 w	19 w	21 m		
Pr 170 beta	7.2 m	8.2 w	11.3 w	15.2 w	16.9 w	25.5 s		
PR 170 gamma	7.2 m	11.3 s	12.8 w	15.2 w	17 m	25.5 s		
PR 179	8 m	11 m	12 s	13.2 m	23.5 s	25 m	27.5 s	29.8 w
PR 188	7.2 s	10.7 s	11.5 w	16.8 w	18.5 m	23.2 m	25.2 s	30.7 w
PR 202 alpha	5.6 m	13.9 s	15.4 m	18.6 w	22.7 m	24–25 w	25.9 m	27.7 s
PR 202 beta	5.7 s	13.4 s	14.8 s	18.2 m	22.6 m	26.2 s	27.2 s	
PR 202 gamma	5.4 m	15.3 m	21.3 w	23 m	26.7 w	27.8 s		
PR 238	5.5 w	13 w	18.2 w	20.5 w	27 m	27.2 s		
PR 254	7.5 m	15.2 m	20.5 w	24.5 m	25.7 m	28.3 s		
PO 16	9.6 s	14.7 m	18.7 w	21 w	26 s	28 m		
PO 34	10 s	26.2 s						26.6 s
PO 36	10.2 m	12 m	14.5 m	18 m	21.2 w	22.5 m	27.3 s	
PY 120	10.3 m	15.5 w	16.4 w	19.6 w	26.5 s			
PY 155	5.5 w	16.5 s	17.2 m	16.5 w	17.5 w	19.2 w	21.7 w	
PY175	6.5 m	1.6 m	15.5 w	19 w	20.5 m	22.7 w	27 s	

21.6
Transmission Electron Microscopy

The Transmission Electron Microscope (TEM) is a powerful instrument that is used to determine the microstructure of materials at very high resolution (5–10nm).

Because the technique requires a very thin specimen, special sample preparation methods have been developed such as ultramicrotomy and ion milling.

Particle morphology and particle size have a considerable effect on the ease of dispersion of the pigment and therefore on the color strength in the medium of application. TEM is extensively used to determine the primary particle size and shape of pigments as well as to evaluate the extent of particle aggregation and agglomeration. High performance pigments usually undergo several processing steps during the finishing stages of their manufacture. These finishing steps can cause the originally well-dispersed particles to form hard aggregates or soft agglomerates. Aggregates are formed when the particles are grown together at their surfaces (face to face) and are not broken down by dispersion processes. Agglomerates are groups of single crystals or aggregates that are joined by their edges or corners and are not grown together. Agglomerates can be separated by dispersion processes. Due to the formation of agglomerates, the end user is required to apply a significant amount of energy to redisperse the particles in order to realize the full potential of the pigment.

21.6.1
Sample Preparation for TEM Analysis of HPOP

TEM has been applied to the analysis of dry powder pigments, flushes, pastes and dispersions. In most cases the sample preparation is quite simple.

For dry colors, 5–10 mg of the sample is dispersed in 5–10 mL of ethanol in a small vial (15 mL size) by sonication for approximately 1 min. One drop of the dispersed sample is then transferred onto a grid, which is placed on a piece of filter paper. If necessary, additional drops of sample are added onto the grid in order to collect a sufficient amount for analysis. The sample on the grid is allowed to dry before TEM analysis is performed.

For flush, dispersions or ink samples, approximately 1–2 mg is placed in 7 ml of toluene and sonicated to disperse the particles. If the sample bleeds in toluene, a weaker solvent such as ether may be used.

The primary particle size of HPOP is in the range 10–500 nm. More opaque pigments may have intentionally grown larger particles. Aggregates and agglomerates can be a few micrometers in size. Figures 21–23 and 21–24 show the TEM micrographs of two copper phthalocyanine blue samples having different degrees of agglomeration.

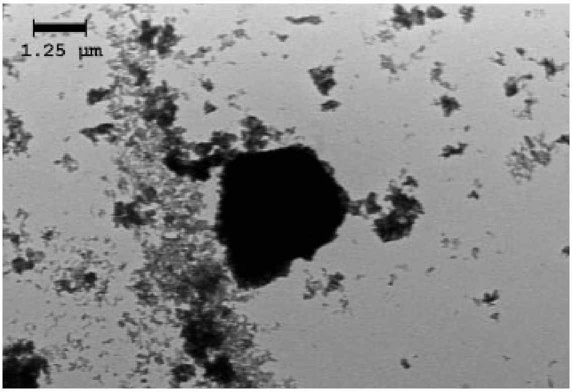


Figure 21–23: TEM micrograph of aggregated PB 15:3.

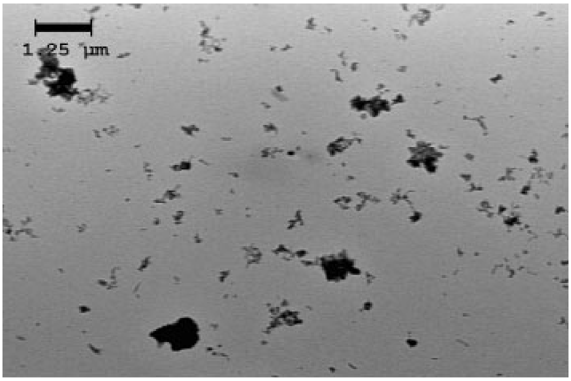


Figure 21–24: TEM micrograph of a less aggregated sample of PB 15:3.

The particle size and shape of red shade (alpha phase) and green shade (beta form) copper phthalocyanine is illustrated in Figures 21–25 and 21–26.

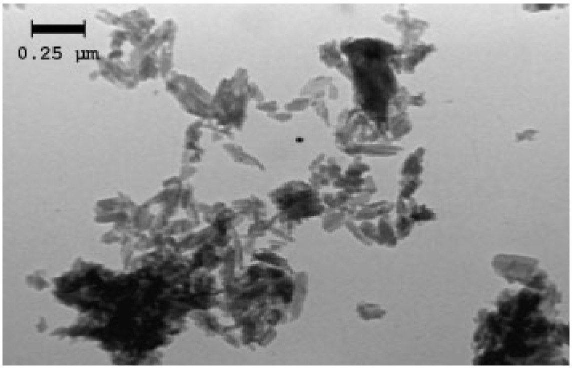


Figure 21–25: TEM micrograph of red shade (alpha phase) PB 15.

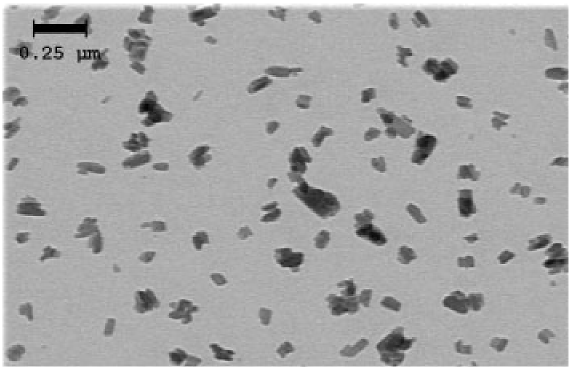


Figure 21–26: TEM micrograph of green shade (beta phase) PB 15.

Figures 21–27 and 21–28 illustrate the difference in particle size and shape between two commercial PR 144 samples.

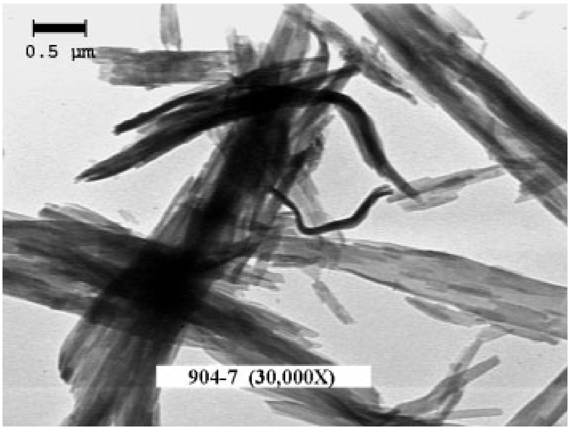


Figure 21–27: TEM micrograph of larger primary particle size PR 144.

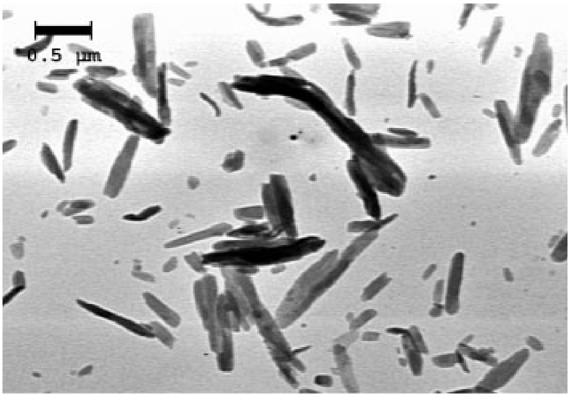


Figure 21–28: TEM micrograph of smaller primary particle size PR 144.

21.7
Optical Microscopy

Because of the physical properties of light (wavelength range) optical microscopy (OM) can only be applied to the observation of particles that are at least one micron in diameter or length. As a result, light microscopy has been used effectively to evaluate the degree or quality of dispersion of agglomerated or flocculated pigment particles in plastics or paints, as well as in aqueous and non-aqueous dispersions and pastes. Other applications include the analysis of large size particles in residues isolated from manufacturing processes or from a customer's equipment.

Like other analytical techniques, sample preparation for OM analysis is critical to the validity and accuracy of the results. Solvent-based paints, pastes or dispersions are often diluted with immersion oil to obtain a suitable particle concentration for examination. They are then pressed between glass slides prior to observation.

For aqueous dispersions, water or dilute surfactant solutions are used for sample preparation.

Thin plastic films may be observed directly without special preparation. For pigments in plastic dispersions or concentrates, a thin slice of the sample is cut using a special knife or preferably using microtome equipment prior to analysis.

The resulting optical micrographs are stored as images on a computer, and image analysis software is used to measure for particle size, particle area and aspect ratio. The size distribution may be plotted as histogram or a line curve for easy evaluation of the results.

A good illustration of the use of optical microscopy in the analysis of HPOP is shown in Figure 21–29. This is a sample of commercial automotive paint that contains PR 254 and PR 202. The OM of the original paint dispersion is shown on the left. When this paint was exposed to heat and shear conditions during the application process, there was considerable color shift to a less yellow shade. Optical microscopy was instrumental in determining that the color shift was due to particle flocculation, as illustrated by the micrograph shown on the right hand side in Figure 21–29.

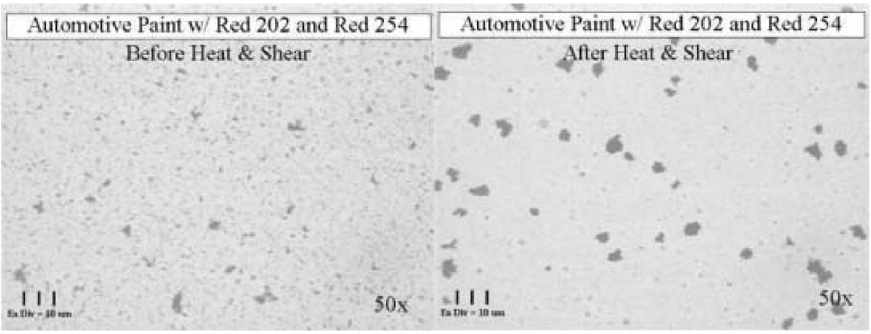


Figure 21–29: Optical micrographs of a non-flocculated automotive paint (left) and a flocculated automotive paint (right) of the same batch containing PR 254 and PR 202.

21.8
Chromatographic Techniques

Because of their very low solubility in organic solvents, HPOPs are not amenable to analysis by chromatographic techniques that require sample dissolution. However, pigment derivatives of HPOP that are soluble in organic solvents can be analyzed by liquid or thin layer chromatography. These include sulfonated derivatives of copper phthalocyanines, quinacridones and perylenes.

Dilute solutions of these derivatives are prepared in DMSO, and the solutions are then analyzed by reverse-phase liquid chromatography with or without ion pair reagents. Photodiode array detectors or UV-Visible detectors may be used for detection. Alternatively, electrospray ionization LC-MS may be used when both separation and identification of the colorants are needed.

Normal phase Thin Layer Chromatography (TLC) has been used for the detection of sulfonated pigment derivatives of copper phthalocyanine, quinacridones, perylenes, copper phthalocyanine sulfonamides, and phthalimido-methyl derivatives of quinacridones and copper phthalocyanines.

Because of the limited solubility and high polarity of these pigment derivatives, very strong solvents are used for elution by TLC. Commonly used solvents are mixtures of DMF, DMSO, acetic acid, toluene and methanol at various ratios.

Figure 21–30 illustrates the HPLC chromatographic separation of sulfonated copper phthalocyanine blue obtained by reverse-phase ion-pair chromatography. The early eluting peaks are higher sulfonated species, whereas the late eluting peaks are the mono- or di-sulfonated species.

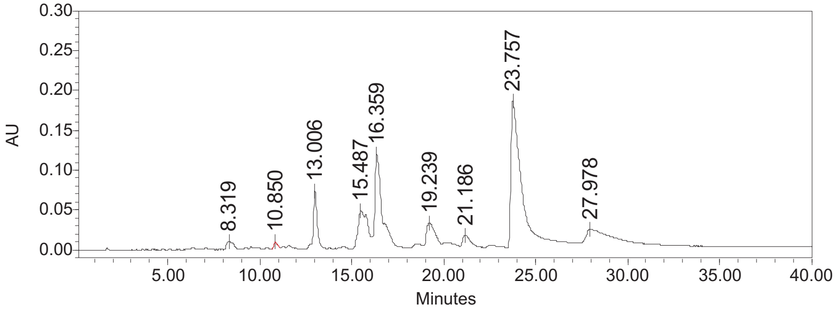


Figure 21–30: High performance liquid chromatogram of copper phthalocyanine sulfonic acid.

21.8.1
Environmental Testing of HPOPs for Impurities

Gas Chromatography with Mass Spectrometry (GC/MS) has been used for the determination of polychlorinated biphenyls (PCBs) as impurities in copper phthalocyanine blue and green, as well as in PR 144. PCBs are suspected carcinogens, and their concentration in commercial products is limited in the United States to a maximum of 25 ppm. Pigment manufacturers are required to monitor their products to ensure that they meet environmental regulations.

Polychlorinated Dibenzo Dioxins (PCDDs) and Furans (PCDFs) are also toxic, and their concentrations are limited to low PPB levels by European and US regulations. Trace levels of these substances have been detected in PV 23 and also in chloranil, the raw material used to manufacture PV 23.

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22

Regulatory Affairs for High Performance Pigments: North America

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22.1

Introduction

It would take a volume larger than this entire publication to provide the reader with a comprehensive review of North American environmental laws and regulations. Moreover, environmental laws and regulations are often delegated to, or the responsibility of, state and local governments. It would not be possible in one volume to review even the structure of these regulatory systems, which cover air, solid waste, water, hazardous waste, work place exposures, commercial chemical review and cleanup of waste and industrial sites.

In the following discussion, we will provide a brief overview of the commercial chemical review and reporting statutes and regulations which apply to organic and inorganic pigments of various types. Following this, we will review current issues which impact specifically on high performance pigments, with a short discussion of the recent issues we have identified which involve specific high performance pigments discussed elsewhere within this volume.

The two themes that have characterized recent changes in chemical regulations in the United States are the international movement toward increased regulation of chemicals that can be described as persistent, bioaccumulative and toxic (PBT) and the technology improvements which are reducing dramatically or eliminating the *de minimis* level. In the course of discussing these two themes, we will describe the basic regulatory schemes controlling the use of new chemicals in the United States.

22.2

Toxic Substances Control Act

New chemicals introduced in the United States are regulated under the Toxic Substances Control Act (TSCA)[1]. Review of new substances before distribution in commerce is incorporated into Section 5 of TSCA. A pre-manufacture notice (PMN) must be submitted to the Environmental Protection Agency (EPA) at least 90 days before the commencement of manufacturing or importing a new chemical. Additionally, a PMN notice must be submitted at least 90 days before the manufacture or processing of a chemical for a significant new use. Pursuant to TSCA, the EPA established an inventory of chemicals manufactured, processed or imported into the United States. The original inventory contained approximately 60 000 substances. Chemicals that are not on the inventory are considered new substances and require a PMN notice in order for manufacture, processing or import to begin. EPA is authorized to restrict or ban the manufacture, processing or import of new chemical substances and significant new uses of existing substances if evaluation indicates that limitations, restrictions, testing requirements or other actions are necessary to protect against an unreasonable risk of injury to health or the environment. Section 4 of TSCA authorizes EPA to promulgate test rules requiring manufacturers or processors to test chemicals or mixtures identified by the EPA for the purpose of assessing their potential risk to human health or the environment. Specific chemicals can be directly regulated under Section 6 of TSCA. Chemicals found to present an unreasonable risk of injury to health or the environment may be prohibited or severely restricted in manufacture, processing or distribution in commerce. TSCA Section 6(e) specifically regulates and restricts the sale and distribution of polychlorinated biphenyl compounds in commerce. The restrictions on the manufacture and sale of PCBs allow for excluded products and processes. Products may contain concentrations of up to 50 ppm of inadvertently generated PCBs with average concentrations which cannot exceed 25 ppm. Monochlorobiphenyl congeners are counted as PCBs at a discount of 50 to 1. Dichlorobiphenyl congeners are counted as PCBs at a discount of 5 to 1. For example, a PCB concentration of 200 ppm which is exclusively a dichlorobiphenyl would contain a concentration of 40 ppm PCBs under the regulations. To qualify as excluded products and processes, the manufacturer or importer must submit to the EPA, and maintain on file, certifications of compliance.

Section 8 of TSCA authorizes the EPA to require the reporting and record keeping of information involving chemical use and exposure. This includes an update of the chemical inventory undertaken by a mandatory survey form for all manufacturers, processors and importers every four years. Section 8(c) of TSCA involves reports of allegations of significant adverse reactions. Section 8(d) of TSCA requires the collection of unpublished health and safety studies on specified chemicals. Section 8(e) of TSCA requires the reporting of information that a substance presents a substantial risk of injury to health or the environment.

Section 12(b) of TSCA requires the notification to the EPA that chemicals regulated under specific sections of TSCA are being exported. Section 13 of TSCA involves notification to the EPA of import activity in violation of TSCA.

Despite its low profile in the EPA, TSCA fines collected for violation of this complex scheme of chemical regulation have often exceeded those collected under the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation and Liability Act, the Clean Air Act and the Federal Water Pollution Control Act. Much of this enforcement is centered on the information collection and reporting requirements of TSCA. Mixtures are not chemical substances under TSCA; however, all ingredients within a mixture can be defined as chemical substances. Articles are not considered chemicals under TSCA. The incorporation of chemicals into an article can be considered processing pursuant to TSCA. Foods, food additives, drugs, cosmetics and devices regulated under the Federal Food, Drug and Cosmetic Act are excluded from regulation as chemicals under TSCA. Also, pesticides regulated under the Federal Insecticide, Fungicide and Rodenticide Act may be excluded from regulation under TSCA as chemicals. In a presentation of this length, a complete review of the regulatory mechanisms developed under TSCA is not possible.

There are a number of pigment products excluded from the TSCA PCB rules as excluded products and processes. EPA now indicates that these excluded products require TSCA Section 12(b) export notification. TSCA Section 12(b) notifications to the EPA are required whenever chemicals regulated under specific parts of the TSCA statute are exported from the United States. The notices only identify the regulated chemical, for example PCBs, not the product the PCBs may be contained in. The notices also contain the name of the receiving country and other basic identification information. EPA, in turn, notifies the receiving country once for each regulated chemical once per year.

In the balance of this chapter, we will emphasize recent activity involving TSCA regulations of interest to pigment manufacturers.

22.3
Canada

Canada, like the United States, has a well developed system for control of new chemicals. The system is preventive and employs a pre-import or pre-manufacture assessment process. This system of regulation is contained in the Canadian Environmental Protection Act (CEPA). The inventory is referred to as the Domestic Substances List (DSL). Substances on the DSL are considered to exist in Canadian commerce and do not require new substance notification. Exclusions which are considered to be on the DSL include hydrates, homogeneous and heterogeneous alloys, special categories including glass, frits, ceramic materials, steel and cement and related chemicals, and substances occurring in nature. Exclusions from the definition of a substance for purposes of the DSL include mixtures, articles and wastes. New substances not requiring notification include those substances for which a premanufacture notice is provided under other Canadian laws, for example the Pest Control Products Act, the Food and Drugs Act, the Atomic Energy Control Act, the Fertilizer Act and the Feeds Act. Other substances not requiring notification include transient reaction intermediates, impurities, incidental reactants and exempt quantities in commerce. Environment Canada (EC) also maintains a separate "Non-Domestic Substances List" (NDSL), which includes substances that are not on the DSL but are believed to be in international commerce. The NDSL comprises substances which are on the TSCA inventory five or more years before the NDSL revision, minus the substances on the DSL. Substances listed on the NDSL require less detailed pre-market notification packages for assessment than substances that are new to both the DSL and TSCA inventories.

The data package required for pre-market notification in Canada varies. Factors include production or import quantities, uses, status under the NDSL and export-only or site-limited intermediate status. Interested readers are referred to the "Guidelines for the Notification of and Testing of New Substances: Chemicals and Polymers", published by EC. Generally, all chemicals new to Canada will require some toxicity and physical testing when production or import quantities exceed 10 000 kg/year.

22.4
Mexico

In order to improve environmental protection and conform to North American Free Trade requirements, Mexico is moving quickly toward increased environmental laws, regulations and related enforcement. Pursuant to the General Ecological Balance and Environmental Protection Law, Environmental Impact Regulations are enacted which include mandatory studies of the impact of products and processes on the health of humans, animals, plants and the environment for all new or already existing Mexican companies. As an example of this movement toward increased regulation, as recently as 1998 a pigment producer in Mexico was required to hold 27 different permits and comply with 256 different official standards. (See Business and Environmental Trends in Mexico, Ms. Alicia Lozano, CPMA Symposium, 1998.)

Mexico is also moving toward a chemical inventory regulation. The key question is whether this new approach will resemble that of the United States, Canada or some other existing system. With the recent dramatic change in government in Mexico, international suppliers should continue to follow these developments closely.

22.5
Toxic Release Inventory Reporting

The EPA also administers the reporting of chemical emissions under the Toxic Release Inventory (TRI). The TRI data collection and publication is part of a broader regulatory scheme established under the Emergency Planning and Community Right to Know Act. Recent changes in the TRI data collection will impact all pigment manufacturers. The TRI requires facilities to report releases of listed substances to the EPA. The list of substances that require TRI reports changes from year to year. EPA makes changes in the TRI inventory by rulemaking in response to petitions from industry, environmental interest groups, and state governments. The information contained in the report is available freely to the public on searchable online databases, both public and private. Until recently, all chemicals listed on the TRI required annual reports when threshold quantities in storage and use during the calendar year exceeded 10 000 pounds for substances used or processed or 25

000 pounds for manufactured substances. Also, until recently, there was in all cases a *de minimis* exemption in the TRI. The *de minimis* exemption allowed reporting facilities to disregard minimal concentrations of reportable substances in mixtures and trade name products processed or otherwise used by the reporting facility. Under new rules recently finalized by the EPA, substances designated as PBTs have dramatically lowered thresholds for reporting and can no longer utilize the *de minimis* exemption.

Canada has recently started an emission inventory similar to the United States TRI. As in the United States, information reported by facilities is freely available to the public. The FDA has recently pronulgated new rules which describe in detail the notice required for treshold analysis of new food contact substances including colors.

22.6
Regulation of *de minimis* Levels

In PBT-TRI rules, discussed in more detail below, *de minimis* levels have been dropped completely from threshold calculations. Additionally, there is no *de minimis* level for Section 12(b) reporting of TSCA regulated exports. In hazardous waste listing rules, parts per trillion (ppt) levels of chlorinated contaminants are now included in descriptions. We have for some time grown accustomed to the notion of parts per trillion concentration values for dioxin. With analytical methods now in use in the past year, we see this language applied to other compounds, PCBs in particular.

As this new technology, which can find virtually any amount in any media, is applied to other areas, it will have profound impacts. We have all seen reports of the new blood and tissue testing of humans which has uncovered lists of trace substances in extremely minute quantities. It is only within the last one to two years that these analytical results became technically possible. Instead, a non-detect level would be given below which we would assume “zero” or a level of no concern. We will now see these methods used in laboratory toxicology tests on test animals and cells. The results will create a never ending equivocal debate over how much is safe, since, for the first time, positive numbers above zero will be reported in final laboratory conclusions.

22.7
Food and Drug Administration

The Federal Food and Drug Administration (FDA) regulates the use of food colors and food contact colors in the United States. Food colors must be approved in an extensive petition process with the FDA. There are two methods by which food contact colors can be used. First there is the traditional food additive petition for use of a food contact substance. If successful, this process leads to listing in the Code of Federal Regulations (CFR) as a new color available for various substrates. Restrictions may be applied to the use of listed colors. The CFR should be consulted and legal advice should be obtained before making food use decisions. The second method by which food contact colors may be used is the threshold of regulation rules. Under this procedure, the manufacturer presents data to the FDA that shows that migration into food from packaging will be less than the daily dietary intake warranting regulation. If successful, the FDA will concede that the food packaging additive is *not* regulated by the FDA. Since the additive is unregulated by the FDA, it can be used in the *specific applications* that were substantiated in the no-migration analysis.

22.8
Color Pigments in General

There are so few issues that would apply to only one pigment that this general discussion should cover most of the issues for all color pigments. We have discussed briefly the shifting and disappearing *de minimis* level.

We now have the PBT-TRI reporting rules for chlorinated contaminants and the PBT-TRI rule for lead. The PBT rule for lead will apply to all pigment production in the United States. First, we should briefly review the background for PBTs and how this evolving scheme developed.

With respect to pigments, the story starts in late 1995. EPA circulated a list of target substances. The list contained only about sixty substances. Interestingly, this list was derived from several sources, including a complex screening method employed by the EPA for the prediction of bioaccumulative substances. Following this, letters were sent to many companies seeking information on a group of chemicals described as bioaccumulative.

There were a number of pigments on this list, including quinacridones. This list of bioaccumulative substances was derived from a complex screening methodology, dating back to 1984, which at first involved predicting the bioaccumulative properties of various substances using computer models. Bioaccumulative substances are generally defined to be those which collect in the fat tissues of fish and animals. With substances which bioconcentrate, the amount of the fat-soluble substance absorbed initially by one organism is concentrated up the food chain in other organisms.

Because of their size and low solubility, many pigment molecules are predicted to be bioaccumulative in the various models for predicting bioaccumulation. However, we know, based on the work of Anliker and Moser in the 1980s, that organic pigments do not bioaccumulate[2]. Organic pigments are extremely insoluble in water and octanol. Anliker and Moser showed that fish do not store organic pigments in fat tissues and, moreover, organic pigments are not soluble in lipids or octanol.

The voluntary data collection in 1995 made clear that EPA was looking for information on substances which may be persistent, bioaccumulative *and* toxic. We know that color pigments are not bioaccumulative, nor are color pigments toxic. Color pigments do persist and, indeed, are designed to persist. The most valuable color pigments, including all of those discussed in this volume, persist the longest in the harshest of environments.

This movement to identify PBTs follows logically from the realization that many of the most difficult environmental problems have been caused by specific organic, generally chlorinated, compounds, which include polychlorinated biphenyls (PCBs), dioxins, DDT, organic mercury and other pesticides. This internationally recognized list has been the subject of bans and restrictions in many countries. The issue for the near future is to find a way to define and eliminate similar compounds.

Through the 1990s, particularly since the list was first published in 1995, the search for a definition of PBTs, and, thereafter, the identification of new PBTs has developed into an international phenomenon involving regulatory efforts by many countries and the United Nations Programme for the Environment. In an attempt to use the PBT concept as a means of restricting much broader classes of chemicals, the EPA has begun to look at not just chlorinated organics, but all organic and inorganic substances as potential PBTs. Additionally, several states have begun to look at restrictions on both organic and inorganic substances based on preliminary classification by EPA as PBTs.

Shortly after the first list of 80 chemicals targeted for voluntary PBT data gathering was complete, the EPA issued the Waste Minimization Prioritization Tool (WMPT). This was originally a software tool given away in unfinished editions by the EPA for public interest groups to assess various substances in commercial waste streams. The WMPT was designed to assess the persistence, bioaccumulation and toxicity characteristics of chemicals. The scoring system used a maximum of nine points, with three points for persistence, three points for bioaccumulation and three points for toxicity.

The problem was that a benign, persistent substance, such as titanium dioxide, would score at least a 5 and in most cases a 6. This is because these benign substances persist and received a maximum score for persistence, together with the minimum scores for bioaccumulation and toxicity (which also contain a persistence sub-parameter). A minimum score in each category was still a score, not a zero. This scoring system, which also used predictive computer models to estimate bioaccumulation, often scored color pigments into a category together with known and far more dangerous substances. Many industry groups opposed the simplistic WMPT analysis.

EPA used the WMPT as a basis for a proposed “voluntary” waste reduction scheme. This has left the manufacturers of color pigments, which were categorized incorrectly in the beginning of this process, to continue arguing for some rational means of removing the unwarranted PBT label. The EPA proposed that industry reduce voluntarily by up to 50 % wastes containing a list of 53 constituents. These constituent chemicals included a list of metals. The listed metals included *all* compounds of lead, cadmium, nickel, arsenic, antimony, copper and zinc[3].

Many trade associations have opposed this new interpretation of metals as PBTs. Since metals are not bioaccumulative and persist as an essential part of the earth’s crust, the attempt to classify metals by a scheme designed originally for fat-soluble chlorinated organics such as PCBs and certain pesticides remains controversial.

Pursuant to TSCA, EPA has for several years examined new chemicals in its premanufacture notice process for PBT characteristics. Since most metals, and trace amounts of metals considered toxic, such as lead, are considered PBTs, and since many pigments, especially high performance pigments, are formulated to persist in the most adverse environments, many new pigment products have been delayed, limited or prevented from entering the market. This trend has been true for both inorganic pigments including the complex inorganic color pigments and organic pigments. (See for example, "Developing Safer Pigments Under TSCA", Ken Moss, USEPA, Presented at CPMA symposium, April 9, 1998.) In the absence of bioaccumulation data, EPA will use estimates based on models to determine bioaccumulation and bioconcentration characteristics. These models are often in error when attempting to predict bioaccumulation parameters for extremely hydrophobic substances, insoluble in both water and octanol or fat[4].

Another PBT area we are monitoring is the review underway in Canada of the chemicals listed on the DSL pursuant to the CEPA. It appears that EC will begin its exhaustive assessment of the Canadian DSL inventory by first reviewing all of the chemicals listed in international HPV programs. The OECD international HPV program includes both inorganic and organic chemicals. This list does include pigments. We know of 14 pigments on the United States HPV testing program list and probably more will follow as United States inventory update years 1994 and 1998 are considered in the future.

22.9 PBT-TRI Rules

We now turn our focus to the PBT-TRI reporting rules. The most significant aspect of these rules is that EPA has withdrawn the *de minimis* exclusion. Without the *de minimis* exclusion, all contaminants at any level, known or estimated, must be considered in determining whether or not reporting thresholds are exceeded and what emissions, if any, occurred at the reporting facility. The final PBT-TRI rule[5] requires that Form R inventory emission reports be submitted for any of the chemicals in Table 22–1 at the noted threshold:

Table 22–1.

	CAS No.	Threshold
Polychlorinated biphenyls	1336-36-3	10 pounds
Hexachlorobenzene	118-74-1	10 pounds
*Dioxin and dioxin-like compounds		0.1 g

* polychlorinated dibenzodioxins and polychlorinated dibenzofurans congeners specifically listed in the Final Rule and EPA's reporting guidance, 17 compounds total.

Therefore, facilities must report under the TRI if any of the above compounds used, processed or manufactured exceed the threshold in the course of a calendar year. The threshold for dioxin applies to initial manufacture or import of the defined dioxin congener. If a substance containing dioxins is purchased for further processing from another manufacturer or importer, those dioxins are not reportable on the TRI since those dioxins already existed and were reported by the manufacturer or importer of the product. It should also be noted that actual analysis of raw materials and products for trace contaminants is not required. However, faced with the prospect of conservatively estimating dioxins or total PCB contents within products, many companies may undertake sampling and analysis plans. Such plans may avoid reporting contaminants that are not actually present. The TSCA definition for PCBs, which discounts mono and dichlorobiphenyl and contains exclusions for inadvertently generated PCBs, does not apply to the Emergency Planning Community Right-to-Know Act (EPCRA).

The TRI is a part of EPCRA. As discussed above, EPCRA defines PCBs for purposes of reporting by the CAS Number cited above. This CAS Number covers all chlorinated congeners of monochlorobiphenyl. It can certainly be argued that these statutes present a contradiction.

The issue to be decided in undertaking a TRI sampling plan is that EPA does not allow for zero or a non-detect level for substances designated PBTs. For example, if you decide to analyze a specific raw material for PCBs and the laboratory returns a none-detected report, you still may have exceeded the threshold. This is due to the fact that if a none-detect level is provided, EPA's guidance indicates that the reporting facility must use that upper bound concentration as a means of calculating the amount of PCBs in the product. In other words, you must assume the PCBs are present even if the best available information indicates that PCBs are probably not present.

This elimination of the *de minimis* level could cause reporting facilities to spend even more resources. If resources are used to obtain the highest resolution analysis by the best methods, lower detection limits can be obtained on the final analytical report. By lowering the upper bound concentration, a more accurate quantification can be obtained for PCBs, in trace amounts, which are actually in the raw material or product. Of course, since these new TRI Rules involve trace quantities, estimations must include not only a finished product, but all of the starting materials that go into the finished product. In practical terms, reporting facilities will complete an extensive spreadsheet analysis to include each congener of each reportable chemical for each product, and will then compile all of those spreadsheets to create a master analysis of all of the products in production in the course of a year. Even if a facility *never* completes a Form R report because the reporting threshold of ten pounds of PCBs is not exceeded, considerable time and effort will be spent preparing a threshold analysis capable of withstanding inspection. If a facility does fill out a TRI report, it is now required to duplicate this effort for each air emission, effluent or solid waste. Reporting facilities can economize and report conservatively by estimation PBTs that may not exist, but the potential costs incurred later in community relations and even lawsuits argue against that strategy.

To turn our attention to laboratory methods, the high resolution method of analyzing for dioxins at extremely low (parts per billion) levels has been available for many years. A new EPA method claims similar and greater accuracy for PCB analysis: EPA method 1668A. We have seen this method used by state authorities to analyze water and sediment samples. There are indications that it will become more prevalent in the future and may be the only means of getting accurate analysis for purposes of completing TRI reports.

Another problem built into the PBT-TRI rules is that these rules will impact customer organizations. While few customer organizations will be impacted by the reporting rule for dioxin, the PCB and lead rules will impact many customer organizations in many industries. This will create more customer pressure to disclose more accurate results for trace amounts of these identified compounds.

The final lead PBT-TRI reporting rule is very similar to the other PBT rules described above. The lead PBT reporting rule was issued as a final rule on January 17, 2001[6]. The threshold for reporting all use, process or manufacture of lead, at any level, is one hundred pounds. Again, like the rules described above, the lead rule requires an extensive analysis of background lead levels in products and raw materials. We should note that when it comes to lead analysis, the raw materials may include the water and water ice used in production.

The lead rule included a statement that the rule was being forwarded to the Science Advisory Board (SAB) for further analysis. A coalition of metal-related trade associations have objected to the classification of metals as PBTs and have requested that EPA withdraw the final rule until the Science Advisory Board has time to thoroughly review the issue. It is certain that if lead is classified as a PBT, many other metals including those identified as human nutrients may also be classified as such.

The TSCA Inventory and the amendments to the review procedures for new PBT substances must be considered, particularly in light of the issues involving metals. Since nickel, antimony, chromium, copper, lead and other metals have been described as PBT substances, a new issue arises with the desire to create new pigments in this segment of the industry. The TSCA chemical inventory review process now requires that each new pigment and each new variation of each new pigment be reviewed for its "bioaccumulative properties". This has reportedly slowed down or even stopped the review of new complex inorganic color pigments. There has also been a dramatic increase in the costs of these applications. Being virtually insoluble in water, oil or even dilute acid, these pigments do not break down and cannot collect in fat tissue.

Many nations are engaged currently in the negotiation of a new treaty for Prior Informed Consent by receiving countries for international chemical shipments. If and when this treaty is complete, the result will likely mean changes in the TSCA Section 12(b) reporting rules. It is possible that PCB-excluded products will at that time be excluded from prior notice requirements.

There are also international developments surrounding the restriction and identification of Persistent Organic Pollutants (POPs). All indications are that any international protocol will have a strong bias toward actual testing results for bioaccumulation and toxicity, rather than computer modeled estimates. While such a protocol may require more testing as specific color pigments are reviewed, erroneous identification of hydrophobic color pigments as bioaccumulators should be reduced under this protocol.

There is also international negotiation underway to decide the extent to which identified POPs should be restricted or eliminated. The POPs already identified include PCBs. Some countries and environmental groups have continued to call for the “precautionary principle”. The precautionary principle allows for regulatory restriction without sufficient data to quantify a significant risk. Under these proposals, unintended trace contaminants would be eliminated, since there would be no *de minimis* level. For example, the current international standard for concentrations of PCBs not exceeding 50 ppm would require change.

The countries opposed specifically to the elimination of unintended trace contaminants have included the United States and Japan. Interestingly, the reasons cited in trade journals for the United States opposition include the manufacture and sale of products that would include inadvertently generated PCBs, such as “paint pigments”.

22.10
High Production Volume (HPV) Substances

Growing out of the search for new PBTs, the High Production Volume (HPV) “voluntary” testing initiative has continued to develop with the first proposed rule for testing a short list of specific HPVs and the publication of controversial final testing guidelines in the Federal Register. HPVs are chemicals produced in amounts that exceed one million pounds per year. The proposed rule contains a list of chemicals for which EPA will require that manufacturers and importers perform a battery of risk related screening tests referred to as the Screening Information Data Set or SIDS. This package of screening tests was copied from an international program. The international program, also involving voluntary industry participation with sponsorship and oversight provided by individual countries, has stepped up the testing of HPV chemicals. International HPV programs are both inorganic and organic. The United States HPV program is specific to organic substances.

By the end of calendar year 2000, a total of 469 companies had sponsored 2155 HPV chemicals in the United States There were 2800 HPV chemicals identified based on the 1990 update of the TSCA inventory. The 37 chemicals included in the proposed rule are a subset of those chemicals that were not sponsored in the voluntary program. The SIDS testing endpoints include: acute toxicity, repeat dose toxicity, developmental and reproductive toxicity, genetic toxicity, ecotoxicity and environmental fate. It should be noted that this test battery includes a number of physical properties including: melting point, boiling point, vapor pressure, *n*-octanol/water partition coefficient, water solubility, photolysis, hydrolysis, transport/distribution and biodegradation. All of the pigments represented in the list of 2800 HPV substances were sponsored with one exception, Alkali Blue. Alkali Blue (CI Pigment Blue 61) is included in the list of 37 substances addressed by the proposed rule[7].

Several pigments are already the subject of international Organization for Economic Cooperation and Development (OECD) SIDS sponsorship. Several more pigments have been added to those already sponsored under the OECD program. In the United States, unnecessary testing can be avoided with the use of Structural Activity Relationship (SAR) analysis, whereby risk assessment data developed for very similar analogous substances are substituted for new data on the target compound. As part of the HPV program, companies or sponsoring consortia may post robust summaries of test data already available for target HPV or structural analogs.

Available data for the pigments that have not been sponsored internationally may reduce or eliminate the need for further testing.

22.11
Phthalocyanine Pigments

Since phthalocyanine pigments are produced using the metal copper, copper phthalocyanines have, at least temporarily, become PBTs. The “voluntary” waste minimization PBT notice included copper as one of the metals declared to be PBTs. As a result, copper phthalocyanine pigments became PBTs.

Phthalocyanine green pigment is listed on the HPV list as one of the substances which will require SIDS testing. There is a wealth of such data available for phthalocyanine pigments. The data available includes several intermediate level feeding studies in both mice and rats. One set of intermediate feeding studies evaluating phthalocyanine blue and green pigments was sponsored by the United States National Toxicology Program. It appears that this HPV testing will be completed under the international initiative, with sponsorship and review in Europe and Japan.

Phthalocyanine pigments may also contain PBTs in the form of trace chlorinated contaminants inadvertently generated during production. In the future, both as a result of POPs developments and PBT regulation, we can expect some regulatory issues to center on these pigments. Phthalocyanine pigments will also be regulated under the new PBT-TRI rule. Manufacturers and users should assess whether TRI reporting thresholds for chlorinated organic contaminants have been met, and whether TRI reports should be submitted to EPA.

22.12
Quinacridone Pigments

Quinacridone pigments are the original pigments to find their way into the EPA PBT focus. Quinacridones were among the potential PBTs that emerged from the screening of the EPA database discussed above. It would appear that this screening was in error. Quinacridone pigments have been tested for bioaccumulation, and they are not bioaccumulative. The original EPA screening was accomplished using computer models to predict fat solubility. The bioaccumulation factors produced by the models do not accurately reflect the characteristics of extremely insoluble compounds. As a result, while these compounds are tested in actual laboratory analysis to be insoluble in octanol and water, the model appears to assume a fat solubility and calculates an erroneous value.

Two quinacridone pigments and two quinacridone intermediate compounds appear on the Interagency Testing Committee (ITC) data submission list. The ITC reviews chemicals in commerce for potential data collection rules under TSCA. The two high performance red pigments are known to be less soluble than the basic unsubstituted quinacridone, C.I. Pigment Violet 19. C.I. Pigment Violet 19 has been extensively tested for bioaccumulation, as well as toxicity parameters. There is no reason to believe that the less soluble and stable varieties (C.I. Pigment Red 122, 207 and 202) are, or could be, toxic or bioaccumulative, while C.I. Pigment Violet 19 is not. With respect to the intermediates, we believe these substances are only produced and used in pigment manufacturing and that exposure is therefore limited.

The quinacridone pigments are represented on the HPV list of substances that require review under SIDS protocol. Again, it would appear likely that sufficient data, much of it currently unpublished, will be available to avoid significant and costly mammalian toxicity testing for the quinacridone pigments represented on the list.

22.13
Carbazole Violet Pigments

Carbazole violet pigments, like most of the other organic pigments types, may possibly contain (CI Pigment Violet 23) chlorinated trace contaminants, at part per billion levels, which may be included in the finished pigments. These trace contaminants are established PBT substances. Therefore, if a manufacturer or importer has sufficient information to estimate the total amount of PBT substances present at trace levels, that manufacturer or importer would be required to assess and if necessary submit a TRI emission form to EPA.

Many domestic manufacturers have reached an agreement with the EPA regarding the quality of pigments and the background levels of chlorinated contaminants that are acceptable. With new imports of carbazole pigments and crudes, concern is now raised that those agreements should be extended to importers through a mandatory significant new use rule. Importers could theoretically use lower quality intermediate chemicals that are not available to domestic manufacturers because of the existing agreements with the EPA to use only high purity ingredient compounds. Since there is no obligation to test new substances under the PBT-TRI rule finalized last year, it is not clear that the requirements applicable to importers have changed at all under the final rule. The final EPA TRI reporting guidelines do clearly identify manufacturers or importers as the only entities required to report in the TRI for carbazole violet pigments, since only these entities could “create” new contaminants. Customers do not have an obligation to report. (See Emergency Planning and Community Right-to-Know Act Section 313: Guidance for Reporting Toxic Chemicals within Dioxin-like Compounds Category.)

22.14
Perylene Pigments

The ITC recently published a voluntary data submission list for “58 Potentially Persistent Dyes and Pigments”. This list, which indicates that the ITC is considering a TSCA data collection under TSCA Section 8, includes two perylene pigments. The

ITC is reviewing many chemicals that do not appear on the HPV lists for possible risk and PBT characteristics. The end result of this process for both perylene and quinacridone pigments may be mandatory information gathering rules under TSCA.

It is apparent that the ITC list is based on computer modeling of PBT parameters. In particular, it appears that estimations of the toxicity and bioaccumulation properties of pigments have been determined using computer modeling techniques.

22.15
Inorganic Pigments

22.15.1
Complex Inorganic Color Pigments

The complex inorganic color pigments are among the most stable of all pigment types. Unfortunately, in the United States many of these pigments have now been identified as PBTs. Three separate regulatory initiatives recently have classified many of these pigments as PBTs: the amendments proposed for the TRI, the waste minimization PBT proposal and the new review parameters for pre-manufacturing (PMN) review of new substances.

The TRI amendments were very surprising for our industry and especially for the complex inorganic color pigment manufacturers. The original idea, first proposed in an advanced notice for proposed rulemaking, was to reduce the reporting threshold for certain “dioxin-like” substances, such as those generated in large scale chemical and refining operations. However, when the rule was actually proposed, there was an extensive, though largely unsubstantiated, discussion of the elements cobalt and vanadium. The implication was that cobalt and vanadium were now “dioxin-like”.

The rule implied that these two metals had somehow become PBTs. The EPA was considering lowering the reporting thresholds under the TRI for cobalt and listing all compounds of vanadium as TRI reporting substances in the future. It is interesting to note that the proposal specifically exempted alloys, such as steel, containing cobalt and vanadium.

The final rule listed bismuth vanadate, as a vanadium compound, as a TRI compound for annual reporting[8]. The rulemaking did not include a reasonable argument for the bioaccumulation of either cobalt or vanadium metals included in insoluble compounds. Nor was there any mention of cobalt blue or vanadium yellow pigments.

The final PBT-TRI rule did not change the TRI reporting requirements for cobalt. Vanadium compounds were added to the list of TRI reportable substances. Reporting thresholds are the same as other substances, 10 000 pounds for chemicals processed or otherwise used or 25 000 pounds for manufactured compounds.

A petition has been submitted to the EPA to delete chrome antimony titanate (CAT) from the list of chemicals reported under the TRI. Facilities are required to report emissions of CAT because of the presence of chromium and antimony. All compounds of chromium are reported under the TRI without regard to valence (usually described as trivalent, hexavalent or metallic). After several years, we are still awaiting the response to that petition at this time.

OECD-HPV testing is now underway for nickel antimony titanate. It is our understanding that mammalian development and toxicity testing are now complete and preliminary results show no toxicity.

The waste minimization PBT rule could also have a dramatic impact on complex inorganic color pigments. This notice, which appeared in the Federal Register[9], requested that industry voluntarily reduce the wastes which contain 53 chemicals (or chemical groups) by 50 % by 2005, compared to a 1991 baseline. The notice made no exceptions for non-bioavailable compounds and wastes. As discussed above, this notice was based on the Waste Minimization Prioritization Tool. Also, with this notice, the EPA proposes to regulate all metal compounds without regard to their bioavailability characteristics and the benefits of individual compounds containing those metals. EPA is expected to finalize the waste minimization program list in the near future.

The Minnesota Toxics in Specified Products Law also impacts on complex inorganic color pigments. The law bans all ink, paint, pigments and dyes which contain lead, mercury, hexavalent chromium and cadmium. The exemptions for the complex inorganic color pigments now cover fourteen pigments which could, in theory, exceed 100 ppm for each of the four listed metals. Of those fourteen pigments, eight pigments were actually documented by survey to contain more than 100 ppm of one or more of the four metals.

The Minnesota Listed Metals Advisory Council (LMAC) has completed its review of color pigments under the Toxics in Specified Products Law. The LMAC voted unanimously in favor of not banning the use of complex inorganic color pigments, lead chromate pigments and cadmium pigments. Specific LMAC reviews of many paint and ink products were also completed in 2000. These include automotive paints, architectural and maintenance coatings.

22.15.2
Cadmium Pigments

Many of the issues discussed above with respect to the complex inorganic color pigments are also applicable to cadmium pigments. Cadmium and all compounds of cadmium, without regard to bioavailability or other characteristics, have been declared to be PBTs. Cadmium and particularly cadmium pigments are not known to be absorbable in animal fat or octanol. The element is ubiquitous, and it is known to persist permanently in the environment. The EPA continues to claim that, since at least some metal compounds are highly soluble and toxic, all other related compounds are also assumed to be toxic. Further, the fact that many metals are absorbed, used and regulated in humans does not appear to change this approach.

Cadmium pigments are included in the waste minimization PBT notice. The long term impact of a requirement to reduce cadmium waste by 50 % could have a dramatic impact on cadmium pigments in the market place. We do not know the form this notice will take, and discussion with metals industry groups and others is ongoing.

The Occupational Safety and Health Administration (OSHA) standard for exposure to cadmium in the workplace was reversed and remanded to OSHA by the United States Court of Appeals for the Eleventh Circuit for the dry color formulator industry. As a result, the standard applicable to the dry color formulator industry is the previous standard (200 micrograms per cubic meter). *Color Pigments Manufacturers Association, et al. v. OSHA*, Case Number 92–3057, March 22, 1994.

The Minnesota Toxics in Specified Products Law remains an important issue for cadmium pigments. The LMAC has voted unanimously not to ban cadmium pigments in Minnesota. Specific product reviews for certain commercial and industrial coatings did result in bans of those products. Pigment consumers should carefully assess the status of product types and pigment availability before manufacturing in Minnesota.

22.16
Conclusion

The PBT regulatory scheme continues to shape regulations in the United States and Europe. These regulations will take different forms in the United States and Europe. In Europe we see a continued push toward product bans and restrictions constructed as exemptions to product bans. In the United States, we have modifications to existing regulatory schemes for existing chemicals and far greater scrutiny of new chemical products.

The elimination of *de minimus* levels, coupled with new, and for the foreseeable future, very expensive analytical methods for trace contaminants, will have a significant impact on the cost of doing business in the United States. These costs will impact both the manufacturer and importer of color pigments. The ongoing debate over the classification of metals as PBTs will also have a significant impact on the color pigments industry. If metals are accorded an automatic toxicological classification equivalent to established PBTs such as pesticides, both organic and inorganic manufacturers and importers could see significant new regulatory burdens for monitoring and reporting in the near term.

References

1 15 U.S.C.A. Sections 2601–2692.

2 Anliker, R. and Moser, P., “Bioaccumulation of Organic Pigments in Fish: Their Relation to the Partition Coefficient and the Solubility in Water and Octanol,” Ecotoxicology and Environmental Safety, (1989) Vol. 13, pp. 43–52.

3 63 Fed. Reg. 60332.

4 64 Fed. Reg. 60194.

5 64 Fed. Reg. 58666.

6 66 Fed. Reg. 4500.

7 65 Fed. Reg. 81658.

8 64 Fed. Reg. 58666.

9 63 Fed. Reg. 60332.

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23

Regulatory and Legislative Aspects of relevance to High Performance Pigments: Europe

Eric Clarke and Herbert Motschi

23.1
Introduction

The aim of this chapter is to provide an overview of the chemical control regulations in Europe of relevance to organic pigments and with emphasis on the European Union (EU) requirements. Many aspects of the complex EU requirements are dealt with in this chapter only briefly, if at all. However, by means of references to further sources of information, it is hoped that the reader will be helped to find the answers to many questions relating to the regulation of the manufacture or import, marketing and use of pigments in Europe. In general, all chemical substances, high performance pigments or otherwise, hazardous or non-hazardous, are subject to European chemical control regulations. There are some exemptions (see Sec. 23.3.1.2) under the individual regulations. In this overview of the general requirements, particular attention is given to those regulations which specifically impact pigments.

23.2
The European Union and its Institutions

Europe comprises many more people and states than the European Union itself.

European Union	Population:	370 million
	GDP:	$ 7600 billion
	Member states:	15
Other European countries	Population:	390 million
	GDP:	$ 1290 billion
	Countries:	25

A simplified organization of the institutions of the European Union is given in Figure 23–1. The responsibilities of these institutions are given in the following sections.

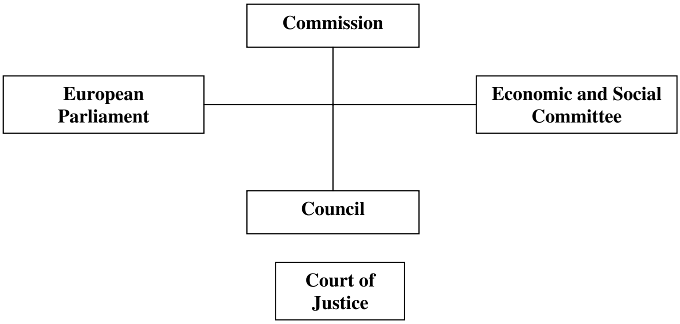

Figure 23–1: Simplified organization of European institutions.

23.2.1
European Commission

The European Commission consists of 20 members. The commissioners are citizens of the 15 member states but are required to act independently and in a non-partisan way. Only the Commission can initiate proposals for new legislation, following consultations with governments, industry, labor and special interest groups and, as required, technical experts. The principle of subsidiarity, enshrined in the Treaty of the European Union, limits legislative proposals to areas where European Union legislation offers benefits over the legislation of individual member states.

The European Commission, with a staff of about 15 000 people, is the largest of the EU institutions. It is organized into 36 directorates-general and specialized services. The directorates-general of most importance to chemical control requirements are listed in Table 23–1.

Table 23–1: European Commission: directorates general involved in aspects of chemicals control regulations.

Enterprise
Environment
Health and Consumer Protection
Internal Market
Joint Research Centre

In addition to initiating Community policy, the European Commission is responsible for:

- safeguarding the EU treaties and ensuring that European legislation is correctly applied and enforced
- negotiating international trade and cooperation agreements

23.2.2
European Parliament (E.P.)

The European Parliament consists of 626 members, elected every 5 years by the citizens of the member states. Given only a consultative role under the 1957 Treaty of Rome, which provided the basis for forming the European Economic Community, the influence of the European Parliament has been extended under subsequent treaties. Differing procedures apply, depending on the legislative aims:

- Consultation
  Parliament gives its opinion on a Commission legislative proposal before it can be adopted by the European Council.
- Co-decision procedure
  This is of particular importance in several areas, including consumer health and environmental protection. Decision-making power is shared equally between the Parliament and Council (see Figure 23–2) and, where necessary, a compromise text is prepared by a conciliation committee. If agreement is not reached, the Parliament can reject the proposal.

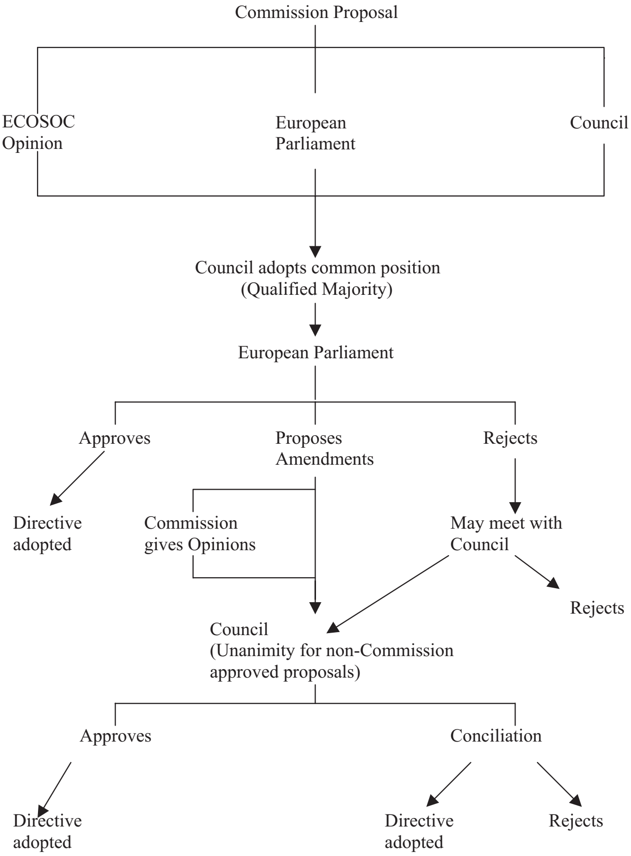

Figure 23–2: Co-decision procedure.

Other important responsibilities of the European Parliament are:

- approval of the European Union budget
- approval of international agreements, including the accession of new member states
- supervision of the executive powers of both the Commission and Council
- approval of the appointment of the full Commission college and president.

23.2.3
The Council of the European Union and other Institutions

The Council of the European Union should not be confused with the Council of Europe, which is an international organization of 40 European countries, based in Strasbourg. The Council of the European Union, also known as the Council of Ministers, sets out the political objectives of the European Union and coordinates national policies. Each member state is represented by one minister on the Council, depending on the subject under discussion (e.g. foreign affairs, finance).

Other important institutions are the Court of Justice, the Economics and Social Committee, the Court of Auditors, the European Investment Bank, the European Central Bank, the Committee of the Regions and the European Ombudsman.

23.2.4
Legal Instruments

European Law consists of three different types of legislation:

Primary legislation: the treaties and other agreements, notably:

1957 The Treaty of Rome (EEC Treaty) establishing the European Economic Community (EEC) as a common trading market

The articles of the EEC Treaty of particular relevance to chemicals control are:

– Article 100 a	Harmonization of requirements, but with the possibility of some exceptions
– Article 118 a	Worker protection
– Articles 130r, 130s, 130t	Environmental protection

1987 The Single European Act (SEA) came into force

1992 The Maastricht Treaty on the European Union (TEU). This created the European Union and consists of three parts:
  - common foreign and security policy
  - home affairs and justice policy
  - amended EC treaty

These Treaties provide the legislative framework for the “secondary legislation”, which consists mainly of directives, regulations and decisions.

- Directives
  A Directive defines the results required but leaves member states to decide the form and means of achieving these results. The member states are

required to implement the necessary laws or regulatory instruments within a designated time limit.

- Regulations

  Regulations are binding and directly applicable to all member states. They automatically enter into force on a specified date, usually several days after publication in the Official Journal of the European Union.
- Decisions

  These are binding, as designated, on member states, companies or individuals.

Additional instruments include “recommendations”, “resolutions”, and “opinions”. These are non-binding and are issued by the “Council”, “Parliament and Council” or “Commission”.

- Case law

  This is founded on the judgments of the European Court of Justice, which is responsible for ensuring that the law is observed in the interpretation and application of the treaties.

23.3
The Major EU Directives Governing Chemical Control

The main EU directives governing chemical control are summarized in Table 23–2.

Table 23–2: Overview of EU chemical control directives and regulations.

	Regulated by:		*Aspects*
Hazard assessment	Dangerous Substances:		
	6th Amendment	79/831/EEC	Notification of new substances
	7th Amendment	92/32/EEC	Testing requirements
			Classification criteria
	General preparations	88/379/EEC	Harmonized labeling
		1999/45/EC	Packaging requirements
Risk assessment	Evaluation and control of risks from:		
	Existing substances	Reg. (EEC) No. 793/93	Data reporting
		Reg. 1488/94	Priority lists
	New substances	93/67/EEC	(See Sec. 23.3.4)
Risk management	Safety data sheets	91/155/EEC	Hazard communication
	Waste	91/689/EEC 91/156/EEC 94/62/EC	Safe handling and disposal
	Integrated pollution prevention and control	96/61/EC	Reducing environmental releases
	Marketing and use	76/769/EEC	Risk reduction

23.3.1
Dangerous Substances (Commission Directive 67/548/EEC)

Commission Directive 67/548/EEC[1] established a harmonized system of classification, packaging and labeling applicable to dangerous chemicals. This basic Directive has already been subject to eight amendments and 28 adaptations to technical progress (ATPs). The most important amendments are the 6th Amendment[2] and the 7th Amendment[3], the most significant aspects of which are summarized in Table 23–3.

Table 23–3: Highlights of requirements under 6th and 7th Amendments to Commission Directive 67/548/EEC.

6^{th} Amendment (79/831/EEC)	***7^{th} Amendment (92/32/EEC)***
Notification of new substances from 100 Kg upwards	Reduction of notifiable amounts of new substances to 10 kg.
Hazard evaluation of new and existing substances	Risk assessment for new substances
Classification of dangerous substances	Reporting of available data for existing substances
Labeling of dangerous chemicals (with hazard symbols, risk and safety phrases)	Obligation for safety data sheets for dangerous substances and preparations
Reporting obligations for certain dangerous substances	

23.3.1.1 Some Differences between EU and US Requirements

Although many parallels can be drawn between the 7th Amendment (92/32/EEC) and the United States Toxic Substances Control Act (TSCA), there are several fundamental differences:

- The 7th Amendment requires pre-marketing notification of new substances whereas the United States requirement is for pre-manufacturing notification.
- Whereas the TSCA inventory is open and includes the existing substances and notified new substances in the European Union, there is a closed inventory of existing substances (European Inventory of Existing Chemical Substances – EINECS) and a separate list of notified new substances (European List of Notified Chemical Substances – ELINCS).
- Under the EU requirements, second or subsequent importers or manufacturers of a new substance must also notify a new substance, whereas under the United States regulations this obligation does not apply once the substance has been added to the TSCA inventory. If the identity of an Inventory substance is confidential, it will be listed in the public Inventory by a generic name. There is a procedure (CFR 720.25) under which the EPA will inform whether a substance is on the confidential Inventory provided a bona fide intent to manufacture or import is established.

- The EU prescribes the information to be provided in the notification dossier including physical-chemical properties and toxicological and ecological test data. The extent of the data package required depends on the amount of substance placed on the EU market. In the USA there is no specified data set, but the EPA is empowered to demand such testing as is deemed necessary to enable a risk assessment to be made or, under Sec. 5(e) of TSCA, testing may be required if the substance is produced in substantial amounts and there is significant human or environmental exposure.
- Notification obligations for polymers differ significantly under the EU and TSCA requirements, which may be relevant for master batches but not for organic pigments themselves.

23.3.1.2 **Notification**

EINECS is an inventory of “existing chemicals” which were commercially available during the period 1971 to 1981 in the then European Economic Community. After September 1981, chemical substances marketed for the first time became subject to notification. There are some exemptions from this notification obligation:

- Substances covered by separate legislation – medicinal products, pesticides, cosmetics, food additives and flavorings, radioactive materials, foodstuffs, animal feedstuffs, waste materials, substances solely for export from the EU,
- “No longer polymer” substances. A list of substances not included in EINECS, but affected by a redefinition of the polymer exclusion,
- Substances placed on the EU market in quantities of less than 10 kg per year,
- Substances for scientific research and development,
- Substances for process-oriented research and development.

Special notification arrangements were also made subsequently for chemical substances of the former German Democratic Republic which were not included in EINECS[4].

Substances listed in EINECS are not subject to the notification requirements and are referred to as “existing substances”. Substances not listed in EINECS are designated “new substances”, and those intended for commercial use must be notified to the competent authorities. Notification involves submitting the competent authority with a technical dossier containing prescribed data on physical-chemical, toxicological and ecotoxicological properties. Information must also be provided on identity, production, proposed uses, safe handling requirements and the proposed classification and labeling. Table 23–4 summarizes the data requirements.

Table 23–4: Summary of new substance notification data requirements and testing costs.

Requirements up to 100 t/y	*< 100 kg/y*	*100–1000 kg/y*	*1–10(0) t/y*[1)] *(Base Set)*
Identification			
Spectra	X	X	X
Analytical method			X
Physical/chemical properties			
Flash point or flammability	X	X	X
Melting point		X	X
Boiling point		X	X
Water solubility		X	X
Partition coefficient		X	X
Relative density			X
Vapour pressure			X
Surface tension			X
Explosive properties			X
Autoflammability			X
Oxidizing properties			X
Particle size distribution			X
Toxicity			
Acute oral toxicity	X	X	X
Skin and eye irritation		X	X
Ames test		X	X
Acute inhalation toxicity			X
Acute dermal toxicity			X
Skin sensitization			X
Subacute (28 d) toxicity			X
Additional mutagenic tests			X
Ecotoxicity			
Biodegradation		X	X
Fish toxicity			X
Daphnia toxicity			X
Algal growth inhibition			X
Bacterial inhibition			X
Hydrolysis			X
Ads./Des. screening test			X

1) A selection from Level 1 (Annex VIII) in agreement with competent authority

Above 100 t/y

10 –1000 t/y	all of Level 1 tests as in Annex VIII
> 1000 t/y	a selection from Level 2 (Annex VIII) in agreement with competent authority

23.3.1.3 Classification and Labeling

The general principles of the classification and the subsequent possible hazard labeling of chemical products are laid down in Art. 4 of the 7th Amendment (Directive 92/32/EEC) to Directive 67/548/EEC for substances and Article 3[6] of the Dangerous Preparations Directive (1999/45/EC) for preparations (mixtures of substances).

There are 15 hazard categories (Annex I to the Directive 67/548/EEC)

Physical-chemical hazards:	"explosive", "oxidizing", "extremely flammable", "highly flammable" and "flammable"
Toxicological hazards:	"very toxic", "toxic", "harmful", "corrosive", "irritant", "sensitizing", "carcinogenic", "mutagenic", "toxic to reproduction"
Ecotoxicological hazards:	"dangerous for the environment"

The criteria for these hazard categories are given in Annex VI, which also includes a labeling guide to the assignment of symbols and the R-(risk) and S-(safety) phrases (listed in Annexes II-IV) to be used on the product label.

There is a requirement to assess all products by comparing the available data with the criteria given in the legislation, whether or not this leads to a subsequent hazard classification and associated hazard labeling.

An important feature of these labeling requirements in the European Union is that they aim not only to provide appropriate hazard warning and safety advice on the label in the interests of worker protection but also, through the application of rigid criteria, to achieve a harmonized approach within the single market. In order to achieve these dual objectives, it is perhaps inevitable that the EU requirements are more prescriptive than their United States counterparts under TSCA and the OSHA Hazard Communication Standard.

Few organic pigments included in EINECS are classified as "dangerous" in the Annex I of the Directive. Annex I consists of the substances which have been officially classified as dangerous, following an evaluation by the Commission Working Group on classification and labeling of dangerous substances, and specifies the classification and the R- and S-phrases.

Barium pigments, which are the barium salts of 1-azo-2-hydroxynaphthalenylarylsulfonic acid[5], are excluded from the generic classification of barium salts as "harmful" (Table 23–5). This generic entry for barium salts mandates the labeling of other barium pigments, regardless of whether or not this would be required on the basis of available experimental results.

Table 23–5: Barium pigments listed in EINECS in sub group "1-azo-2-hydroxynaphthalenyl aryl sulfonic acid, barium salts".

CAS No.	*Chemical name*	*EINECS No.*	*C.I. Generic name*	*C.I. Constitution No.*
1103-38-4	1-Naphthalenesulfonic acid, 2-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (2:1)	2141606	Pigment Red 49:1	15630:1
5160-02-1	Benzenesulfonic acid, 5-chloro-2-[(2-hydroxy-1-naphthalenyl)azo]-4-methyl-, barium salt (2:1)	2259353	Pigment Red 53:1	15585:1
5850-87-3	Benzenesulfonic acid, 4-[(2-hydroxy-1-naphthalenyl)azo]-2-methyl-, barium salt (2:1)	2274591	Pigment Red 51	15580
7585-41-3	2-Naphthalenecarboxylic acid, 4-[(5-chloro-4-methyl-2-sulfophenyl)azo]-3-hydroxy-, barium salt (1:1)	2314948	Pigment Red 48:1	15865:1
15782-04-4	Benzenesulfonic acid, 4-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (2:1)	2398787	Pigment Orange 17	15510:1
17814-20-9	2-Naphthalenecarboxylic acid, 4-[(4-chloro-5-methyl-2-sulfophenyl) azo]-3-hydroxy-, barium salt (1:1)	2417804	Pigment Red 52	15860
17852-98-1	2-Naphthalenecarboxylic acid, 3-hydroxy-4-[(4-methyl-2-sulfophenyl) azo]-, barium salt (1:1)	2418064	Pigment Red 57:2	15850:2
24530-53-8	1-Naphthalenesulfonic acid, 2-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (1:1)	2462993		
50326-33-5	Benzenesulfonic acid, 4-chloro-2-[[2-hydroxy-3-[[(2-methoxyphenyl)amino]-carbonyl]-1-naphthalenyl]azo]-5-methyl-, barium salt (2:1)	2565430	Pigment Red 243	15910
61013-97-6	Benzenesulfonic acid, 2-[[2-hydroxy-3-[[(4-sulfophenyl)amino]carbonyl]-1-naphthalenyl]azo]-, barium salt (1:1)	2625599	Pigment Red 151	15892
67801-01-8	Benzenesulfonic acid, 5-chloro-4-ethyl-2-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (2:1)	2671226	Pigment Orange 46	15602
67892-38-0	Benzenesulfonic acid, 3-chloro-4-ethyl-5-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (2:1)	2675702		
67892-41-5	2-Naphthalenecarboxylic acid, 4-[(3-chloro-2-methyl-5-sulfophenyl)azo]-3-hydroxy-, barium salt (1:1)	2675739		
67892-47-1	1,5-Naphthalenedisulfonic acid, 2-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (1:1)	2675807		

Table 23–5: Continued

CAS No.	*Chemical name*	*EINECS No.*	*C.I. Generic name*	*C.I. Constitution No.*
67892-50-6	Benzenesulfonic acid, 3-chloro-5-[(2-hydroxy-1-naphthalenyl)azo]-4-methyl-, barium salt (2:1)	2675833		
67990-34-5	1,5-Naphthalenedisulfonic acid, 3-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (1:1)	2680560		
68189-25-3	2-Naphthalenesulfonic acid, 1-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt (2:1)	2691834		
68368-34-3	Benzenesulfonic acid, 3-chloro-6-[(2-hydroxy-1-naphthalenyl)azo]-2-methyl-, barium salt (2:1)	2698651		
68368-35-4	Benzenesulfonic acid, 3,6-dichloro-2-[(2-hydroxy-1-naphthalenyl)azo]-4-methyl-, barium salt (2:1)	2698667		
68368-36-5	Benzenesulfonic acid, 3,5-dichloro-2-[(2-hydroxy-1-naphthalenyl)azo]-4-methyl-, barium salt (2:1)	2698672		
68959-10-4	2,7-Naphthalenedisulfonic acid, 4-[(5-chloro-4-methyl-2-sulfophenyl)azo]-3-hydroxy-, barium salt (2:3)	2733968		
73612-34-7	Benzenesulfonic acid, 4-chloro-2-[(2-hydroxy-1-naphthalenyl)azo]-5-methyl-, barium salt (2:1)	2775531		
84030-33-1	Benzenesulfonic acid, 4-chloro-2-[(2-hydroxy-1-naphthalenyl)azo]-5-methyl-, barium salt	2818061		
84030-38-6	1,5-Naphthalenedisufonic acid, 3-[(2-hydroxy-1-naphthalenyl)azo]-, barium salt	2818119		
84696-57-1	2-Naphthalenecarboxylic acid, 4-[(4-ethoxy-2-sulfophenyl)azo]-3-hydroxy-, barium salt	2836625		
85005-86-3	2-Naphthalenecarboxylic acid, 4-[(5-chloro-4-methyl-2-sulfophenyl)azo]-3-hydroxy-, barium calcium salt	2850173		
85005-87-4	2-Naphthalenecarboxylic acid, 3-hydroxy-4-[(1-sulfo-2-naphthalenyl) azo]-. barium calcium salt	2850189		
94109-21-4	2,.7-Naphthalenedisulfonic acid, 4-[(4-chloro-3-sulfophenyl)azo]-3-hydroxy-, barium salt (2:3)	3024600		

Although only exceptionally has the need to classify organic pigments as dangerous arisen, the criteria for the application of the risk phrase R53 "may cause long-term adverse effects in the aquatic environment" do raise some questions of interpretation.

The R53 phrase is required for substances with a water solubility of less than 1 mg/L if:

(i) the substance is not readily degradable and
(ii) the log Pow ≥ 3.0 (unless the experimentally determined bioconcentration factor is ≤ 100).

If these criteria are fulfilled, then the R53 phrase is required unless e.g. there is evidence of an absence of chronic toxicity effects at the solubility limit. The underlying concern is the possibility that such substances might bioconcentrate in aquatic species to harmful levels. This issue has also been raised in the case of the Danish "List of Undesirable Substances" which is discussed later in Sec. 23.6.3.

23.3.2
Dangerous Preparations (E.P. and Council Directive 1999/45/EEC)

Directive 1999/45/EC, amending Directive 88/379/EEC, will be enacted by the EU member states from 30th July 2002. There is no provision for a transition period[6]. This new Directive introduces the hazard classification "dangerous for the environment" for preparations, which was previously only required for dangerous substances. Organic pigments are generally not toxic to aquatic organisms because of their limited bioavailability and therefore do not normally require classification.

23.3.3
Safety Data Sheets (Commission Directive 2001/58/EC)

Commission Directive 2001/58/EC[7] specifies the information to be included in a safety data sheet (SDS). A safety data sheet must be provided for all dangerous chemical products with or before the first supply and irrespective of the mode of supply. Responsible suppliers provide SDSs for all products whether these are classified as dangerous or not. Should further significant information arise, the supplier is also obliged to revise the SDS and supply this update to all those who received the product within the preceding twelve months. The information supplied in the SDS must be sufficient to enable the user to determine how best to protect persons coming into contact with the hazardous chemical and how to protect the environment.

The required information must be given under sixteen specific headings covering identification of the chemical product and its supplier: composition information, hazard identification, first aid measures, handling and storage, exposure control and personal protection, physical and chemical properties, stability and reactivity, toxicological information, ecotoxicological information, disposal, transport requirements, regulatory information, and any other information which might facilitate the safe use of the product.

23.3.4
Existing Substances, Priority Lists, Risk Assessment (Council Regulation EEC 793/93)

The Council Regulation (EEC) No. 793/93 was adopted in March 1993 and came into force on June 4, 1993[8]. The Regulation contains three basic elements: data collection, priority setting and risk assessment.

The aim of the Regulation is to set up a framework for the systematic evaluation of the risks posed by chemical substances which are available within the European Union. These so-called "Existing Chemicals" are those substances which were in use in the EU before September 1981 and are listed in EINECS (i.e. not subject to notification).

From the EINECS list a EU-HPVC list (EU high production volume compounds expected to be produced or imported at above 1000 tonnes/year) was compiled in two phases.

For the data collection, the HEDSET software package (Harmonized Electronic Data SET), a special computer programme, was developed. Industry must use this software for the compilation and submission of the data. The software has been designed to run on standard personal computers and is available in 9 EU-languages.

A final phase involved the reporting of all substances on the market in amounts between 10 and 1000 tonnes. In this case only the amounts, identities and hazard classifications are required.

The safe management of chemicals in the EU is based on the stepwise approach illustrated in Figure 23–3. In April 1996 a Technical Guidance Document was published[9] to provide guidance on the risk assessment of both notified substances (as required under Commission Directive 93/67/EEC)[10] and existing substances (under EC Regulation No. 1488/94)[11]. This guidance document deals with the risk assessment for human health and the environment, and covers also the use of (quantitative) structure-activity relationships. Of particular importance for the outcome of the risk assessment are the emission scenario documents, especially with respect to the default values, which will be applied if experimental data are not available.

Each Member State Authority is given the responsibility for a sub-set of the priority substances and must carry out a risk assessment following the Commission Regulation (EC) No. 1488/94 and guidance given in the "Technical Guidance Document

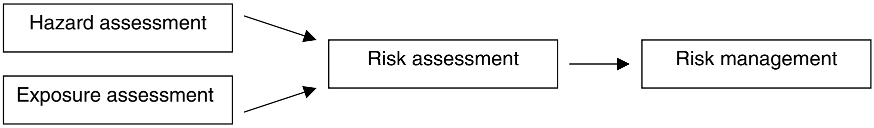

Figure 23–3: Step-wise approach to the safe management of chemicals.

for Risk Assessment on Existing Substances". The final risk assessment report, created by the "rapporteurs", and the validated data sheet will be included in IUCLID (International Uniform Chemical Information Database), which is the basic tool for the data collection and evaluation in the frame of the European Risk Assessment Programme on Existing Substances.

23.3.5
Restrictions of Marketing and Use

Council Directive 76/769/EEC[12] seeks a harmonization of the regulatory measures to protect the public and environment by regulating the marketing and use of certain dangerous substances and preparations. Restrictions of marketing and use can be an effective and necessary means to reduce risk. Already the subject of 18 amendments and 6 adaptations to technical progress, the publication of a consolidated version is much needed. Few of the amendments have any impact on organic pigments:

Council Directive 89/677/EEC[13] reduced the limit of polychlorobiphenyls and polychloroterphenyls in preparations to 50 ppm. It also introduced a 0.1 % by weight limit on 2-naphthylamine, benzidine, 4-nitrobiphenyl and 4-aminobiphenyl in substances sold to the general public.

A proposal for a 19th Amendment[14] aims at harmonizing the diverse restrictions on certain azo colorants in several EU member states. It applies only to azo dyes (see additional comments in Sec. 23.4.1.1) which would liberate any one of 21 listed aromatic amines on reductive cleavage of one or more azo bonds (Table 23–6).

Table 23–6: List of carcinogenic aromatic amines referred to in Sec. 23.3.5. and Sec. 23.4.1.1.

		Classification as carcinogen		
Aromatic amine	***CAS-No.***	***EU (Annex I)***	***IARC***	***MAK III***
o-Anisidine*	90-04-0	Cat. 2		2
2-Naphthylamine	91-59-8	Cat. 1	Group 1	1
3,3′-Dichlorobenzidine	91-94-1	Cat. 2	Group 2B	2
4-Aminodiphenyl	92-67-1	Cat. 1	Group 1	1
Benzidine	92-87-5	Cat. 1	Group 1	1
o-Toluidine	95-53-4	Cat. 2	Group 2B	2
4-Chloro-*o*-toluidine	95-69-2	**	Group 2A	1
4-Methyl-1,3-phenylenediamine	95-80-7	Cat. 2	Group 2B	2
o-Aminoazotoluene	97-56-3	Cat. 2	Group 2B	2
5-Nitro-*o*-toluidine	99-55-8	**	Group 3	2
4,4'-Methylene-bis-(2-chloraniline)	101-14-4	Cat. 2	Group 2A	2
4,4'-Methylenedianiline	101-77-9	Cat. 2	Group 2B	2
4,4'-Oxydianiline	101-80-4	**	Group 2B	2
p-Chloraniline	106-47-8	Cat. 2	Group 2B	2
3,3′-Dimethoxybenzidine	119-90-4	Cat. 2	Group 2B	2

Table 23–6: Continued

		Classification as carcinogen		
Aromatic amine	***CAS-No.***	***EU (Annex I)***	***IARC***	***MAK III***
3,3′-Dimethylbenzidine	119-93-7	Cat. 2	Group 2B	2
p-Cresidine	120-71-8	**	Group 2B	2
2,4,5-Trimethylaniline	137-17-7	**	Group 3	2
4,4’-Thiodianiline	139-65-1	**	Group 2B	2
4-methoxy-*m*-phenylenediamine	615-05-4	**	Group 2B	2
4,4’-Methylenedi-*o*-toluidine	838-88-0	Cat. 2	Group 2B	2

* not yet regulated under German Consumer Goods Ordinance (ref. 28)
** EU classification pending

23.3.6
Pollution Control

The Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC) must be implemented in all Member States by 31 October 1999[15]. It is being introduced across Europe to improve the standard of environmental protection. The purpose of the Directive is to achieve prevention and control of pollution arising from the range of activities listed in Annex 1 of the Directive. It lays down measures designed to prevent, or where that is not practicable, to reduce emissions to air, land and water from these activities, including measures concerning waste.

Annex 1, under 4.1. (j), lists dyes and pigments as falling under the Directive because of their chemical production on an industrial scale.

23.3.7
Packaging and Packaging Waste (E.P. and Council Directive 94/62/EC)

The objective of the E.P. and Council Directive (94/62/EC)[16] is to reduce the amount of packaging waste requiring disposal by means of a combination of reuse, recycling or recovery measures. A further aim is to harmonize the regulations in the individual member states to prevent obstacles to trade within the single market whilst providing for a high level of environmental protection.

Although all pigment manufacturers are impacted by the general requirements of this directive, the key issue regarding organic pigments is the limitation under Article 11 of certain heavy metals present in packaging. Article 11 requires the sum of the concentration levels of lead, cadmium, mercury and hexavalent chromium in packaging or packaging components to be reduced to:

600 ppm	by 30 June 1998
250 ppm	by 30 June 1999
100 ppm	by 30 June 2001.

23.3.8
Eco-Labels

The EU eco-label scheme aims to stimulate the supply and demand of products with a reduced environmental impact and to give consumers the means of informed environmental choices.

The basic legal framework for an eco-label in the EU is Council Regulation (EEC) No 880/92[17]. Consumer goods are divided into 22 product groups for which ecological criteria are normally established for a period of three years. This allows for technical improvements and changes in the market to be reflected when the criteria are revised.

One of the first eco-labels with impact on organic pigments is that for bed linen and T-shirts, issued under Commission Decision (96/304/EC)[18]. This has recently been superseded by the more general eco-label for textile products[19], which sets specific limits on the levels of certain ionic metal impurities in dyes and organic pigments (Table 23–7). Although some categories of dyes may not be used, no organic pigments are excluded from use.

Table 23–7: Trace metal limits (ppm) for ionic impurities in colorants under the EU eco-label criteria for general textile products (Commission Decision 1999/178/EC).

	Dyes	*Pigments*
Arsenic	50	50
Cadmium	20	50
Chromium	100	100
Copper	250	–
Mercury	4	25
Nickel	200	–
Lead	100	100
Antimony	50	250
Tin	250	–
Zinc	1500	1000

Unfortunately, there are some inconsistencies between this eco-label for textiles and the eco-label for bed mattresses, which was enacted in October 1998[20] and excludes the use of metal-complexed dyes or pigments based on chromium, copper, nickel and lead. It is hoped that this restriction will be removed by the next revision.

So far, relatively few products have received an EU eco-label award. This may be due to the fact that there are already numerous national, international and independent schemes in place. One of the earliest eco-labeling schemes was the Blue Angel, introduced in Germany in 1977. The Nordic Countries (Sweden, Finland, Norway, Denmark and Iceland) have been particularly active with several eco-labels in operation (e.g. the Nordic or White Swan). Within the European textile industry the Öko-tex label is widely promoted by the textile retailers.

23.3.9
Food Packaging Legislation

The EU Framework Directive 76/893/EEC on materials and articles intended to come into contact with foodstuffs was first adopted in 1976[21], but was subsequently replaced by Directive 89/109/EEC[22]. As a general requirement this framework directive requires that all food contact materials must be manufactured according to Good Manufacturing Practice (GMP), and that they do not transfer their constituents to foodstuffs in quantities which could endanger human health or “bring an unacceptable change in the composition of the foodstuff or a deterioration in the organoleptic properties”. It was foreseen that the framework directive would be supplemented by directives for specific groups of materials and articles (Figure 23–4).

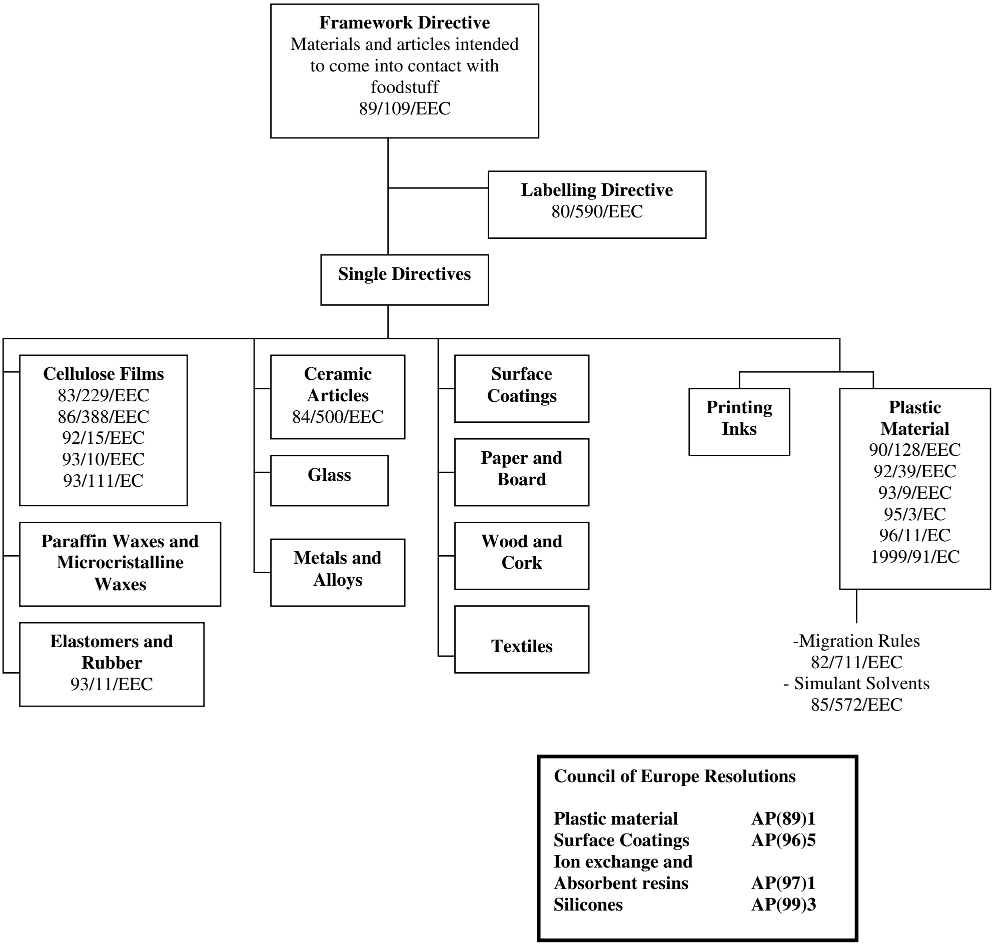

Figure 23–4: Framework Directive 89/109/EEC (food packaging).

Many significant pigment applications can be affected by the EU food contact legislation, e.g. printing inks, mass coloration of food packaging plastics, coatings. This is a complex area of regulation which can only be described briefly in this chapter. A supplier of pigments for these applications needs to be aware of:

(i) The current status of specific EU requirements
The Scientific Committee for Food (SCF) Guidelines lays down the requirements for toxicological evaluation of substances to be used in materials and articles intended to come into contact with foodstuffs (Table 23–8);

Table 23–8: Summary of toxicological data requirements at various migration levels

Migration (mg/kg food simulant)		*Test data requirements*
<0.05	Level 1	3 mutagenicity tests: gene mutation in bacteria, chromosomal aberration in mammalian cells (in vitro), gene mutation in mammalian cells (in vitro)
0.05–5	Level 2	– absence of bioaccumulation in animals (e.g. partition coefficient) – absence of mutagenicity (3 tests) – 90-day oral toxicity
>5	Level 3	– 90 day oral toxicity – 3 mutagenicity tests – absorption, distribution, metabolism, excretion – reproductive toxicity – teratogenicity –long-term toxicity/carcinogenicity

(ii) The relevant Council of Europe resolutions
Although Council of Europe resolutions do not have a regulatory basis, they reflect a consensus of the experts in the EU and other Council of Europe member states, and influence the likely approach within the EU to harmonizing requirements within the single market.
Two Council of Europe resolutions of relevance to pigments have been finalized:

Resolution AP (89)1	Plastics materials coming into contact with food
Resolution AP (96)5	Surface coatings intended to come into contact with foodstuffs

Resolutions are also in preparation for food packaging inks (on non-food contact surface) and for paper and board intended to come into contact with foodstuffs.

(iii) Specific requirements in individual member states
Currently a diversity of regulatory requirements applies in the EU member states. Harmonization is being sought but will inevitably take time. In the interim period the principle of mutual recognition, derived from Articles 30–36 of the EU Treaty, plays an important role in the operation of the single

> market. Under this principle, a member state may not forbid the sale of a product produced lawfully in another member state unless the product presents a demonstrated risk to public health.

Pending the development of harmonizing EU requirements, it is necessary to comply with the diverse requirements of individual European countries (see also Sec. 23.4.2.1).

23.3.10
Technical Barriers to Trade

The procedure under which member states are required to notify the Commission before introducing technical standards and regulations was laid down in Council Directive 83/189/EEC[23]. This procedure aims at providing transparency and control with regard to regulations which could create unwarranted trade barriers within the single market. National provisions cannot be enforced if they should have been notified and were not[24]. Subsequent amendments under Council Directive 88/182/EEC and Directive 94/10/EC of the EP and of the Council introduced the need (Article 8) to include a risk analysis, and have been codified by Directive 98/34/EC[25].

The importance of this procedure has recently been exemplified in the area of the restriction and marketing of certain azo colorants (see Sec. 23.4.1.1).

23.4
National Regulations

Substantial progress has been made in harmonizing the regulatory requirements throughout the EU member states in the interests of achieving a single market. This does not, of course, mean that there are not substantial differences in terms of compliance and enforcement in the individual member states. Nevertheless, a pigment supplier needs to be aware that unique national regulations may exist. Some examples are highlighted in the following sections.

23.4.1
Germany

23.4.1.1 Consumer Goods Ordinance

A second amendment to the German Consumer Goods Ordinance[26] had unexpected repercussions in certain azo pigments. This amendment banned the use of azo dyes which on cleavage of one or more azo bonds would form any one of 20 listed aromatic amines (see Table 23–6) in consumer goods intended for more than temporary contact with the skin. Although the original intent of the German authorities is unclear, a subsequent 4th Amendment[27] confirmed, or extended, the scope of the restriction to include azo pigments. The basis for the restriction, i.e. that the restricted dyes are possible carcinogens, is plausible and supported by the available test data. However, the extension of this reasoning to include the corresponding azo pigments is questionable. The available test data and the fact that pigments have a low bioavailability do not support the supposition that these organic pigments are potential carcinogens.

The 5th Amendment of the Consumer Goods Ordinance[28] limited the impact on azo pigments to a few products, e.g. C.I. Pigment Reds 8, 22 and 38, which generate more than 30 mg listed aromatic amine/kg commodity using a less aggressive test method. This German restriction inevitably stimulated similar restrictions in other member states, e.g. the Netherlands[29] and Austria[30], and it is hoped that harmonization at EU level will be reached through a proposed 19th Amendment to Directive 76/769/EEC[14].

23.4.1.2 **Wassergefährdungsklassen (Water-hazard classes)**

Regardless of the harmonized EU requirements for the classification and labeling of dangerous substances and preparations (mixtures), a recently amended administrative regulation on substances hazardous to waters[31] requires the classification of substances and preparations into three water hazard classes, i.e.

WGK 1:	slightly hazardous to water
WGK 2:	hazardous to water
WGK 3:	highly water hazardous

The classification of substances is laid down in four annexes.

Annex 1

Substances listed in Annex 1 are “non-hazardous to waters”. Included in this annex are copper phthalocyanine and “plastics, including granulates, preformed parts, fibers, sheets and plastic resins, if solid, non-dispergated, not water-soluble and inert”.

Annex 2

Substances previously classified in WGK 1 to 3.

Annex 3

This annex lays down the procedure for self-classification of substances based on the applicable R-phrases. Points are assigned not only to R-phrases based on ecotoxicological hazards but also to toxicological hazard R-phrases. The WGK is determined by the sum of the points assigned to the R-phrases or the default values if test data are not available.

Score 0–4 → WGK 1
Score 5–8 → WGK 2
Score ≥ 9 → WGK 3

Annex 4

This annex lays down the procedure for self-classification of mixtures based either on limit values for content of classified components or the experimental data available for the mixture.

The self-classifications must be submitted to the authorities for registration and publication purposes. From 2001 substances not registered will be considered to be WGK 3.

23.4.1.3 Dioxin Limits

The “Chemikalien-Verbotsverordnung”[32] lays down limit values for polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) which may not be exceeded in substances, preparations or articles manufactured in Germany or placed on the German market. The stringent limits are detailed in Table 23–9.

Table 23–9: Limits for polychlorinated dibenzodioxins / furans under the German Chemicals Prohibition Ordinance, 1996.

Group 1	2,3,7,8-TCDD	Limit for Groups 1,2 and 3: 100 µg/kg (ppb)	Limit for Groups 1 and 2: 5 µg/kg (ppb)	Limit for Group 1: 1 µg/kg (ppb)
	2,3,7,8-TCDF			
	1,2,3,7,8-PeCDD			
	2,3,4,7,8-PeCDF			
Group 2	1,2,3,4,7,8-HxCDD			
	1,2,3,6,7,8-HxCDD			
	1,2,3,7,8,9-HxCDD			
	1,2,3,7,8-PeCDF			
	1,2,3,4,7,8-HxCDF			
	1,2,3,6,7,8-HxCDF			
	1,2,3,7,8,9-HxCDF			
	2,3,4,6,7,8-HxCDF			
Group 3	1,2,3,4,6,7,8-HpCDD			
	OCDD			
	OCDF			
	1,2,3,4,6,7,8-HpCDF			
	1,2,3,4,7,8,9-HpCDF			

Abbreviations		***No. of chlorine atoms***
TCDD	Tetrachlorodibenzodioxin	4
TCDF	Tetrachlorodibenzofuran	4
PeCDD	Pentachlorodibenzodioxin	5
PeCDF	Pentachlorodibenzofuran	5
HxCDD	Hexachlorodibenzodioxin	6
HxCDF	Hexachlorodibenzofuran	6
HpCDD	Heptachlorodibenzodioxin	7
HpCDF	Heptachlorodibenzofuran	7
OCDD	Octachlorodibenzodioxin	8
OCDF	Octachlorodibenzofuran	8

23.4.2
France

23.4.2.1 Food Packaging Regulations

Particular reference to the French regulatory approach for colorants used in food contact packaging is warranted because of its prescriptive and restrictive nature. Since the original food law of 1905, three decrees have been published (in 1912, 1973 and 1992), dealing with food contact materials.

Under the French regulations the use of a colorant is subject to three conditions:

- being authorized
- meeting the specified purity criteria
- non-migration to food.

The first positive list of colorants for food packaging materials was published in Circular No. 176 in 1959. It consists primarily of colorants for use in plastics. Since then numerous additions have been published. Consolidated texts are published in the booklet No. 1227[33].

Table 23–10 illustrates the many differences in the purity specifications applicable in several European countries. In France the trace metal limits for lead and arsenic relate to total content and not extractable in 0.1M hydrochloric acid, except in the case of printing inks[34].

Whereas organic pigments based on 3,3′-dichlorobenzidine were removed from the French positive list for plastics, their use in food packaging inks is still permitted[35].

Table 23–10: Trace metal and impurity limits (ppm) for colorants used in food packaging plastics in various European countries.

	As	*Ba*	*Cd*	*Cr*	*Hg*	*Pb*	*Sb*	*Se*	*Zn*	*Aromatic amines (a)*	*Carcinogenic amines (b)*	*Sulfonated amines (c)*	*PCBs (d)*
Belgium (1)	100	100	100	1000	50	100	500	100		500	10	–	–
France (2)	50 (e)	100	1000	–	50	100 (e)	–	100	2000	500	–	–	–
Germany (3)	100	100	100	1000	50	100	500	100	–	500	–	–	–
Greece (4)	100	100	100	1000	50	100	500	100	–	500			
Italy (5)	50	100	100	1000	50	100	500	100	–	500	10	–	–
Netherlands (6)	100	100	1000	1000	50	100	2000	100	–	500			
Portugal (7)	100	100	100	1000	50	100	500	100	2000				
Spain (8)	100	1000	2000	1000	50	100	2000	100	–	500			
Switzerland (9)	100	100	100	1000	50	100	500	100	–	500		500	25
Great Britain (10)	100	100	100	1000	50	100	500	100	–	500		500	25
Council of Eur.(11)	100	100	100	1000	50	100	500	100		500		500	25

23.4.3
Switzerland

Chemical regulations in Switzerland are the responsibility of two institutions: the Swiss Federal Office of Public Health, BAG (Bundesamt für Gesundheitswesen), and the Swiss Agency for the Environment, Forests and Landscape, BUWAL (Bundesamt für Umwelt, Wald und Landschaft). Although the requirements for the notification of new chemical substances are very similar to those of the EU, there are some specific features. Any manufacturer or importer of a chemical substance has to perform an environmental compatibility assessment as part of a self-control according to the Ordinance on Substances[36]. This is not just for notified substances; it includes all products. Furthermore, products have to be either classified by BAG according to the BAG's "Poison Lists" and criteria or submitted by the manufacturer or importer to BAG as a self-classification[37].

Currently, a draft chemical substances law[38] which will replace and amend the Poison Law and the Ordinance on Substances has been submitted to the Parliament. It is expected that this will bring further harmonization with EU legislation. This will eliminate the present requirement for Swiss manufacturers to apply, where necessary, Swiss hazard labeling, which is not equivalent to the EU hazard labeling. At present, EU manufacturers may use EU labeling for exports to Switzerland but must quote the BAG-T number and poison class.

The Ordinance on Consumer Goods[39] of 1 March 1995 under Art. 20 issues requirements on the coloration of articles with food contact. Chapter 5 of GebrV gives migration limits for certain metals and aromatic amines for articles intended for use by children. Similar requirements are specified in Art. 11 which refers to the Ordinance on Materials and Articles from Plastic[40].

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(1) Belgisch Staadsblad, 24 July 1992, 16719

(2) Circulaire No. 176 du 2 décembre 1959, J. officiel du 30.12.1959.

(3) BgVV Empfehlung IX, Bundesgesundheitsblatt 37, 364 (1 June 1994)

(4) Greek Code for substances and articles in contact with food and beverages, Governmental decision No 714/20 of 20 August 1996.

(5) Gazzetta Ufficiale della Repubblica Italiana, No. 228, 30 September, 1998.

(6) Verpakkingen-en Gebruiksartikelen Besluit (Warenwet) of 1 October 1979, 10th supplement April 1997.

(7) Food contact plastics, Law NP 3254 (1990).

(8) Boletin Oficial del Estado, No. 282 of 24 November 1982.

(9) Kunststoffverordnung (KsV) of 26 June 1995.

(10) Statutory instruments 1987 No. 1523 and Update 1988, The Materials and Articles in Contact with Food Regulations 1987.

(11) Council of Europe Resolution AP (89) 1, adopted on 13.9.1989.

(a) extractables, expressed as aniline

(b) total extractable benzidine, 2-naphthylamine and 4-aminobiphenyl

(c) extractables, expressed as sulfanilic acid

(d) extractables, expressed as decachlorobiphenyl

(e) total content.

Art. 22 refers to the Ordinance on Cosmetic Ingredients[41] as last amended 31 January 2000, which lists colorants with certain specifications under which these are permitted and also lists certain dyes and organic pigments which are excluded from cosmetic products.

23.5

Future Enlargement of the EU (PHARE and similar programs)

The PHARE Programme is a European Community initiative to help the countries of central Europe and the Baltic states to join the European Union in the near future (Table 23–11).

Table 23–11: Development of the European Union and its future candidates.

Year	*Member states*
1952	Belgium, France, Germany, Italy, Luxembourg, Netherlands (Treaty of Paris)
1973	As above plus Denmark, Ireland and the United Kingdom
1981	As above plus Greece
1986	As above plus Spain and Portugal
1995	As above plus Austria, Finland and Sweden
Future candidates:	• Cyprus, Czech Republic, Estonia, Hungary, Poland, Slovenia • Bulgaria, Latvia, Lithuania, Malta, Romania, Slovakia, Turkey

Amongst the main priorities for PHARE fundings are reform of institutions, legislation and public administration, reform of social services, employment, education and health, development of energy, transport and telecommunications infrastructure, and environment and nuclear safety. For countries that have signed Europe Agreements, PHARE is the financial instrument of the European Union's pre-accession strategy which will lead them to full membership. The PHARE programme is the world's largest grant assistance effort for central and Eastern Europe.

A key development in this respect was the signature by the European Commission of an important contract with CEFIC to study the impact of the Commission's "White Paper" on the preparation of the Associated Countries of Central and Eastern Europe for integration into the Internal Market of the Union, especially in the area of harmonization of chemical legislation. The contract applied to Poland, Hungary, the Czech Republic, Slovakia, Slovenia, the three Baltic States, Romania and Bulgaria.

Establishing an extensive network of contacts with the relevant authorities and chemical companies at European and national level, they have created a unique forum for dialogue between industry and the authorities on the ongoing legislative issues. The Programme also meets one of the priority lines as defined in the "Commission Communication on the Competitiveness of the Chemical Industry"[42].

One point emphasized in the general conclusions, addressed to the Commission and CEE authorities, is the need for additional efforts within the approximation process in order to achieve the harmonization and integration of notification, registration and authorization procedures throughout Europe, harmonization of classification, packaging and labeling requirements, exclusion of all non-tariff barriers, and international co-operation in the chemical control, including the risk assessment of chemicals. Specific proposals were made in order to accomplish this objective. A similar approach was proposed also to other parts of the "acquis" governed by Article 100 a of the Treaty, in order to progress with the "regulatory enlargement" which would pave the way for successful enlargement of the Internal Market to the benefit of all stakeholders, and could lead to creation of a wider European economic and regulatory area.

The findings of the Project and the conclusions and recommendations are considered by the CEECs' authorities involved in the legislative process, and considerable changes were made or are going to be made in the national legislation being developed in order to align it with the EU laws and rules.

The Programme drew the EU and CEE chemical companies operating in the CEECs closer together in terms of co-operation on the issues of common interest and contributed to the mutual trust essential for its future development.

23.6
Non-Regulatory Initiatives

Regulation is not the only means of achieving higher levels of safety in the manufacture, use, storage and disposal of chemicals. Self-regulation by the industry, pressure by environmental groups and dissemination of relevant information by authorities are examples of non-regulatory initiatives. From the perspective of industry, self-regulation can offer benefits in terms of lower costs and improved image, but unless a high level of voluntary participation is reached, the competitive situation can be distorted to an unacceptable level in favor of the non-participants. On the other hand, the regulators and public are more likely to regard self-regulation as complementary to regulation, rather than an alternative.

23.6.1
High Production Volume (HPV) Chemicals Testing Initiative

A current voluntary initiative by the chemical industry is the HPV chemicals testing initiative, which aims to improve the current database by completing an internationally agreed set of data (the OECD Screening Information Data Set, SIDS) for approximately 1000 HPV chemicals by 2004. The global industry initiative is being coordinated by the International Council of Chemical Associations (ICCA) by a work group representing national chemical federations and companies, with particular responsibility being taken by the United States, Japanese and European associations (ACC, JCIA and CEFIC respectively).

23.6.2
Precautionary Principle

The EU approach to chemicals control is based on a stepwise process of hazard assessment, risk assessment and risk management. This process assists a rational prioritization in the allocation of limited resources to achieve a high level of health and environmental protection. Because this process often involves uncertainties due to insufficient or inconclusive scientific evidence, the "precautionary principle" may need to be applied in cases where there are indeed reasonable grounds for concern that health or the environment may be seriously endangered. The precautionary principle was first recognized in international law in the World Charter for Nature, adopted by the UN General Assembly in 1992. At the Rio Conference on the Environment and Development, Principle 15 states that "in order to protect the environment, the precautionary approach shall be widely applied by States according to their capability. Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation". In the EU there is a reference to the precautionary principle, in the context of the environment, in Article 174 of the 1992 EC Treaty, but the principle is not defined. In 1999 the Council of Ministers adopted a resolution calling on the Commission to consider the principle when preparing proposals for legislation.

Overly zealous application of the precautionary principle could have a serious impact on the chemical industry and deprive society of the benefits of products without counterbalancing improvements in health and safety. The issue by the European Commission of a Communication[43] on the use of the precautionary principle affirms that it is neither the politicization of science nor the acceptance of zero-risk. This Communication states that measures based on the precautionary principle should be:

- proportional to the chosen level of protection
- non-discriminatory in their application
- consistent with similar measures already taken
- based on an examination of the potential benefits and costs of action or lack of action
- subject to review in the light of new scientific data
- capable of assigning responsibility for producing the scientific evidence necessary for a more comprehensive risk assessment.

3.6.3
Black-listing

In the context of this chapter, “black-listing” refers to the designation of a specific chemical substance or group of substances as undesirable, unwanted or warranting exclusion from use. Although “black-listing” does not occur within the European regulatory framework, it is mentioned because it is increasingly used in Europe and can cause serious damage to the market potential of a listed substance.

Blacklisting manifests itself in three main forms:

- exclusion lists issued by downstream industries, usually based solely on hazard considerations
- private eco-label criteria
- “Sunset” or “Undesirable Substances” lists prepared by regulatory authorities or public institutions.

Although voluntary initiatives can offer benefits over regulation, there is concern about the unsound and often arbitrary nature of black-listing. Because black-listing is not a regulatory measure, its use by authorities to discourage application of specific substances circumvents the notification obligations under Commission Directive 83/189/EEC, which are aimed at avoiding technical barriers within the single market (see also Sec. 23.3.10).

23.7
Confidentiality

The chemical control regulations in the EU have already resulted in a substantial and inexorable erosion of the industry’s ability to protect confidential information, especially with regard to product composition. The principles of responsible care require adequate information to be provided by the chemical manufacturer to the user industry and public authorities, but all too often the main beneficiaries are the competitors of the innovative companies.

As many colorants are marketed as preparations, confidentiality includes both

(a) specific identity of the components, and
(b) quantitative composition.

In general, disclosure of composition is the more important issue, although process details, production and marketing information, and test reports can often be valuable confidential business information.

A clear distinction should be made between public disclosure (i.e. to public and competitors) and disclosure to responsible authorities. Provided adequate security for confidential information is assured, disclosure to responsible institutions, e.g. Poison Centres, cannot be denied.

23.8
Availability of Information on Current Regulations

Table 23–12 lists some of the major website addresses of European and other international institutions and some selected homepages of national regulatory agencies.

Table 23–12: Selection of websites of European regulatory authorities and institutions.

European Commission	http://www.europa.eu.int/comm/
European Parliament	http://www.europarl.eu.int/
Council of the European Union	http://ue.eu.int/en/summ.htm
The Court of Justice of the European Communities	http://europa.eu.int/cj/en/index.htm
European Union Law	http://europa.eu.int/eur-lex/
European Chemicals Bureau	http://ecb.ei.jrc.it/
Database concerning export/import of certain dangerous chemicals	http://edexim.ei.jrc.it/
UNEP chemicals	http://irptc.unep.ch/
OECD's Work on Environmental Health and Safety	http://www.oecd.org/EHS/
International Occupational Safety and Health Information Centre	http://www.ilo.org/public/english/protection/safework/cis/
Austrian Federal Environment Agency	http://www.ubavie.gv.at/
Danish EPA	http://www.mst.dk/homepage/
Finland: Ministry of Social Affairs and Health	http://www.vn.fi/stm/
France: INRS	http://www.inrs.fr
France: Ministry for the Environment	http://www.environnement.gouv.fr./english
German BgVV	http://www.bgvv.de/
German Federal Environmental Agency	http://www.umweltbundesamt.de/
Ireland: Health and Safety Authority	http://www.hsa.ie
Italy: Istituto Superiore di Sanità	http://www.iss.it
Netherlands: VROM	http://www.minvrom.nl
Norway: Pollution Control Authority	http://www.sft.no/english
Schweiz: Amtliche Sammlung des Bundesrechts	http://www.admin.ch/ch/d/as/
Spain: Ministerio de Medio Ambiente	http://www.mma.es
Spain: Ministerio de Sanidad y Consumo	http://www.msc.es
Sweden: KEMI	http://www.kemi.se
UK: DETR	http://www.environment.detr.gov.uk
UK: HSE	http://www.hse.gov.uk

23.9
Future Outlook

Even in the highly regulated European market there is a constant flow of new regulations. This inevitably means that any publication like this chapter will soon be outdated. Two white papers signal the plans for far-reaching changes to the chemical control measures in the European Union:

- White Paper on Food Safety
- White Paper: Strategy for a future Chemicals Policy

The main aim, to improve the level of safety and implementation, will significantly increase the regulatory burden on the industry. Based on past experience, it can be expected that the regulations will indeed be rigorous and complex, and that enforcement will be insufficient to ensure a high level of compliance. This leads to a damaging distortion of the competitive situation, but may fail to achieve the projected benefits in terms of health and environmental safety.

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4 Commission Decision 92/3/EEC of 9 December 1991, O.J. L003, 8.1.92, 26.
5 Commission Directive 96/54/EC of 30 July 1996, O.J. L248, 30.9.96, 30.
6 Directive 1999/45/EC of the E.P. and of the Council of 31 May 1999, O.J. L200, 30.7.99, 1.
7 Commission Directive 2001/58/EC of 27 July 2001, O.J. L212, 7.8.2001, 24.
8 Council Regulation (EEC) No. 793/93 of 23 March 1993, O.J. L84, 5.4.93, 1.
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24

Toxicology and Ecotoxicology Issues with High Performance Pigments

Hugh M. Smith

24.1

Introduction

From a careful reading of the comments made in the preceding chapters of this volume, a number of seemingly paradoxical conclusions can be drawn. First, no toxicological or ecotoxicological shortcomings are admitted by the authors for any of the High Performance Pigments (HPPs) which they have addressed. Secondly, motivation in developing several new classes of pigments stems from a perception that certain existing pigment classes need to be replaced because of toxicological/ecotoxicological considerations, for example, organic yellows as substitutes for lead chromates, and cerium sulfides for cadmium pigments.

How can one rationalize such seemingly divergent views? Will we have a major retrenchment of HPP pigment classes in the future? Or will we see a “kindlier”, “friendlier” view of all HPPs in the years ahead?

It is not the purpose of this chapter to replace the excellent monographs already published, which detail known data on HPPs in the areas of toxicology and ecotoxicology[1–5]. Instead, we will merely add a small amount of new information, develop a commentary on the rationale between the above two views, and emphasize the necessity for vigilance on the part of the pigment producing and using communities worldwide, to preserve good science in toxicology and ecotoxicology, and preclude the possibility of “political science” rather than true science becoming the change agent upon which future toxicological and ecotoxicological decisions are made.

24.2

Recent Toxicological Testing of High Performance Pigments

Perhaps the best place to start in our commentary is to review some recent testing in the HPP area, and to acknowledge the important role that ETAD continues to play in this field. In recent years, in response to the intention of the Danish Miljøstyrelsen (EPA) to include several organic pigments in their list of substances “dangerous to the environment”, ETAD sponsored aquatic toxicological testing of a number of HPPs, including Pigment Red 122, Pigment Blue 15:1, and Pigment Blue 60.

The work was carried out successfully and the negative results given to the Danish Agency, and it is now accepted that such HPP families do not represent an ecotoxicological threat to human health and the environment.

Again, on the inorganic HPP side, perhaps the pigment class with the greatest likelihood of being fully replaced as a threat to human health and the environment, in favor of organic substitutes, is that of the cadmium family, which has suffered from restrictions in a number of countries[1, 4, 6]. But as Chap. 3 now explains, a recent scientific review for the UK authorities concludes unequivocally that this pigment family should not be considered a threat to health and the environment!

What has brought about this distrust of certain pigment classes? I would suggest that the following six factors have at least partly contributed in past years to roday's distrust and confusion.

23.3
Past Confusion in Assessment of HPPs

23.3.1
Confusion between Water Soluble Salts of Inorganic Metals and Related but Insoluble Pigments

All too often, there is a seeming lack of understanding on the part of regulatory authorities, after having reviewed positive evidence of toxic/ecotoxic effects with water soluble metal salts, that pigments, and particularly high performance pigments, exhibit mega-insolubility in water and solvents, and that biological availability is essentially absent from the latter.

A personal anecdote in this area might be appropriate at this time. In the 1980s, the United States Toxic Substances Interagency Testing Committee (TITC) were evaluating whether or not aquatic testing of Copper Phthalocyanine Green (C.I. Pigment Green 7) should be made mandatory for United States Pigment manufacturers and importers, on the grounds that it was an organo-metallic substance containing copper, which, when present in soluble inorganic salts, is well known as a systemic poison in plants and trees. Accordingly, one day I was telephoned by a representative of a well known Contractor to the EPA, and advised that earlier aquatic toxicological testing on Copper Phthalocyanine Green carried out for my company by a reputable independent testing laboratory, with negative results, and submitted to the TITC, could not be used in their evaluation. On further discussion with my caller, I was informed in no uncertain terms that the reason for rejecting the submitted "ecotox" tests was that the pigment had not been put into solution to ensure maximum bioavailability to the test organisms. In turn, I suggested to him that such would be impractical because of the extreme insolubility of the pigment in water. I can still recall his reply: "Oh, we have ways of solubilizing any product for aquatic testing." Upon a moment's reflection, I agreed with his statement, but suggested that the two effective solubilizing agents for the pigment (molten aluminum chloride and chlorosulfonic acid) would unfortunately dissolve the fish and daphnia as well as the pigment! Not surprisingly, TITC dropped its plan to evaluate the ecotoxicology of C.I. Pigment Green 7 soon afterwards.

24.3.2
Confusion between Pigments and their Associated Impurities

Today we live in an “age of enlightenment” where we have to control the processes involved in pigment manufacture so as to minimize or remove unwelcome inadvertent impurities, by-products, or starting materials from our pigment products. Accordingly, today’s pigments may bear little resemblance to those produced several years ago, and positive results from toxicological testing of these older products may no longer be valid. A case in point is to be found in the “Ames” tests carried out several years ago on C.I. Pigments Red 3 and Red 23 by the United States National Toxicology Program, when equivocal results were obtained in both cases[5]. In light of today’s knowledge regarding the formulation of the pigments and the low purity in both cases, it seems logical that little faith can be placed on the “positive” results of the tests, as these were due more to impurities than to the pigments themselves.

24.3.3
False Positives in Genotoxicity Testing of Organic HPPs

The use of dimethyl sulfoxide (DMSO) as an aid to mutagenic testing of organic HPPs is to be deprecated. This technique is commonly used to render the substance being tested at least partially soluble and thus more bioavailable. In the case of organic pigments, however, any solubilization which may take place essentially transforms the pigment into a bio-available dyestuff, rather than an inert, unreactive, and non-bioavailable substance, and can produce “false positive” test results.

24.3.3
Over-reliance on Structure Activity Relationship (SAR) Assessment of HPPs

QSAR (quantitative structure activity relationship) assessment involves an elegant comparison of structural elements within known substances with similar elements in the substance under evaluation, and predicts with fair success in most substances their toxicological/ecotoxicological profile. Where QSAR can fail, however, is that it does not take into consideration the mega-insolubility in HPPs referred to in Sec. 24.3.1 above, and assumes that the pigment is always bio-available, which is not the case.

24.3.4
Confusion over Inaccurate “PBT” Classifications of HPPs

By virtue of their inertness and permanence in their desired applications, high performance pigments must definitely be considered “persistent”. The idea of a non-persistent HPP is, in fact, unthinkable! However, in recent years, the term “Persistent”, together with the related terms, “Bioaccumulative”, and “Toxic” (or PBT), has become something of a “red flag” to government authorities and NGOs alike, in substances which they believe should be considered candidates for substitution, regulation or even outright banning as POPs (Persistent Organic Pollutants). While it is correct that substances that are persistent and bioaccumulative and toxic to human health or the environment are true “PBTs”, and should be treated as such, there has all too often been poor science exercised in categorizing HPP pigments as PBTs on various governmental lists, where persistence alone has been enough to qualify these substances as PBTs, even though there may be no positive bioaccumulation or toxicity data. Because of such lapses in good science, great stress has been placed by pigment producers and users in the United States and the EU on the idea that in order to qualify as a “PBT” substance it must combine all three categories of persistence and bioaccumulation as well as toxicity! See also Chap. 22 for additional insight into this area.

24.3.4
Inadequacy of Recent Computer-Driven Models for Substance Profiling

Over the last few years, there has been a proliferation of computer-driven models developed to predict product safety and environmental behavior of chemical substances. Again, however, while good results have been documented with “straightforward” substances, most models do not yet appear applicable to “HPP” type levels of insolubility, to inorganic substances, or in some cases to polymers.

24.3.5
Inadequacy of Partition Coefficient Calculations in Evaluating Bioaccumulation

Use of partition coefficients (log Kow) is key to today’s environmental profiling of chemical substances. Kow is the ratio of the solubility of the substance in *n*-octanol to its solubility in water. While such measurements of this ratio work well in the majority of “straightforward” substances, and are part of a normal base set of testing parameters, there is an obvious difficulty with HPPs. In the case of inorganic HPPs, for example, both solubilities are essentially zero. And so we arrive at the impossible task of assessing the log of 0/0! The case of organic HPPs is very similar. With a solubility in water of essentially zero and a low parts per million or billion solubility in *n*-octanol, we have another untenable calculation for most high performance pigments. In view of this anomaly, some years ago Drs. Anliker and Moser of ETAD compared predicted bioaccumulation data for pigments, using log Kow figures from solubility measurements, with results obtained from actual bioaccumulation experiments[9]. This exercise clearly shows the folly of relying on predicted calculations for HPPs and underlines the need to disregard such calculations in favor of actual experimentation.

24.3.6
Continued Polarization between Environmental NGOs and Industry Groups

In the United States, serious attempts have been made in recent years to reconcile past differences between industry groups and environmentalist organizations in order to understand each other's perspective more clearly and help accelerate progress in the testing of chemicals. These efforts, however, appear to be short-lived. A PBS special investigative television program shown in the United States called "Trade Secrets" portrayed an alleged massive cover-up by the American Chemistry Council and its sister organization, the American Vinyl Institute over health problems experienced by employees working with vinyl chloride monomer in the 1950s and 1960s. Subsequent rebuttal statements as to the film's perspective and bias, made by the American Chemistry Council, only enflamed Environmental Defense and the Environmental Working Group, who became occupied in distributing the video of the PBS program to State and Local Governments around the nation, together with a commentary on the lack of trust with which the public should regard the chemical industry.

While this has nothing to do with pigments per se, it has everything to do with explaining why polarization still continues between industry and NGOs.

In the early 1990s I had the opportunity of participating with a group from CPMA in a meeting with one of the chief environmentalist action groups in the United States. While there, I explained that my company, in addition to its pigments production facilities in the United States, had similar facilities in Europe. I still remember the comment made by one well-meaning environmentalist who told me in no uncertain manner that our United States manufacturing facilities were unwelcome to his group, and that we could do no better than to produce our HPPs exclusively in Europe and import them into USA! Today, when industry hears of the need for "greater transparency", and the public's "right to know", it sometimes translates this into "a need for greater transparency, so that the NGOs can use the raw data provided for their own benefit, and interpret it in ways that maximize their position before the public". Obviously, this is an area where much improvement is still critical.

24.4
Current Programs for Toxicological and Ecotoxicological Assessment of HPPs

In recent years, an international effort has gained momentum to evaluate the key toxicological and ecotoxicological characteristics of High Production Volume Substances, defined in the United States as substances with an annual production volume greater than 1 million pounds and in the EU as substances with an annual production volume greater than 1 million kgs. Among HPPs being tested in Europe are copper phthalocyanine green (C.I. Pigment Green 7), while in the United States Quinacridone Reds 122 and 202 have been selected for possible future testing[10–12]. With the concept of "filling in the blanks", compiling a "robust" summary of tox/ecotox test results for the authorities to review, and posting this on the internet for all to see, the next few years should greatly expand our understanding of the inherent safety to human health and the environment of high production volume substances, including high performance pigments.

24.5
The Way Ahead

24.5.1
Future Protocols for HPPs

A recent “White Paper” from the European Commission has unveiled the shape of things to come in the area of toxicological testing and authorization of chemicals[13]. The Paper proposes that industry perform toxicological and ecotoxicological testing of all existing commercial substances and prepare risk assessments to demonstrate either that they are safe or should be authorized for future use only in restricted ways.

A tiered testing process will be phased in over a twenty year period, and is expected to cost industry approximately $2.5 billion, with an administrative staff of almost 200, to be paid for by a service fee levied on industry. Of major concern with HPPs is a “fast track” authorization provision for PBTs. As already noted in Sec. 24.3.4 above, HPP producers and importers must ensure accuracy of the definition of PBTs as (P+B+T)s or face the specter of across-the-board regulatory restrictions on their products due to exercise of the Precautionary Principle.

The White Paper is now being submitted to the European Parliament. If signed into law, this strategy will ensure the largest volume of toxicological and ecotoxicological testing that has yet been seen.

24.5.2
Implementation of the Prior Informed Consent (PIC) Treaty

Under the auspices of the United Nations Environmental Programme (UNEP), an international conference of plenipotentiaries meeting in Rotterdam in September 1998 approved a Prior Informed Consent (PIC) procedure for certain hazardous chemicals and pesticides in international trade[14]. Once ratified by 50 nations, PIC will swing into action and become a major player in international commerce by ensuring that certain listed products can only be exported once the receiving (importing) country, has officially given its “Informed Consent” for that importation.

At the time of writing this chapter, the passage of this program appears inevitable, and should provide help in generating much needed “right to know” on import/export of materials in international commerce.

One issue, however, requires addressing before the pigments community can fully welcome PIC as a way of doing business. At this time, three of the inadvertent trace impurities, which may be present in some HPPs, are polychlorinated biphenyls, polychlorinated dibenzodioxins, and polychlorinated dibenzofurans. While these impurities are fully compliant with TSCA, and may only be present in low parts per million or billion, USEPA's Enforcement Division currently requires that, if analytically detectable, any listed trace impurities must still be reportable when exported out of the United States. To compound the difficulty, USEPA then informs the importing country, not that a product is to be exported from the United States containing a trifling impurity of "xyz", but rather that a shipment of "xyz" is being exported to them, without any hint as to it only being a trace impurity.

Until USEPA changes its philosophy and admits that trace impurities are trace impurities and not products, and need not be reported as products to importing countries, there will be little likelihood of an easy implementation of the PIC procedures.

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Appendix

Colour Index Name	***Pigment Family***	***CAS No.***	***EINECS No.***
Pigment Yellow 35	Cadmium	12442-27-2	235-672-6
Pigment Yellow 53	CICP	8007-18-9	232-353-3
Pigment Yellow 93	Disazocondensation	5580-57-4	226-970-7
Pigment Yellow 94	Disazocondensation	5580-58-5	226-971-2
Pigment Yellow 95	Disazocondensation	5280-80-8	226-107-4
Pigment Yellow 109	Isoindolinone	5045-40-9	225-744-5
Pigment Yellow 110	Isoindolinone	5590-18-1	226-999-5
Pigment Yellow 120	Benzimidazolone	29920-31-8	249-955-7
Pigment Yellow 128	Disazocondensation	79953-85-8	279-356-6
Pigment Yellow 138	Quinophthalone	30125-47-4	250-063-5
Pigment Yellow 139	Isoindoline	36888-99-0	253-256-2
Pigment Yellow 151	Benzimidazolone	31837-42-0	250-830-4
Pigment Yellow 154	Benzimidazolone	68134-22-5	268-734-6
Pigment Yellow 157	CICP	68610-24-2	271-853-6
Pigment Yellow 161	CICP	68611-43-8	271-892-9
Pigment Yellow 162	CICP	68611-42-7	271-891-3
Pigment Yellow 163	CICP	68186-92-5	269-054-2
Pigment Yellow 164	CICP	68412-38-4	270-185-2
Pigment Yellow 166	Disazocondensation	76233-82-4	–
Pigment Yellow 175	Benzimidazolone	35636-63-6	252-650-1
Pigment Yellow 180	Benzimidazolone	77804-81-0	278-770-4
Pigment Yellow 181	Benzimidazolone	77441-05-7	277-873-1
Pigment Yellow 184	Bismuth Vanadate	14059-33-7	237-898-0
Pigment Yellow 185	Isoindoline	76199-85-4	278-388-8/253-256-0
Pigment Yellow 189	CICP	69011-05-8	273-686-4
Pigment Yellow 194	Benzimidazolone	82199-12-0	279-914-9
Pigment Yellow 213	Quinoxalinedione	–	–
Pigment Orange 20	Cadmium	12656-57-4	235-758-3
Pigment Orange 31	Disazocondensation	12286-58-7	226-105-3
Pigment Orange 36	Benzimidazolone	12236-62-3	235-462-4
Pigment Orange 55	Disazocondensation	304891-88-1	–
Pigment Orange 62	Benzimidazolone	52846-56-7	258-221-5
Pigment Orange 64	Benzimidazolone	72102-84-2	276-344-2
Pigment Orange 66	Isoindoline	68808-69-5	272-330-5
Pigment Orange 69	Isoindoline	85959-60-0	289-055-1
Pigment Orange 71	Diketopyrrolopyrrole	–	–

Colour Index Name	*Pigment Family*	*CAS No.*	*EINECS No.*
Pigment Orange 72	Benzimidazolone	–	–
Pigment Orange 73	Diketopyrrolopyrrole	–	–
Pigment Orange 75	Cerium	12014-93-6	234-603-7
Pigment Orange 78	Cerium	12014-93-6/12031-49-1	234-603-7/234-752-8
Pigment Red 108	Cadmium	58339-34-7	261-218-1
Pigment Red 122	Quinacridone	980-26-7	213-561-3
Pigment Red 123	Perylene	24108-89-2	246-018-4
Pigment Red 139	Disazocondensation	12262-44-1	–
Pigment Red 140	Disazocondensation	–	–
Pigment Red 141	Disazocondensation	3864-06-0	–
Pigment Red 142	Disazocondensation	109944-97-0/ 6166-65-0	–
Pigment Red 143	Disazocondensation	122286-63-4	–
Pigment Red 144	Disazocondensation	5280-78-4	226-106-9
Pigment Red 149	Perylene	4948-15-6	225-590-9
Pigment Red 166	Disazocondensation	3905-19-9	223-460-6
Pigment Red 175	Benzimidazolone	6985-92-8	230-249-2
Pigment Red 176	Benzimidazolone	12225-06-8	235-425-2
Pigment Red 178	Perylene	3049-71-6	221-264-5
Pigment Red 179	Perylene	5521-31-3	226-866-1
Pigment Red 185	Benzimidazolone	51920-12-8	257-515-0
Pigment Red 190	Perylene	6424-77-7	229-187-9
Pigment Red 202	Quinacridone	3089-17-6	221-424-4
Pigment Red 206	Quinacridone	71819-76-6	216-125-0
Pigment Red 207	Quinacridone	71819-77-7	–
Pigment Red 208	Benzimidazolone	31778-10-6	250-800-0
Pigment Red 209	Quinacridone	3573-01-1	–
Pigment Red 214	Disazocondensation	82643-43-4	255-055-2
Pigment Red 217	Disazocondensation	56358-42-0	260-129-5
Pigment Red 218	Disazocondensation	56418-72-5	260-167-2
Pigment Red 220	Disazocondensation	68259-05-2	269-507-4
Pigment Red 221	Disazocondensation	71566-54-6	275-639-3
Pigment Red 224	Perylene	128-69-8	204-905-3
Pigment Red 230	CICP	68187-27-9	269-083-0
Pigment Red 231	CICP	68186-99-2	269-061-0
Pigment Red 232	CICP	68412-79-3	270-210-7
Pigment Red 233	CICP	68187-12-2	269-073-6
Pigment Red 235	CICP	68201-65-0	269-230-9
Pigment Red 236	CICP	68187-53-1	269-104-3
Pigment Red 242	Disazocondensation	52238-92-3	257-776-0
Pigment Red 248	Disazocondensation	211502-18-0	–
Pigment Red 254	Diketopyrrolopyrrole	84632-65-5	402-400-4
Pigment Red 255	Diketopyrrolopyrrole	88949-37-5	–
Pigment Red 260	Isoindoline	71552-60-8	275-616-8
Pigment Red 262	Disazocondensation	211502-19-1	–
Pigment Red 264	Diketopyrrolopyrrole	–	–
Pigment Red 265	Cerium	12014-96-6/12014-93-6	234-603-7
Pigment Red 271	Isoindoline metal complex	–	–
Pigment Red 272	Diketopyrrolopyrrole	–	–
Pigment Red 275	Cerium	12014-93-06	234-603-7

Colour Index Name	*Pigment Family*	*CAS No.*	*EINECS No.*
Pigment Violet 19	Quinacridone	1047-16-1	213-879-2
Pigment Violet 23	Dioxazine	6358-30-1/215247-95-3	228-767-9
Pigment Violet 29	Perylene	81-33-4	201-344-6
Pigment Violet 32	Benzimidazolone	12225-08-0	235-426-8
Pigment Violet 37	Dioxazine	57971-98-9/17741-63-8	241-734-3
Pigment Violet 42	Quinacridone	1047-16-1	213-879-2
Pigment Violet 47	CICP	68610-13-9	271-849-4
Pigment Blue 15	Phthalocyanine	147-14-8	205-685-1
Pigment Blue 16	Phthalocyanine	574-93-6	209-378-3
Pigment Blue 36	CICP	68187-11-1	269-072-0
Pigment Blue 71	CICP	68186-95-8	269-057-9
Pigment Blue 72	CICP	68186-87-8	269-049-5
Pigment Blue 73	CICP	68187-40-6	269-093-5
Pigment Blue 74	CICP	68412-74-8	270-208-6
Pigment Blue 75	Phthalocyanine	3317-67-7	222-012-7
Pigment Blue 76	Phthalocyanine	68987-63-3	273-501-7
Pigment Blue 79	Phthalocyanine	14154-42-8	237-998-4
Pigment Green 7	Phthalocyanine	1328-53-6	215-524-7
Pigment Green 26	CICP	68187-49-5	269-101-7
Pigment Green 36	Phthalocyanine	14302-13-7	238-238-4
Pigment Green 50	CICP	68186-85-6	269-047-4
Pigment Brown 11	CICP	64294-89-9	–
Pigment Brown 23	Disazocondensation	35869-64-8	252-772-5
Pigment Brown 24	CICP	68186-90-3	269-052-1
Pigment Brown 25	Benzimidazolone	6992-11-6	230-258-1
Pigment Brown 31	CICP	68187-51-9	269-103-8
Pigment Brown 33	CICP	68186-88-9	269-050-0
Pigment Brown 34	CICP	68187-10-0	269-071-5
Pigment Brown 35	CICP	68187-09-7	269-069-4
Pigment Brown 37	CICP	70248-09-8	274-508-8
Pigment Brown 39	CICP	71750-83-9	275-985-5
Pigment Brown 40	CICP	68991-68-0	274-248-5
Pigment Brown 42	Disazocondensation	80648-58-4	–
Pigment Brown 43	CICP	12062-81-6	235-049-9
Pigment Brown 44	CICP	144437-67-2	–
Pigment Brown 45	CICP	144437-66-1	–
Pigment Black 23	CICP	68187-54-2	269-105-9
Pigment Black 24	CICP	68187-00-8	269-062-6
Pigment Black 25	CICP	68186-89-0	269-051-6
Pigment Black 26	CICP	68186-94-7	269-056-3
Pigment Black 27	CICP	68186-97-0	269-060-5
Pigment Black 28	CICP	68186-91-4	269-053-7
Pigment Black 29	CICP	68187-50-8	269-102-2
Pigment Black 30	CICP	71631-15-7	275-738-1
Pigment Black 31	Perylene	67075-37-0	266-564-7
Pigment Black 32	Perylene	83524-75-8	280-472-4