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Alternatives for elimination of polychlorinated biphenyls (PCBs) in pigments used for printing inks and architectural paints

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Alternatives for elimination of polychlorinated biphenyls (PCBs) in pigments used for printing inks and architectural paints

by

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Executive Summary¹

It has long been known that polychlorinated biphenyls (PCBs) are inadvertently generated during manufacture of some pigments. This has become more of an issue in Washington State because of allowances of up to 50 ppm PCBs in most products under the federal Toxics Substances Control Act (TSCA) and much lower allowances for PCBs in waterways under the Clean Water Act (CWA). PCBs are addressed in the state PBT Rule (WAC 173-333) on persistent, bioaccumulative and toxic chemicals (PBTs) that remain in the environment and people for a long time and build up within organisms and in the food chain. It is beneficial to reduce sources of PBTs like PCBs wherever possible to reduce exposure to people and the environment. There are many challenges to PCB-free pigments, which must show potential to be used for widely distributed applications, including large-volume, low-cost printing of magazines, newspapers, and architectural paints.

This report addresses:

- Chemistry of pigments and PCB formation during manufacture of pigments
- Uses of different pigments
- Challenges related to the availability of PCB-free pigments
 - Summary of assessments already performed (including effectiveness, economical and ecological considerations) on PCB-free pigment options.
 - Current market dissemination of the most promising PCB-free pigments.
 - Factors inhibiting further market acceptance.
- Alternative reaction mechanism designed to avoid the formation of PCBs.
 - Compilation of research on alternative pathway mechanisms with literature references, where available.
 - Factors inhibiting further research and commercialization of pathways.

The conclusions include:

- Azo and CuPc pigment manufacture in recent decades has transferred substantially, though not completely, from the USA, Europe and Japan, to China and India. Western users of these pigments now rely heavily on imported products.
- Inadvertent PCB formation in pigment manufacture, although long recognized, appears to be emerging as an issue of growing concern for pigment manufacturers and users, based on recent environmental studies using increasingly-sophisticated analytical techniques.
- Analytical data from current Japanese studies is beginning to identify azo pigment product types causing concern, although more extensive evidence to confirm the conclusions is required.

¹ The Executive Summary was written by Ecology and the rest of the document was written by Prof. Christie.

- This paper proposes free radical mechanisms for PCB formation that are consistent with structural features of the azo pigments implicated in the Japanese study.
- Short-medium term action to address confirmed issues will need to focus on existing pigment ranges. New pigment development is a long-term project
- There are no obvious immediate replacements available for the diarylide pigments as extensively use in printing inks. Such issues require to be addressed by manufacturers through enhanced understanding of PCB formation mechanisms within their processes to ensure reduced levels.
- Phthalocyanine pigments are implicated in the US study but not the Japanese study and thus clarification is needed. If the source of PCBs in CuPc blue is confirmed as the use of chlorinated aromatic solvents, as appears mechanistically reasonable, then alternatives are available. The situation with CuPc greens appears less well understood and would benefit from clarification on the basis of experimental and analytical studies

Purpose of the report

This report, together with a presentation at the 17th Annual Green Chemistry Conference and in a webinar in June 2013 has been prepared on the basis of a contract with the Department of Ecology, State of Washington, USA. The report addresses the following:

A. Challenges related to the availability of PCB-free pigments that can substitute diarylide, azo or phthalocyanine pigments (note that diarylide pigments are a subset of azo pigments). PCB-free pigments must show potential to be used for widely distributed applications, including large-volume, low-cost printing of magazines, newspapers, and architectural paints. Details include:

(a) Summary of assessments already performed (including effectiveness, economical and ecological considerations) on PCB-free pigment options.

(b) Current market dissemination of the most promising PCB-free pigments.

(c) Factors inhibiting further market acceptance.

B. Alternative reaction mechanism designed to avoid the formation of PCBs.

(a) Compilation of research on alternative pathway mechanisms with literature references, where available.

(b) Factors inhibiting further research and commercialization of pathways.

Strategy

The report is based on both general review of internet sources and specific literature surveys using keyword searches, with Web of Knowledge for academic literature and with Google Patents for patent literature. In relation to the chemistry of the potential mechanisms of PCB formation in pigments, specific textbooks and review articles have proved informative. The report also draws significantly from the author's breadth and depth of personal experience and knowledge of pigment manufacture over several decades, and books, monographs and articles published over a long career. The author emphasizes that he has insight into manufacturing processes and procedures adopted to address environmental issues in organizations that have manufactured the pigments in Europe and North America, but has comparatively less insight into the practices in Asia, notably in China and India, where most pigment manufacture now takes place.

Literature review confirmed the author's initial opinion that there was unlikely to be significant specific relevant information openly published by the pigment industry. Keyword searching of academic literature using (pcb or synonyms) and (pigment or dye) in article titles identified only one article, and it was not relevant. A broader search in article topics gave 480 hits. The titles of all of the publications were scrutinized for relevance. Mostly, they concerned health and toxicity studies and some dealt with analytical studies. Importantly, recent papers reporting environmental studies in the US have raised the profile of the issue of trace levels of PCBs in certain pigments. Only a limited number of patents referring to PCB in pigments were identified but these provide some insight into the ways in which the industry has sought to address the issues over the years. Critically, reports from Japan, including one in May 2013 which provides analytical data on PCB levels in specific industrial pigment samples, have provided important preliminary information on current commercial products.

The report is structured so that relevant background information is presented initially. Section 3 provides a summary, in some detail, of the extensive and diverse range of pigments in current commercial use. This coverage was included to allow assessment of the potential of products to be manufactured 'PCB-free' and on the basis that a requirement for alternatives or substitutes in a short-medium timeframe would need to be found from existing ranges. Section 4 provides a summary of the contrasting requirements for pigments used in the two ubiquitous applications on which the report is focussed, printing inks and architectural paints. Section 5 presents a general overview of the issue of PCB levels in pigments, with special reference to recent developments. The issues specified in (A) and (B) above are dealt with specifically in sections 6 and 7 respectively. Section 8 provides a summary of the general conclusions from the study, with references given in section 9.

PCBs

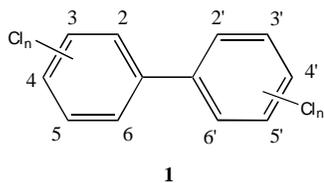


Figure 1- General PCB structure

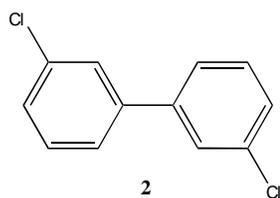


Figure 2-PCB-11

PCB is the commonly-used abbreviation for organochlorine compounds referred to as polychlorinated biphenyls or polychlorobiphenyls. [1] These materials, which are of serious toxicological and environmental concern, are characterized by general structure (Figure 1) and formula $C_{12}H_{10-x}Cl_x$, consisting of 209 possible congeners. A particular congener, PCB 11 (Figure 2), is discussed later in this report in the context of diarylide pigments. PCBs were formerly used as insulating materials in electrical equipment, hydraulic oils and heat transfer systems with smaller quantities used for other industrial purposes. Their stability, while formerly a technical advantage, means that they are highly persistent in the environment, and they are thus classified as persistent organic pollutants. PCBs were manufactured by the chlorination of biphenyl. Most PCBs used in the USA were produced the Monsanto Chemical Company and marketed as mixtures of congeners under the brand name Aroclor. Their production is long-discontinued but quantities remain in the environment. Their disposal is problematic and expensive.

Pigments

The distinction between pigments and dyes is that, with a few exceptions, pigments are insoluble in their application medium and dyes are soluble.[2-5] Pigments are used mostly in the coloration of paints, printing inks and plastics, but also to an extent in a wider range of substrates, including paper, textiles, rubber, glass, ceramics, cosmetics, crayons and building materials such as cement and concrete. Dyes are used mainly in textile coloration. The ability of pigments to provide color is not their only optical function. They may be required to provide opacity, most importantly in paints. In contrast, in multicolor printing, generally using inks of 4 colors, the 3 subtractive primaries, yellow, magenta and cyan, together with black, transparency is needed to ensure that subsequently printed colors do not obscure previously-printed colors. Pigments are required to be fast to light, weathering (if external exposure is envisaged), heat, solvents and chemicals such as acids and alkalis, to a degree dependent on the demands of the particular application.

Chemically, pigments are classified as either *inorganic* or *organic*. These two broad groups are roughly comparable in industrial importance. In general, inorganic pigments provide excellent fastness properties, in this respect offering technical advantage over organic pigments, and are less expensive than typical organics. However, they commonly provide inferior color properties. Organic pigments provide high color strength and brightness although with variable fastness properties. There is a range of high performance organic pigments which offer excellent durability while retaining superior color properties, although they are more expensive.[6] In general, inorganic pigments give high opacity, while organic pigments are transparent. Pigments are solid crystalline materials manufactured in a finely divided form.[7] Commercial products are rarely pure species, often treated with surface active agents or resins to modify physical characteristics. A particular product may contain small quantities of other pigments to modify the color. They may also contain impurities arising from the manufacturing process which tend to be strongly retained because of the high surface area of pigments.

Inorganic pigments [3]

By far the most important white pigment is titanium dioxide (TiO_2), used widely in paints, plastics, printing inks, rubber, paper, ceramics, textiles and cosmetics. Its dominant industrial position is due to high opacity and whiteness, excellent durability and non-toxicity. The most important colored inorganic pigments are iron oxides, with colors ranging from yellow and red to brown and black. They are used in paints, plastics and in building materials. Iron oxide pigments are characterized by excellent durability, high opacity, low toxicity and low cost. The main deficiency is that the colors lack brightness and intensity. Chromium (III) oxide, Cr_2O_3 , is a weak, dull green pigment but shows outstanding durability. Mixed metal oxides, including cobalt

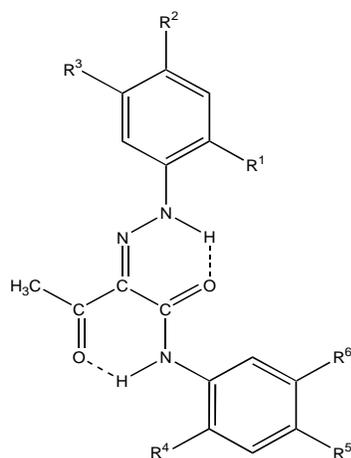
aluminate blue and nickel antimony titanium yellow, are inorganic pigments used in ceramics and plastics because of outstanding heat stability combined with moderate color strength and brightness. Cadmium sulfides provide moderately intense yellow to red colors, of importance in plastics because of high heat stability. Lead chromate pigments provide bright colors from greenish-yellow through to yellowish-red which offer good fastness properties and high opacity, at relatively low cost. The use of Cd- and Pb-containing pigments is restricted on the grounds of potential toxicity associated with the presence of heavy metals. Bismuth vanadates are relatively-recently introduced pigments with high opacity and good durability. They give bright deep yellow shades in industrial and automotive paints and have been growing steadily in importance since their industrial introduction. Ultramarine blue offers excellent fastness to light and heat at moderate cost, providing brilliant reddish-blue colors, but low color strength. Prussian blue retains moderate importance as a low cost blue pigment. Carbon blacks are the dominant black pigments, providing outstanding technical properties at low cost and are used in virtually all pigment applications, including black coatings, plastics and printing inks.

Organic pigments [2]

Organic pigments are categorized as either *classical*, long-established products with good coloristics and moderate technical performance at relatively low cost, or as *high performance*, providing superior durability, generally at higher cost. The most important organic pigments belong to the *azo* and *phthalocyanine* classes, although other chemical types have individual significance. An additional relevant group of classical organic pigments for printing ink applications are *basic dye complex pigments*.

Azo pigments

Azo pigments dominate yellow, orange and red classical products. Although usually defined as containing one or more azo groups (-N=N-), in reality they exist in the ketohydrazone form, as illustrated in this report. Most yellow azo pigments are azoacetanilides, of both monoazo and disazo types. Compounds in Figure 3 and Table 1 a-k are the most important monoazo yellow pigments, traditionally known as *Hansa Yellows*. In general, they give bright yellow colors of moderate intensity and good lightfastness but poor resistance to organic solvents, and are used in applications such as water-based paints where this deficiency is not critical.



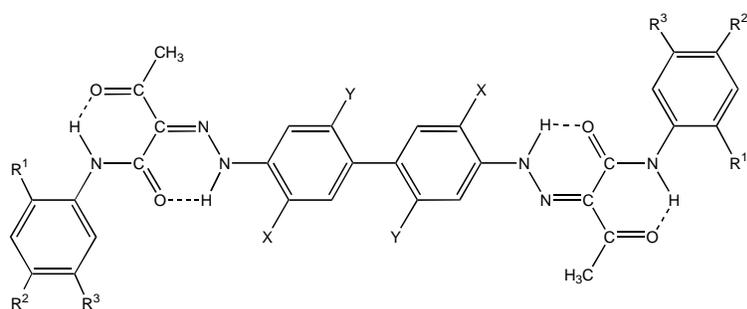
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Figure 3-Azo pigment general structure

Table 1 Azo pigment R groups

Compound	CI Pigment	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
	Yellow						
3a	1	NO ₂	CH ₃	H	H	H	H
3b	3	NO ₂	Cl	H	Cl	H	H
3c	6	NO ₂	Cl	H	H	H	H
3d	65	NO ₂	OCH ₃	H	OCH ₃	H	H
3e	73	NO ₂	Cl	H	OCH ₃	H	H
3f	74	OCH ₃	NO ₂	H	OCH ₃	H	H
3g	75	NO ₂	Cl	H	H	OC ₂ H ₅	H
3h	97	OCH ₃	SO ₂ NHPh	OCH ₃	OCH ₃	Cl	OCH ₃
3i	98	NO ₂	Cl	H	CH ₃	Cl	H
3j	111	OCH ₃	NO ₂	H	OCH ₃	H	Cl
3k	116	Cl	CONH ₂	H	H	NHCOCH ₃	H

Disazoacetoacetanilides (Figure 4 and Table 2 a-q), or *diarylides*, provide the most important yellow and orange organic pigments. Diarylide pigments are especially well-suited to printing ink applications, with Yellows 12, 13 and 14 (Table 2 4a-c) of prime importance. Their lightfastness is generally inadequate for paints and plastics but a few, for example Yellow 83 (Table 2 4i), have sufficient photostability for some paint applications. CI Pigments Yellow 16 (Figure 5a) and 155 (Figure 5b) are examples of disazoacetoacetanilides with a contrasting structural arrangement, which are not described as diarylides. The important diarylide (or pyrazolone) oranges, notably 6a and 6b in Table 3, are similar structurally and in also application properties to the diarylide yellows. The azonaphthols (Table 4 7a-d) are orange and red monoazo pigments with application properties similar to the Hansa Yellows (Figure 3).



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Figure 4- Disazoacetanilides (diarylides) general structure

Table 2- Diarylide R groups

Compound	CI Pigment Yellow or Orange	R ¹	R ²	R ³	X	Y
4a	Y12	H	H	H	Cl	H
4b	Y13	CH ₃	CH ₃	H	Cl	H
4c	Y14	CH ₃	H	H	Cl	H
4d	Y17	OCH ₃	H	H	Cl	H
4e	Y55	H	CH ₃	H	Cl	H
4f	Y63	Cl	H	H	Cl	H
4g	Y77	CH ₃	H	Cl	Cl	H
4h	Y81	CH ₃	CH ₃	H	Cl	Cl
4i	Y83	OCH ₃	Cl	OCH ₃	Cl	H
4j	Y113	CH ₃	Cl	H	Cl	Cl
4k	Y124	OCH ₃	OCH ₃	H	Cl	H
4l	Y152	H	OC ₂ H ₅	H	Cl	H
4m	Y170	H	OCH ₃	H	Cl	H
4n	Y171	CH ₃	Cl	H	Cl	H
4o	Y172	OCH ₃	H	Cl	Cl	H
4p	O15	H	H	H	CH ₃	H
4q	O16	H	H	H	OCH ₃	H

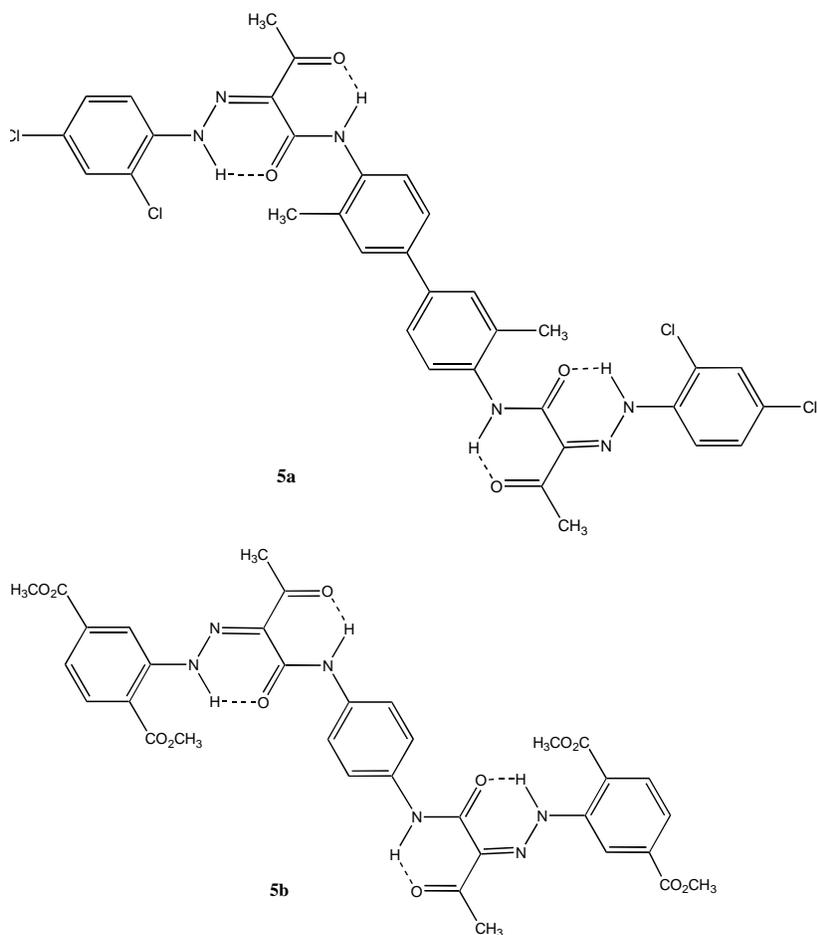


Figure 5- Structure of CI Pigments Yellow 16 (5a) and 155 (5b)

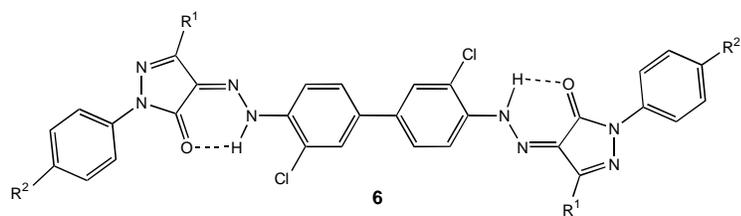


Figure 6- Structure of diarylide (or pyrazolone) oranges

Table 3- Diarylide (or pyrazolone) oranges R groups

Compound	CI Pigment	R ¹	R ²
6a	Orange 13	CH ₃	H
6b	Orange 34	CH ₃	CH ₃

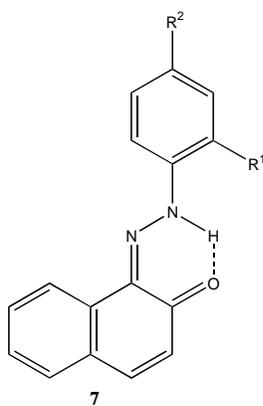


Figure 7- Structure of azonaphthols

Table 4- Azonaphthols R groups

Compound	CI Pigment	R ¹	R ²
7a	Orange 5	NO ₂	NO ₂
7b	Red 3	NO ₂	CH ₃
7c	Red 4	Cl	NO ₂
7d	Red 6	NO ₂	Cl

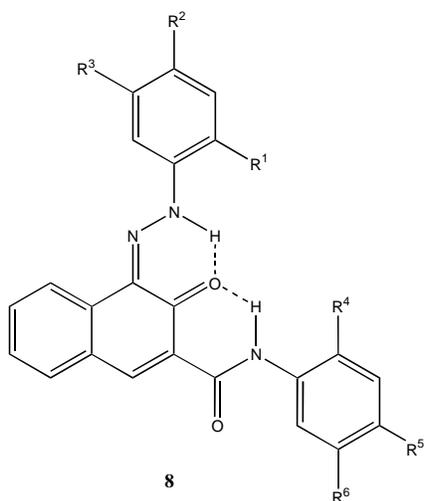


Figure 8- General structure for Naphthol AS or naphtharylamide oranges and reds

Naphthol AS or naphtharylamide oranges and reds, represented by the general structure in Figure 8, are used in printing ink, paint and plastics applications. Group 1 products (Table 5) are simpler structurally, while the more complex Group 2 pigments (Table 6) offer superior properties and some of these products have been growing in commercial importance.

Table 5- Naphthol AS pigments (Group 1)

Compound	C.I. Pigment Red	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
8a	2	Cl	H	Cl	H	H	H
8b	8	CH ₃	H	NO ₂	H	Cl	H
8c	9	Cl	H	Cl	OCH ₃	H	H
8d	10	Cl	H	Cl	H	CH ₃	H
8e	12	CH ₃	NO ₂	H	CH ₃	H	H
8f	14	NO ₂	Cl	H	CH ₃	H	H
8g	22	CH ₃	H	NO ₂	H	H	H
8h	23	OCH ₃	H	NO ₂	H	H	NO ₂
8i	95	OCH ₃	H	SO ₂ OC ₆ H ₄ NO ₂ (<i>p</i>)	CH ₃	H	H
8j	112	Cl	Cl	Cl	CH ₃	H	H

Table 6- Naphthol AS pigments (Group 2)

Compound	C.I. Pigment Red	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
8k	5	OCH ₃	H	SO ₂ N(C ₂ H ₅) ₂	OCH ₃	OCH ₃	Cl
8l	146	OCH ₃	H	CONHC ₆ H ₅	OCH ₃	Cl	OCH ₃
8m	147	OCH ₃	H	CONHC ₆ H ₅	CH ₃	H	Cl
8n	170	H	CONH ₂	H	OC ₂ H ₅	H	H
8o	187	OCH ₃	H	CONHC ₆ H ₅ - <i>p</i> - CONH ₂	OCH ₃	OCH ₃	Cl
8p	188	CO ₂ CH ₃	H	CONHC ₆ H ₅ - Cl ₂ (2,5)	OCH ₃	H	H

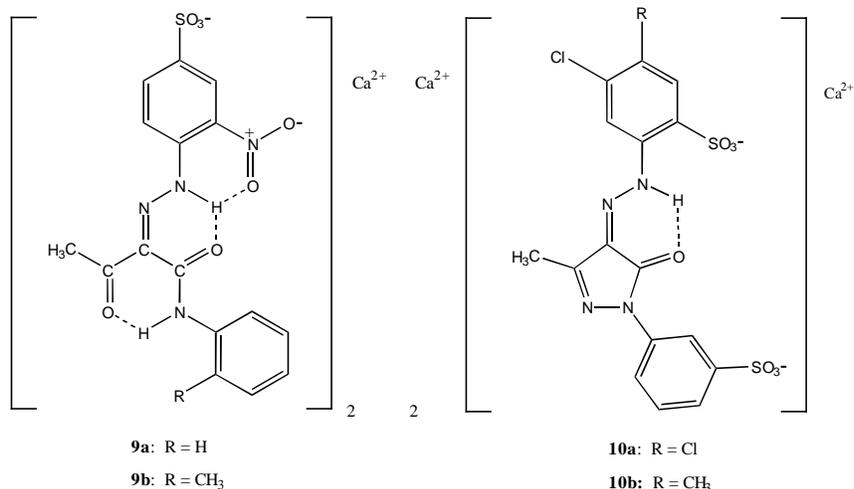


Figure 9- Structure for azoacetoacetanilides

Figure 10- Structure for azopyrazolones

Metal salt azo pigments have evolved from very early products referred to as *lakes*, which were essentially anionic azo dyes precipitated on to inorganic substrates such as alumina or barium sulphate. There are only a few industrial yellow metal salt pigments, azoacetoacetanilides (Figure 9a,b) and azopyrazolones (Figure 10a,b), of modest importance in plastics. In contrast, many of the most important classical red azo pigments are metal salts, especially for printing inks. The pigments may be grouped into 3 types. The most important 2-naphthol based pigments are Lithol Reds (Figure 11a,b) and lake red C (Figure 12). Pigments derived from 3-hydroxy-2-naphthoic acid (Figure 13 and Table 7 13a-h) are particularly important. Red 57:1 (Table 7 13h), commonly referred to as Ca4B toner, is the worldwide standard magenta printing ink pigment.

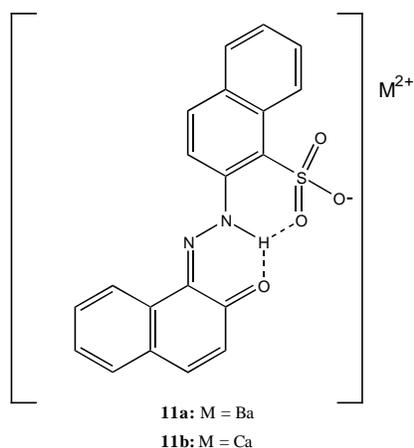


Figure 11- Structure of Lithol Reds

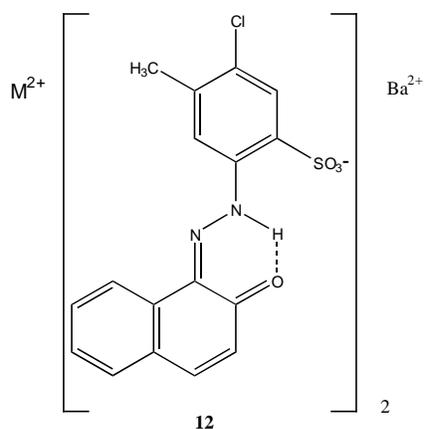


Figure 12- Structure of lake red C

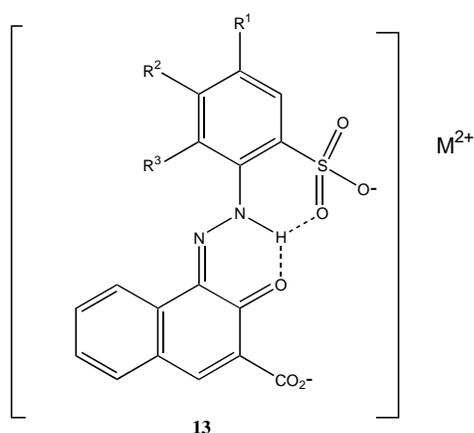


Figure 13- Structure of Pigments derived from 3-hydroxy-2-naphthoic acid

Table 7- R groups for pigments derived from 3-hydroxy-2-naphthoic acid

Compound	C.I. Pigment Red	R ¹	R ²	R ³	M
13a	48:1	CH ₃	Cl	H	Ba
13b	48:2	CH ₃	Cl	H	Ca
13c	48:3	CH ₃	Cl	H	Sr
13d	48:4	CH ₃	Cl	H	Mn
13e	48:5	CH ₃	Cl	H	Mg
13f	52:1	Cl	CH ₃	H	Ca
13g	52:2	Cl	CH ₃	H	Mn
13h	57:1	CH ₃	H	H	Ca

There are two types of *high performance azo pigments*, disazo condensation pigments benzimidazolone pigments, both groups giving durable yellow, red, violet and brown products.

Phthalocyanine pigments

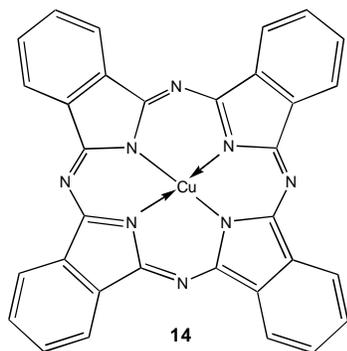


Figure 14- Structure of copper phthalocyanine

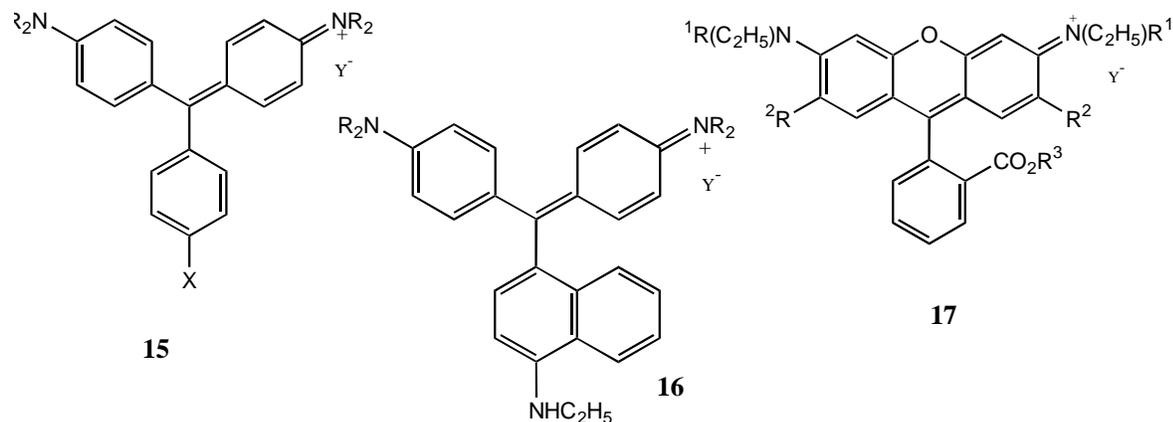
The single most important organic pigment is copper phthalocyanine (CuPc, CI Pigment Blue 15, Figure 14). In addition to a brilliant intense blue color, CuPc offers exceptionally high stability to light, heat, solvents, acids and alkalis at modest cost and finds universal use in the range of pigment applications. The most important green organic pigments are halogenated copper phthalocyanines, CI Pigment Green 7, in which the 16 ring H-atoms are replaced virtually completely by chlorine, and CI Pigment Green 36, which incorporates a range of bromo and bromochloro CuPcs. The CuPc greens exhibit the same outstanding coloristic and technical performance as the blue pigments and are used widely in paints, printing inks and plastics.

High performance organic pigments, encompassing a wide variety of structural types, have been developed in an attempt to match the properties of CuPcs in the yellow, orange, red and violet shades. [6] These products, though industrially important, are more expensive than the comparable classical pigments. They include so-called vat pigments, e.g., anthraquinones, Indanthrone Blue, (CI Pigment Blue 60), Flavanthrone Yellow, (CI Pigment Yellow 24) and perinone (CI Pigment Orange 43), other high performance carbonyl pigments, such as quinacridone, (CI Pigment Violet 19), diketopyrrolopyrrole (DPP) pigments, e.g., CI Pigment Red 254, perylenes, e.g., CI Pigment Red 179, and isoindoline CI Pigment Yellow 139, and other chemical types exemplified by tetrachloroisoindolinone, (CI Pigment Yellow 110) and dioxazine (Carbazole Violet, CI Pigment Violet 23).

Basic dye complex pigments

A further group of classical products of moderate significance are *basic dye complex pigments*. These pigments are derived from water-soluble basic (cationic) dyes rendered insoluble by precipitation with large polymeric counteranions, notably phosphomolybdates, phosphotungstates and copper ferrocyanide. They provide reds, violets, blues and greens,

exhibiting high brilliance and intensity of color and high transparency at relatively low cost. Their main use is in printing ink applications when good fastness to light and heat, and stability to alkali is not essential. Basic dyes of three structural types (Figures 15-17) are used to prepare these pigments.



Figures 15, 16, 17- Structures of basic dye complex pigments

Table 8- R groups for basic dye complex pigments

Compound	C. I. Pigment	X	R		
15a	Violet 3	NHCH ₃	CH ₃		
15b	Violet 39	N(CH ₃) ₂	CH ₃		
15c	Green 1	H	CH ₂ CH ₃		
Compound	C. I. Pigment	R			
16a	Blue 1	CH ₃			
16b	Blue 62	CH ₂ CH ₃			
Compound	C. I. Pigment	R ¹	R ²	R ³	
17a	Red 81	H	CH ₃	CH ₂ CH ₃	
17b	Violet 1	CH ₂ CH ₃	H	H	
17c	Violet 2	CH ₂ CH ₃	H	CH ₂ CH ₃	

Printing ink and architectural paint applications of pigments

This report deals with two specific applications which use pigments in large amounts. There are some distinct differences in the requirements of pigments for these two broad application areas, and consequent differences in pigment selection. [8]

The printing industry, together with associated industries such as publishing and packaging, is a major component of most national economies. Printing predominantly uses pigment-based inks on substrates including paper (books, newspapers, magazines, banknotes, stamps, posters, etc.), board, plastic film and containers, metal foils and textiles. The main pigment requirements for printing inks are high intensity and brightness of color, transparency for multicolor printing, and low cost, while durability requirements are often modest. These features explain why classical organic pigments predominate in printing inks. High volume multicolor printing mainly uses pigments of the subtractive primaries, yellow, magenta and cyan, together with black. Predominantly, these employ diarylide yellows, especially Yellows 12, 13 and 14 (Figure 4 and Table 2 4a-c), Ca4B (Figure 13 and Table 7 13h) as magenta, CuPc (Figure 14) as cyan and carbon black. Other classical organics are used in printing inks, for example where specific colors are required.

For the purpose of this report, architectural paints are assumed to mean paints used in and around the home and office for decorative and protective purposes. Pigments for these paints are required to provide opacity since the coating is designed to obscure the surface. Durability is an important requirement, especially for exterior applications. Inorganic pigments are thus commonly used, with the white pigment, TiO_2 , the dominant product. Selection of colored pigments depends on the color required. The disadvantage of inorganic pigments is that they cannot generally provide bright colors, in which case organic pigments are used, including certain azo pigments, CuPcs and high performance organics.

PCBs in Pigments

It has been known for some time that certain commercial organic pigments may contain trace quantities of PCBs. Awareness of the issue developed as the serious environmental consequences arising from the industrial PCBs was recognized, and also as analytical techniques capable of quantifying trace amounts became increasingly sophisticated and sensitive. Pigment manufacturers, conscious of the situation with specific products, have addressed the issues through optimization of manufacturing processes, aiming to ensure compliance with regulations specifying maximum permissible PCB levels. There is little evidence in the open literature to allow an assessment of the depth of understanding that exist within manufacturing organizations of the mechanisms leading to the formation of PCBs during pigment manufacture. The level of internal understanding may well vary within different industrial organizations and in different geographical regions.

Very recent studies in the US leading to a series of articles have opened a wider debate on the presence and consequence of PCB in pigments. Two key papers were published in 2010. Rodenburg et al presented evidence for the ubiquitous presence of 3,3'-dichlorobiphenyl (PCB11, Figure 2) , referred to as a non-Aroclor PCB, in a variety of environmental situations.[9] The paper proposes that a source of PCB11 in the environment may be discarded consumer goods, such as newspapers, magazines, packaging and plastic bags, the link made to its inadvertent presence in diarylide yellow pigments used in printing inks. Hu and Hornbuckle have presented evidence for their hypothesis that PCB congeners, and PCB11 in particular, may be present in commercial paint formulations.[10] 33 paint pigments acquired from local paint stores were analysed for all 209 PCB congeners. The chemical compositions of the pigments analyzed were either identified in terms of the general product class, or were unidentified. No PCBs were detected in inorganic pigments, including titanium dioxide, iron oxides and carbon black. PCBs were detected in certain organic pigments, notably in azo and phthalocyanine pigments. In the azo pigments, lower PCB congeners (including PCB 11) were prevalent, while the phthalocyanine green pigments showed high levels of PCB209. The assignment to particular chemical species from this study, especially in the case of azo pigments, should be treated with some caution in view of the possibility of misidentification. The authors also propose interesting mechanistic suggestions for inadvertent PCB formation during pigment manufacture, which this report deals with in a later section on alternate reaction mechanisms. Studies have now confirmed the environmental occurrence of PCB 11 in a wide range of locations.[11]

In January 2011, a report by the Ecological and Toxicological Association of Dyes and Organic Pigment Manufacturers (ETAD) confirmed that PCBs may be unintentionally generated during the manufacture of certain organic pigments.[12] They stated that their formation is product and process dependent and may be influenced by the quality and impurity profile of raw materials and intermediates. The report expressed opinions that there is no information which justifies the

conclusion that all or even a predominant source of PCB11 is associated with pigments, that PCB traces in ETAD member products do not constitute a hazard to human health or the environment, and that best available techniques are used to ensure that PCB formation is kept to an absolute minimum, and so that the products meet the regulatory limits.

In February 2012, the Ministry of Economy, Trade and Industry (METI), Japan, based on a report from the Japan Dyestuff and Industrial Chemicals Association (JDICA), requested that businesses that either manufacture or import certain organic pigments that had been detected as containing 0.5ppm or more PCB, analyze the levels in the pigments that they deal with and disclose those pigments containing 50ppm or more. A METI report in May 2013 identified those pigments exceeding the limits as monoazo pigments CI Pigment Red 2 (Figure 8 and Table 5 8a), Red 112 (Figure 8 and Table 5 8j) and Yellow 165, and diarylide pigments, CI Pigments Yellow 12 (Figure 4 and Table 2 4a), 13 (Figure 4 and Table 2 4b), 17 (Figure 4 and Table 2 4d), 55 (Figure 4 and Table 2 4e), 81 (Figure 4 and Table 2 4h), 83 (Figure 4 and Table 2 4i) and Orange 34 (Figure 6 and Table 3 6b).[13] It is of interest that the specific pigments implicated show common molecular structural features. The monoazo pigments are derived from the diazotisation of either a di- or trichloroaniline. The diarylide pigments are derived from tetrazotisation either of 3,3'-dichlorobenzidine or 3,3',5,5'-tetrachlorobenzidine. Copper phthalocyanine pigments do not appear to be implicated in the Japanese study.

Challenges related to the availability of PCB-free pigments

The organic pigment industry has not traditionally promoted the term ‘PCB-free.’ A primary concern has been to ensure that inadvertent PCB formation is minimized and that the products comply with regulatory limits. The term ‘PCB-free’ is indeed misleading as it may be impossible to assert that there is a zero level in a particular product under all circumstances, especially as the sophistication and sensitivity of modern analytical detection methods increase. For the purpose of this report, the author has assumed a meaning based on an assessment of the mechanistic potential to form PCBs. Literature review has revealed, at least until very recently, virtually no meaningful analytical data on PCB levels in the range of commercial products available openly. The results from the US research [10] and the analytical data emerging currently from Japan [13] has started to provide relevant information and to identify certain products causing concern. It is to be hoped that more extensive studies will now follow to ensure an accurate evaluation of the situation with regard to the range of commercial products. At this stage, the limited amount of data on selected single samples of pigments means that the results should be treated with some caution. Significant differences might be anticipated depending on particular manufacturing processes, with batch variation a distinct possibility.

This section attempts to address the issues given in (A) for the purpose of this report.

- (a) Summary of assessments already performed (including effectiveness, economical and ecological considerations) on PCB-free pigment options.
- (b) Current market dissemination of the most promising PCB-free pigments.
- © Factors inhibiting further market acceptance.

The author has formed the opinion that there is little meaningful disclosure by the industry or their representatives dealing directly with the particular issues listed above on which an evaluation may be made. The industry may historically have regarded the issue of inadvertent PCB as localized to a few specific products for which process optimization and control was used to ensure that levels were below the regulatory limits. There is some recent limited evidence for promotion by manufacturers of ‘PCB-free’ products which might be considered as market dissemination of alternatives to PCB-containing products. This suggests that there has historically been limited recognition or perception by the industry of a requirement for such products either from legislative bodies or the commercial marketplace. Recent emergent evidence and a widening of the debate based on environmental concerns, particularly on diarylide pigments if those issues are corroborated with certainty, may require the manufacturing industry to re-evaluate this situation.

In view of this conclusion, this report has dealt with these issues in a less direct but more meaningful way. They are addressed with particular reference to the types of azo pigment implicated in the Japanese study [13], and the copper phthalocyanines implicated in the US study [10], taking account also of likely mechanisms for inadvertent PCB formation (as discussed in the following section on alternative reaction mechanisms). There are certain obvious criteria in deciding that specific pigments might have the potential to be described as PCB-free. As proposed by ETAD [12], these are the absence of chlorine-containing raw materials or solvents in the manufacture. The discussion that follows deals initially with the potential to provide substitutes from the range of existing range of commercial pigments, as summarized in section 3, and the requirements of the specific applications, as summarized in section 4, followed by an overview of approaches towards potential alternative pigments, as yet not industrialized. Suggestions for alternatives given are to be interpreted as potential examples as no single pigment is an exact match for another in all respects.

The challenges in relation to the potential to select a substitute product are broadly to provide:

- (a) the required coloristic performance;
- (b) the required degree of transparency or opacity;
- (c) the level of fastness (to light, solvents, heat, chemicals, etc.) demanded by the application;
- (d) cost effectiveness, in turn dependent on the manufacturing process, including the nature and cost of raw materials, ease and efficiency of the process, product yield, etc.
- (e) an acceptable toxicological and environmental profile.

As described earlier, the color, optical and fastness requirements are different for the two specific applications, printing inks and paints. In the search for substitutes, inorganic pigments might be considered for paint applications but they will be unsuitable for printing inks, where alternative organic pigments are likely to be more appropriate.

Alternatives to the azo pigments.

The recent Japanese study [13] identified a number of azo pigments as exceeding the limits. These pigments may be separated into 2 groups: (a) monoazo pigments derived from a di- or trichloroaniline as the diazo component; (b) diarylide pigments derived from either 3,3'-dichlorobenzidine or 3,3',5,5'-tetrachlorobenzidine as tetraazo component. In both cases, it is of interest that reasonable mechanisms may be proposed for PCB formation as discussed in the following section on alternative mechanisms.

- (a) monoazo pigments from polychloroanilines.

Three pigments are implicated. Of these, Yellow 165 derived from a dichloroaniline as diazo component and a pyrazolone coupling component was not included in section 3 as, although a minor product in Japan, it is barely used elsewhere. It could presumably thus be relatively easily substituted if necessary. Inspection of the structures of the range of other monoazo yellow pigments described in section 3 does not suggest other candidates likely to show high PCB levels. There are several products which contain Cl, but which also contain other substituents that would most likely be retained in impurity formation. The reported presence of PCB in a sample of CI Pigment Yellow 1 (Figure 3 and Table 1 3a) proposed in the US study [10] requires verification as this pigment contains no chlorine.

CI Pigment Reds 2 (Figure 8 and Table 5 8a) and 112 (Figure 8 and Table 5 8h) are moderately significant commercial products, especially the latter. Red 2 is a relatively low cost mid-red pigment used primarily in printing inks. Red 112 is a higher performing product used in printing inks, paints and plastics. There are no suitable red inorganic pigments, so that substitutes, if required, would need to be found from the range of organics. Higher performance naphthol AS pigments, such as CI Pigment Red 170 (Figure 8 and Table 6 8n), or candidates from the metal salt azo pigments, may provide potential alternatives. Inspection of the structures of the range of other monoazo red pigments described earlier suggest that the only other structurally similar pigments which might form PCBs in an analogous way are CI Pigment Reds 9 (Figure 8 and Table 5 8c) and 10 (Figure 8 and Table 5 8d), both yellowish reds, but neither extensively used.

(b) (diarylide (disazo) pigments from polychlorobenzidines

These pigments have for nearly a century been the dominant yellow products for the inks used in high volume, low cost printing of magazines, newspapers and other printed material. Only a few of the products are also used widely in paint applications, the most notable being CI Pigment Yellow 83 (Figure 4 and Table 2 4i). The presence of PCBs in this group of pigments appears to have been raising serious concern only recently, and there is little obvious evidence of the promotion of 'PCB-free' alternatives.

However, there has been a different concern over the years with diarylide pigments associated with the toxicity of the common starting material, 3,3'-dichlorobenzidine (DCB) which has motivated some research towards potential replacements. The use of DCB in pigment manufacture requires careful, controlled handling, generally with specifically-devised handling procedures and equipment, and ideally involving no human contact. Although reassurances are given that the pigments themselves are essentially non-toxic, evidence has been reported that they may cleave thermally at temperatures above 200°C to give a monoazo compound and that prolonged heating above 240°C causes further decomposition leading to release of DCB [14]. As a result of these observations, the use of diarylide pigments has declined in applications where high temperatures are likely to be encountered, especially in thermoplastics. In these applications, alternative pigments have been proposed which do not give rise to this issue, often

at higher cost, including some monoazo pigments and high performance yellow pigments, including benzimidazolone azos, disazo condensation products, isoindolines and isoindolinones, and inorganic pigments such as bismuth vanadate.

However, for printing ink applications, finding substitute products from the existing commercial range is problematic, arguably not possible. No inorganic pigments provide anything approaching the level of color strength and transparency required. There are no alternative yellow and orange azo pigments available that can match the color and transparency requirements at a similar cost. The monoazo pigments are invariably almost half of the color strength of the disazo products. There has been some development of printing ink grades of pigments normally considered primarily for paint applications, a notable example being CI Pigment Yellow 74 (Figure 3 and Table 1 3f). Yellow 155 (Figure 5b) is an example of a disazo pigment with a different structural arrangement compared with the diarylide pigments which has suitability for printing ink applications and does not present the same mechanistic potential to form PCBs. This pigment appears to be growing in commercial importance. In contrast, the analogous Yellow 16 (Figure 5a) is derived from a dichloroaniline and thus structurally has potential for PCB formation. In principle, the development of printing ink grades of the high performance yellow organics might offer alternative possibilities, at higher cost.

For the more limited range of paint applications in which the diarylide pigments are used, a similar group of high performance pigments as are used in plastics may provide alternatives, at much higher cost to the user. Inorganic yellow pigments, such as iron oxides and nickel antimony titanium yellow, are not capable of matching the colors of the organics, while lead chromates and cadmium sulphides are restricted on toxicological grounds. However, bismuth vanadate is a relatively-recently industrialized yellow inorganic pigment which is growing in industrial importance for paint applications because of its bright color, good durability and hiding power, although at a higher cost than is normal for inorganic pigments, and thus offers the possibility of providing a substitute product.[3]

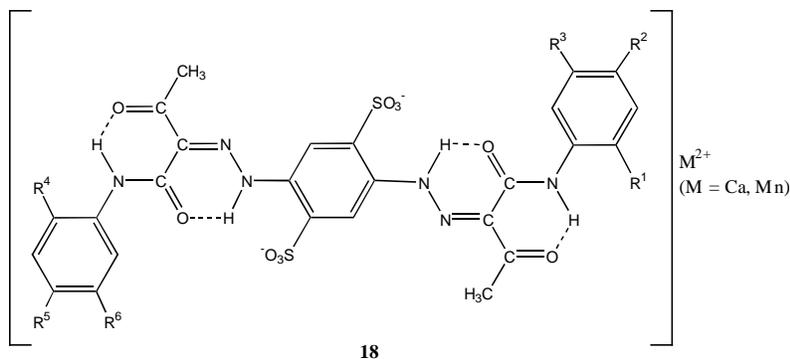


Figure 18- Structure of metal salt pigments

There have been two notable academic studies aimed at investigating new chemical types of disazo pigments, as potential alternatives for diarylide yellows. These studies were based on exploring alternative diamines which have the potential to replace DCB as the tetrazo component. The strategy in the studies involved design or selection of diamines on the basis of low toxicity. Nevertheless, while not a stated aim at the time, the products did not contain chlorine and thus have the potential to be ‘PCB-free’. Our research group has reported the synthesis and properties of yellow pigments based on *p*-phenylenediamines. [15] Of particular interest are some metal salt pigments (Figure 18). Freeman *et al* report investigations of a range of disazo pigments based on alternative benzidine derivatives designed for non-mutogenicity.[16] On the basis of the variable technical and color performance of the range of products as reported, although undoubtedly with potential for improvement through process and product optimisation, and the use of specialist starting materials which might impact on cost-effectiveness, the products were not immediately proposed as suitable technical replacements for the commercial diarylide yellows. However, the publications demonstrate research approaches that may be useful for new product development, either in academic or industrial environments, over a longer timeframe. Other potential products may be found in relatively old patents, the properties of which may be known to the manufacturers who carried out the original investigations, and may be worth re-investigation in view of new information. On the basis of industrial patent activity, there appears to have been recent interest in disazo pigments based on bis-coupling components, structurally analogous to CI Pigment Yellow 155 (Figure 5b). [17,18] The main barrier to the development of pigments based on new chemical species is the requirement for extensive, and expensive, toxicological evaluation before a new commodity industrial chemical can be introduced. Thus, it would appear that the most likely short term approach to the diarylide pigments is to attempt to eliminate or minimize the PCB issues associated with the products, as discussed in the following section on alternative mechanisms.

Alternatives to CuPc blue and green pigments

Copper phthalocyanine blue has been described as the ‘perfect’ blue pigment, providing all-round excellent color and technical performance at low cost. There has consequently been little incentive to develop alternative blue pigments. CuPcs are apparently not implicated at this stage in the Japanese study, although there is some implication from the US study, which requires verification. The available inorganic blue pigments, ultramarine, Prussian blue and cobalt aluminate blue, provide much weaker colors and they each have specific technical weaknesses. There are only a few blue azo pigments and they are of little consequence and a limited number of high performance anthraquinone based pigments, but they are aimed at specialist applications and lack the versatility of copper phthalocyanine. For reasons given in the following section on alternative mechanism, the reduction of PCBs in CuPc blue to acceptable levels might be addressed more easily than new product development.

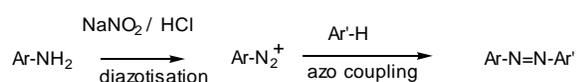
Copper phthalocyanine greens present a more complex situation. These are polychlorinated (and polybrominated) CuPcs, and the formation of higher PCB congeners as suggested by the US publication [10] seems a distinct possibility mechanistically. They are used in printing inks and paints when the desired color demands it. Green colors may of course be obtained by mixing blue and yellow pigments, and under certain circumstances with careful pigment selection, this provides an alternative with the potential to reduce the PCB congeners associated with the CuPc green pigments if confirmed, although it is only be useful if the less intense, less bright color than would be given by the use of copper phthalocyanine greens is acceptable. In this context, copper phthalocyanine blue is most useful used in combination with appropriate azo pigments, or with high performance organic yellows in applications where the durability of copper phthalocyanine greens needs to be matched. Inevitably, the latter approach would add to the cost. The only major green inorganic pigment is chromium oxide, although the color is dull. There has been some recent industrial patent activity claiming alternative green pigments which contain no halogen, thus apparently aimed at addressing potential PCB formation issues, which may be directed towards replacements in the long term.[19-22]

Basic dye complex pigments (Figures 15-17) are suitable for printing ink applications on the basis of strong bright red, violet, blue and green colors, transparency and relatively low cost. CI Pigment Green 1 (Figure 15 and Table 8 15c), for example, is a potential substitute for copper phthalocyanine green although with significantly inferior durability. This group of pigments provides no yellow colors, although it may be speculated that there could, in principle, be products developed based on the modern range of yellow water-soluble cationic dyes for printing applications.

Alternative reaction mechanisms designed to avoid the formation of PCBs.

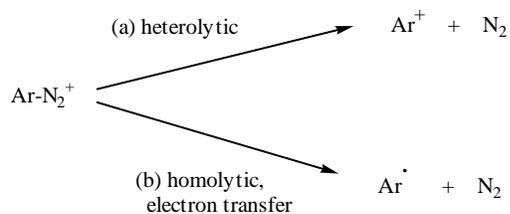
This section presents informed speculation on potential mechanisms by which PCBs may form inadvertently which during the manufacture of certain pigments. The hypotheses would need to be confirmed by experimental investigation. Proposals are made concerning how these side reactions might be minimized to provide products with reduced PCB levels.

Azo pigments



Scheme 1- Synthesis of azo pigments

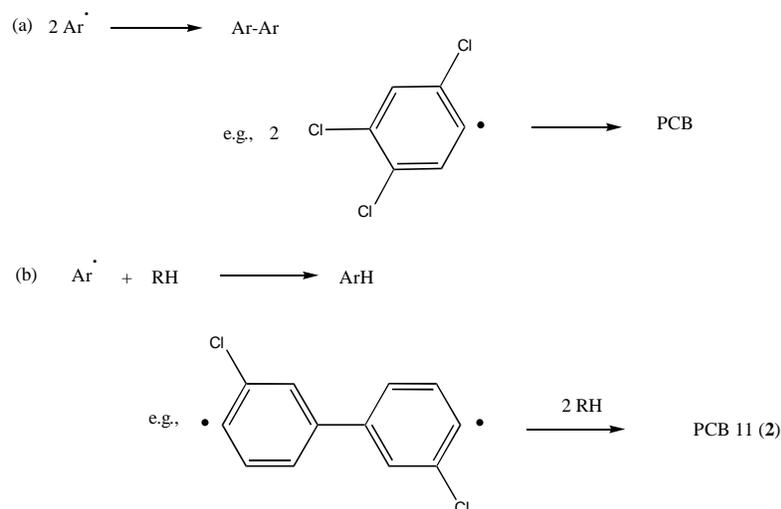
All classical azo pigments are synthesized by variations on the same standard synthetic route.[23] The synthesis involves a two-stage sequence of reactions known as *diazotisation* and *azo coupling* (Scheme 1), carried out in water. It is important to control the synthesis conditions carefully to maximize the yields and to minimize side reactions which can lead to impurities which adversely affect product quality and environmental acceptability. Diazotisation involves the treatment of a primary aromatic amine (ArNH₂), the diazo component, with nitrous acid to form a diazonium salt (ArN₂⁺Cl⁻). Nitrous acid, HNO₂, is generated by treating sodium nitrite with a strong acid, usually hydrochloric acid. It is important to maintain careful control of the temperature, usually in the range 0-5°C. The main reason is the instability of diazonium salts which decompose readily with the evolution of nitrogen. Diazonium salts are almost always prepared in solution as required and used immediately to synthesize the azo pigment. Azo coupling involves reaction of the diazonium salt with appropriate coupling components at or just below ambient temperatures. There is usually an optimum pH range for a specific azo coupling reaction, dependent on the coupling component used. As a general rule, it is desirable to carry out the reaction at the lowest pH at which coupling takes place at a reasonable rate. The rate of addition of the diazonium salt to the coupling component is controlled to ensure that a diazonium salt excess is never allowed to build up in the coupling medium. Disazo pigments (Figure 4) are prepared by tetrazotisation (bis-diazotisation) of a diamine, most commonly 3,3'-dichlorobenzidine, and reaction with two equivalents of the coupling component. For this report, the two groups of azo pigments identified in the Japanese study [13] have been highlighted (see earlier sections). Based on an inspection of the structures and a consideration of the mechanistic possibilities, it appears most likely that the source of the PCBs is the diazo component, a di- or trichloroaniline in the case of the monoazo pigments and 3,3'-dichlorobenzidine (DCB) in the case of the diarylide pigments.



Scheme 2- General mechanisms of dediazonation

In the azo coupling reaction that forms the pigment, the nitrogen atoms of the diazonium salt are retained. However, diazonium salts also undergo a range of reactions in which the nitrogen is eliminated, referred to collectively by the term *dediazonation*. [24] There are 2 principal mechanisms for such reactions, illustrated generally in Scheme 2: (a) involving a heterolytic process and (b) a homolytic process. A third mechanism invokes the intermediacy of arynes. The heterolytic process forms an aryl cation (Ar^+) which commonly undergoes reaction with nucleophiles present in the reacting system, e.g., with water to form phenols and with chloride ions to form chloroaromatics. The latter reaction, although involving chlorine, does not, at first sight at least, suggest a potential source of PCB formation.

It appears that a more likely mechanism involves homolytic processes and the intermediacy of aryl free radicals, especially since it is known that PCBs are commonly formed in free radical reactions.[1] The topic has been the subject of systematic reviews.[24,25] Complications in applying literature reports in attempts to speculate on the formation of trace amounts of inadvertent materials include the numerous mechanistic possibilities and the fact that these reactions have been most extensively studied with a view to optimizing their preparative qualities, with much less investigation into prevention or minimization. As shown in Scheme 2, the process is initiated by electron transfer from a reducing agent and the aryl radical is formed following nitrogen elimination. Reduction processes at an electrode, by gamma-radiation or photoinitiation are known are not obviously relevant to pigment manufacture. Initiation by reducing metal ions is well-established, most commonly with Cu(I), but also by Sn(II), Cr(II), Ti(III), V(II) and Fe(II). Organic reducing agents such as ferrocene and ascorbic acid may also initiate the process. The most commonly encountered anion leading to radical formation is iodide. Chloride and oxygen anions are reported to be insufficiently reducing to cause electron transfer. It has been tentatively suggested that the nitrite anion, used in the diazotisation, may have sufficient reducing properties.[25]



Scheme 3- Potential mechanism for PCB formation from aryl radicals

Scheme 3 shows two potential general reactions (a) and (b) of the aryl radical. Radical combination (a) can lead to biphenyl derivatives, apparently providing a plausible mechanism for inadvertent PCB formation in the case of pigments, such as CI Pigment Red 2 (Figure 8 and Table 5 8a), Red 112 (Figure 8 and Table 5 8j) and Yellow 165, derived from diazotized di- and trichloroanilines. A further frequently-encountered reaction of aryl radicals is hydrogen abstraction (b) from an appropriate hydrogen donor. Preparatively, reagents such as hypophosphorus acid may be used to carry out this reaction. Alternatively, the reaction solvent may provide the source of hydrogen, for example ethanol at high temperatures. This reaction presents a plausible mechanism for inadvertent formation of PCB 11 in the manufacture of diarylide pigments, as a result of bis-dediazoni-ation of the tetrazonium salt, either as illustrated in Scheme 3 or in separate stages. It is emphasized that these are hypothetical mechanistic proposals that need to be tested by experimental investigation. On the basis of the suggestions, possible approaches to minimize PCB formation during azo pigment manufacture are discussed. It is conceivable, indeed likely, that pigment manufacturers might already have considered at least some of these approaches.

Removal of PCBs once formed from the pigments appears problematic. Organic pigments are of fine particle size and strongly absorb aromatic compounds on the surface of or occluded into the crystal structures. Removal by vacuum-assisted evaporation may be considered in view of the reported volatility of PCB 11, but may be inefficient and would require disposal of the removed materials. Chemical degradation methods that can remove the PCBs without harming the pigment appear unlikely. Approaches that involve modification of synthesis conditions to minimize, ideally avoid, PCB formation appear more promising. Some options are discussed, based on the premise that free radical reactions of the type illustrated in Scheme 3 are involved.

To ensure product quality, azo pigment manufacturers use ‘best available techniques’ in manufacturing operations.[12] Diazotisation is carried out under optimized conditions and the

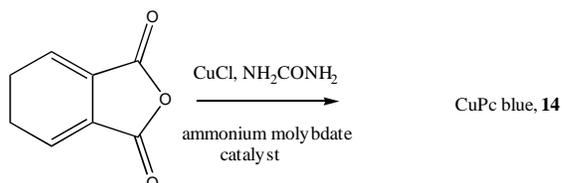
diazonium salt is used as soon as possible in azo coupling to form the pigment. It is self-evident that minimizing the lifetime of the diazonium salt is likely to minimize the possibility of side reactions. The chemical process factors involved are broadly recognized by industry. A Hoechst patent [26] describes how such practice is used to minimize PCB levels in monoazo pigments derived from di- and trichloroanilines, such as those implicated in the Japanese study.[13] However, in view of growing awareness of the inadvertent PCB issues, experimental investigations, for example using the principles of statistical design, to quantify rigorously the effect of individual process factors on PCB levels should prove valuable. The obvious parameters include starting material purity, concentrations and relative quantities of reactants, reaction temperatures, pH levels, rates of addition and the industrial mixing technology. These may inform industry in a re-assessment of the need for stricter process control measures to minimize PCB formation and also batch variation.

Aryl radical formation from diazonium salts is initiated by reduction. Manufacturers might consider whether there are potentially reducing species present, even in small amounts, for example reducing metals and ions, process additives or impurities in starting materials.

If hydrogen abstraction is confirmed in the formation of PCB 11, consideration may be given to the hydrogen source. It is not immediately clear from literature the extent to which water can act as this source. Organic CH is a recognized source.

It is well-known that free radical reactions may be inhibited by radical scavengers or antioxidants. Experimentation with these proprietary materials would be of interest as a means to test the free radical hypothesis and as a potential means to reduce PCB levels. In this context, a Hoechst patent claims that PCB levels in azo pigments may be reduced by carrying out the preparation in the presence of alkenes.[27] It is known that the specific alkenes cited are capable of reaction with free radicals.[25]

Copper Phthalocyanines



Scheme 4- The manufacturing process for copper phthalocyanine

Although the structure of CuPc is complex, its synthesis is straightforward.[28] In the most commonly-used process, phthalic anhydride is treated with urea, copper (I) chloride and a catalytic amount of ammonium molybdate at high temperatures. Mechanistic schemes have been proposed to explain the course of this synthesis but much of the detail remains to be established unequivocally. The organic starting materials contain no chlorine. Inorganic chlorine is present in copper (I) chloride. This chlorine has the potential to be incorporated into the organic system, but this does not appear to be a potentially significant source of PCB. A proposal has been made that the source of PCBs may be dichlorobenzene or trichlorobenzene used as solvent for the reaction, and a free radical mechanism based on pyrolysis of the chloroaromatic solvents has been proposed, supported by literature precedent.[10,29] If this source of PCB is confirmed, then there is a clear solution. Alternative chlorine-free solvents may be used, for example as promoted by SBS Pigments, India,[30] and it is also long-established that it is possible to manufacture CuPc in a solvent-free 'dry-bake' processes.

Synthesis of phthalocyanine green pigments involves direct exhaustive halogenation of CuPc blue with chlorine (or bromine or a halogen mixture) at elevated temperatures in a suitable solvent, commonly an AlCl₃/NaCl melt. It has been proposed that higher PCB congeners may be formed from chlorination of the PCBs present in the CuPc from which the green pigments are manufactured.[10] BASF quote that their Heliogen pigments contain levels of less than 2ppm PCB in CuPc blue and 2-25ppm in CuPc green.[31] The issues for these pigments thus appear to be complex and require further systematic experimental and analytical investigation, for example of the mechanistic processes involved in PCB formation and the influence of individual process parameters.

Conclusions

- Azo and CuPc pigment manufacture in recent decades has transferred substantially, though not completely, from the USA, Europe and Japan, to China and India. Western users of these pigments now rely heavily on imported products.
- Inadvertent PCB formation in pigment manufacture, although long recognized, appears to be emerging as an issue of growing concern for pigment manufacturers and users, based on recent environmental studies using increasingly-sophisticated analytical techniques
- Analytical data from current Japanese studies is beginning to identify azo pigment product types causing concern, although more extensive evidence to confirm the conclusions is required.
- This paper proposes free radical mechanisms for PCB formation that are consistent with structural features of the azo pigments implicated in the Japanese study.
- Short-medium term action to address confirmed issues will need to focus on existing pigment ranges. New pigment development is a long-term project
- Possible general approaches for substitution with alternative 'PCB-free' products are discussed.
- There are no obvious immediate replacements available for the diarylide pigments as extensively used in printing inks. Such issues require to be addressed by manufacturers through enhanced understanding of PCB formation mechanisms within their processes to ensure reduced levels.
- Phthalocyanine pigments are implicated in the US study but not the Japanese study and thus clarification is needed. If the source of PCBs in CuPc blue is confirmed as the use of chlorinated aromatic solvents, as appears mechanistically reasonable, then alternatives are available. The situation with CuPc greens appears less well understood and would benefit from clarification on the basis of experimental and analytical studies.

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