Colourants
for
Food Contact Plastics

Aspects of Product Safety

Disclaimer

This brochure provides information to the processors of colourants on product safety aspects relating to their use in the manufacture of plastic food packaging and food contact articles.

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Should additional information or explanation concerning the product safety of the products described in this publication be required, the reader is requested to contact the manufacturer or supplier directly.

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1 Preface and objective

The objective of this brochure is to show the measures taken by the colourant manufacturers, represented by ETAD and VdMi, to ensure that the colourants used in plastic food contact articles and packaging do not present a health risk for consumers.

This brochure describes examples from the colourant classes which are currently used in the manufacture of plastic food packaging and containers. The main themes are consumer protection and the obligation for a continuing improvement of health, safety and environmental protection, in line with principles of the Responsible Care® initiative of the European Chemical Industry Council.

The greater part of our food is marketed in packaged form. Proper packaging is now regarded as important for public health and a component of a high standard of living. The variety of packaging materials, forms and functions increases continuously. Proper packaging has become essential for the hygienic transport and storage of food.

Plastics are increasingly coloured to enhance the attractiveness of packaging, to protect the contents from the adverse effects of light or to differentiate between products. Depending on the type of packaging, the contents and the storage conditions, it is possible that components in the packaging, including colourants, could migrate to the food. It must therefore be ensured that the packaging components, including colourants, do not pose a health hazard for the consumer. This is also the aim of the relevant Directives, laws and regulations.

Positive lists of colourants used for the colouration of plastics supplement, but do not replace, the legally prescribed test procedures and responsibilities. For example, certain purity requirements, migration behaviour and toxicological properties must be satisfied before a colourant is included in the French Positive list. The selection of a listed colourant does not automatically mean that it is suitable for a specific application. Furthermore, the listing of a colourant, for example by a Generic Name, is not a basis for concluding that one or all corresponding commercial products are suitable or permitted. Commercial products can contain different amounts of impurities, e.g. intermediates and by-products, and also additives.

The processor must therefore always obtain confirmation from the manufacturer that a particular commercial product is suitable. This declaration of suitability does not relieve the processor of his duty of due care. He must process the colourant properly, pay attention to possible incompatibility with other additives and, in particular, check the fastness to migration of the finished product under practical conditions.

The colouration of plastics, which come into contact with food, is an important application for the colourants industry. The following basic criteria are decisive for the safe use of colourants for the colouration of food contact articles and packaging:

1. purity criteria of the colourant,
2. its fastness to migration,
3. the tested toxicological properties.

The colourant manufacturers guarantee that the colourants have been toxicologically tested and that the purity criteria are met. The manufacturers of the food contact article or packaging material are responsible for the migration testing. These three criteria for safe use are explained in more detail in Section 3.

New scientific knowledge, new consumer desires, technical innovations in materials and their processing necessitate constant scrutiny and development.

Consumer protection is a cooperative task for industry, commerce and lawmakers. It can only be assured through the cooperation of authorities, manufacturers, processors and importers on a national and international basis. In an era of global trade it is essential that all face up to the challenge of guaranteeing consumer protection regardless of where the packaging is manufactured or from where the starting materials are sourced.

The ETAD member companies have exemplified their commitment to responsible practices by developing in the mid 1970s, without legal pressures, a safety data sheet format which later served as a prototype for other chemical sectors. Standard test methods were agreed by the member companies: a base set of physical-chemical, toxicological and ecological data were generated for colourants. These data provide the user with a basis for safe handling of colourants.

The colourant manufacturers face the demand for a continuous improvement in consumer protection and offer not only suitable products but also a willingness to cooperate constructively with all the parties involved.

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2 Definitions

2.1 Responsible Care®

The member companies of the associations publishing this brochure fully support the *Responsible Care®* initiative of the European Chemical Industry Council. The pigment industry plays an active rôle in the development and implementation of the guidelines, activities, recommendations and voluntary restrictions in the interest of health and environmental protection.

For the companies, *Responsible Care®* is a commitment to continuing improvement of measures for the benefit of health, safety and the environment (1). The companies are assisted to fulfil this commitment by means of guidelines and management codes issued by the national chemical associations. Suitable management systems are available, which lay down the responsibilities for environmental and safety measures together with the corresponding test procedures.

Product stewardship, which is the application of *Responsible Care®* to products (2) embraces the development, use and disposal of the products. Aspects of environmental protection and safety are paid attention from an early stage in the research and development.

Literature

(1) Responsible Care: A chemical industry commitment to improve performance in health, safety and the environment. CEFIC, 1993

(2) Product stewardship: Responsible care applied to products – Guiding principles. CEFIC, 1994

2.2 Colour Index International

Pigments and dyes are listed in the Colour Index International by their Generic Name and their chemical structure. The Colour Index is published by *The British Society of Dyers and Colourists* and the *American Association of Textile Chemists and Colorists*. The C.I. Generic Name relates only to the coloured component of the product. The C.I. Constitution No is issued as soon as the manufacturer has disclosed the chemical structure. The entry of a particular commercial product in the Colour Index is at the instigation of the manufacturing company; however, a C.I. Constitution No is not available for all colourants in the market.

2.3 Colourants

"Colourant" is a collective term for all substances which impart colour (including black and white) to substrates. The technical literature differentiates between pigments and dyes. Both are included in the collective term "colourants". "Pigments" are by definition practically insoluble inorganic or organic colourants. In contrast, "dyestuffs" are organic colourants and are soluble in the application medium

2.4 Food contact articles

The EU Framework Directive 89/109/EEC defines food contact articles in Article 1 as "materials and articles which, in their finished state are intended to be brought into contact with foodstuffs. … Covering or coating substances, such as the materials covering cheese rinds, prepared meat products or fruit, which form part of foodstuffs and may be consumed together with those foodstuffs, shall not be subject to this Directive."

2.5 Packaging

In general, food is only placed on the market in packaged form. Food packaging must fulfil several conditions:

- protection of the food from environmental influences (e.g. light, moisture, impurities);
- providing information concerning contents (concerning composition, components, dietary advice etc.);
- providing information concerning storage conditions, sell-by date, processing instructions, manufacturer details etc.;
- attractive appearance to encourage purchase.

In order to reduce the environmental burden resulting from the increasing amounts of packaging wastes, the EU Packaging and Packaging Waste Directive introduced measures aimed at avoiding generation of packaging wastes.

To facilitate the recycling and recovery of material from used packaging and to reduce adverse environmental influences resulting from disposal, the four most environmentally relevant metals – lead, cadmium, mercury and chromium(VI) – were limited to a total content of 100 mg/kg. This limit value was taken from the U.S. CONEG model legislation, which had the same objective.

The majority of organic colourants produced nowadays fulfil the CONEG requirements. Some inorganic pigments can however, depending on the raw materials used, contain impurities in excess of the limit values. The packaging manufacturer must seek confirmation from his colourant suppliers that the limit values are met.

3 Criteria for the use of colourants in food contact applications

The assessment of possible health risks to consumers from colourants in articles and packaging materials involving direct food contact is based on the following criteria:

a) purity criteria for the colourants (products);

b) their fastness to migration,

c) their toxicological properties.

The risk assessment, based on the hazard potential of colourants including their impurities and/or additives and the exposure resulting from migration from the plastic material into the food (simulant), provides the basis for deciding the suitability of colourants (products) in particular applications.

The colourant manufacturers are committed to providing the manufacturers of consumer articles with all available data in a form which enables them to make an informed decision regarding consumer safety in the recommended use of their product throughout its lifetime and to ensure compliance with the regulatory requirements.

3.1 Purity criteria

Compliance with the regulatory purity criteria is an important factor for the product safety of colourants in food packaging. This is ensured by the colourant manufacturers through regular testing and confirmed in writing at the request of the user. Most colourant manufacturers make lists of tested commercial products available to their customers.

3.1.1 Heavy metals

The regulator has laid down limits on the content of certain metals (Pb, Hg, Cd, Cr and Ba) and semi-metals (As, Sb and Se) in colourants used in consumer articles. As the concentration of the colourant in the article is normally less than 1 %, the limits in the article are correspondingly lower. Furthermore, the colouration process involves imbedding the colourant in a hydrophobic plastic matrix. This means that any significant migration of the above elements to the food is practically excluded.

Important for migration in practice is not the total content of these elements but their soluble portion. For historical reasons some of the national regulations within the EU applied limits to the total content, others to the acid-soluble content (extractable). Moreover, the limits were not harmonised.

Now, with only some minor deviations, the EU member states apply the limits agreed under the Council of Europe Resolution AP(89)1 on the use of colourants in plastic materials coming into contact with food. These limits apply to the amount extractable by 0.1 M hydrochloric acid, and relate to the colourant itself, not the coloured finished article.

Element	acid-soluble portion according to AP(89)1, mg/kg	Element	acid-soluble portion according to AP(89)1, mg/kg
Antimony	500	Chromium	1000
Arsenic	100	Lead	100
Barium	100	Mercury	50
Cadmium	100	Selenium	100

Resolution AP(89)1 also lays down additional requirements with respect to certain organic substances.

3.1.2 Aromatic amines

The content of primary unsulphonated aromatic amines, extractable in 1 M hydrochloric acid may not exceed 500 mg/kg (expressed as aniline). The content of benzidine, 2-naphthylamine and 4-aminobiphenyl may not exceed, individually or in total, 10 mg/kg. 2-Amino-5-chlorotoluene should be treated in the same way.

3.1.3 Sulphonated aromatic amines

The content of extractable sulphonated aromatic amines may not exceed 500 mg/kg, expressed as sulphanilic acid.

3.1.4 Polychlorobiphenyls (PCBs)

The PCB content may not exceed 25 mg/kg, expressed as decachlorobiphenyl.

3.2 Migration fastness

3.2.1 General

The most relevant criterion for the suitability of colourants for the colouration of food contact articles is that migration from the article be as low as possible. In contrast to the colourless additives used in food contact articles, the intense colour of the colourant provides a simple means of establishing its migration or non-migration. Nowadays, additional robust detection methods are available which enable detection of extremely low levels of migration.

Colourant manufacturers check their colourants for fastness to migration in certain systems and provide their customers with corresponding recommendations. However, the fastness to migration depends above all on the appropriate processing and on the type and amount of additives used (and their possible interactions with the colourant), on the food and its storage conditions, as well as any later treatments. It remains the responsibility of the user, as prescribed by the regulator, to check the fastness to migration of the colourant under practical conditions in the finished food packaging. The technical application departments of the colourant manufacturers can provide their customers with advice and support.

3.2.2 Plastic food contact articles

The EU Framework Directive 89/109/EEC lays down in Article 2 that

> “materials and articles must be manufactured in compliance with good manufacturing practice so that, under their normal or foreseeable conditions of use, they do not transfer their constituents to foodstuffs in quantities which could:

– endanger human health

or

– bring about an unacceptable change in the composition of the foodstuffs or a deterioration in the organoleptic characteristics thereof."

The Framework Directive foresees that the manufacture of food contact articles will be regulated by individual Directives. In the case of plastic articles this has already been achieved through Directive 90/128/EEC and its amendments, 2001/62/EC.

This "Plastics Directive" has in the meantime been amended several times and contains lists of permitted monomers for the manufacture of plastic food contact articles, additives and other starting materials, in some cases with restrictions on SML (specific migration limit in food or food simulants), QM (maximum permitted quantity of the "residual" substance in the material or article) or additional specifications.

Article 2 of Directive 90/128/EEC lays down that the overall migration of components from the article to the food may not exceed 10 mg/dm^2. In the following cases the applicable limit is 60 mg/kg food:

- fillable articles with a capacity of 0.5 to 10 litres;
- fillable articles, for which an estimation of the surface area coming into contact with food is not possible;
- caps, gaskets, stoppers or similar devices for sealing.

These limits apply to all substances for which no specific migration limit has been laid down, and represent a limitation on the total migration (global migration) from the article.

Food contact articles coloured with azo colourants may not, in accordance with Directive 2001/62/EC, release detectable quantities of primary aromatic amines. The applicable detection limit is 0.02 mg amine (calculated as aniline) pro kg food or food simulant

3.2.3 Colourants

In preparation for a harmonised regulation of plastic food contact articles the Council of Europe passed the Resolution AP(89)1 on the use of colourants. This resolution, in addition to limits for extractable heavy metals, aromatic amines and sulphonated aromatic amines, also includes the requirement of "no visible migration" to the food. The so-called "Abklatschtest" is described as a test method for the determination of visible migration, as adopted, also, in various national regulations. As a result of further development of the methods, sensitive analytical procedures are now available. For example for inclusion of colourants in the French positive list it is now necessary to determine the specific migration by the methods described in Directive 82/711/EEC and its amendments.

Indications of the fastness to migration of colourants can be deduced from their insolubility in water (as simulant for aqueous foodstuffs) and e.g. in n-octanol (as fat simulant). For this reason the solubility of the individual pigments in these two media is referred to throughout this brochure.

Determination of the visible migration limit for organic pigments

ETAD has investigated the visible migration limit for 19 pigments (ETAD Project A4006: Visible detection limits for selected pigments using ETAD Analytical Method No. 221). The average value for all the pigments investigated was 8.5 $\mu g/dm^2$, and 7.3 $\mu g/dm^2$ for the 7 pigments used in plastics.

In comparison with the limits laid down in Directives 90/128/EEC and 2001/62/EC for total migration of all constituents from the finished article to the foodstuff of 10 mg/dm^2, the amount corresponding to a visually recognisable migration (limit of visible migration) is 3 orders of magnitude lower.

3.3 Tested toxicological properties

Toxicological data requirements differ in the EU for the so-called existing chemicals and new substances. The Regulation 793/93/EEC for existing chemicals placed on the market in amounts exceeding 10 tonnes/year required that industry provides the available toxicological data for the authorities to carry out a hazard assessment and a risk assessment. This purely European program is supported by various voluntary High Production Volume Chemicals initiatives of the chemical industry and by the umbrella organisations in America (ACC), Europe (CEFIC) and Asia (JHOSPA) as well as by the ICCA and the OECD.

In the case of new substances the data requirements are volume dependent and laid down in Directive 67/548/EEC and its Annexes.

These regulatory requirements, including the corresponding chemical controls elsewhere, e.g. USA and Japan, bring the marketing and handling of chemicals to a level of safety for man and the environment which is accepted, generally, by the national authorities.

Nevertheless, specific product applications, e.g. in food packaging, call for additional toxicological and exposure data for the assessment of consumer risk. In Europe, the Directives 90/128/EEC and 2001/62/EU regulate the different substance classes which can be used in food contact applications of plastics. In addition, there are national requirements (e.g. French Positive list, BgVV etc.) and also the FDA in the USA and JHOSPA in Japan. Although these regulatory systems differ in their requirements, they have the common aim of a high level of consumer protection. This means, for example, that even in the case of an extremely low migration, as is typical for organic pigments, a mutagenicity test may be required.

The above regulatory frameworks specify for the listed chemicals the concentration limit in the plastic or the limit on migration to the food (or food simulant), and, in some cases, the particular application (e.g. “hot fill”): compliance with these constraints is regarded as assuring the safety of the finished article for the consumer.

In the introductory phase of many of these regulatory frameworks the authorities have included in their lists those colourants which at that time were widely used: the so-called grandfather clause. Since then colourants, for which a manufacturer submits an application for listing, require the toxicological and exposure data to comply with the relevant regulatory regime.

Commercial colourants can also contain other components in addition to the colourant itself, in order to optimise the application properties. In these cases it is essential that the colourant manufacturer and processor check the consumer safety in the likely applications. It is therefore important that the colourant processor, in addition to consulting the positive lists, makes contact with the colourant manufacturer. Some manufacturers already describe in their brochures whether their commercial products are suitable for certain applications and satisfy the regulations.

3.4 Summary

Colourant manufacturers check the purity, fastness to migration, and the toxicological properties of colourants (products). On this basis they can evaluate the possible risks to consumers and the suitability for particular applications. It remains the responsibility of the manufacturer of the finished article to ensure consumer safety and the compliance with regulatory requirements.

Consumer safety is a joint responsibility of manufacturers, processors and authorities. For the consumer the safe use of coloured plastic food contact articles is already provided for by the current regulations in combination with a responsible approach by the pigment manufacturers and processors. Nevertheless, new knowledge must always be taken into account.

The member companies of the associations responsible for publishing this brochure are committed to a high safety standard. Inadequate checks of regulatory purity requirements for pigments of uncertain origin can create imbalances in the market and lead to market disadvantages.

4 Description of substances and substance classes

With respect to product safety the following chapters do not offer complete listing of all colourants suitable for the colouration of food contact plastics. Instead, examples of pigments and solvent dyes are described.

The examples are grouped in classes of chemically similar colourants with similar properties. With respect to product safety the chemical description and the most important toxicological data are provided.

Solubility data and information on migration characterize the migration behaviour. Entries in the French Positive List and FDA registers of commercialized products are available from the suppliers of colourants.

4.1 Titanium dioxide

C.I. Pigment White 6

C.I. 77891 CAS No. 13463-67-7 EINECS No. 236-675-5

Titanium dioxide is of outstanding importance as a white pigment because of its light scattering properties, chemical stability, and its biological inertness. In terms of quantities, it is the most important pigment (1). Furthermore, titanium dioxide is used as a sub-pigment because of its UV shielding property.

Titanium dioxide meets the purity criteria as laid down in AP(89)1 and the requirements of the FDA Regulation 21 CFR 178.3297 “Colourants for Polymers”.

Short chemical description

Titanium dioxide occurs in the nature in the three modifications rutile, anatase, and brookite. Rutile pigments are industrially produced by the chloride process or the sulphate process. Anatase pigments are obtained by the sulphate process (1). The sub-pigment grade of titanium dioxide is synthesized from titanium tetrachloride by a high temperature hydrolysis process.

Titanium dioxide is usually coated with colourless organic or inorganic compounds of low solubility to improve weather resistance, light fastness and dispersibility.

Toxicological data

Titanium dioxide is not considered as toxic: LD_{50} value (rats, oral) > 5 000 mg/kg (2). Titanium dioxide does not irritate the skin, but can, like all fine particles, take up moisture and natural fats from the skin surface. A possible drying of the skin can be avoided by the use of good protective measures for the skin.

Titanium dioxide is produced and processed for about 80 years. No acute or chronic adverse health effects are known to result from the use of titanium dioxide.

Migration

Titanium dioxide has an excellent migration fastness.

Solubilities (water, octanol)

Titanium dioxide is virtually insoluble in water and in organic solvents. Small portions of coatings made of titanium dioxide can be soluble under strong acidic or alkaline conditions.

References

(1) Römpps Chemie-Lexikon, “Titandioxid”. 9. Auflage; Georg Thieme Verlag, Stuttgart, New York, 1992

(2) IUCLID Data Sheet, Titanium dioxide

4.2 Zinc sulphide, lithopone, barium sulphate

4.2a Zinc sulphide

C.I. Pigment White 7

C.I. 77975 CAS No. 1314-98-3 EINECS No. 215-251-3

With the exception of titanium dioxide, zinc sulphide pigments are the most widely used white pigments. Zinc sulphide white pigments are optically less efficient than titanium dioxide, but they cover a considerable market due to their specific technical properties.

Thanks to their soft texture and low Mohs' hardness, these pigments are less abrasive than other white pigments. The outstanding characteristics of zinc sulphide pigments are high brightness and low colour hue, low absorption in the near UV range as well as good light fastness, low binder demand and favourable rheological properties, good wetting properties and dispersibility.

Zinc sulphide is listed in the FDA Regulation 21 CFR 178.3297 as an allowed component (up to 10 %) of packaging materials with direct food contact.

Short chemical description

Zinc sulphide suitable for the colouration of consumer goods for food contact is produced by precipitation of purified solutions (zinc sulphate and sodium sulphide) and subsequent calcining.

Toxicological data

Zinc sulphide is not a dangerous substance according to the Dangerous Substances Directive or other EU regulations and has therefore not to be labelled accordingly. Zinc sulphide shows no toxicity after a single oral, dermal, or inhalation exposure. There is no evidence of mutagenic effects of zinc.

LD_{50} (rat, oral): > 15 000 mg/kg
LC_{50} (rat, inhalative): > 5 040 mg/m^3/4 h
LD_{50} (rat, dermal): > 2 000 mg/kg
LC_{50} (aquatic toxicity, golden orfe): > 5 155 mg/l (OECD 203)
EC_{50} (aquatic toxicity, water flea): > 100 mg/l (OECD 202)

Solubilities (water, octanol)

Zinc sulphide is virtually insoluble in water and in n-octanol. Under the influence of acids, hydrogen sulphide is released at pH values below 3.

Advice for safe handling

Zinc sulphide has generally a good system tolerance. In combination with some HALS stabilizers, however, an interaction can occur which reduces the stabilizing effect. There are also a few additives known with a pH value below 3. When using these additives it is recommended to add pH buffers, e. g. calcium carbonate or aluminium trihydrate.

4.2b Lithopone

C.I. Pigment White 5
C.I. 77115 CAS No. 1345-05-7 EINECS No. 215-715-5

Lithopone is a co-precipitate consisting of zinc sulphide (see section 4.2a) and barium sulphate (see section 4.2c).

4.2c Barium sulphate

Name: Blanc fixe
C.I. Pigment White 21
C.I. 77120 CAS No. 7727-43-7 EINECS No. 231-784-4

Blanc fixe is a very pure, synthetic barium sulphate with the highest degree of whiteness. It is used in all polymers rather as a functional additive than a filler. Because of its exceptional technical properties, blanc fixe is indispensable in a variety of high-quality applications for adjusting certain essential properties of composites. One example is the optimization of mechanical or optical properties. The variety of types offered in the market results from adjustment of particle sizes, different particle forms, and, as with titanium dioxide pigments, of different inorganic and organic coatings.

Blanc fixe is listed in the FDA Regulation 21 CFR 178.3297 as an allowed component of packaging materials with direct food contact.

Short chemical description

Blanc fixe is a synthetic barium sulphate of high purity, precipitated from purified solutions (e. g. barium sulphide and sodium sulphate).

Toxicological data

Blanc fixe is not a dangerous substance according to the Dangerous Substances Directive or other EU regulations and has therefore not to be labelled accordingly.

LD_{50} (rats, oral): > 15 000 mg/kg.

There are no known toxic effects using Blanc fixe. It is, as a pharmaceutical quality, allowed as an X-ray contrast medium and to be directly ingested as aqueous suspension.

In the USA, barium sulphate is the only barium compound which is not subject to report according to SARA Title III.

Solubilities (water, octanol)

Barium sulphate is virtually insoluble in water and in n-octanol.

4.3 Synthetic amorphous silica

Name: highly dispersed silica or highly dispersed silicon dioxide

C.I. – CAS No. 112945-52-5 ex 7631-86-9 EINECS No. 231-545-4

Name: precipitated synthetic amorphous silica

C.I. – CAS No. 112926-00-8 ex 7631-86-9 EINECS No. 231-545-4

Synthetic amorphous silica is used in very different branches of industry, for example as a component of high-quality thermal insulating materials. In addition, it serves as a free flowing agent of sticky powders, as active filler in polymers (amongst others: silicone rubber, thermoplastics), to adjust the rheological properties of paints and varnishes and as a matting agent. The marketed products differ mainly by the specific surface area, the densification and the type of surface treatment.

Synthetic amorphous silica, also the silanized ones, are according to EU Directive 90/128/EEC and the subsequent Directives as well as to the BgVV Recommendation LII, allowed to be used in food contact plastics. Synthetic amorphous silica meets the requirements according to the FDA 21 Code of Federal Regulations (CFR) part 172.480 and 21 CFR parts 175–178 to the Food Chemical Codex V and to the EU Directive 95/2/EC and its subsequent Directives.

Short chemical description

Synthetic amorphous silica is synthesized by high temperature hydrolysis of chlorosilanes or by precipitation from alkali silicate solutions with acids. The product properties can be varied by choosing appropriate reaction conditions and surface modifications. There are hydrophilic as well as hydrophobic products on the market.

Toxicological data

Synthetic amorphous silica shows no acute toxic effects after oral application to rats; LD_{50} (rat, oral) > 3 300 mg/kg.

Synthetic amorphous silica does not irritate the skin or eyes. During decades of producing and using these compounds, there has not been reported any evidence of its sensitization potential.

In long-term studies, synthetic amorphous silica showed no toxic effect. In animal assays and in epidemiological studies, no silicosis occurred after long-term inhalation exposure.

Solubilities (water, octanol)

Synthetic amorphous silica is virtually insoluble in water and in n-octanol.

Purity criteria

Unmodified synthetic amorphous silica consists of, after the elimination of the physically and chemically bound water, at least 99.8 % (highly dispersed silica) or over 98.0 % (precipitated silica) of pure silicon dioxide. In case of chemical surface treatments the manufacturers provide the appropriate information.

References

Aerosil, Degussa AG

4.4 Iron oxides

Iron oxide red, hematite Fe_2O_3
C.I. Pigment Red 101

C.I. 77491	CAS No. 1309-37-1	EINECS No. 215-168-2

Iron oxide black, magnetite Fe_3O_4
C.I. Pigment Black 11

C.I. 77499	CAS No. 1317-61-9 12227-89-3	EINECS No. 215-277-5

Iron oxide yellow, goethite FeOOH
C.I. Pigment Yellow 42

C.I. 77492	CAS No. 20344-49-4 51274-00-1	EINECS No. 243-746-4

$(Mn,Fe)_2O_3$
C.I. Pigment Black 33

C.I. 77537	CAS No. 12062-81-6	EINECS No. 235-049-9

$(Mn,Fe)_2O_3$
C.I. Pigment Brown 43

C.I. 77536	CAS No. 12062-81-6	EINECS No. 235-049-9

Short chemical description

Iron oxide pigments are colourants which are chemically and physically similar to the iron oxide pigments widely found in nature. The red types are oxides of trivalent iron, crystallizing in the corundum lattice. The colour range covers orange terra-cotta to burgundy. Their saturation is less than that of organic red pigments. The yellow types are oxide-hydroxides of trivalent iron. When heated, they can lose water of crystallisation and recrystallize to iron oxide red. With the yellow shades, a natural-like ochre shade can be achieved. The black types are (inverse) spinels in which a part of the iron exists in the bivalent form. Due to the content of bivalent iron, these pigments can oxidize under certain conditions. Iron oxide black is ferromagnetic (mineralogical name: magnetite) and can oxidize at temperatures above 80 °C. Depending on the crystallisation, bluish-black shades can be achieved.

Iron oxides are listed in the French Positive List. The FDA Regulation 21 CFR 178.3297 allows them as components of food contact plastics. (The FDA approval does not apply to Mn containing types.) Iron oxides of high purity are allowed in Europe and in the USA for the colouration of food, pharmaceutical products and cosmetics.

Toxicological data

Iron oxides in their natural form are ubiquitous components of our environment. They are responsible for the red colour of soils and rocks. Primitive life emerged and developed in an environment rich of iron. Hence, these substances are the least problematic substances. Iron is the metallic element most frequently found in the human organism.

A large number of toxicological tests revealed no evidence of harmful effects of iron oxides on the human organism. The LD_{50} value (acute toxicity) of iron oxides is above 5 000 mg/kg. During decades and centuries of using iron oxides, no chronic diseases caused by these substances are known. Furthermore, ecotoxicological studies did not yield any indications of harmful effects on aquatic organisms.

Migration

Because of the low solubility in aqueous or organic media no migration into food is expected from coloured plastics. Therefore, iron oxides are used world-wide for the colouration of food contact plastics. The regulations can differ from country to country. Therefore, the user should check the information with his supplier or manufacturer.

Solubilities (water, octanol)

Iron oxides are insoluble in organic media. In an aqueous environment, their solubility is negligible or low. Only under strongly acidic conditions (pH < 2), does the solubility increase.

Purity criteria

Contents of critical metals

Iron oxides are usually produced from the scrap of the iron producing industry. These raw materials include mordant bathes, scrap and other materials, for example chips of waste from cast iron or turnings. The metal spectrum found in the metallic and liquid raw materials, including the iron ores, can also be detected in the iron oxide pigments. During the production of the iron oxide pigments, no heavy metals are intentionally added.

Normally, most of the iron oxides meet the requirements for applications with food contact, in packagings and in toys. Manufacturers offer detailed information about these topics.

Aromatic amines

Some iron oxides are produced by the so-called Laux process, which yields aniline and iron oxide pigments. The red pigments obtained by this process are calcined after the oxidation of the iron, so that they are completely free of aniline.

The black and the yellow pigments obtained by this process are washed several times in concentrators until only traces of aniline are detectable. The residual contents are without toxicological relevance.

In addition to the Laux process, there are the precipitation process and the Penniman process. Both of these processes are purely inorganic, and aromatic amines are not formed.

References

(1) IUCLID Data Sheets
among others: CAS No. 1309-37-1, CAS No. 1317-61-9, CAS No. 20344-49-4

(2) Studies performed by Bayer AG

(3) Buxbaum, Gunter. Industrial Inorganic Pigments. Second Edition, Wiley-VCH, Weinheim, 1998

(4) Endriß, Hartmut. Aktuelle anorganische Buntpigmente. Vincentz-Verlag, Hannover, 1997

4.5 Chromium oxide

Chromium oxide, chromium oxide green Cr_2O_3
C.I. Pigment Green 17
C.I. 77288 CAS No. 1308-38-9 EINECS No. 215-160-9

Short chemical description

Chromium oxide green is a synthetic representative of the naturally occurring mineral escolaite, which is found in basalts all over the world. This synthetic pigment is known for its dark olive shade. Under natural conditions, it is chemically inert and physically very resistant. Plastics coloured with chromium oxide are characterized by excellent light fastness and high weather resistance. Because of their high light scattering power and their high absorption, chromium oxide pigments exhibit excellent hiding power in a number of media. As highly effective UV absorbers they improve the weather resistance of some paint and plastic systems.

Chromium oxide crystallizes in the same lattice type as sapphire and ruby and has a comparable hardness and thermal stability.

Chromium oxide is listed in the French Positive List. The FDA Regulation 21 CFR 178.3297 permits them as a component of food packaging.

Toxicological data

When assessing the toxicity of chromium, one has to distinguish between the trivalent and the hexavalent states. Trivalent chromium is an important trace element for the human organism. In animal assays, individuals subjected to a deficiency of trivalent chromium showed arteriosclerosis, diabetes, growth defects and clouding of the lens of the eye. The uptake of trivalent chromium with food tends to be too low rather than too high. The acute toxicity is correspondingly low; the LD_{50} value is above 5 000 mg/kg.

In contrast to the trivalent chromium, the hexavalent chromium is sensitizing and carcinogenic. Accordingly, it is classified by the German MAK commission in the group 2 (positive results in animal assays; considered to be carcinogenic for humans).

Chromium oxide that does not contain hexavalent chromium is neither sensitizing nor irritating to the skin. At contents of hexavalent chromium greater than about 10 ppm Cr(VI) there is a risk of sensitizing of the skin and the respiratory tract.

Chromium oxide dust can cause irritation of the respiratory tract when overloading takes place. These effects are not specific and occur also with other inert dusts. They are clearly distinguishable from the effects of *soluble* compounds of trivalent chromium to the respiratory tract.

Chromium oxide (with the appropriate purity) is approved in the USA and in Europe for the colouration of cosmetics. In the USA, it is approved for the colouration of pharmaceuticals for external application only.

Migration

Because of its chemically and physically inert behaviour, chromium oxide green is particularly suitable for applications in which migration has to be prevented, for example food contact, toys, cosmetics and pharmaceuticals.

Solubilities (water, octanol)

Chromium oxide green produced by reputable manufacturers consists only of the insoluble oxide of trivalent chromium. It is therefore not toxic and is not labelled as a dangerous substance. During the processing of coloured plastics when the coloured products are used, a release of chromium ions is impossible. Even under highly acidic conditions (pH 1–2), chromium oxide green is chemically stable. An oxidation to hexavalent chromium occurs only under extremely alkaline conditions at temperatures of several hundred degrees Celsius. During normal usage, an oxidation to hexavalent chromium is impossible.

Purity criteria

Contents of critical metals

Although less dense than iron, chromium is usually considered to be a heavy metal. Because of the production process and the raw materials, chromium oxides contain other metals but only in toxicologically negligible traces.

Its suitability for the colouration of plastics for food contact is determined by the content of hexavalent chromium which should, preferably, be less than 10 ppm. At higher contents of hexavalent chromium the coloured plastic has to be tested for migration of chromium.

References

(1) IUCLID Data Sheet CAS No. 1308-38-9, British Chrome & Chemicals, 26.4.94

(2) Toxicological studies performed by Bayer AG

(3) Korallus, U., Ehrlicher, H., Wüstefeld, E. Dreiwertige Chromverbindungen – Ergebnisse einer arbeitsmedizinischen Untersuchung. Arbeitsmedizin, Sozialmedizin, Präventivmedizin; Heft 11, 1974, S. 248–252

(4) Derelanko et al. Thirteen-week subchronic rat inhalation toxicity study with a recovery phase of trivalent chromium compounds, chromic oxide and basic chromium sulfate. Toxicological sciences 52, 278-288 (1999)

(5) Buxbaum, Gunter. Industrial Inorganic Pigments. Second Edition, Wiley-VCH, Weinheim, 1998
(6) Endriß, Hartmut. Aktuelle anorganische Bunt-Pigmente. Vincentz-Verlag, Hannover, 1997

4.6 Carbon black

Name: pigment black

Formula: Carbon

C.I. Pigment Black 6

C.I. 77266 CAS No. 1333-86-4 EINECS No. 215-609-9

C.I. Pigment Black 7

C.I. 77266 CAS No. 1333-86-4 EINECS No. 215-609-9

Short chemical description

Carbon black pigments are produced on an industrial scale by incomplete combustion or by thermal decomposition of hydrocarbons under strictly controlled conditions. For the production of carbon black pigments there are three different processes:
- furnace process,
- gas process,
- lamp process.

This results in a very wide range of extremely different carbon black types, which allows coverage of the various market demands.

The properties, which are given by carbon black pigments to printing inks, paints, plastics, and special applications can be attributed to the following fundamental features of the carbon blacks themselves:
- particle size and particle surface,
- porosity,
- structure,
- surface chemistry.

In addition, the purity of carbon black pigments is important, as well as other properties, related to the outer shape, the handling and the processibility of the carbon black pigments. These physico-chemical properties can be specifically adjusted via the selection of raw material, the production process, the production conditions as well as oxidative and mechanical after-treatments.

Toxicological data

The acute toxicity LD_{50} (oral, rat) is above 8 000 mg/kg. An acute toxic effect is therefore impossible. The application of carbon black pigments to unbroken skin and to the eye of a rabbit does not cause any irritating effect. There is no evidence for a sensitizing effect of carbon black pigments.

Long-term studies on rats gave some indications that, when the lung is overloaded, respirable very fine particles can cause lung tumours in this animal species. The same studies performed on mice and hamsters did not confirm these results.

The implications of these studies for humans are not yet known. During decades of producing and processing the carbon black pigments, no significantly harmful effects habe been recorded. Morbidity studies, which examined the incidences of diseases, and mortality studies which examine the causes of death, did not show significant risks to human health caused by carbon blacks.

Solubilities (water, octanol)

Carbon black pigments are virtually insoluble in water and in n-octanol.

Purity criteria

According to the FDA Regulation 21 CFR 178.3297, the limiting values for high-purity furnace carbon blacks are 0.5 ppm PAH (polyaromatic hydrocarbons) and 5 ppb benzo(a)pyrene.

Contents of critical metals

Carbon blacks meet the specifications of Council of Europe Resolution AP(89)1.

Aromatic amines

Primary aromatic amines $\leq$ 500 ppm

In toluene extractable content

$\leq$ 0.15 %

Advice for safe handling

An important criterion for the *handling* of carbon blacks and their *processing* is the form in which they are delivered. Depending on the particular requirements, carbon black pigments are used as a powder or as beads (dry, wet, oil beaded), which considerably facilitates their processing.

References

(1) Was ist Ruß? Degussa AG
(2) Schriftenreihe Pigmente Nr.10. Degussa AG
(3) Schriftenreihe Pigmente Nr.14. Degussa AG
(4) Pigmentruße, Technische Daten. Degussa AG
(5) Technische Information 1217; FDA-Konformität von Pigmentrußen. Degussa AG
(6) Ferch, Horst. Pigmentruße. Vincentz Verlag, 1995
(7) Ullmann’s Encyclopedia of Industrial Chemistry. VCH, Weinheim

4.7 Rutiles

Chromium titanium yellow $(Ti,Cr,Sb)O_2$
C.I. Pigment Brown 24
C.I. 77310 CAS No. 68186-90-3 EINECS No. 269-052-1

Nickel titanium yellow $(Ti,Ni,Sb)O_2$
C.I. Pigment Yellow 53
C.I. 77788 CAS No. 8007-18-9 EINECS No. 232-353-3

Manganese titanium brown $(Ti,Mn,Sb)O_2$
C.I. Pigment Yellow 164
C.I. 77899 CAS No. 68412-38-4 EINECS No. 270-185-2

Chromium titanium yellow, with niobium substitution $(Ti,Cr,Nb)O_2$
C.I. Pigment Yellow 162
C.I. 77896 CAS No. 68611-42-7 EINECS No. 271-891-3

Short chemical description

Different metal cations can be incorporated into the stable host lattice of the titanium dioxide rutile. So, these pigments are described as doped rutiles. The rutile lattice of titanium dioxide can incorporate nickel(II) oxide, chromium(III) oxide or manganese(II) oxide as colouring components, as well as antimony(V) oxide for balancing the valencies, so that an average valency of four like that of titanium is achieved. The basic structure of the host lattice is not being altered by the incorporation; only the dimensions of the unit cell, the so-called lattice constants, are increasing as a result of the incorporation of the foreign ions.

By incorporation in the host lattice, the metal oxides lose their original chemical, physical and physiological properties. In the rutile pigment, they do not further exist as chemical species of their own. The properties of the newly formed chemical compounds are mainly determined by the host lattice, the titanium dioxide rutile. The pigments are produced by a calcination process at temperatures between 1100 and 1200 °C and are therefore very stable pigments.

Nickel titanium yellow is a lemon-coloured pigment, chromium titanium yellow varies in its colour from a light to a medium ochre, and manganese titanium brown varies from brown to dark brown, depending on the manganese content.

Nickel titanium yellow and chromium titanium yellow, as well as those with niobium substitution, are listed in the Circulaire 176, the so-called French Positive List, as colourants approved for the colouration of food contact materials.

In addition, nickel titanium yellow and chromium titanium yellow, with the exception of Pigment Yellow 162, are approved in the USA under FDA Regulation 21 CFR 178.3297 for the colouration of consumer goods for food contact, with a maximum dosage of 1 % for all polymers. The quantity limit is explained by the migration data (with 1 % colouration) which were submitted to the authority.

Toxicological data

When assessing the toxicity, one has to consider that the incorporated metal oxides do not exist as separate chemical species, but are components of the rutile lattice. Hence, a toxicological evaluation of these pigments cannot be based on the toxicological data of the metal oxides.

The doped rutiles do not show acute toxicity. In a Japanese study on the chronic toxicity, rats were fed with nickel titanium yellow over a period of three months with doses of 1.5 g and 10 g per kg feed, without any adverse toxicological effect.

In a subchronic animal assay, the bioavailability of the different metal ions in nickel titanium yellow and chromium titanium yellow was tested. In the study, rats were fed during a three month period with up to 10 000 mg/kg of these pigments. Clinical-chemical and histo-pathological studies did not show any alterations compared to the control group of rats. Thus, the pigments showed no toxicity and bioavailability.

The results of Ames tests and of tests on mouse lymphocytes to check the mutagenic effect of nickel titanium pigments and of chromium titanium pigments were negative.

Soluble nickel compounds and nickel metal can cause allergic reactions. Even after several years of using nickel titanium yellow pigments, no allergic reactions were observed.

Migration

The doped rutiles are characterized by an absence of migration from the coloured plastics. Extraction tests were performed with chromium titanium yellow as 1 % colouration in eight different plastics. The extraction conditions were 10 days at 40 °C with the four food simulants distilled water, 3 % acetic acid, 10 % alcohol and test fat HB 307. The extraction tests showed no detectable migration, even at very low detection limits (0.2 µg/l chromium and 0.25 µg/l antimony).

Corresponding tests with nickel titanium yellow as 1 % colouration in six different plastics with the detection limits 0.3 µg/l nickel and 0.25 µg/l antimony showed also no detectable migration.

Corresponding tests with manganese titanium brown as 1 % colouration with the detection limits 1 µg/l manganese and 0.25 µg/l antimony showed also no detectable migration.

By listing in the FDA Regulation 21 CFR 170.39, these pigments are likewise excluded from the regulation for direct food contact, with a maximum dosage of up to 2 % in all polymers.

Solubilities (water, octanol)

The doped rutiles are virtually insoluble (< 0.1 mg/l) in water and in organic solvents.

References

(1) IUCLID Data Sheet CAS No. 68186-90-3
(2) Studies performed by BASF AG
(3) Buxbaum, Gunter. Industrial Inorganic Pigments. Second Edition, Wiley-VCH, Weinheim, 1998
(4) Endriß, Hartmut. Aktuelle anorganische Bunt-Pigmente. Vincentz-Verlag, Hannover, 1997

4.8 Spinels

Cobalt blue $CoAl_2O_4$
C.I. Pigment Blue 28
C.I. 77346 CAS No. 1345-16-0 EINECS No. 310-193-6

Cobalt blue $Co(Al,Cr)_2O_4$
C.I. Pigment Blue 36
C.I. 77343 CAS No. 68187-11-1 EINECS No. 269-072-0

Cobalt green $(Co,Ni,Zn)_2TiO_4$
C.I. Pigment Green 50
C.I. 77377 CAS No. 68186-85-6 EINECS No. 269-047-4

Zinc iron brown $(Zn,Fe)Fe_2O_4$
C.I. Pigment Yellow 119
C.I. 77496 CAS No. 68187-51-9 EINECS No. 269-103-8

Spinel black $Co(Cr,Fe)_2O_4$
C.I. Pigment Black 27
C.I. 77502 CAS No. 68186-97-0 EINECS No. 269-060-5

Spinel black $Cu(Cr,Fe,Mn)_2O_4$
C.I. Pigment Black 28
C.I. 77428 CAS No. 68186-91-4 EINECS No. 269-053-7

Short chemical description

Cobalt blue pigments are obtained by a complete or partial replacement of magnesium by cobalt or by cobalt and chromium(III) in the $MgAl_2O_4$ lattice.

The incorporation of cobalt and nickel in both the inverse titanium spinels Mg_2TiO_4 and Zn_2TiO_4 yields cobalt green pigments.

Zinc iron brown is a spinel based on zinc and iron.

Spinel black pigments are copper chromium(III) oxides, $CuCr_2O_4$, in which chromium is partially replaced by manganese and iron. But in the chromium iron spinel, $Fe(Cr,Fe)_2O_4$, the iron can be partially replaced by cobalt.

The pigments are produced at high temperatures by a calcining process. Hence, they are very stable pigments.

The products are listed in the Circulaire 176, the so-called French Positive List, as colourants approved for the colouration of consumer goods for food contact.

In addition, some products are approved in the USA according to the FDA Regulation 21 CFR 178.3297 for the colouration of consumer goods for food contact.

Toxicological data

When assessing the toxicity, one has to consider that the incorporated metal oxides do not exist as separate chemical species, but are components of the spinel lattice. Therefore, toxicological evaluations of these pigments, on the basis of the knowledge of the component metal oxides only, is incorrect.

The above-mentioned spinels show no acute toxicity. Except for the zinc iron brown, no relevant heavy metals are soluble in hydrochloric acid at concentrations similar to that in the stomach. The pigments are therefore not to be considered as bioavailable. The acid-soluble zinc contents of zinc iron brown are toxicologically harmless.

Migration

The above-mentioned spinels are characterized by an absence of migration from plastics. In the case of zinc iron brown, harmless amounts of zinc, in the ppb range, can be dissolved if acidic materials are packaged.

The production of the spinel black pigments can be based on metal oxides of different purities. Before using these pigments for the colouration of consumer goods, the required purity of the products must be confirmed by the manufacturer.

Solubilities (water, octanol)

The above-mentioned spinels are virtually insoluble (< 0.1 mg/l) in water and in organic solvents.

References

(1) Studies performed by BASF AG

(2) Buxbaum, Gunter. Industrial Inorganic Pigments. Second Edition, Wiley-VCH, Weinheim, 1998

(3) Endriß, Hartmut. Aktuelle anorganische Bunt-Pigmente. Vincentz-Verlag, Hannover, 1997

4.9 Bismuth vanadate

C.I. Pigment Yellow 184

C.I. – CAS No. 14059-33-7 EINECS No. 237-898-0

Bismuth vanadate pigments are used to obtain lead-free, brilliant shades for original automotive coatings, repair coatings and industrial coatings of very high quality. The thermostable bismuth vanadate pigment grades are mainly used for the colouration of plastics. Very brilliant shades can be achieved in combination with organic pigments.

Short chemical description

Bismuth vanadate occurs in nature, amongst others, as a brown mineral called pucherite. The development of pigments based on bismuth vanadate started more than 20 years ago. Bismuth vanadate pigments are high-quality inorganic brilliant yellow pigments. Their composition varies from the $BiVO_4$ to the complex pigment $4\ BiVO_4 \cdot 3\ Bi_2MoO_6$. To improve stability and thereby their fastness properties, the products may contain stabilizing coatings, which are mainly oxides of boron, aluminium, zinc, silicon, and phosphorous.

Toxicological data

Animal assays did not result in toxicity by oral or inhalative application.

- LD_{50} rat, oral: > 5 000 mg/kg
- LC_{50} rat, inhalative: 4.15 mg / liter / 4 h
- LC_{50} (aquatic toxicity, golden orfe): > 10 000 mg/l
- skin tolerability: not irritating (tested on rabbit)
- mucous membrane tolerability: not irritating (tested on rabbit eye)
- mutagenicity (Ames test): negative (tested on 5 bacteria strains, with and without enzymatic activation)
- sensitization: not sensitizing (tested on guinea pig)

There are indications of effects caused by chronic inhalation exposure, but they are not relevant for food safety.

Solubilities (water, octanol)

Bismuth vanadate pigments are sparingly soluble in water. Only at pH values less than 2, do they become noticeably soluble.

Bismuth vanadate pigments are very resistant to organic solvents.

4.10 Effect pigments

4.10a Pearlescent pigments

Pearlescent pigments are regarded as preparations in chemical law. Therefore, possible components are listed as follows.

Al_2O_3	CAS No. 1344-28-1 EINECS No. 215-691-6 C.I. –
Cr_2O_3	CAS No. 1308-38-9 EINECS No. 215-160-9 C.I. 77288 / C.I. Pigment Green 17
Fe_2O_3	CAS No. 1309-37-1 EINECS No. 215-168-2 C.I. 77491 / C.I. Pigment Red 101, 102
Fe_3O_4	CAS No. 1317-61-9 EINECS No. 215-277-5 C.I. 77499 / C.I. Pigment Black 11
FeO(OH)	CAS No. 20344-49-4 EINECS No. 243-746-4 C.I. 77492 / C.I. Pigment Yellow 42, 43

Mica	CAS No. 12001-26-2
	EINECS No. 310-127-6 (natural substance)
	C.I. 77019 / C.I. Pigment White 20, 26
SiO_2	CAS No. 7631-86-9
	EINECS No. 231-545-4
	C.I. –
SnO_2	CAS No. 18282-10-5
	EINECS No. 242-159-0
	C.I. 77861 / C.I. Pigment White 15
TiO_2	CAS No. 13463-67-7
	EINECS No. 236-675-5
	C.I. 77891 / C.I. Pigment White 6

The most important fields of application are plastics, coatings, and printing inks.

Short chemical description

Pearlescent pigments are synthetic pigments, which are known for their high gloss, brilliance and iridescent colour effect caused by optically thin layers. The visual impression results from reflection and refraction of the light in thin multiple layers.

Particularly well known are mica-based pigments. In this case, colour and gloss are achieved by covering of mica flakes with one or more metal oxides, e. g. TiO_2 or Fe_2O_3. Pearlescent pigments are used to obtain brilliant two-tone flops in transparent colour formulations. These pigments can be divided, roughly, into the following groups: silver pigments, interference pigments, golden pigments and metal gloss pigments.

The components of pearlescent pigments are essentially inorganic substances. For special applications, the pigments can be submitted to surface coating (e. g. for exterior applications) or pasted (to facilitate the processability). In these cases, the additives can be polymers, resins, fatty acids (e. g. stearic acid, myristic acid) and various solvents (e. g. hydrocarbons). The particle size of these pigments is mainly between 5 and 125 µm.

Toxicological data

Pearlescent pigments are toxicologically harmless. The acute oral toxicity (LD_{50}, rats) is above 5 000 mg/kg (1). Investigations of the inhalation toxicity (two studies) resulted in LC_{50} values of 4.6 to 14.9 mg/l and of > 14.9 mg/l and 10.1 mg/l, resp. (1). Most probably, the observed non-specific effects are due to the very high concentrations overloading the respiratory tract rather than truly toxic effects.

Pearlescent pigments are neither irritating nor sensitizing to the skin and mucous membranes (1).

No adverse effects of pearlescent pigments for the human health were observed at normal occupational exposure (2). According to several studies, chronic effects can be ruled out as well (3).

Migration

Pearlescent pigments have an excellent migration fastness.

Solubilities (water, octanol)

Pearlescent pigments are virtually insoluble in water, dilute acids and bases. The same holds for organic solvents.

References

(1) Eberstein, M. V.; Heusener, A; Jacobs, M.: E. Merck Institute of Toxicology, Darmstadt, Germany, 22 Reports, 1970–1991

(2) Bruch, "J. Expert report on Health and Hazards caused by Pearl Lustre Pigments". Occupational Medicine and Toxicology, Institute of Hygiene and Occupational Medicine, University Clinic Essen, Germany, 1990
(3) Bernhard, B. K. et al.: "Toxicology and carcinogenesis studies of dietary titanium dioxide-coated mica in male and female Fischer 344 rats." J. Toxicol. Environ. Health 1989, 28, pp. 415–426

4.10b Metal pigments

Aluminium
C.I. Pigment Metal 1
C.I. 77 000
CAS No.: 7429-90-5 for Aluminium metal
EINECS No.: 231-072-3

Copper and gold bronze (copper-zinc alloy)
C.I. Pigment Metal 2
C.I. 77400
CAS No.: 7440-50-8 for copper metal, 7440-66-6 for zinc metal
EINECS No.: copper: 231-159-6, zinc: 231-175-3

Short chemical description

Metal pigments are flakes consisting of aluminium, copper or gold bronze (copper-zinc alloy) in form of powders or pastes. The flakes have a maximum length of about 1 to 350 μm and a thickness of about 0.1 to 1 μm. In the production of metal pigments, metal powder obtained by spraying is ground in a ball mill in the presence of milling agents (usually stearic acid or oleic acid), which inhibit cold welding of the pigment particles.

Optically very demanding metal pigments are produced by the pvd process. Metal pigments provide the means to obtain silver and copper-red to greenish shades with the essential light-reflecting, metallic effect.

Aluminium pigments meet the standards of the FDA Regulation 21 CFR 178.3297 for the colouration of consumer goods for food contact and of the French Positive List (Circulaire 176).

Toxicological data

Aluminium powders do not show any acute toxicity. The medical white oil (according to DAB) contained in metal pigment pastes is not toxic. At normal exposure, no chronic effects caused by aluminium powder are known. Metallic copper and gold bronze are also not toxic.

Solubilities (water, octanol)

Metal pigments are insoluble in n-octanol. All metal pigments can be destroyed oxidatively by acids and bases. Aluminium pigments can react already in water only, depending on the conditions (pigment type, temperature). But as soon as the metal pigments are embedded in plastic or in a binder, they are largely protected against such an attack.

References

Merian, E. Metalle in der Umwelt. VCH, Weinheim, 1994

4.11 Monoazo pigments

Monoazo yellow pigments were discovered at the beginning of the last century. Known as HANSA Yellow, they were so successful on the market, that the name “Hansa” is often used as a general descriptive term for these simple “classical” monoazo pigments.

They cover the colour range from yellow with an intense greenish hue through orange to brilliant red.

The earlier pigments showed a certain solubility in organic solvents and a rather poor migration resistance, as well as a perturbing tendency towards recrystallization and insufficient fastness. By incorporating additional polar groups – e. g. carbonamides or sulphonamides, which enable intermolecular interactions – their properties were gradually improved enabling their use in food contact applications.

C.I. Pigment Red 170

C.I. 12475 CAS No. 2786-76-7 EINECS No. 220-509-3

In plastic applications, this pigment is used for the colouration of unplasticized PVC. It is listed in the French Positive List, with some restrictions concerning the use in the final product.

Short chemical description

The pigment is synthesized by coupling of diazotized p-aminobenzamide with 2'-ethoxy-3-hydroxy-2-naphthanilide.

Toxicological data

The pigment is not acutely toxic (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. In a 28-day feeding study, there was no significant effect due to this substance, up to the highest dosage of 12 500 mg per kg feed (1).
The pigment was not mutagenic in the Ames test.

Solubilities (water, octanol)

C.I. Pigment Red 170 is virtually insoluble in water.

References

Studies performed by Clariant GmbH

4.12 Pigment lakes

C.I. Pigment Yellow 62
C.I. 13940 CAS No. 12286-66-7 EINECS No. 235-558-6

C.I. Pigment Yellow 168
C.I. 13960 CAS No. 71832-85-4 EINECS No. 276-057-2

C.I. Pigment Yellow 183
C.I. 18792 CAS No. 65212-77-3 EINECS No. 265-634-4

C.I. Pigment Yellow 191
C.I. 18795 CAS No. 129423-54-7 EC No. 403-530-4

C.I. Pigment Yellow 191:1
C.I. 18795:1 CAS No. 154946-66-4 EC No. (not yet assigned)

Yellow monoazo pigment lakes are structurally similar to other monoazo yellow pigments, except that in these pigments aminosulphonic acids have been introduced instead of aromatic amines as diazo components and that a salt formation follows. Furthermore, the coupling component may contain an additional sulphonic acid group.

4.12a C.I. Pigment Yellow 62 and C.I. Pigment Yellow 168

Both of these monoazo pigments, laked with calcium, are listed in the French Positive List, with some restrictions concerning the use in the final product.

Short chemical description

Both pigments are synthesized by coupling relatively simple diazotized aromatic sulphonic acids with acetoacetic derivatives and subsequent laking with calcium.

Toxicological data

The toxicological properties of C.I. Pigment Yellow 62 and C.I. Pigment Yellow 168 are identical: they are not acutely toxic (LD_{50} > 2 000 mg/kg) and not irritating to the skin or eyes. Mutagenicity tests (Ames tests) gave negative results (1).

Solubilities (water, octanol)

The water solubility of these pigments is between 10 and 50 mg/l.

4.12b C.I. Pigment Yellow 183

This monoazo pigment laked with calcium is listed in the French Positive List and is approved in the USA according to 21 CFR 178.3297 for the colouration of consumer goods with food contact, up to a maximum dosage of 1 % by weight of polymers.

Short chemical description

C.I. Pigment Yellow 183 is synthesized by coupling of diazotized 2-amino-4,5-dichlorobenzenesulphonic acid with 1-(3'-sulphophenyl)-3-methyl-5-pyrazolone and subsequent laking with calcium.

Toxicological data

The C.I. Pigment Yellow 183 is not acutely toxic. The Ames test showed no mutagenicity (2).

Solubilities (water, octanol)

The water solubility of this pigment is greater than 10 mg/l.

4.12c C.I. Pigment Yellow 191 and C.I. Pigment Yellow 191:1

These monoazo pigment lakes are suitable for the colouration of polyolefins and PVC. The user should perform tests with his own formulation to ensure, that no interaction takes place between the components in his system, e. g. stabilizers and colourants.

Short chemical description

These pigments are synthesized by coupling of diazotized 4-amino-6-chlorotoluene-3-sulphonic acid with 1-(3'-sulphophenyl)-3-methyl-5-pyrazolone (3). The laking takes place by addition of calcium chloride or ammonium chloride, respectively.

C.I. Pigment Yellow 191 is listed in the French Positive List. The FDA allows the use of this pigment according to CFR 21, 178.3297 in all polymers up to 1 %.

C.I. Pigment Yellow 191:1 is listed in the French Positive List as well in 21 CFR 178.3297, with a maximum dosage of 0.5 % per weight of the polymers. The final product can come into contact with food under the application conditions A to H, as described in table 2 of section 176.170(c).

Toxicological data

C.I. Pigment Yellow 191 is not acutely toxic (LD_{50} > 2 000 mg/kg) and not irritating to skin or mucous membranes. In the Ames test and in an *in vivo* test the pigment showed no mutagenicity (4).

C.I. Pigment Yellow 191:1 shows toxicologic properties similar to those of C.I. Pigment Yellow 191; the LD_{50} is above 2 000 mg/kg; it is not irritating to skin or eyes and shows no mutagenicity in the Ames test and the micronucleus test (1).

Solubilities (water, octanol)

The solubility of C.I. Pigment Yellow 191 in water is about 50 mg/l (4), and that of C.I. Pigment Yellow 191:1 is about 1.2 g/l (1).

References

(1) Studies performed by Ciba Specialty Chemicals Inc.
(2) Studies performed by BASF AG
(3) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997
(4) Studies performed by Clariant GmbH

4.13 Disazo pigments

C.I. Pigment Yellow 83
C.I. 21108 CAS No. 5567-15-7 EINECS No. 226-939-8

C.I. Pigment Yellow 155
C.I. 200310 CAS No. 68516-73-4 EINECS No. 271-176-6

Diarylide pigments are synthesized by bis-diazotizing diamino-diphenyl derivatives, mainly 3,3'-dichlorobenzidine (DCB), and coupling with acetoacetarylides or aryl-substituted pyrazolones (1).

Their shades are primarily in the range of yellow, orange or red.

Bis-acetoacetarylide pigments are disazo pigments with bifunctional coupling components.

4.13a C.I. Pigment Yellow 83

Of all the diarylide pigments, C.I. Pigment Yellow 83 is used because of its fastness properties mainly for the mass colouration of plastics. The processing temperatures must not exceed 200 °C.

Plastics coloured with C.I. Pigment Yellow 83 show a good to very good fastness to migration. The bleed fastness in plasticized PVC, for example, lies near level 5.

Short chemical description

C.I. Pigment Yellow 83 is synthesized by coupling of bis-diazotized DCB with 4'-chloro-2',5'-dimethoxyacetoacetanilide.

Toxicological data

Many diarylide pigments are derived from the 3,3'-dichlorobenzidine (DCB). Therefore, the diarylide pigments on DCB basis have been tested toxicologically very extensively.

Diarylide pigments with their LD_{50} values above 2 000 mg/kg show no acute toxicity according to the EU classification criteria. They are not irritating to the skin or mucous membranes.

Long-term feeding studies with several diarylide pigments, e. g. Pigment Yellow 83, showed no evidence of a carcinogenic potential (2–6).

In studies of the bioavailability of several representatives of this group of pigments, no carcinogenic cleavage product was released in detectable amounts after oral, inhalative or intratracheal application on rats.

One further study of the bioavailability of DCB (DCB haemoglobin adduct) has been performed with the diarylide pigments C.I. Pigment Yellow 13 and C.I. Pigment Yellow 17 (see ref. 7). In this study, no release of carcinogenic DCB from the pigments has been detected. This indicates the absence of metabolism to DCB under the test conditions.

It can be summarized, that, according to the known studies, diarylide pigments do not represent any health risk.

Solubilities (water, octanol)

Diarylide pigments (e. g. C.I. Pigment Yellow 83) possess an extremely low water solubility (< 0.02 mg/l, not detectable). The solubility of C.I. Pigment Yellow 83 and of other diarylide pigments in n-octanol is also less than 0.02 mg/l (not detectable).

4.13b C.I. Pigment Yellow 155

Of all the bis-acetoacetarylide pigments, mainly the C.I. Pigment Yellow 155 is used for the colouration of plastics.

This pigment is listed in the French Positive List.

Short chemical description

C.I. Pigment Yellow 155 is synthesized by coupling two equivalents of diazotized dimethyl-2-aminoterephthalate with 1,4-bis-(acetoacetylamino)-benzene.

Toxicological data

This pigment is not acutely toxic (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. In the Ames test, it was not mutagenic (8).

Solubilities (water, octanol)

C.I. Pigment Yellow 155 is virtually insoluble in water .

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997

(2) On the carcinogenic potential of diarylide pigments based on 3.3'-dichlorobenzidine. ETAD-Report T 2028-BB (E), 1990
(3) Nony, C. Metabolism of Azo Dyes to Potentially Carcinogenic Aromatic aminess. NCTR Technical Report, 1979
(4) Mondino, A.; Achari, R. et. al. Absence of dichlorobenzidine in the urine of rats and monkeys treated with C.I. Pigment Yellow 13. Med. Lav. 1978, **69**, 693–697
(5) Leuschner, F. Carcinogenicity study of different diarylide yellow pigments in mice and rats. Toxicol. Lett. 1978, **2**, 253–260
(6) Bioassay of Diarylide Yellow for Possible Carcinogenicity. NCI, DHEW Publication No. (NIH) 77–830, 1977
(7) Sagelsdorff, R. et. al. Lack of bioavailability of dichlorobenzidine from diarylide azo pigments: molecular dosimetry for hemoglobin and DNA adducts, Carcinogenesis, 1996, **17**, 507–514
(8) Studies performed by Clariant GmbH

4.14 Benzimidazolone pigments

C.I. Pigment Orange 72
C.I. 211095 CAS No. 78245-94-0 EC No. 407-660-2

C.I. Pigment Yellow 180
C.I. 21290 CAS No. 77804-81-0 EINECS No. 278-770-4

The common characteristic of this group of pigments is the benzimidazolone group, usually present in the coupling component.

4.14a C.I. Pigment Orange 72

This pigment is particularly suitable for the colouration of plastics. It is an intensely coloured and brilliant orange pigment with a heat resistance of 290 °C in polyolefins. It has a high light fastness and shows no distortion in HDPE.

C.I. Pigment Orange 72 is listed in the French Positive List, with some restrictions concerning the use in the final product.

Short chemical description

In literature, C.I. Pigment Orange 72 is described as a benzimidazolone pigment (1). The components for its synthesis are 3,3'-dichlorobenzidine (DCB) and 5-acetoacetylaminobenzamidazolone. The benzimidazolone unit is responsible for the above-mentioned properties and for the outstandingly stable crystal structure.

Toxicological data

C.I. Pigment Orange 72 is not acutely toxic (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. In a 28-day feeding study, no significant effect due to this substance was observed up to the highest dosage of 1000 mg per kg body weight.

In a maximization test on guinea pigs, the pigment was not skin-sensitizing. The pigment has shown no mutagenicity in the Ames test or in an *in vivo* test. In an inhalation study, no dichlorobenzidine was released from the pigment after repeated application (2).

Solubilities (water, octanol)

C.I. Pigment Orange 72 has no measurable solubility in water (< 0.02 mg/l, detection limit) and in n-octanol (< 0.02 mg/l, detection limit). Investigations of several solvent fastnesses have shown, that C.I. Pigment Orange 72 is one of the least soluble organic compounds. Its exceptional properties are explained by an intermolecular network of hydrogen bonds which stabilize the crystal lattice. These hydrogen bonds are formed by the benzimidazolone group. This effect is documented comprehensively in reference (3). It produces a pigment that has outstanding thermal stability and solvent fastness characteristics.

4.14b C.I. Pigment Yellow 180

This disazo pigment is also particularly interesting for the colouration of plastics. It has a heat stability in HDPE up to 290 °C and has low distortion. C.I. Pigment Yellow 180 is listed in the French Positive List. The FDA allows its use, according to 21 CFR 178.3297, in all polymers up to 1%.

Short chemical description

C.I. Pigment Yellow 180 is synthesized by coupling bis-diazotized 1,2-bis-(2-amino-phenoxy)-ethane with 5-acetoacetylaminobenzimidazolone.

Toxicological data

This pigment is not acutely toxic (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. In the Ames test it was not mutagenic.

Solubilities (water, octanol)

The pigment shows no measurable solubility in water (< 0.02 mg/l, detection limit).

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997
(2) Studies performed by Clariant GmbH
(3) Hunger; Paulus. farbe + lack **86** (1980), 116 and **88** (1982), 453

4.15 Disazo condensation pigments

C.I. Pigment Red 95
C.I. 20034 CAS No. 5280-80-8 EINECS No. 226-107-4

C.I. Pigment Red 214
C.I. 200660 CAS No. 40618-31-3 EINECS No. 255-005-2

C.I. Pigment Red 220
C.I. 20055 CAS No. 68259-05-2 EINECS No. 269-507-4

C.I. Pigment Red 242
C.I. 20067 CAS No. 52238-92-3 EINECS No. 257-776-0

The solvent resistance and the migration resistance of simple azo pigments can be increased by chemical and/or physical modifications.

The target of the chemical modifications is the formation of bigger and thereby more stable molecules. This method was first applied in the early 1950s. At that time, pigments with relatively high molecular weight were synthesized, the so-called disazo condensation pigments.

An example of these substances are the formamyl types, in which two monoazo units are bridged by an aromatic diamino-carbonamide (1).

The red disazo pigments can be regarded as dimerization products of two Naphthol AS type pigments. (On the other hand, to obtain the yellow pigments the azo units have to be connected, either via the coupling component or via the disazo unit.)

4.15a C.I. Pigment Yellow 95

In plastic colouration, this pigment is used mainly for the colouration of PVC and polyolefins. It has an excellent heat stability (up to 280 °C in HDPE).

C.I. Pigment Yellow 95 is listed in the FDA Regulation 21 CFR 178.3297 for applications in all polymers up to 1 % and for the conditions B to H, as described in the table 2 § 176.170(c). It is also listed in the French Positive List.

Short chemical description

The synthesis of C.I. Pigment Yellow 95 starts from a bis-acetoacetylated aromatic diamine. Subsequently, this is coupled in a diazotization reaction with an aminobenzoic acid. In a final step, condensation with an additional aromatic amine results in the desired enlargement of the molecule.

Toxicological data

C.I. Pigment Yellow 95 shows no acute toxicity (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. In the Ames test, the pigment was not mutagenic (2).

Solubilities (water, octanol)

The pigment is virtually insoluble in water and in n-octanol.

4.15b C.I. Pigment Red 214

This pigment is mainly used for the colouration of PVC and polyolefins. It has an excellent heat stability (up to 300 °C in HDPE).

It is listed in the French Positive List.

Short chemical description

The synthesis of C.I. Pigment Red 214 starts with the coupling of diazotized 2,5-dichloroaniline with 3-hydroxy-2-naphthoic acid. The product is then converted into the acid chloride. Subsequently, two equivalents of this acid chloride are condensed with one equivalent 1,4-diamino-2,5-dichlorobenzene.

Toxicological data

C.I. Pigment Red 214 shows no acute toxicity (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. In the Ames test, the pigment was not mutagenic (2)

Solubilities (water, octanol)

The pigment is virtually insoluble in water and in n-octanol.

4.15c C.I. Pigment Red 220

This pigment is mainly used for the colouration of polyolefins and PVC. It has an excellent heat stability (up to 300 °C in HDPE).

It is listed in the French Positive List and in the FDA Regulation 21 CFR 178.3297.

Short chemical description

The synthesis of C.I. Pigment Red 220 starts with the coupling of diazotized 2'-chloroethyl-3-amino-4-methylbenzoate with 3-hydroxy-2-naphthoic acid. The product is then converted to the acid chloride. Subsequently, two equivalents of this acid chloride are condensed with one equivalent of 1,4-diamino-2,5-dichlorobenzene.

Toxicological data

C.I. Pigment Red 220 shows no acute toxicity (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes.

Solubilities (water, octanol)

The pigment is virtually insoluble in water and in n-octanol.

4.15d C.I. Pigment Red 242

In plastic colouration, this pigment is mainly used for the colouration of polyolefins and PVC. It is also suitable for the colouration of polystyrene and other technical plastics.

C.I. Pigment Red 242 is listed in the French Positive List.

Short chemical description

The synthesis of C.I. Pigment Red 242 starts with the coupling of diazotized 2-chloro-5-trifluoromethylaniline with 3-hydroxy-2-naphthoic acid. The product it then converted to the acid chloride. Subsequently, two equivalents of this acid chloride are condensed with one equivalent of 1,4-diamino-2,5-dichlorobenzene.

Toxicological data

C.I. Pigment Red 242 is not acutely toxic (LD_{50} > 2 000 mg/kg) and is not irritating to the skin or mucous membranes. The pigment was not mutagenic in the Ames test and in an *in vitro* chromosomal aberration test (3).

Solubilities (water, octanol)

The pigment is virtually insoluble in water and in n-octanol.

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997

(2) Studies performed by Ciba Spezialitätenchemie AG

(3) Studies performed by Clariant GmbH

4.16 Phthalocyanine pigments

C.I. Pigment Blue 15, 15:1, 15:2, 15:3, 15:4 and 15:6
C.I. 74160 CAS No. 147-14-8 EINECS No. 205-685-1

C.I. Pigment Green 7
C.I. 74260 CAS No. 1328-53-6 EINECS No. 215-524-7

C.I. Pigment Green 36
C.I. 74265 CAS No. 14302-13-7 EINECS No. 238-238-4

Chemically, the phthalocyanine system belongs to the aza-(18)-annulene family, an aromatic, macrocyclic hetero-system with 18 π electrons which form conjugated double bonds.

Increasing halogenation of the ring positions shifts the colour shade of phthalocyanines from the original blue to the green colour region.

4.16a C.I. Pigment Blue 15

The excellent chemical stability of the copper phthalocyanine pigments and their high thermal resistance during the processing steps lead to a broad range of possible applications in plastics.

C.I. Pigment Blue 15 is listed in the Circulaire 176, the French Positive List. The pigment is also approved in the USA according to the FDA Regulation 21 CFR 178.3297 for the colouration of consumer goods for food contact.

Short chemical description

Copper phthalocyanine blue is the copper(II) complex of the tetraazatetrabenzoporphine. The copper phthalocyanine blue pigments can occur in different crystal modifications. The technically most important forms are the alpha form (reddish-blue) and the beta form (greenish-blue). By partial chlorination (0.5 chlorine atoms per molecule copper phthalocyanine), the alpha modification is stabilized.

Copper phthalocyanine is synthesized either by the phthalodinitrile process, in a solvent or without a solvent, from o-phthalodinitrile and copper bronze or copper(I) chloride or by the phthalic anhydride/urea process.

Toxicological data

In animal assays, copper phthalocyanine pigments did not show any acute toxicity. Irritation tests indicated no acute irritation effect to the skin or mucous membranes. The mutagenicity tests (Ames tests) were negative. In tests on guinea pigs, no indications to a sensitizing effect were observed.

A 13-week feeding study on rats to test the chronic toxicity, with up to 5 000 mg per kg body weight, resulted in no toxicological effects. The copper, in the pigment bound in a complex, is not bioavailable. The pigment does not show the toxicity which is characteristic of soluble inorganic copper compounds. An investigation in mice, where phthalocyanine blue pigment was injected during a period of eight months, resulted in no indication to a carcinogenic potential.

Solubilities (water, octanol)

Blue copper phthalocyanine pigments are virtually insoluble (< 0.1 mg/l) in water and in organic solvents. The water-soluble copper contents are usually lower than 5 ppm.

4.16b C.I. Pigment Green 7

By the incorporation of chlorine atoms, the shade of copper phthalocyanine pigments shifts from blue to green. The pigment has excellent fastnesses in plastics.

The pigment is listed in the French Positive List. According to the FDA Regulation 21 CFR 178.3297, it is also approved for the colouration of consumer goods for food contact.

Short chemical description

The copper phthalocyanine molecule of the C.I. Pigment Green 7 contains about 15 chlorine atoms. The synthesis is carried out by direct chlorination of copper phthalocyanine in molten sodium chloride / aluminium chloride.

Toxicological data

The pigment is not acutely toxic. In the Ames test it was not mutagenic. Two subchronic studies in rats and mice (90 days each) resulted in no toxic effects.

Solubilities (water, octanol)

C.I. Pigment Green 7 is virtually insoluble (< 0.1 mg/l) in water and in organic solvents.

4.16c C.I. Pigment Green 36

These pigments give green shades with an intense yellow shade. The colour is substantially more yellowish than that of the C.I. Pigment Green 7 types. The shade is the yellower, the more chlorine in the copper phthalocyanine molecule is replaced by bromine.

Short chemical description

The copper phthalocyanine molecule of the C.I. Pigment Green 36 contains 4 to 5 chlorine atoms and 11 to 12 bromine atoms

The synthesis involves a mixed halogenation. To achieve the green pigment, potassium bromide is added to the reaction melt. This leads to the formation of elemental bromine, which further reacts to form the brominated types.

Toxicological data

C.I. Pigment Green 36 is not acutely toxic. In the Ames test it is not mutagenic.

Solubilities (water, octanol)

C.I. Pigment Green 36 is virtually insoluble (< 0.1 mg/l) in water and in organic solvents.

References

(1) IUCLID Data Sheet CAS 147-14-8 and 1328-53-6

(2) Studies performed by BASF AG

(3) Löbbert, G. Phthalocyanines. Ullmann’s Encyclopaedia of Industrial Chemistry Vol. A20. VCH, Weinheim, 1992

(4) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997

(5) Battelle’s Columbus Laboratories, USA (1979)

4.17 Quinacridone pigments

C.I. Pigment Violet 19
C.I. 73900 CAS No. 1047-16-1 EINECS No. 213-879-2

C.I. Pigment Red 122
C.I. 73915 CAS No. 980-26-7 EINECS No. 213-561-3

The basic structure of the quinacridone pigments is a heterocyclic ring system, consisting of five anellated rings. Varying shades are generated by changing the substituents on the outer rings. Appropriate additional treatment of the crude quinacridone or specific process control leads to different crystal morphologies.

4.17a C.I. Pigment Violet 19

This pigment is suitable for almost every application, particularly for the pigmentation of plastics. It is listed in the French Positive List. The FDA allows its use in all polymers and does not restrict the contact with food in any way.

Short chemical description

C.I. Pigment Violet 19 is the most important quinacridone pigment. It exists in two crystal modifications, both of which are marketed.

Toxicological data

This pigment has no acute toxicity by the oral route (LD_{50} > 2 000 mg/kg). It is not irritating to skin or eyes. Mutagenicity tests were negative.

Solubilities (water, octanol)

C.I. Pigment Violet 19 is virtually insoluble in water and in organic solvents.

4.17b C.I. Pigment Red 122

This pigment is suitable for the colouration of polymers, paints and printing inks.

It is a bluish-red pigment (magenta). It is listed in the French Positive List.

Short chemical description

C.I. Pigment Red 122 is 2,9-dimethylquinacridone.

Toxicological data

This pigment has no acute toxicity by the oral route and is not irritating to skin or eyes. In a subacute daphnia test, no effects were found.

Solubilities (water, octanol)

C.I. Pigment Red 122 is virtually insoluble in water and in organic solvents.

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997

(2) Studies performed by Clariant GmbH and by Ciba Spezialitätenchemie AG

4.18 Diketopyrrolopyrrole pigments

C.I. Pigment Red 254
C.I. 56110 CAS No. 84632-65-5 EC No. 401-540-3

C.I. Pigment Orange 71
C.I. 561200 CAS No. 84632-50-8 EC No. (not yet assigned)

This group embodies the recently introduced class of diketopyrrolopyrrole pigments. The basic structure consists of two anellated five-membered rings, each of which contains a carbonamide group.

4.18a C.I. Pigment Red 254

This pigment is particularly suitable for the colouration of plastics and paints as well as special printing inks. It is listed in the French Positive List and in the FDA Regulation 21 CFR 178.3297. The FDA allows the use of this pigment in all polymers up to 1 %.

Toxicological data

This pigment has no acute toxicity by the oral route (LD_{50} > 5 000 mg/kg) or by skin contact (LD_{50} > 2 000 mg/kg). The acute inhalation toxicity is above 2 250 mg/kg. The pigment is not irritating to the skin or eyes. In the guinea pig skin sensitization test, it showed no sensitizing effect. No adverse effects were observed in a 28-day toxicity study with doses of up to 1 000 mg/kg. No evidence of mutagenicity was detected in mutagenicity tests, *in vitro* or *in vivo*.

Solubilities (water, octanol)

C.I. Pigment Red 254 is sparingly soluble in water (< 0.01 g/l at 20 °C). In fat simulants < 10 mg/100 g are soluble at 37 °C. The partition coefficient (log P_{OW}) is calculated to be 3.

4.18b C.I. Pigment Orange 71

This pigment is particularly suitable for the colouration of plastics and paints as well as special printing inks. It is listed in the French Positive List.

Toxicological data

This pigment has no acute toxicity by the oral route (LD_{50} > 5 000 mg/kg) or by skin contact (LD_{50} > 2 000 mg/kg). It is not irritating to the skin or eyes. No evidence of mutagenicity was detected in mutagenicity tests, *in vitro* or *in vivo*.

Solubilities (water, octanol)

C.I. Pigment Orange 71 is sparingly soluble in water (< 0.012 mg/l at 20 °C). In fat simulants < 0.059 mg/100 g are soluble at 37 °C. The partition coefficient (log P_{OW}) is calculated to be 0.2 to 0.6.

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997
(2) Studies performed by Ciba Spezialitätenchemie AG

4.19 Isoindolinone pigments

C.I. Pigment Yellow 109
C.I. 56284 CAS No. 5045-40-9 EINECS No. 225-744-5

C.I. Pigment Yellow 110
C.I. 56280 CAS No. 5590-18-1 EINECS No. 226-999-5

These pigments are suitable for use in plastics and printing inks. They are listed in the French Positive List. The FDA allows the use of C.I. Pigment Yellow 110 at up to 1 % for the colouration of all polymers with food contact, with the exception of condition A.

Short chemical description

The isoindolinone pigments are chemically classified as heterocyclic azomethines.

Toxicological data

Isoindolinone pigments have no acute toxicity by the oral route (LD_{50} > 5 000 mg/kg) or by inhalation (LD_{50} > 1 000 mg/m^3). They do not irritate the skin or eyes.

Solubilities (water, octanol)

This pigments are virtually insoluble in water and in organic solvents.

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997
(2) Studies performed by Ciba Spezialitätenchemie AG

4.20 Isoindoline pigments

C.I. Pigment Yellow 139
C.I. 56298 CAS No. 36888-99-0 EINECS No. 253-256-2

C.I. Pigment Yellow 185
C.I. 56290 CAS No. 76199-85-4 EINECS No. 278-388-8

The molecules of the isoindoline pigments contain an isoindoline ring, which is connected via methine bridges to two substituents.

4.20a C.I. Pigment Yellow 139

The reddish C.I. Pigment Yellow 139 is suitable for the colouration of plastics. It is listed in the French Positive List. This pigment is mainly used in all technologies of polyolefin colouration, e. g. the colouration of foils, ribbons and fibres, but is also very well suited for use in PVC.

Short chemical description

The isoindoline ring of the C.I. Pigment Yellow 139 molecule is connected via methine bridges to two barbituric acid residues. C.I. Pigment Yellow 139 is synthesized from diimino-isoindoline and barbituric acid.

Toxicological data

The data available for C.I. Pigment Yellow 139 give no indication of acute toxic properties. In the Ames test, the pigment was not mutagenic.

Solubilities (water, octanol)

The water solubility of C.I. Pigment Yellow 139 was determined to be < 10 mg/l.

4.20b C.I. Pigment Yellow 185

The greenish C.I. Pigment Yellow 185 is offered in the form of a pigment preparation for the colouration of plastics.

Short chemical description

The isoindoline ring of the C.I. Pigment Yellow 185 molecule is connected via methine bridges to two asymmetrical residues: a methyl-cyanacetamide residue and a barbituric acid residue.

Toxicological data

C.I. Pigment Yellow 185 is not acutely toxic by the oral route. In the Ames test and in the chromosomal aberration test, it showed no mutagenic properties. In a 28-day (subacute) feeding study with C.I. Pigment Yellow 185, no toxic effects were found.

Solubilities (water, octanol)

The water solubility of this pigment is less than 10 mg/l. The partition coefficient (log P_{OW}) is 1.4.

References

Studies performed by BASF AG

4.21 Anthraquinone pigments

C.I. Pigment Red 177
C.I. 65300 CAS No. 4051-63-2 EINECS No. 223-754-4

This pigment is suitable for almost every application. It is mainly used for the colouration of polyolefin and PVC as well as for industrial paints and for spin dyeing.

The pigment is listed in the French Positive List. The FDA Regulation 21 CFR 178.3297 allows the use of this pigment in all polymers up to 1 % and for materials with food contact, with the exception of condition A.

Short chemical description

The molecule of the C.I. Pigment Red 177 consists of two anthraquinone derivatives connected to each other.

Toxicological data

This pigment is not acutely toxic by the oral route ($LD_{50} > 5\,000$ mg/kg). It is not irritating to the skin or eyes.

Solubilities (water, octanol)

C.I. Pigment Red 177 is virtually insoluble in water and in organic solvents.

References

(1) Herbst, W.; Hunger, K. Industrial Organic Pigments. Second Edition, Wiley-VCH, Weinheim, 1997
(2) Studies performed by Ciba Spezialitätenchemie AG

4.22 Perylene pigments

C.I. Pigment Red 178
C.I. 71155 CAS No. 3049-71-6 EINECS No. 221-264-5

C.I. Pigment Red 179
C.I. 71130 CAS No. 5521-31-3 EINECS No. 226-866-1

The perylene pigments are derivatives of the perylenetetracarboxylic acid. These compounds were first used as vat dyes, and only since 1950 as pigments for the colouration of plastics and for high-quality industrial paints.

4.22a C.I. Pigment Red 178

This pigment is listed in the French Positive List.

Short chemical description

C.I. Pigment Red 178 is synthesized by the reaction of the dianhydride of the perylenetetracarboxylic acid with p-aminoazobenzene.

Toxicological data

C.I. Pigment Red 178 does not show acute toxic effects.

Solubilities (water, octanol)

This pigment is virtually insoluble in water and in organic solvents.

4.22b C.I. Pigment Red 179

In the USA, the C.I. Pigment Red 179 is, according to the FDA Regulation 21 CFR 178.3297, approved for the colouration of polymers with food contact, but not exceeding 1 % by weight of the polymer.

Short chemical description

C.I. Pigment Red 179 is sythesized by the reaction of the dianhydride of the perylenetetracarboxylic acid with N-methylamine.

Toxicological data

In animal assays, this pigment did not show acute toxic effects. In the Ames test, it was not mutagenic.

Solubilities (water, octanol)

The pigment is virtually insoluble in water and in organic solvents.

References

Studies performed by BASF AG

4.23 Quinophthalone pigments

C.I. Pigment Yellow 138
C.I. 56300 CAS No. 30125-47-4 EINECS No. 250-063-5

This class of pigments is based on the quinophthalone structure, which is formed from quinaldine and phthalic anhydride.

C.I. Pigment Yellow 138

Of all the quinophthalone pigments, only C.I. Pigment Yellow 138 is of importance for the colouration of plastics. The pigment is listed in the French Positive List. In the USA it is, according to the FDA Regulation 21 CFR 178.3297, approved for the colouration of consumer goods for food contact, but not exceeding 1 % by weight of the polymer.

Short chemical description

This pigment is synthesized by the reaction of 8-aminoquinaldine with the double molar amount of tetrachlorophthalic anhydride.

Toxicological data

In toxicological studies, C.I. Pigment Yellow 138 did not show any acute toxic effects. The investigation for mutagenicity by the Ames test and the micronucleus test resulted in no indications of mutagenic properties.

Solubilities (water, octanol)

C.I. Pigment Yellow 138 is sparingly soluble in water and in organic solvents.

References

Studies performed by BASF AG

5 Solvent dyes

Solvent dyes are colourants which, in contrast to pigments, are soluble in the application medium. Therefore, they are suitable for transparent colourations and are of growing importance in consumer goods and many other applications.

Solvent dyes are preferred for the colouration of high melting point polymers such as polyamide or polycarbonate. If opaque colourations are required, they can be mixed with light scattering and colour enhancing inorganic pigments such as complex inorganic pigments (rutiles or spinels), iron oxides or titanium dioxide.

The main application of solvent dyes is the colouration of amorphous thermoplastics. They are usually not recommended for the colouration of crystalline systems such as polyolefins.

Solvent dyes dissolve in the plastic melts at the required processing temperature. They appear in the melt in molecular dispersion, which facilitates the achievement of high colour yield and the reproducibility of colouristic properties.

Solubilities (water, octanol)

Solvent dyes are soluble in organic solvents such as aromatic esters or halogenated hydrocarbons, but only sparingly in water or in diluted aqueous solutions of acetic acid or ethanol.

For detailed data, e. g. about the solubility of the solvent dyes and their suitability for the colouration of consumer goods with food contact, please consult the individual manufacturer.

Migration

The low solubility in the above-mentioned media makes the solvent dyes suitable for the colouration of articles used as toys or in food contact applications. However, any formulation should be checked in appropriate tests for its bleeding (migration) properties, as already mentioned in section 3.2

6 Annexes

6.1 Relevant legal requirements

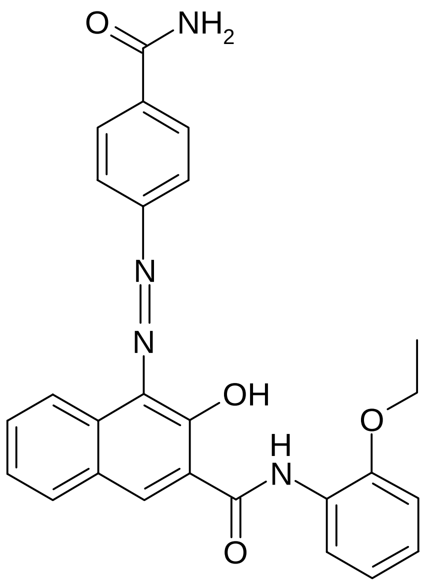
This chapter lists some of the regulations relevant for food contact applications. This list is not comprehensive, but cites American and European legislation, currently used as reference.

- Code of Federal Regulations, Title 21, Vol 3, Sec. 178.3297 „Colourants for polymers“
- Materiaux au contact des denrées alimentaires produits de nettoyage de ces matériaux, No. 1227, Direction des Journaux Officiels, Paris
- Council of Europe Resolution AP(89)1 „On the use of colourants in plastic materials coming into contact with food“, adopted on 13 September 1989
- Council Directive 89/109/EEC of 21. December 1988 on the approximation of the laws of the Member States relating to materials and articles intended to come into contact with foodstuffs, O.J. L40, 11.2.1989, 38–44
- Lebensmittel- und Bedarfsgegenständegesetz (LMBG), 9. September 1997, Bundesgesetzblatt III/FNA 2125-40-1-2
- Verordnung zur Neuordnung lebensmittelrechtlicher Vorschriften über Zusatzstoffe, 29. Januar 1998, Bundesgesetzblatt 1998, Teil 1 Nr. 8, S. 230–320 (5.2.1998)
- Bedarfsgegenstände-Verordnung vom 23. Dezember 1997,
Bundesgesetzblatt I 1998, S. 5, S. 3492
1999, S. 2059
2000, S. 179
- Council Directive 82/711/EEC of 18. October 1982 laying down the basic rules necessary for testing migration of the constituents of plastic materials and articles intended to come into contact with foodstuffs, O.J. L297, 23.10.1982, 26–30
.

6.2 Chemical structures (examples)

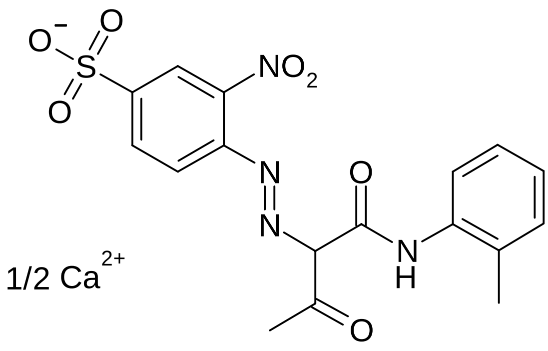
4.11 Monoazo pigments

C.I. Pigment Red 170,
CAS No. 2786-76-7



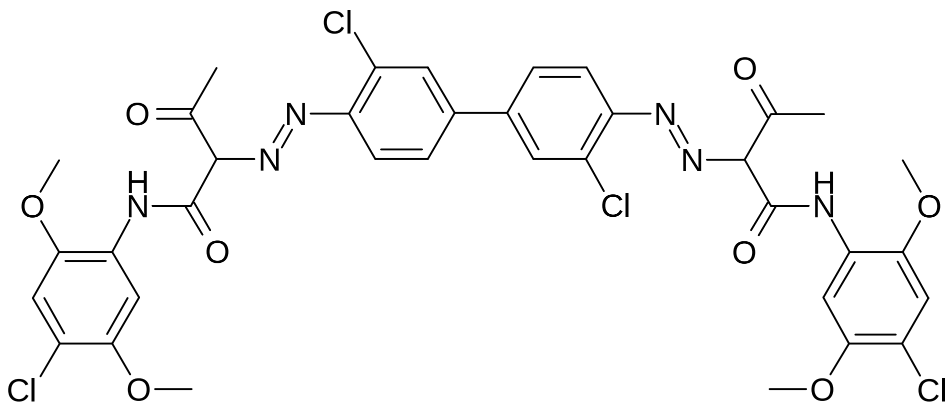
4.12 Pigment lakes

C.I. Pigment Yellow 62, CAS No. 12286-66-7



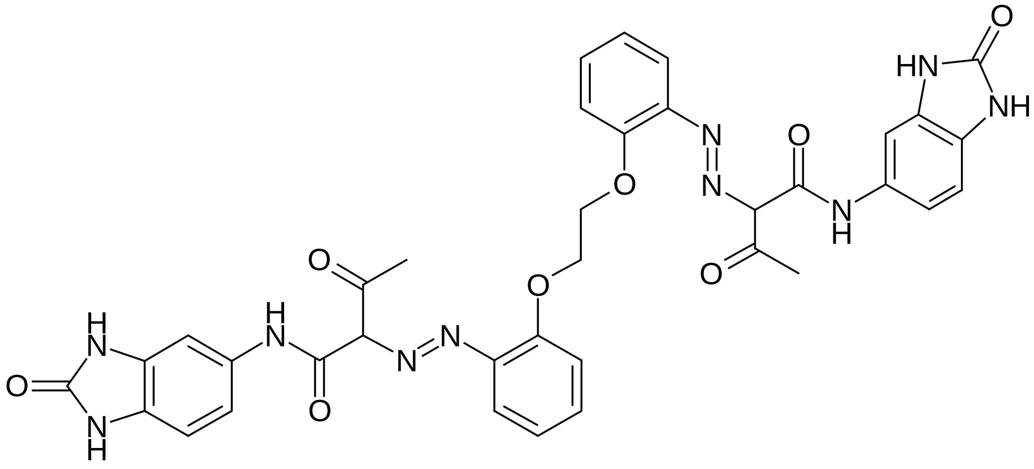
4.13 Disazo pigments

C.I. Pigment Yellow 83, CAS No. 5567-15-7



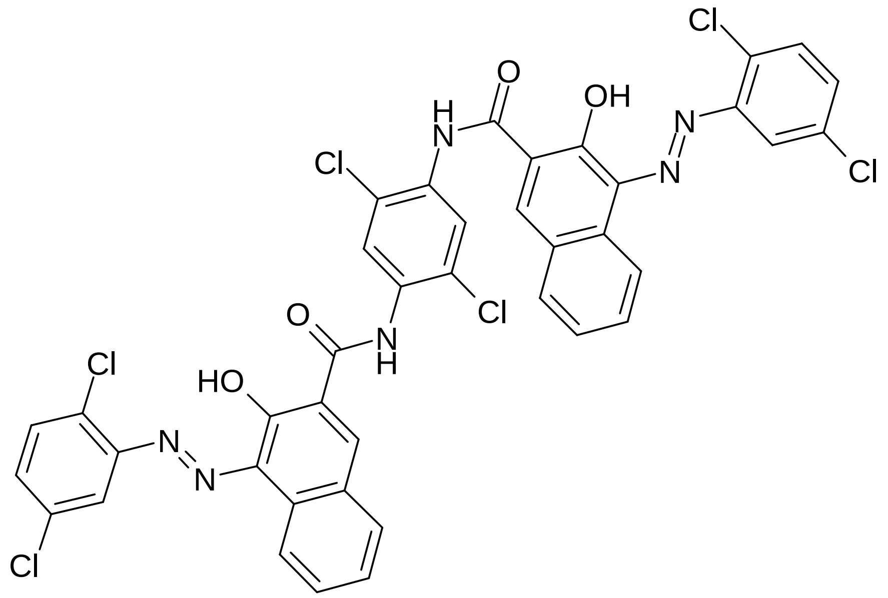
4.14 Benzimidazolone pigments

C.I. Pigment Yellow 180, CAS No. 77804-81-0



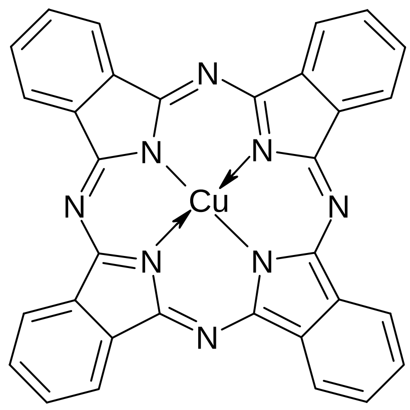
4.15 Disazo condensation pigments

C.I. Pigment Red 214, CAS No. 40618-31-3



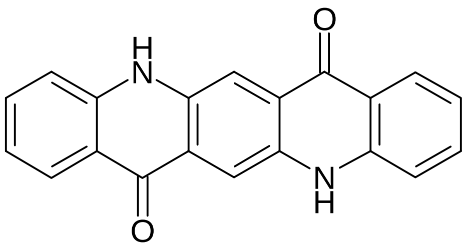
4.16 Phthalocyanine pigments

C.I. Pigment Blue 15, CAS No. 147-14-8



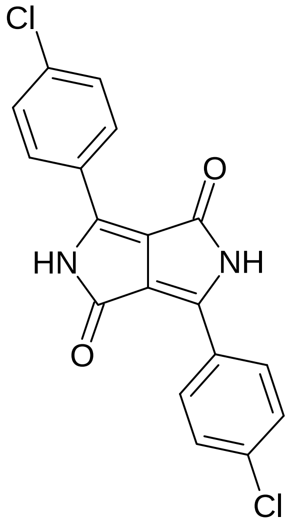
4.17 Quinacridone pigments

C.I. Pigment Violet 19, CAS No. 1047-16-1



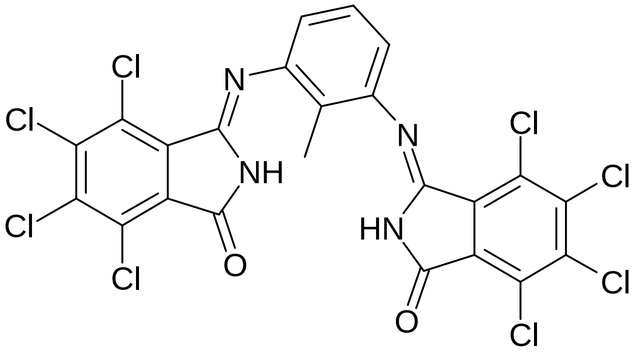
4.18 Diketopyrrolopyrrole pigments

C.I. Pigment Red 254, CAS No. 84632-65-5



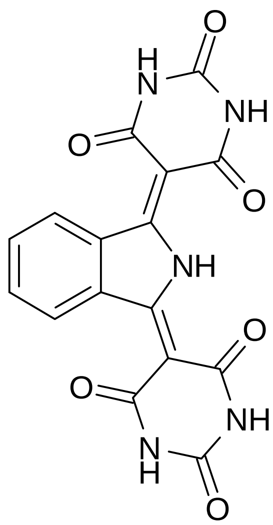
4.19 Isoindolinone pigments

C.I. Pigment Yellow 109, CAS No. 5045-40-9



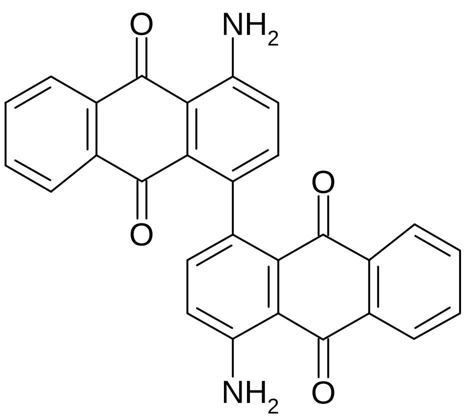
4.20 Isoindoline pigments

C.I. Pigment Yellow 139,
CAS No. 36888-99-0



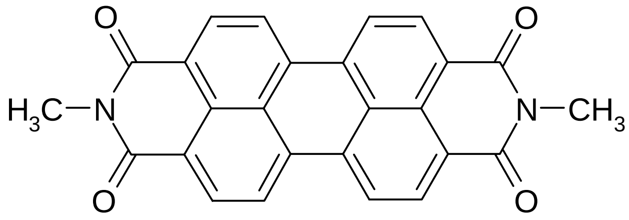
4.21 Anthraquinone pigments

C.I. Pigment Red 177,
CAS No. 4051-63-2



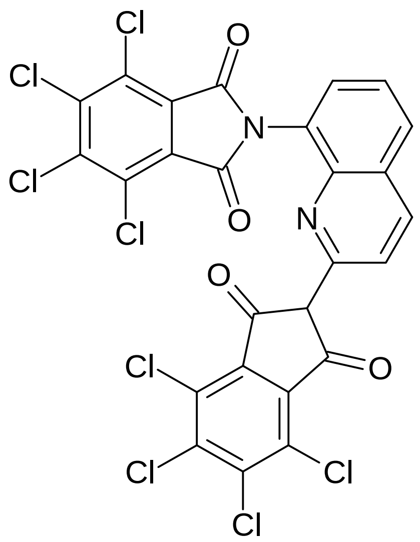
4.22 Perylene pigments

C.I. Pigment Red 179, CAS No. 5521-31-3



4.23 Quinophthalone pigments

C.I. Pigment Yellow 138, CAS No. 30125-47-4



6.3 Definitions / Glossary

ABS copolymer of acrylonitrile, butadiene and styrene (plastic)

ACC American Chemistry Council

acute toxicity describes all short-term health effects of the respective substance to humans and animals

Ames test a pre-screening *in vitro* test for gene mutation, carried out with bacteria (*Salmonella*)

BgVV Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin (Germany)

bleed fastness see migration fastness

CAS No. Chemical Abstract Service registry number

CEFIC The European Chemical Industry Council (CEFIC, Conseil Européen des Fédérations de l'Industrie Chimique)

chromosomal aberration test test to investigate for chemical-induced chromosomal damages

colourant generic term for all colouring materials (i. e. dyes and pigments)

CONEG Coalition of Northeastern Governors (USA)

DAB Deutsches Arzneimittel-Buch (German pharmaceutical register)

dermal (literally: of the skin) administration of chemicals or uptake of substances by the skin

dyes colourants, other than pigments; soluble in the application medium

EAK EU Waste Catalogue (EAK, Europäischer Abfallarten-Katalog)

EINECS European Inventory of Existing Commercial Chemical Substances

FDA Food and Drug Administration (USA)

fillers substances, consisting of insoluble particles, for enhancing the volume and for influencing some technical and optical properties

FPL French Positive List

heat stability describes the stability against temperatures, which are common in the processing of plastics

heavy metals metals with a density above 4.5 g/cm^3

ICCA International Council of Chemical Associations

***in vitro* test** toxicity study with cell cultures or tissues, conducted outside of a living organism (e. g. cytogenetic *in vitro* test)

***in vivo* test** toxicity study, conducted on living organisms (e. g. micronucleus *in vivo* test)

irritation the production of reversible inflammatory changes in the respective tissue (skin, eye, mucous membranes or respiratory tract)

IUCLID International Uniform Chemical Information Database

JHOSPA	Japan Hygienic Olefin and Styrene Plastics Association
KBWS	Kommission zur Bewertung wassergefährdender Stoffe (Germany)
lattice / crystal lattice	regular arrangement of atoms or molecules in a solid; the lattice type describes the crystal structure
LC_{50}	lethal concentration 50; the concentration of the respective substance required to kill 50 % of the organisms exposed to it (generally: algae, fish, daphnia)
LD_{50} (oral)	lethal dose 50, the measure for the acute toxicity; this is the dose of the respective substance, which kills, administered once by the oral route, 50 % of a group of animals experimentally exposed to it
light fastness	describes the resistance of colours (paints, printing inks, plastics) to the action of light
LMBG	Lebensmittel- und Bedarfsgegenständegesetz (Germany)
masterbatches	colourants and/or additive concentrates in a solid plastic matrix or plastic-like matrix with contents of colourants and/or additives, which are higher than in the final application
METI	Ministry of Economy, Trade and Industry (Japan)
migration	mass transfer of a substance through a boundary surface
migration fastness	describes the migration stability of the used colourants against the accepting boundary surface (food, skin, materials), with which it is in direct contact
modifications	designation for different states of elements or compounds, which have the same composition, but not the same physical properties; example: graphite and diamond
mutagenicity	the capability of a substance or agent to alter the genetic material in a living cell. An important pre-screening *in vitro* test is the Ames test on bacteria. Definite conclusions regarding a mutagenic potential can not be drawn from the outcome of a single mutagenicity test.
OECD	Organisation for Economic Cooperation and Development
oral	(literally: of the mouth) administration of chemicals or uptake of substances by the mouth
PA	polyamide plastic
partition coefficient	describes the concentration ratio of a substance in two adjacent, not miscible phases (solvents, gases); usually, its logarithm (log P_{OW}) is denoted
PBT, PBTP	polybutylene terephthalate plastic
PC	polycarbonate plastic
PCB	polychlorinated biphenyls
PE	polyethylene plastic
PET	polyethylene terephthalate plastic
pigment	colourant, insoluble in the application medium

PMMA	polymethyl methacrylate plastic
polymers	a class of substances, formed of such molecules, in which one type or several types of atoms or atom groups are repeatedly lined up (definition according to IUPAC). Colloquially, polymers are understood as plastics like ABS, PA, PBT, PC, PE, PET, PMMA, PP, PS and PVC.
polyolefin plastics	polymers on the basis of (generally) polypropylene or polyethylene
PP	polypropylene plastic
PS	polystyrene plastic
PVC	polyvinyl chloride plastic
SARA	Superfund Amendments and Reauthorization Act (1986; U.S.)
sensitization	is characterized by the immunologically mediated reaction of the organism after repeated or long-term exposure to a substance, so that the organism shows an allergic response. Therefore, the contact with such chemicals must be restricted to a minimum.
toxicity, acute	describes all short-term health effects of the respective substance to humans and animals
TSCA	Toxic Substances Control Act (USA)
VCI	Verband der Chemischen Industrie e.V. (Germany)
weather fastness	describes the resistance against the action of daylight and moisture

Eurocolour

Non-profit organisation, representing the interests of the European colourants industry.

Eurocolour is a cluster of Cefic (European Chemistry Industry Council).

Address: CEFIC, Avenue E. van Nieuwenhuyse 4, B–1160 Bruxelles / Belgium
Tel.: +49 (69) 2556 - 1351
Fax: +49 (69) 25 30 87
E-Mail: rfischer@vdmi.vci.de

Homepage: http://www.cefic.org

Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD)

An international association of manufacturers of organic pigments and dyes, which was established in 1974 to address health and environmental issues. Its international membership of 44 companies is based in 13 nations and includes 16 European members. Secretariats of the *Operating Committees* are based in Basel, Sao Paulo, Tokyo and Washington (D.C.). In the U.S., ETAD represents only the interests of the dye manufacturers.

Address: ETAD, P.O. Box, CH–4005 Basel / Switzerland
Tel.: +41 (61) 690 99 66
Fax: +41 (61) 691 42 78
E-Mail: info@etad.com

Homepage: http://www.etad.com

Verband der Mineralfarbenindustrie (VdMi)

Association of the German manufacturers of inorganic pigments, printing inks, carbon black pigments, white reinforcing fillers, chemicals for enamel, glass and ceramics as well as artists and school colours, food colourants and masterbatches.

Address: VdMi, Karlstrasse 21, D–60329 Frankfurt (Main) / Germany
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