Inorganic Pigments

LANXESS

Technical Information
Competence Center Specialities

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Inorganic Pigments for the Paper Industry

1 Introduction

When talking about the use of pigments in the paper industry, it is primarily extenders such as chalk or kaolin which are meant.

Pigments in the true sense, i.e. in accordance with DIN 55 943, are only used in special papers requiring, for example, very good dry and wet opacity. This applies to both white and coloured special papers. The extender and/or pigment can either be added directly to the pulp (mass colouring) or a paper coating can be applied on the finished paper at the end of the manufacturing process. Which of these two options is chosen depends on the end-use of the paper.

2 General properties of inorganic pigments

2.1 Optical properties

It goes without saying that the optical properties (colouring properties, tinting strength, hiding power/opacity) of colorants such as inorganic pigments are of key importance. Of these, the colouring properties come under scrutiny first because they determine whether or not the pigment can be used to create the required colour or to match a given reference.

The colouring properties are the result of the interaction between light absorption (K) and light scattering power (S). Pigments which have stronger light absorption than light scattering power exhibit greater depth of colour. Those of which the opposite is the case produce relatively pale shades. The K/S quotient can be used to classify colorants in three groups.

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a) In the first group, the scattering coefficient S is very much larger than the absorption coefficient K.

b) In the second group of colorants, the relationship is inverted. The absorption coefficient K and thus the light absorption of the pigments are significantly greater than the scattering power. This group includes organic colour pigments, dyestuffs, which have no scattering power at all, and transparent inorganic colour pigments. The size of the absorption coefficient K correlates with the tinting strength of a colorant, a feature which will be discussed later.

c) In the third group of colorants, the absorption coefficient K is roughly the same as the scattering coefficient S. This is true of inorganic colour pigments. These pigments normally exhibit both good tinting strength and hiding power, determined above all by the scattering power but also by the absorption. The absorption coefficient is largely governed by the chemical composition of the pigment and the particle size. The scattering coefficient is also greatly influenced by the particle size which means that the colouring properties, a result of the interaction between absorption and scattering, are affected by the particle size in inorganic colour pigments. This can be seen very clearly in the case of Bayferrox® red pigments.

The colouring properties of a pigment can be assessed objectively by means of colorimetry and either characterised by colour values or plotted in a colour system. The further away a pigment is from the achromatic point, i.e. from perceived (white, grey and black) the more brilliant or saturated is the colour of the pigment .

If a certain colour requirement is satisfied by a pigment, the question automatically follows as to the cost of using that pigment. However, it is not only the price of the colorant which should be considered. Its optical properties such as tinting strength and hiding power must also be included in the equation.

The tinting strength of a pigment is a measure of its ability to colour other substances such as paper because of its absorption properties. Generally speaking, the relative tinting strength of a colour pigment is determined in white reductions against a similar pigment. The relative tinting strength, at least in white reductions, is a reciprocal relationship and therefore enables conclusions to be drawn as to the cost-effectiveness of a colour pigment. In the case of blends made up of several pigments, the proportions of the individual components are primarily determined by their tinting strengths.

The tinting strength of a colour pigment is equivalent to the reducing power of a white pigment.

Apart from the tinting strength of a colour pigment or the reducing power of a white pigment, the opacity is also very important. In the paper industry, opacity is measured by determining the contrast ratio against a black or white substrate.

$$\text{Opacity} = \frac{\text{Ry against black} \cdot 100}{\text{Ry against white}}$$

2.2 Dispersibility

In order to fully exploit the optical properties of an inorganic pigment, determined by the particle size produced during manufacture, it is essential that the pigment can be easily dispersed, i.e. broken down into its primary particles and distributed evenly in the pulp. Good results are obtained if an aqueous pigment suspension (slurry) is made up first and then added to the pulp. However, it is still more common in practice to mix the pigment with the cellulose and other components in the pulper and to disperse it to a non-defined degree in the refiner. Better dispersibility will certainly make it possible to improve the opacity.

2.3 Migration resistance

Inorganic pigments are completely insoluble in water and therefore totally resistant to migration. Problems associated with bleeding, blooming or insufficient solvent resistance, such as can occur when using organic pigments, will not occur at all if inorganic pigments are used. Furthermore, colour changes resulting from partial dissolution of the pigments at high processing temperatures will not occur if inorganic pigments are used.

2.4 Physiological properties

2.4.1 Toxicology

The safety data sheets compiled for each type of pigment include the following data for all inorganic pigments manufactured by LANXESS Deutschland GmbH.

Acute toxicity: LD_{50}, oral, rat > 10,000 mg/kg
Skin and mucous membrane irritation: none

Germany's Senate Commission for testing substances which are hazardous to health reviews the maximum permissible workplace concentration each year. This is the concentration at which no harm to health can be expected (German MAK value). The following values were specified for titanium dioxide and iron oxide in Bulletin XXV (1989) of the Senate Commission:

6 mg/m³ fine dust (< 5 µm)

Titanium dioxide and iron oxide dusts are classified as inert and are neither toxic nor fibrogenic. No MAK values have yet been specified for chrome(III) oxide and mixed phase pigments.

None of the inorganic pigments manufactured by LANXESS Deutschland GmbH are classified as hazardous substances in the context of EC Directive

67/548/EEC and its subsequent amendments. They are not therefore subject to labelling requirements.

2.4.2 Ecology

The fish and bacterial (golden orfe resp. Pseudomonas putida) toxicity of all inorganic pigments manufactured by LANXESS Deutschland GmbH is greater than 1,000 mg/l which is above the maximum permissible test concentration.

Because of the virtual insolubility of the pigments in water, separation can be achieved using any effective filtration or sedimentation process. LANXESS' own test have shown that the pigments can be classified as generally non-hazardous to water (WGK 0 = German water hazard classification).

As all the pigments are virtually insoluble in water, no problems are to be expected with landfill disposal. Nevertheless, the relevant local authority regulations must be observed.

The pigments are also inert when incinerated. Only in the case of pigments containing chrome is partial oxidation to hexavalent chrome possible, depending on the composition of the slag.

3 The use of pigments or extenders

In understanding the reasons for using pigments and extenders, it is important to know the functions they are intended to fulfil. In addition to economic aspects, it is primarily optical considerations which determine the use of extenders. Improvements in the optical properties may increase the degree of whiteness of alter the colour but also produce wider-reaching benefits such as improved printing properties. It may also be the intention to increase the opacity of white paper, i.e. to improve the ability of the paper to hide a substrate of a different colour. This is important in the case of graphic, decorative and photocopying papers. The refractive index n of the extender is of major importance here. The greater the difference between the refractive index of the extender and that of the surrounding matrix (air or binder), the greater the opacity of the paper. The key is therefore the difference between the refractive indices of the extender/pigment and the ambient phase. Extenders usually fulfil the requirements for standard papers. The difference between their refractive index and that of air is sufficient to produce light scattering and, as a result, opacity.

However, if good wet opacity is required, conventional extenders are not sufficient. A product with a higher refractive index is required, e.g. titanium dioxide. The table below shows that paper pigmented with just an extender has no wet opacity.

	Refractive index n	**Difference in refractive compared with binder Δn**	**Wet opacity**
Vacuum/air	0	—	—
Binder e.g. resin, oil, water etc.	1.6	—	—
Cellulose	1.6	0	none
Kaolin	1.6	0	none
Chalk	1.6	0	none
Anatase	2.5	0.9	high
Rutile	2.7	1.1	very high

In contrast, papers pigmented with titanium dioxide have high wet opacity due to the high refractive index of the pigment. For the same reason, they retain their high opacity after impregnation with resins. In such a case, the air is displaced from the paper web. The important factor is therefore the difference between the refractive index of the pigment and that of the ambient organic matrix. The hiding power/opacity or wet-opacity of the papers is raised by the high absorption behaviour with application of Bayferrox® and Chrome Oxide Green pigments also clearly.

Even in the case of very fine printing papers in which only the dry opacity is of importance, the use of TiO_2 is absolutely essential.

4 Pigments in decorative papers

The bulk of the inorganic pigments processed by the paper industry is used to colour decorative papers. The pigments are added directly to the pulp (mass colouring). The decorative papers are later used in laminates or decorative films which are pressed onto chipboard for use primarily in the furniture industry.

The required concentration of white pigments is between approx. 10 and 40 %, calculated on the dry paper. In the case of coloured papers, e.g. those pigmented with Bayferrox®, the pigment concentration is between approx. 10 and 20 %. It is common to use mixtures of these pigments.

There is a large demand for coloured laminates, particularly wood imitations, in which the decorative paper is yellow-brown or red-brown and has a wood-grain print.

Bayferrox® pigments are normally used in this application (see the tabular overview on page 11).

Inorganic pigments have excellent lightfastness in decorative papers and are therefore superior to organic pigments. The same is true of their opacity.

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5 Pigments in standard papers

As mentioned earlier, extenders are sufficient in standard papers where only the whiteness and dry opacity are important. Precipitated silicates such as Baysical® A and Baysical KN can be used in such papers.

However, very thin printing papers (e.g. bible papers) or papers requiring a certain degree of wet opacity require the use of TiO_2 pigments such as anatase or rutile. Cigarette papers also contain TiO_2, e.g. special anatase (supplied with purity certificate). With the exception of cigarette filter papers, which are coloured with Bayferrox® Yellow 920 Z, organic dyestuffs are normally used to colour standard papers.

6 Pigments in paper coatings

Special white papers for printing, e.g. those for calendars, magazines, etc., are often coated. The coating consists of a binder (latex, starch) and an extender (chalk, kaolin, talc). It is similar in composition to an emulsion paint. TiO_2 is rarely used in this application as extenders usually produce the required opacity.

As a rule, unbleached cellulose with a high content of waste paper is used in the manufacture of cardboard and paperboard. These papers are therefore inherently brown or grey. In order to ensure the good opacity of the coating, a TiO_2 pigment must be added. The maximum TiO_2 content is 15 % by wt., calculated on the total weight of the coating.

Adequate optical hiding of the substrate is easier to achieve using rutile pigments than using anatase pigments. This is because the rutile pigment has the higher refractive index - approx. 2.7 compared with approx. 2.5 for the anatase pigment. However, the reducing and hiding power also depend on the particle size distribution, the dispersibility and the degree of dispersion (which may be affected by flocculation) of the pigment in the coating.

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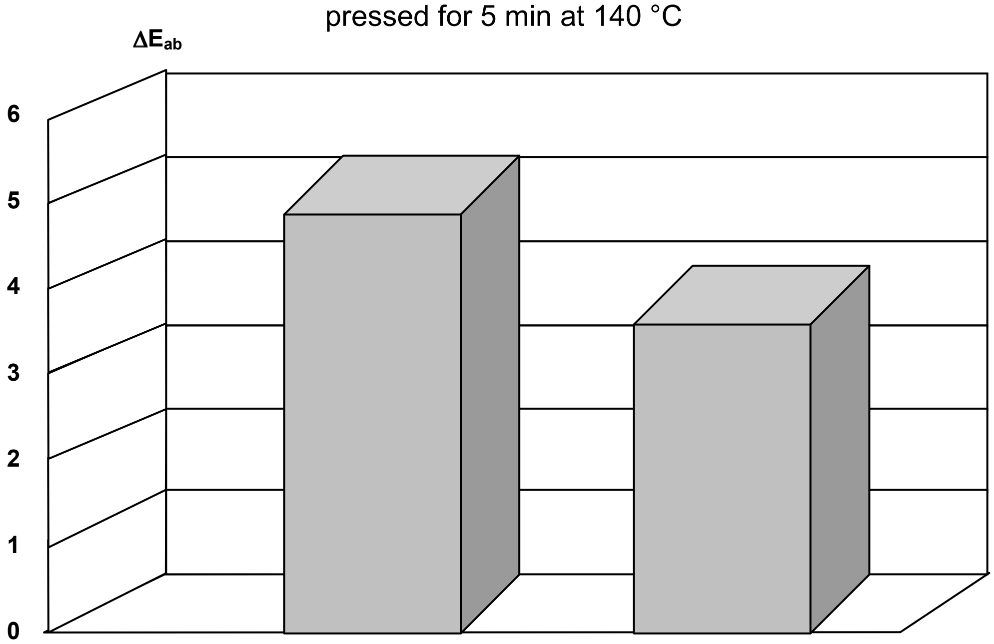
7 Special properties and notes on the use of inorganic pigments in paper

7.1 Pressing temperature stability

Particularly in the case of decorative papers coloured with iron oxide yellow, pressing with melamine resins at temperatures above 140 °C may result in colour changes due to reduction of the trivalent iron. The pressing temperature of these papers should therefore not exceed 150 °C. The pressing time is just as important. A pressing time of less than 90 seconds at approx. 200 °C (short cycle process) may result in less of a colour change than a pressing time of 5 minutes or more at a temperature of 150 °C.

Pressing Temperature Stability
compared against Bayferrox 420,
pressed for 5 min at 140 °C



Bayferrox 420
pressed for
5 min at 180 °C

Bayferrox 420
pressed for 90 s
at 210 °C (short cycle)

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7.2 Lightfastness

Lightfastness (see also section 4) is only of importance in the case of decorative papers which are pressed with melamine resins to produce laminated papers. The lightfastness is determined in accordance with DIN EN ISO 105-B02 (wool scale > 6). As described in section 7.1, the use of Bayferrox® Yellow may result in slight discolouration but this is reversible, as is the case for white laminated papers.

8 The range of LANXESS inorganic pigments and the options for their use in the paper industry

The tabular overview on the next page shows the inorganic pigments from LANXESS suitable for colouring paper and the main applications. The following paragraphs examine the pigment groups in more detail.

8.1 Bayferrox® pigments

In terms of quantity, iron oxide pigments are the leading inorganic colour pigments. They include yellows, reds, browns and blacks. Chemically speaking, iron oxide yellow pigments are needle-shaped iron (III) oxide hydrates. Iron oxide reds are iron (III) oxides and iron oxide blacks iron (II,III) oxides, both with spherical particles. Standard iron oxide brown pigments are mixtures of iron oxide red and iron oxide black and sometimes iron oxide yellow.

Some of the Bayferrox® pigments (see the tabular overview on the next page) can be used to colour paper, particularly decorative papers. Iron oxide pigments are largely inert during processing. The pressing temperature stability and lightfastness of iron oxide yellow pigments must always be tested (see sections 7.1 and 7.2).

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8.2 Chrome Oxide Green pigments

This type of pigment are rarely used in paper because of the cost. Organic pigments are preferred. There are no problems as far as the processing of these pigments in paper is concerned.

Tabular overview

Pigment	Application
Bayferrox® 110, 120, 120 N, 130, 140, 180, TP LXS 5250	All papers
Bayferrox® 420, 1420, 3910, 920, 920 Z, 943, 960	All papers
Bayferrox® 610, 655, 663	All papers
Bayferrox® 306, 318 M, 318 MB, 360, 360 Z	All papers
Colortherm® 10	Lightfast decorative papers with pressing temperature stability
Chrome Oxide Green GN-M	Paper pulp, decorative papers

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LANXESS Deutschland GmbH
Business Unit Inorganic Pigments
Rheinuferstraße 7-9
47829 Krefeld
Germany

Fax +49 2151 88 4133

www.lanxess.com
www.bayferrox.com