German Standard DIN 53 237: Pigments for colouring cement-based and lime-based building materials (Pigments: Quality management and standardization in the light of DIN 53 237, Draft 9/92)

Dr. G. Schöpwinkel (Referent)
R. Tebbe

Bayer AG
Inorganic Products
Marketing Iron Oxide / Technical Service
Germany

0 Summary

DIN 53 237 establishes test methods and requirements to assess whether an inorganic pigment is suitable for colouring cement-based and lime-based building materials.

Pigments intended to colour such materials must satisfy various requirements. These requirements are described in DIN 53 237.

The standard defines specified values for various technical characteristics and fixes the permissible deviations from those values.

The requirements concern the pigment's effect on the properties of the concrete, i.e. its influence on the setting of the cement and on the compressive strength of the mortar, furthermore the effect of the water-soluble matter the pigment contains.

In addition, the requirements concern technical data such as tinting strength, sieve residue, oil absorption pH value, and the main components of the pigment.

In the third place, the standard defines the pigment properties the interested parties are to agree upon: besides the relative tinting strength in cement, the colour stability in cement as well as weather resistance and heat stability.

The paper reports how these pigment properties tend to influence the quality of the coloured concrete.

1 DIN 53 237 - Introduction

With the increased demand for designing and accordingly also for colouring concrete products, the use of pigments in this field has grown steadily. With the increased use of pigments, especially synthetic iron oxides, in colouring cement-bound building materials in particular, the question has also arisen as to whether, besides the usual aggregates, the pigments can have an effect on the properties of the concrete and, if so, what this effect is.

This question is answered by DIN 1045 which describes the pigments used to colour concrete as concrete additives (Section 2.1.3.6).

The suitability of pigments for colouring concrete must then be verified by fulfilling the requirements of a further standard, DIN 53 237 ("Pigments for colouring cement- and lime-bound building materials"). There is no duty to display a quality test mark (DIN 1045, 6.3.2).

DIN 53 237 was first issued in 1977. It defines test methods for determining the suitability of a pigment for use in colouring cement- and lime-bound building materials.

Inorganic pigments are inert concrete additives. Because of their granulometry, they are classified as ultrafine additives or as fines, from the view of the concrete technologist.

DIN 53 237 has been revised with the aim of widening the scope of the tests on pigments and making the tests more stringent (Draft of September 1992). There were four reasons for this - to determine whether the properties of concrete are affected by these additives; to identify and limit the effects; to define the material; and to define the necessary colouristic properties.

2 Test concept and quality verification

In contrast to the existing DIN 53 237 (Edition 2/1977), Draft 9/1992 contains a definitive test concept for determining certain pigment characteristics. The results of the tests are to be verified in the form of a certificate (manufacturer's specific test report in accordance with EN 10204 - 2.3).

2.1 Test concept and requirements

The test concept is based on the following requirements which must be fulfilled in accordance with the standard.

2.1.1 Basic test

The basic test is a test with requirements for individual pigments in their supply forms. It is carried out once a year by an external testing centre appointed by the Institute for Building Technology.

2.1.2 Tests within the framework of production control

Tests within the framework of production control are to be carried out by both the producer and the supplier, if the supplier alters the products supplied by the producer.

2.1.3 Agreed requirements and related tests

These are requirements made of the pigments which must be agreed between the pigment manufacturer (and supplier) and the user.

Three measures are applied to guarantee quality:

- independent testing (basic test)
- own testing (production control)
- controls agreed between supplier and user.

2.2 Explanation of terms

Some explanation of certain terms is necessary.

Individual pigment in the context of the draft standard does not mean each individual pigment in a product range but a typical representative of various product groups. Taking the pigments of the Bayferrox range as an example, either a red, yellow or black pigment could be used. The various red, yellow and black grades differ in their chemical composition and their crystal structure. However, the red, yellow and black pigments in the individual groups are identical in their chemical composition and their crystal structure. It is therefore sufficient to select a typical representative of a group as the individual pigment.

Draft 9/1992 also prescribes that the basic test of the individual pigments must be carried out using the supply form in which the pigment is traded commercially (powder, granules, aqueous preparation).

As the Bayferrox brown grades are physical blends of individual pigments which do not react with each other and have already been tested, there is no need to apply the basic test to the brown pigments. It is the physical blending of the individual pigments which results in the brown pigments.

3 Test scope

3.1 Basic test

Table 1 summarises the requirements made of individual pigments by the basic test. It also shows the test methods to be used.

The following paragraphs describe the pigment properties which are determined by the basic test in order to verify the suitability of a pigment.

3.1.1 Influence of pigments on the compressive strength of mortar after 28 days

The compressive strength of a pigmented sample may be a maximum of 5 % lower than that of an unpigmented sample. The test method used is in accordance with DIN EN 196, Part 1.

3.1.2 Influence of pigments on initial setting

Initial setting should begin a minimum of 1 h after mixing and end after a maximum of 12 h. The difference between pigmented and unpigmented samples should not be more than ± 60 min (DIN 1164, Part 1, 4.2)

These threshold values are still controversial points in the discussion of the final version of the standard. The test method is in accordance with DIN EN 196, Part 3.

3.1.3 Content of water-soluble salts

The total content of salts (including sulphates) is determined. In non-reinforced concrete the content may not exceed 5 % and in steel-reinforced concrete 0.5 %. The test method is in accordance with DIN ISO 787, Part 3.

Limiting the content of water-soluble salts in non-reinforced concrete to 5 % is intended to give the pigment manufacturer the option of modifying the supply form with additives yet to prevent the non-disclosed use of concrete additives.

When using a pigment to colour steel-reinforced concrete, the content of water-soluble halides, including pseudo-halides, is of particular significance. The content of these substances in a pigment may not exceed 0.10 %.

The test method is in accordance with DIN ISO 787, Part 13 or similar.

The content of water-soluble substances in some products of the Bayferrox range is at the limit of the range defined by the standard (see Table).

The values shown in the Table are the results of individual measurements and should therefore be viewed as guide values. Separate tests must be carried out in addition to determine the suitability of the pigments concerned.

Because of the threshold values defined in the Draft, it must be emphasized that pigment preparations

such as granules and suspensions do not usually satisfy the requirements for use in steel-reinforced concrete. This is because the preparations contain auxiliaries needed in their manufacture. These auxiliaries are water-soluble and would result in the threshold values being exceeded.

3.1.4 Composition of pigments

This involves determining the content of the main constituents, e.g. Fe_2O_3, Cr_2O_3 or TiO_2. The test method used must be detailed.

3.2 Tests carried out by the producer and supplier within the framework of production control

3.2.1 Overview of the test scope

As described in Section 3.1, the basic test investigates the effect of certain pigment characteristics on the properties of concrete. Once a pigment has been characterized on the basis of its main constituent, the content of water-soluble salts and the influence of the pigment on the compressive strength of the mortar and on initial setting are determined. This allows conclusions to be drawn as to the basic suitability of the pigment for colouring concrete.

Pigment-specific properties are determined in a second series of tests which must be carried out on each batch (of each supply form) by the manufacturer and the supplier.

As well as determining the content of water-soluble salts, these tests determine the sieve residue, oil absorption, pH and, most importantly, the tinting strength.

3.2.2 Tinting strength/colour

The tinting strength and the colour are the actual properties of a pigment and thus the most important quality criteria. The user of a pigment expects that his products will always be the same colour if he uses the same pigment - provided that his formulation is unchanged. Such important pigment properties must therefore be defined and specified exactly. This has been done with various standards. Visual assessment has now been given considerable support with the use of colorimetry.

The perception of colour is characterized by:

- shade
- lightness
- saturation or purity

The phenomenon of colour can be represented in a three-dimensional system known as the colour space. The light/dark axis is vertical to the shade plane. The further down one moves on this axis, the darker and less distinctive colours become until they reach black.

A similar pattern is seen moving up the axis. The colours become lighter and lighter until they reach white.

The big problem of representing colours in a three-dimensional coordinate system is soon revealed. The human eye is varyingly sensitive to colour differences. Geometrically equal colour differences in the colour space are not perceived as equal by the eye.

Nowadays, the CIELAB System recommended in 1976 by the Commission Internationale de l'Eclairage (CIE) is the most widely used. In all sectors of the CIELAB System, geometrically equal colour differences are roughly equivalent to visually perceived colour differences.

The CIELAB System is a three-dimensional right-angled coordinate system. It consists of a shade plane formed by a red-green (a*) axis and a yellow-blue (b*) axis.

The lightness or L* axis is vertical to the shade plane. A perception of colour can be characterized by the three values L*, a* and b*.

The **colour of a pigment** cannot be determined from the appearance of the pigment powder in its dry state. One and the same pigment can appear quite different depending on its moisture content and the degree of compacting. The pigment must first be dispersed to a defined degree and then fixed. As well as assessing the perceived colour of individual pigments, it is very common to determine the **colour difference** between a pigment and an agreed pigment standard. Both are used under identical conditions to produce blends which are then evaluated colorimetrically to determine the colour difference (ΔE^*).

It is not only the colour of a pigment which is important but its **tinting strength** in particular. The tinting strength is a measure of the ability of a pigment to colour other substances by virtue of its absorption properties. Testing determines the amount of pigment needed to produce the same tinting strength as a reference pigment (standard). As a rule, the lightness (CIELAB lightness L*) is used as the measure of tinting strength. This makes it possible to determine this relative tinting strength which is given as a percentage mass ratio of reference and sample. A pigment which has greater tinting strength than the reference will result in a numerical value above 100 %.

Three special test methods can be used to determine the possible relative tinting strength when colouring cement-bound building materials. Comparison is always against an agreed standard. It may be necessary to adjust the lightness before testing.

1. The relative tinting strength of a **powdered** pigment is measured in a **dry mixture** with a powdered white substance (e.g. heavy spar). The tinting strength is determined by comparing parallel lines of powder after adjustment of the lightness.
2. To test the relative tinting strength of **aqueous pigment preparations** and **granules**, an aqueous slurry of the reduction (pigment + heavy spar) is produced (**wet mixture**). After this has dried, the relative tinting strength is measured in the now powdery samples using the parallel line technique described above.
3. A **wet mixture** is also used to determine the **relative tinting strength in cement**. The sample and reference are both used to make pigmented mortar samples. Once these have hardened, the tinting strength can be assessed visually and colorimetrically.

(Example for colours produced by oxide pigments in mixes with white cement see figure 8.)

3.2.3 Pigment-specific properties dependent on particle size

Characteristic of the iron oxide pigments and also of all other pigments is the phenomenon that many properties are dependent on particle size. This dependency can be seen particularly clearly in properties such as shade, tinting strength, specific surface and oil absorption.

In order for the colouristic properties of a pigment to develop optimally, it is necessary to keep within a certain, very limited particle size range during manufacture. In the case of the Bayferrox red pigments, this range is between around 0.09 and 0.7 µm. The highest and narrowest possible particle size distribution curve is required for a pure shade with high tinting strength.

Particle size is not mentioned in DIN 53 237. It is not suitable as a quality criterion for pigment end-products as it is very difficult to be determined with any accuracy. The primary particle size cannot be determined at all. However, the close relationship between particle size and shade must be discussed here. It is of fundamental importance in a pigment. The dependency of colour and tinting strength on the particle size and particle size distribution can be exploited in the manufacture of, for example, Bayferrox red pigments in order to create various shades of red. The particle size specified and produced during the first stage of manufacture determines the colour of the end-product, i.e. whether it is a yellowish red or violet-red.

This phenomenon can be demonstrated very clearly using Bayferrox red pigments (Bayferrox 110 - 180). As has already been said, these are identical in terms of their composition, crystal structure and particle shape. They differ only in their **particle size** which increases with the product numbers. Electron micrographs reveal the increase in particle size from Bayferrox 110 to Bayferrox 180.

With increasing product number, the oil absorption and specific surface of the pigments decrease. The shades vary from a brick red (110) to a violet-red (180). The tinting strength reaches a peak in Bayferrox 130 and decreases slightly on either side of the peak. 11.

This change in shade occurs with very small increases in the particle size. For example, there are two Bayferrox grades (120 N and 120) between Bayferrox 110 and 130 which have predominant particle sizes of 0.09 µm and 0.17 µm respectively. These have their own property profile and, therefore, measurable colour differences. 12.

3.2.4 Oil absorption

In accordance with DIN ISO 787, Part 5, the oil absorption is defined as the amount of linseed oil absorbed by a pigment sample under specific conditions. In practical application, the oil absorption is the amount of linseed oil needed to work 100 g of pigment powder into a paste which is not quite runny. 5.

Related to the oil absorption and of more significance to the building material industry is the water absorption. This is determined in the same way but using water instead of linseed oil. 4.

The water absorption is a measure of the water requirement of a pigment. This is important in colouring concrete, for example, in the manufacture of aqueous pigment slurries. The higher the water absorption is, the more water is required to maintain a free-flowing suspension.

3.2.5 Sieve residue

When using pigments, it is important to know whether the pigment contains particles which are larger than the others and, if so, what amount. These particles could be contaminants, pigment aggregates or agglomerates. 5.

Pigment agglomerates may form during the pigment manufacturing process. Important stages of the process such as calcination and drying may cause the pigment particles to cake together. These agglomerates must be broken down again by a subsequent grinding process. Determining the sieve residue indicates the efficiency of the grinding process.

The sieve residue is determined by pouring an aqueous slurry of the pigment through a sieve with 45 µm mesh. The residue in the sieve is then rinsed thoroughly. What are left are the coarse particles which cannot be broken down any further. Although these particles would have no effect on the concrete, the efficiency of grinding is important in that a well-ground product is easier to disperse in the concrete than a poorly ground product.

DIN 53 237, Draft 9/1992, specifies a maximum sieve residue of 0.1 % in a sieve with 90 µm mesh. Bayferrox pigments are very fine and therefore easily satisfy this requirement. In their case, determining the sieve residue serves only to identify the presence of any coarse constituents. 4.

3.2.6 pH

The pH of a pigment should be considered in conjunction with its content of water-soluble salts. These have a slightly acidic or slightly alkaline reaction. The measure of this reaction is the pH. 5.

Concrete has a highly alkaline reaction. In comparison, the slightly acidic or slightly alkaline reaction of the pigment is not that important. However, it may have an effect on viscosity in the manufacture of aqueous pigment slurries. If pigments with an acidic pH are used, significant corrosion may result to the iron containers used in mixing the slurries. 4.

3.3 Tests necessitated by agreed requirements

The third part of the test concept detailed in the draft of DIN 53 237 deals with the testing of pigment 13.

properties based on requirements agreed between the pigment manufacturer (and supplier) and the user.

3.3.1 Relative tinting strength in cement

The relative tinting strength in cement is determined in a wet mixture, as described in Section 3.2.2. The test method used must be detailed in a manufacturer's specific test report, if this has been agreed.

3.3.2 Colourfastness in cement

This test is only a rough assessment of the cement resistance of a pigment. It can only be applied to assess pigments used in building materials which will not be exposed to weathering. It must be pointed out that any colour changes (lightening) observed in the test samples may be the result of efflorescence and must therefore be taken into account. In principle, oxide pigments are colourfast in cement due to their material properties.

3.3.3 Weather stability of pigments in building materials

Weather stability should be determined by outdoor weathering tests. Experience has shown that only this test method provides a conclusive evaluation. Accelerated laboratory tests are not sufficient.

As well as this basic principle and the rule that naturally weathered samples should only be compared against unweathered samples, there are a number of other conditions to be observed in outdoor weathering tests. The result of such tests may be affected by a number of factors such as the composition of the concrete, the water/cement ratio and compacting. These must be determined before testing begins. Accurate evaluation of the test samples can only be made once any efflorescence has been weathered away.

The test samples should be placed in a south-facing position at an angle of 45 °. A further important factor is the weathering duration.

Testing at one location only provides a reliable conclusion about weathering behaviour at that location. To enable a generalized conclusion to be made, the samples must be tested at various locations with different climates (industrial/marine climate). Bayer therefore operates various outdoor weathering stations, one near its production facilities. It also has one near the North Sea coast of the Netherlands. The samples used are extruded concrete roof tiles. Their smooth and homogeneous surfaces allow accurate colorimetric determination of colour differences during the course of weathering. Concrete pavers are also tested in the same way. The only problem here is that they are placed under little or no mechanical stress by pedestrians or traffic as they would be in actual use.

Bayferrox pigments are weather-stable. Organic pigments in particular and also carbon black pigments fade after outdoor weathering. Organic pigments are therefore not covered by this standard.

3.3.4 Heat stability

Given their chemical composition and structure, the pigments are fundamentally heat-stable. However, it is still necessary to determine the heat stability if it is to be expected that the thermal load during the manufacture and later use of the pigmented material will be above normal levels (80 - 100 °C). The determination of this property must then be agreed.

This is likely in the case of some building materials, for example, in the manufacture of sand granules for concrete roof tiles or in the production of fibrous cement slabs or calcium silicate bricks. These are hardened in saturated water vapour at temperatures of up to around 200 °C.

In the light of the facts just mentioned, one limitation must be mentioned as far as black iron oxide

pigments are concerned. Their heat stability is already exceeded at such high temperatures. Expensive special grades must be used for these particular applications.

4 Bibliography

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Dr.-Ing. Gert Schöpwinkel
Roland Tebbe

Bayer AG
Werk Uerdingen
Anorganische Industrieprodukte
Marketing Eisenoxid/Technik
Rheinuferstraße 7 - 9
D-47829 Krefeld

Telefax: (0 21 51) 88-41 33

Compressive strength of mortar after 28 days	maximum of 5% lower than that of the unpigmented sample		DIN EN 196 part 1
Influence of pigments on initial setting - Setting start - Setting end Tolerance of the setting start between pigmented and unpigmented samples	min. of 1h (after mixing) max. of 12 h not more than +/- 60 min.		DIN EN 196 part 3
content of watersoluble salts	non-reinforced concrete	steel-reinforced concrete	
- total content including sulphates	max 5.0%	max. 0.5%	DIN ISO 787 part 3
- water-soluble halides, including pseudo-halides	---	max. 0.1%	DIN ISO 787 part 13
Content of the main constituents, e.g. content of Fe_2O_3	Values corresponding to the actual state of the analysis methods		

Fig. 1 **DIN 53 237 (Provisional Draft 9/92)**
The Requirements individual Pigments have to meet in order to satisfy the Basic Test Methods.

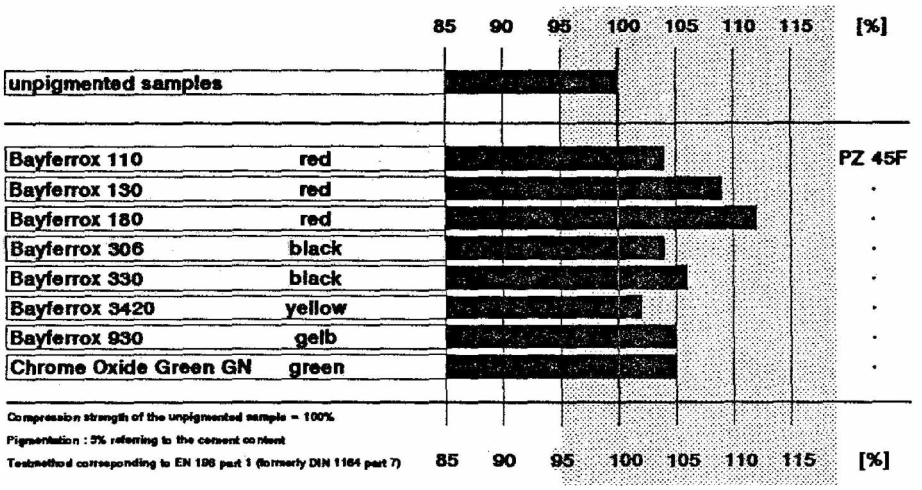


Fig.2 **Influence of the Pigmentation on the Compressive Strength**

Pigment	Colour	Initial setting time start (difference values)	Initial setting time end (difference values)	Water-soluble components (total) [%]	Main constituents
Bayferrox 110	red	– 20	+/– 0	0,11	95,8 % Fe203
Bayferrox 130	red	– 25	– 10	0,08	96,3 % Fe203
Bayferrox 180	red	– 10	– 20	0,09	97,1 % Fe203
Bayferrox 222	red	+/– 0	+ 15	0,18	95,5 % Fe203
Bayferrox 3420	yellow	– 15	+ 5	0,31	86,3 % Fe203
Bayferrox 930	yellow	+/– 0	+ 20	0,31	86,3 % Fe203
Bayferrox 306	black	– 10	+ 10	0,40	95,4 % Fe203
Bayferrox 330	black	+ 5	+ 25	0,81	93,1 % Fe203
Bayer Titan A	white	– 35	+ 5	0,25	97,2 % Ti02
Chrome Oxide green GN	green	– 10	+ 5	0,25	99,0 % Cr203
180 : 3420 : 306 1 : 1 : 1	--------	– 25	– 30	-----	--------
110 : 930 : 330 1 : 1 : 1	--------	– 25	– 5	-----	--------
		DIN EN 196 part 3		DIN ISO 787 part 3	dör 1377e/94

Fig.3 **Results of Production Control**

Pigment	Colour	Water-soluble components				Pigment technical data		
		total [%]	sulphate [%]	chloride [%]	I; Br; F; Thiocyanate Cyanate	sieve residue [%]	oil absorption [ml/100g]	pH
Bayferrox 110	red	0,11	<0,01	0,0050	not	0,002	30	7,3
Bayferrox 130	red	0,08	<0,01	0,0050	traceable	0,020	27	7,9
Bayferrox 180	red	0,09	<0,01	0,0030	I	0,004	20	7,7
Bayferrox 222	red	0,18	0,08	0,0050	I	0,007	20	7,9
Bayferrox 3420	yellow	0,31	0,03	0,1100	I	0,001	32	4,8
Bayferrox 930	yellow	0,31	0,14	0,0340	I	0,002	68	5,4
Bayferrox 306	black	0,40	0,03	0,0960	I	0,020	20	4,4
Bayferrox 330	black	0,81	0,04	0,0750	I	0,030	25	4,6
Bayer Titan A	white	0,25	<0,01	0,0011	I	0,030	19	7,0
Chrome Oxide green GN	green	0,25	0,13	0,0047	V	0,003	16	5,9
180 : 3420 : 306 1 : 1 : 1	----------	-----	-----	-----	----------	-------	23	-------
110 : 930 : 330 1 : 1 : 1	----------	-----	-----	-----	----------	-------	35	-------
		DIN ISO 787 Teil 3			DIN ISO 787 part 13	DIN 53 195	DIN ISO 787 part 5	DIN ISO 787 part 9

Fig.4 Results of Production Control

Pigment properties	Requirements		Testing to
Relative tinting strength dry mixture wet mixture	100 +/- 5%		DIN 55 913
Water-soluble components	non-reinforced concrete	steel-reinforced concrete	DIN ISO 787 part 3
Total content including sulphates Water-soluble halides including pseudo-halides	max. 5.0% ----	max. 0.5% max. 0.1%	
Absorption	Deviation from standard not more than 15%		DIN ISO 787 part 5
Sieve residue (45 µm Sieve)	max. 0.1%		DIN 53 195
pH	+/- 2		DIN ISO 787 part 9

Fig. 5

DIN 53 237 (Provisional Draft)
The Requirements for Pigments in their delivered Form and applied Test Methods.

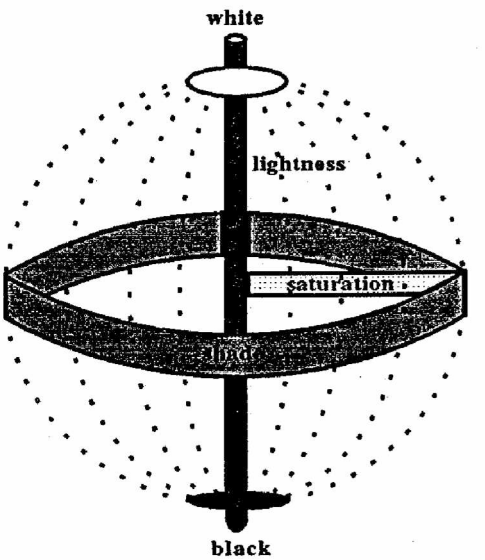
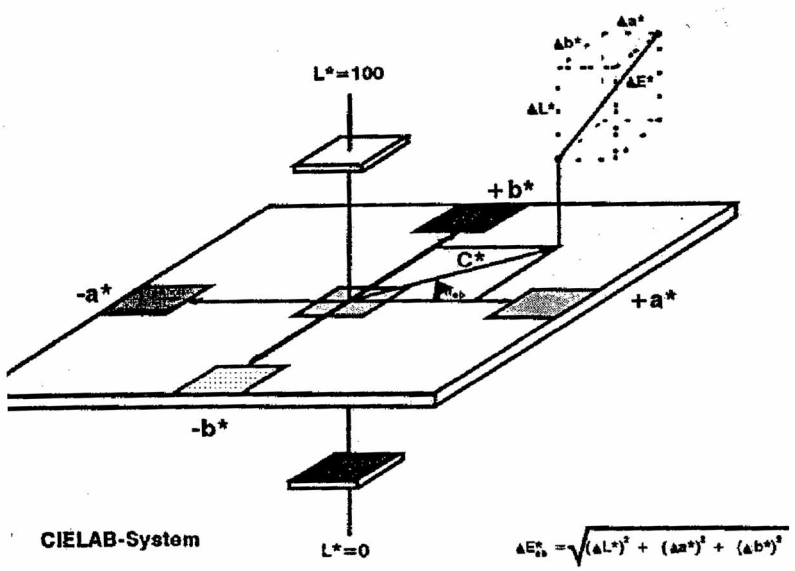


Fig.6 Three-dimensional Colour System



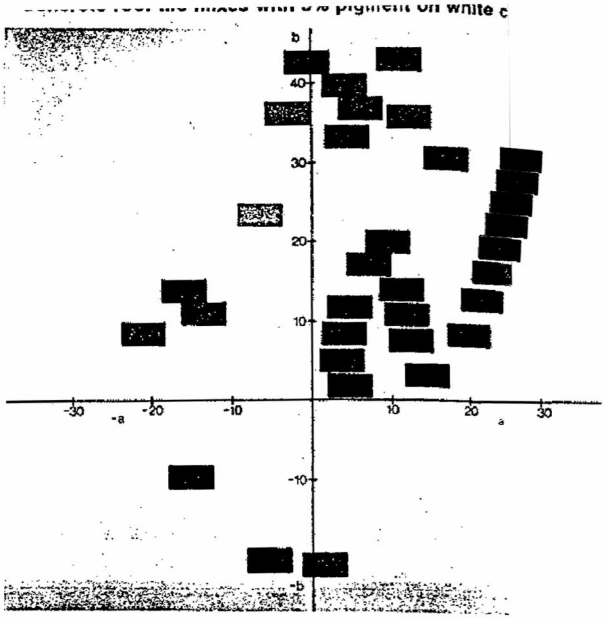


Fig.8 Colours produced by Oxide Pigments (CIELA

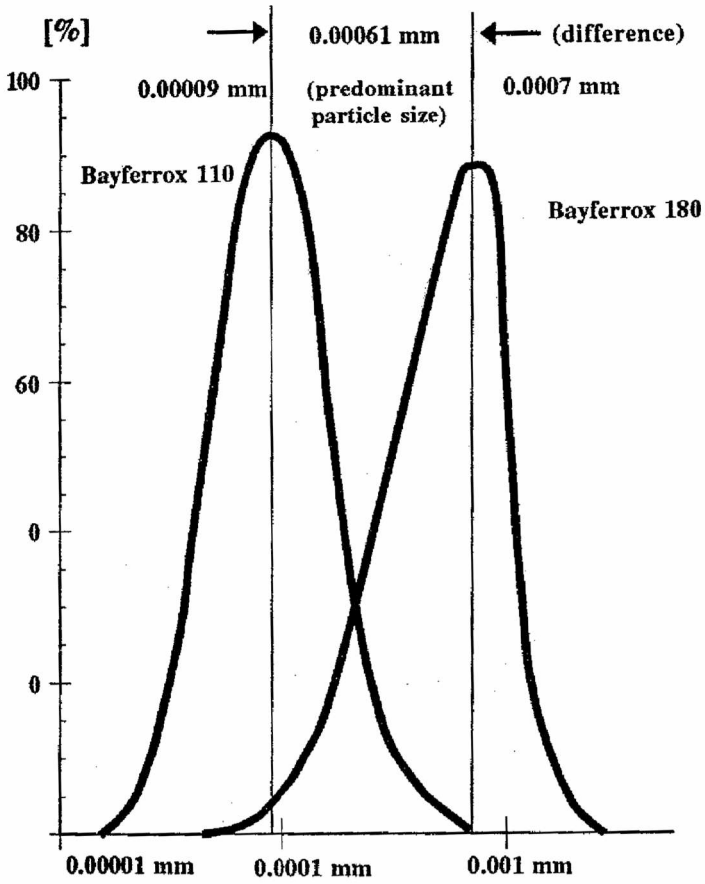


Fig.9 Particle Size Distribution

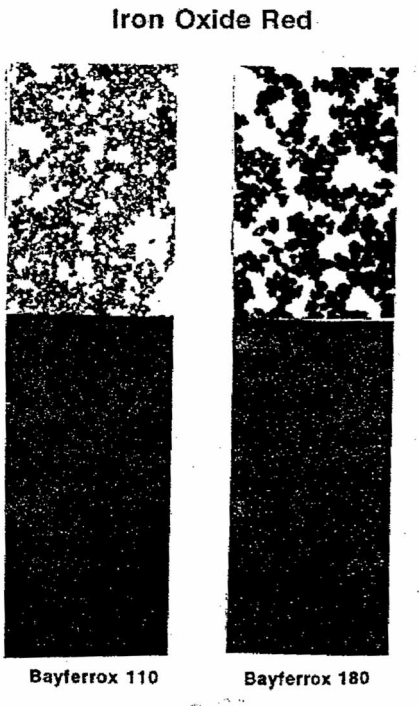


Fig. 10 The Dependence of the Shade on the Particle Size

Bayferrox Red	110	120N	120	130	130B	140	160	180
Predominant particle size [µm]	0,09	0,11	0,12	0,17	0,22	0,30	0,40	0,70
Shade	yellow-red →							violet-red
Tinting strength	← decreasing →							
Specific surface	→ decreasing →							
Oil absorption	→ decreasing →							

Fig.11 Bayferrox-Red-Pigments

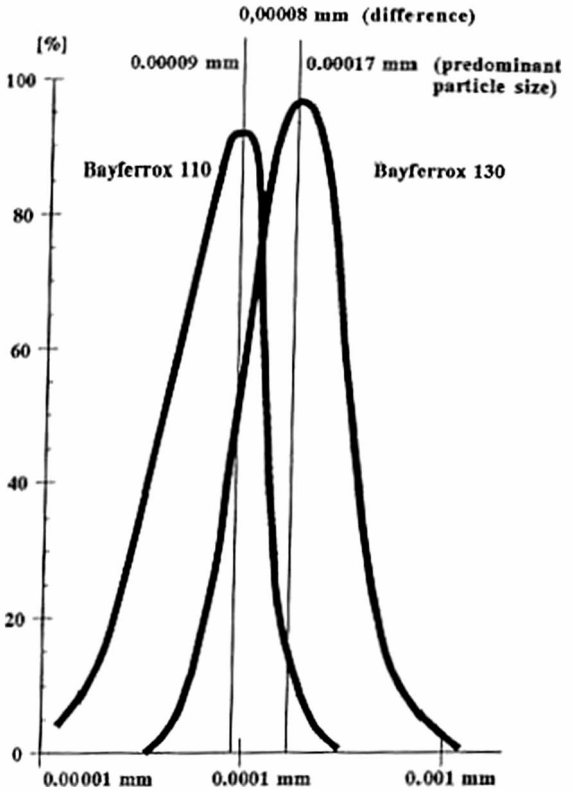


Fig.12 Particle Size Distribution

Pigment properties	Requirements
Relative tinting strength in cement (with regard to the standard)	100 +/- 5%
Colourfastness in cement	The stability of the pigment with regard to the colour and the influence of the temperature must be obtained under the schedule of application conditions. The required details have to be agreed upon between the interested parties.
Weather stability	
Heat stability	

Fig.13 DIN 53 237 (Provisional Draft 9/92)
Test Methods and Properties to be agreed upon.



Fig.14 Weathering Station Krefeld (Concrete Roof Tiles)

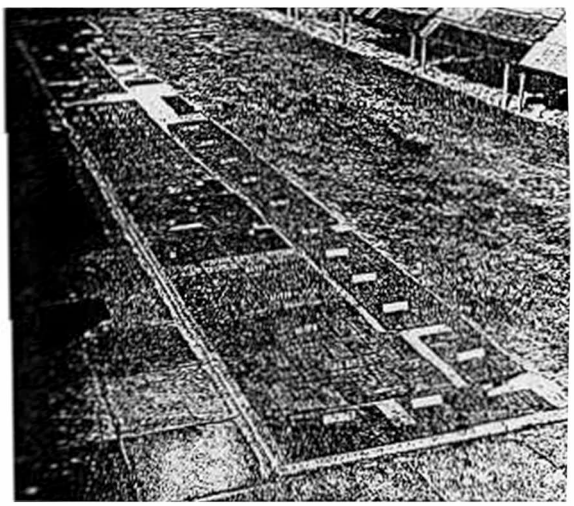


Fig.15 Weathering Station Krefeld (Concrete Pavers)



Fig.16 Weather Stability of Inorganic Pigments

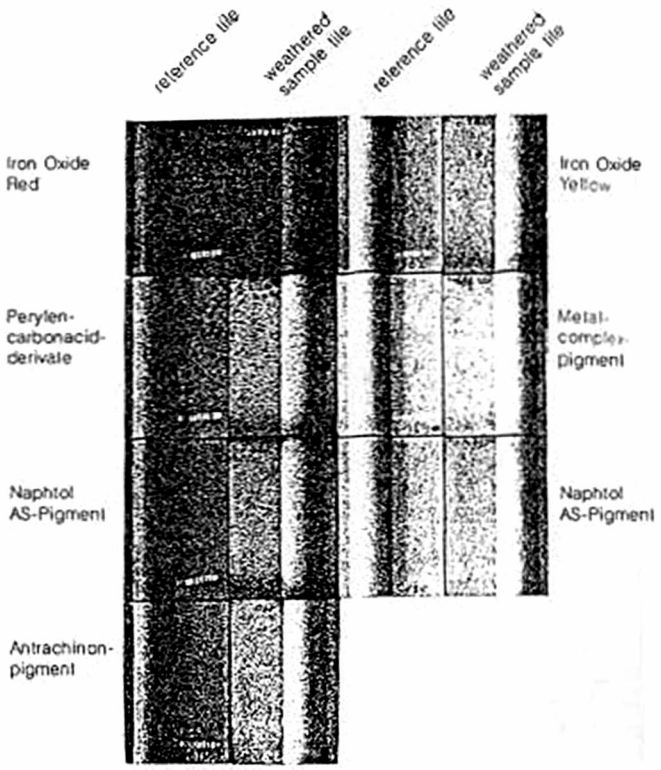


Fig.17 Weathering of Different Pigments (Krefeld, 21 months)