Inorganic Pigments

LANXESS

Technical Information
Competence Center Construction

Edition: May 2002
Replaces edition: July 1998

The Manufacture of Colored Sand Using Inorganic Bayferrox® Pigments

1 Introduction

Colored sand is mainly used to dress the surfaces of roofing materials. This not only produces an attractive, rough surface texture but creates a colorful appearance.

This technique is primarily used on concrete roof tiles. Bituminous roof felt too is often colored by scattering colored sand onto the still warm and tacky surface.

Since the roofing materials mentioned, particularly the concrete roof tiles, are very durable, the colorfastness of the colored sand used must be correspondingly high. This is not only dependent on the lightfastness and weather stability of the pigments but also on the resistance of the binder used to fix the pigment to the sand particles. As a rule, organic binders do not satisfy the requirements specified so inorganic binders are nearly always used nowadays.

This publication describes the manufacture of colored sand, the suitable pigments and the properties of the finished product. In this case, sodium silicate is used as the binder but other substances may also be used.

2 The manufacture of colored sand

2.1 Raw materials

2.1.1 Pigments

The pigments which should be used in the manufacture of colored sand must have the following properties:

a) lightfastness and weather stability
b) alkali resistance
c) thermal stability

These requirements are satisfied by a number of metallic oxide pigments, as shown in Table 1:

Table 1: Range and chemical composition of inorganic Bayferrox® pigments for the manufacture of colored sand

Color	Suitable-product	Chemical composition
Red	all Bayferrox® red grades	α-Fe_2O_3
Brown	Bayferrox® 645 T	mixed phase $(Fe, Mn)_2O_3$
Black	Bayferrox® 303 T	mixed phase $(Fe,Mn)_2O_3$
Yellow	Colortherm 3950	zinc ferrite
Green	Chrome Oxide Green GN, GX	α-Cr_2O_3

These pigments are chemically stable at temperatures of 1,000 °C and above. There may be some color change at temperatures above 800 °C as the result of particle size increase (see Section 3).

Bayferrox® 110 and 130 are particularly recommended because they can be used to create the brick-red shade most frequently required.

2.1.2 Sand

The purest possible quartz sand is normally preferred for the manufacture of colored sand. Of course, normal river sand can also be used, provided the particles are the right size. It must be remembered that this type of sand contains a certain proportion of iron oxide and will turn reddish brown at the necessary firing temperature. This has a negative effect on the final shade of the colored sand (mixed color). Sand containing carbonates such as calcite or dolomite should never be used because the carbonates decompose at the firing temperature to form carbon dioxide with calcium and magnesium oxide respectively.

Edition: May 2002
Replaces edition: July 1998

The Manufacture of Colored Sand Using Inorganic Bayferrox® Pigments

The particle size is selected according to the application. In order to obtain the right color effect, it must be ensured that the sand is well-bonded to the carrier material (cement slurry, bitumen layer) but that it does not sink in too deep. If the sand is too coarse, it will not sink deep enough into the carrier material and the bond will be relatively poor. The most suitable particle sizes for most applications are between 0.5 and 1.2 mm. It is of no great importance whether the sand particles are round or broken.

2.1.3 Binder

As was already mentioned in the introduction, inorganic binders are ideal for the manufacture of colored sand, both in terms of weather stability and price. The most frequently used binder is sodium silicate because it is inexpensive. However, mono-aluminium phosphate (refractory binder) is also suitable. At high temperatures both these binders form highly polymeric, glass-like compounds in which the pigment is embedded and fixed onto the surface of the sand. The resultant weather stability is dependent on the firing temperature, the firing time and the binder content. This will be discussed further in Section 4. Generally speaking, 2 to 3 % binder (calculated on the weight of the sand) is used.

2.2 Manufacturing process

The manufacture of colored sand is divided into three stages:

2.2.1 Mixing

The sand, pigment and binder are mixed in a standard forced circulation mixer, such as is commonly used in the concrete industry, with a capacity of 150 to 250 liters. The sand is weighed into the mixer. The weighed pigment is added with the mixer running. The correct amount of binder is then added as well. However, no difference has been observed if the binder is added before the pigment. The composition should be mixed for 3 to 5 minutes. Longer mixing is more of a disadvantage than an advantage. The addition of 1 to 1.5 liters of water for every 100 kg of sand is recommended if the sand is air-dry. This results in better distribution of the pigment on the surface of the sand particles as the amount of liquid added with the binder is very low. If the sand is too wet, however, too much binder and pigment will stick to the walls of the mixer and the pigment will be distributed unevenly on the surface of the sand particles. It is therefore best to work with air-dry sand as the moisture content is easier to control. Sodium silicate is highly alkaline. Safety regulations should be observed during manufacture and workers should wear safety goggles and protective gloves.

2.2.2 Firing

In order to ensure the weather-stable bonding of the pigment to the sand particles, the inorganic binder (sodium silicate or mono-aluminium phosphate) must be fired at temperatures between 600 and 1,000 °C. Directly heated rotary kilns (oil-fired) are suitable for this purpose. The mixture produced as described in Section 2.2.1 is best transferred to the kiln using a screw conveyor and via a buffer silo. It is ideal if, before it actually reaches the kiln, the mixture can be pre-dried with the hot exhaust gases as it is moved along. This improves the flow properties and thus the flow rate of the mixture and is particularly recommended when using small rotary kilns with a length of about 5 m.

The size of rotary kiln used depends on the amount of colored sand to be produced. Generally speaking, kilns between 5 and 10 m in length and 0.8 to 1.2 m in diameter are used. The larger the kiln, the easier it is to control and the more evenly the sand is fired. Because a firing temperature of around 900 °C is necessary to produce weather-stable colored sand, as will be discussed in Section 4, the kiln used should be capable of producing a maximum temperature of 1,000 °C. The flow rate is governed by the length of the kiln, the angle of incline and the speed at which it rotates. The dwell time of the colored sand between entering and leaving the kiln can be regulated by adjusting these parameters and should be at least 5 minutes, with the sand exposed to the maximum firing temperature for 2 to 3 minutes. Temperature measurement is essential to ensure the weather stability and even color of the sand. A temperature sensor should be fitted close to the kiln exit where the maximum temperature is reached. It should measure the temperature in or directly above the sand to give an exact value for the effective temperature of the moving sand. It is to be expected that some of the sand will stick at the exit of the kiln. The kiln should be open so the stuck sand can be removed, e.g. with an iron bar. A more elegant method is to fit a water-cooled stripper device. The burner must be operated with a surplus of air so that there is an oxidizing atmosphere in the kiln. The color of iron oxide and iron oxide/mananese compounds may alter in a reducing atmosphere.

2.2.3 Cooling and storage

As a rule, the colored sand has a temperature of about 900 °C when it leaves the kiln. Since sand has a relatively high thermal retention capacity, it must be cooled before storage. This can be done in two ways. The sand can be passed through a water-cooled cooling drum mounted adjacent to the kiln exit. Alternatively it can be passed along vibrating steel troughs where, because of the relatively thin layer formed, it cools fairly quickly through contact with the ambient air. There are also two ways of storing the sand. It is cheapest and easiest to store in open boxes. A more elegant but more expensive option is to transfer the cooled sand by means of elevators or other conveyor systems into storage silos. The sand can then be withdrawn as required and transported to the site where it is needed.

3 The relationship between shade and pigment concentration and firing conditions

3.1 Pigment concentration

The amount of pigment added is calculated as a percentage of the weight of the sand used. As sodium silicate and mono-aluminium phosphate binders are colorless, it is the opacity of the pigment rather than its tinting strength which are important although there is, of course, a close relationship between the opacity and tinting strength of inorganic color pigments. Optimum coloring is achieved if the pigment embedded in the binder completely covers the surface of the sand particle. In the case of the pigments listed in Table 1, this is usually the case with a pigment concentration of 2 to 3 %. If the pigment concentration is lower, the sand particle will not be completely covered and the white sand will show through. The result is that the final color appears paler. Moreover, the pigment first fills the irregularities in the surface of the sand particle before covering the entire surface.

3.2 Firing temperature and time

As will be discussed further in Sections 4.2 and 4.3, the firing temperature and time have a significant influence on the adhesion of the pigment to the sand particles. It is only at a temperature of around 900 °C that a weather-stable sodium silicate layer is formed. Furthermore, it is in the range of 850 to 1,000 °C that the final shade of the colored sand is most affected by the firing temperature and time. Our investigations have found that this is particularly true of the iron oxide reds and of Bayferrox® 645 T whereas there is a less pronounced change in color when using chrome oxides and Bayferrox® 303 T.

This color change is not caused by a chemical change in the compounds on which the pigments are based but by an increase in the size of the pigment particles. Darker shades result from this particle size increase - the shade produced with iron oxide red, for example, becomes bluer. If the temperature is very high (above 1,000 °C) or the firing time very long, the sand will appear very black and metallic (overfired). The firing temperature and time must therefore be kept as constant as possible to ensure evenly colored sand. The relationship between shade and firing temperature can be exploited to vary the nuance of color produced by a single pigment. This is possible within certain limits and without any great effect on the adhesion of the pigment to the sand (see also Section 4.2). However, temperatures above 900 °C are critical as the sodium silicate layer begins to soften and the sand near to the burner (maximum temperature) tends to stick to the kiln walls. This should be avoided as far as possible or a stripping device should be fitted. The reasons for this are not only technical. The sand which sticks to the kiln walls has a longer dwell time in the kiln than the bulk of the sand which passes through normally. By the time it leaves the kiln, having fallen from the walls as the result of the kiln's rotation or been removed by some other method, these particles are darker in color and show up as dark flecks in the sand. It is therefore necessary to reach a compromise between firing temperature, achievable adhesion and shade. It should be remembered that the shade can also be influenced by adding other pigments. It has been found in practice that firing at a temperature of around 900 °C largely prevents any of the problems described above. Good adhesion is achieved and the required weather stability of the colored sand is therefore ensured.

4 Adhesion of the pigments on the surface of the sand

4.1 Test methods

The only way of testing the adhesion of the pigments to the sand particles in relation to various parameters (firing temperature, binder content and firing time) is by accelerated testing. Although the results of most accelerated tests do not correlate exactly with the results of outdoor weathering, they are a very good way of establishing what relationships exist and of indicating what behavior might be expected on exposure to outdoor weathering.

The usual adhesion test involves soaking the colored sand briefly (approximately 10 minutes) in boiling, diluted acid (hydrochloric or acetic acid) or sodium hydroxide solution and then assessing the solution to see whether if it has been discolored by dissolved pigment. Our investigations have shown that reliable results can also be obtained by boiling the sand for 1 hour in pure water. The amount of pigment which dissolves, calculated as a percentage of the original amount used, can then be plotted in relation to the parameters (firing temperature, binder content and firing time). However, as it is generally not possible to assess the quantity of pigment dissolved, the durability of the colored sand can be tested in the following way. Water attacks sodium silicate which has been fired at too low a temperature and has not polymerized or silicified fully. Some decomposes to form sodium hydroxide and aqueous silicic acid. The curve shown in **Figure 1** is obtained by plotting the pH values of the water after boiling samples of colored sand fired for 3 minutes at various temperatures. This curve shows a characteristic drop from pH 10 (alkaline) to pH 6 (slightly acidic) between 800 and 900 °C. The conclusion from this is that sodium silicate fired at a temperature of 900 °C or above is not vulnerable to attack. Nowadays, pH measurements are very easy to take using indicator paper. It can be assumed that the colored sand is weather-stable if a pH of 6 to 7 and no or only slight discoloration is observed after the accelerated test described above. Slight discoloration is usual in most cases because not all of the pigment is wetted with sodium silicate during mixing and because the firing and rapid cooling processes cause a certain degree of abrasion, resulting in the presence of a certain amount of pigment dust. As pigments are very fine, just a small amount produces noticeable discoloration, although there is no decrease in pigment content. If severe discoloration is observed despite a neutral pH, insufficient binder was used. This is discussed further in Section 4.4.

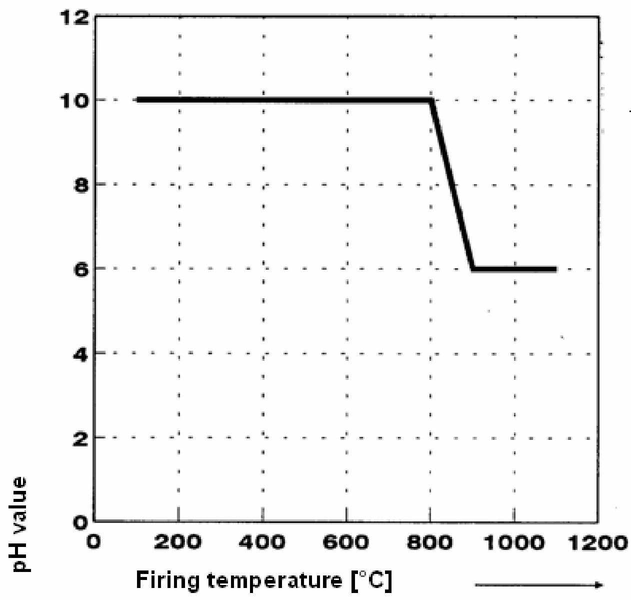

Figure 1

pH values of the water in relation to the firing temperature after accelerated testing

Inorganic Pigments

Technical Information
Competence Center Construction

Edition: May 2002
Replaces edition: July 1998

The Manufacture of Colored Sand Using Inorganic Bayferrox® Pigments

4.2 The influence of the firing temperature

As has already been mentioned several times, the firing temperature is a decisive factor in the weather stability of colored sand. The relationship between the adhesion of the pigment and the firing temperature is shown by the three examples in **Figure 2**. The following formulation was used.

100 kg	quartz sand
2.5 l	sodium silicate, density = 1.35 (38 - 40 °Bé)
1.5 l	water
3 kg	pigment

Firing time: 3 minutes at the temperatures specified

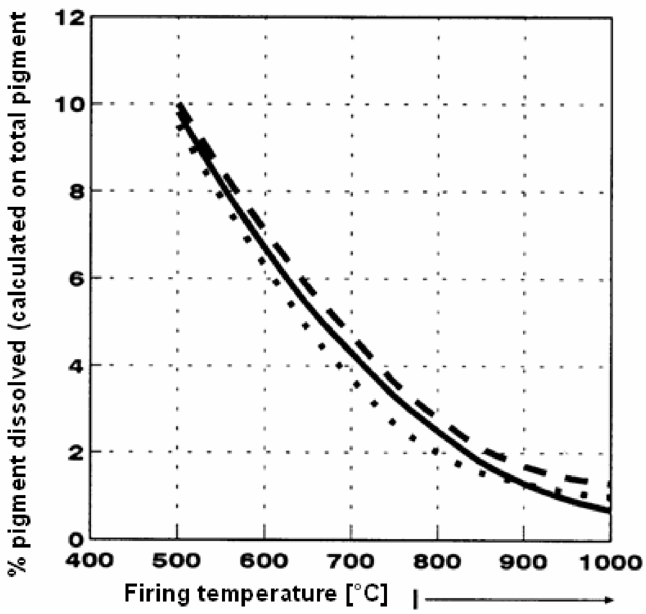

Figure 2

Adhesion of various pigments in relation to the firing temperature (firing time: 3 minutes)

The tests documented in **Figure 2** showed that there was a marked improvement in adhesion up to around 900 °C. No significant further improvement was achieved at temperatures above this. In principle it can be said that if the amount of pigment dissolved in the accelerated test described above is 2 % or less, the sand will have very good weather stability and colorfastness in outdoor weathering tests. The largest proportion of dissolved pigment consists of lightly fixed pigment dust particles. If the colored sand samples are boiled for a second time in water, it will be seen that virtually none of the pigment dissolves.

4.3 Influence of the binder content

Each pigment requires a certain amount of binder to wet its surface and to ensure that it is completely embedded in the binder film. The amount of binder required depends on the surface of the pigment, the surface structure and the particle shape. **Figure 3** shows the adhesion of the pigment in relation to the firing temperature and the binder content (1, 2 and 4 liters of sodium silicate for every 100 kg of quartz sand with 3 kg of Bayferrox® 110).

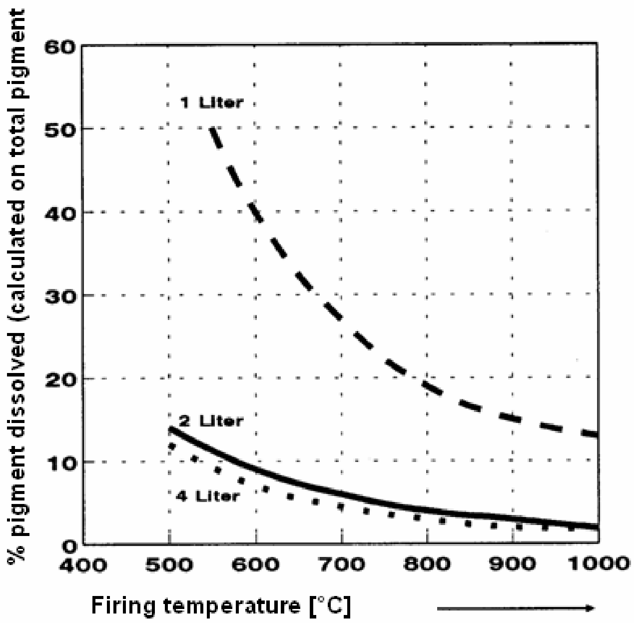

Figure 3

Adhesion of Bayferrox® 110 in relation to the sodium silicate content (litres per 100 kg quartz sand) and the firing temperature (firing time: 3 minutes)

The firing time was again 3 minutes at the temperatures specified. The results show that 1 liter of the binder is not sufficient to bind the pigment and produce a weather-stable product. 2 liters of binder is the absolute minimum. However, doubling this amount produces no significant improvement. To be on the safe side, the formulation should be made up using about 2.5 liters of sodium silicate for every 100 kg of sand. If too much binder is used, there is the risk that the sand will become tacky after firing. Of the pigments normally used in the manufacture of colored sand (Bayferrox® 110, 120 and 130, Bayferrox® 645 T, Colortherm 3950, Bayferrox® 303 T and Chrome Oxide Green GN), all require the same as or slightly less binder than Bayferrox® 110. Therefore, a binder content of approximately 2.5 liters can be assumed to be the optimum unless the pigment concentration is increased which, given the comments made in Section 3.1, makes little sense. However, it should be ensured that the correct sodium silicate concentration is used. The statements here apply to sodium silicate with a density of 1.35 (38 - 40 °Bé). On the question of sodium silicate, tests of the products available on the market have shown that the best results are obtained using a compound with the density specified.

4.4 Influence of the firing time

It goes without saying that the firing time, i.e. the dwell time at a given temperature, also influences adhesion. However, as can be seen from **Figure 4**, the influence of the firing time at a high temperature (900 °C) is significantly smaller than at a lower temperature (750 °C).

At this lower temperature, an increase in the firing time produces a significant improvement in adhesion. Good results can therefore also be achieved with a firing time of approximately 10 minutes at 750 °C. However, the alkaline reaction of the water in which samples of the sand fired at 750 °C were boiled for 1 hour shows that the sodium silicate is attacked. Despite the small amount of pigment dissolved from the sand with a longer firing time, the results in outdoor weathering are not expected to be so good as for sand fired at a temperature of 900 °C or above.

Edition: May 2002
Replaces edition: July 1998

The Manufacture of Colored Sand Using Inorganic Bayferrox® Pigments

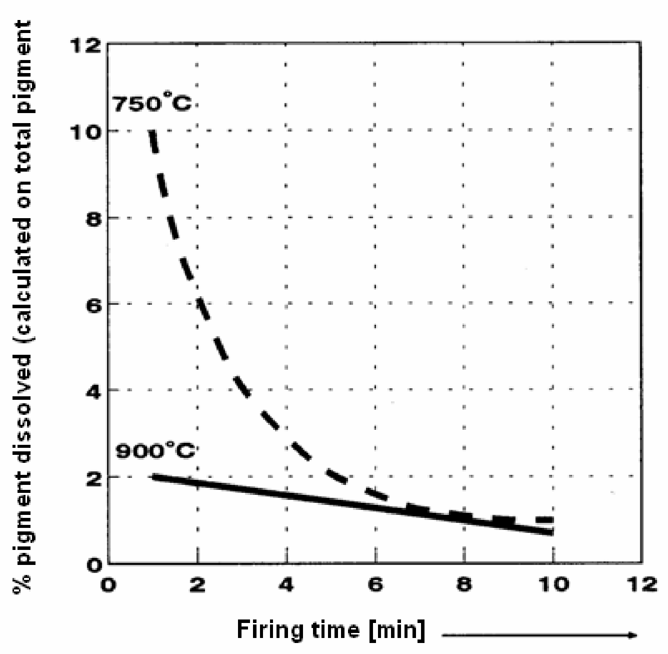

Figure 4

Adhesion in relation to the firing time at 750 °C and 900 °C

5 Guide formulations

5.1 Sodium silicate

100 kg	sand
2.5 l	sodium silicate, density = 1.35 (38 - 40 °Bé)
1.5 l	water
1 - 3 kg	pigment

Firing temperature: 900 °C / 3 minutes

5.2 Mono-aluminium phosphate (refractory binder)

100 kg	sand
0.9 l	refractory binder (50 % solution), density = 1.5
0.7 l	water
1 - 3 kg	pigment

Firing temperature: 300 - 600 °C / 15 minutes

5.3 Sodium silicate and zinc oxide

100 kg	sand
3.7 l	sodium silicate, density = 1.35 (38 - 40 °Bé)
0.8 l	potassium silicate, density = 1.25
0.8kg	Zinc Oxide Active
1 – 3 kg	pigment

Firing temperature: 250 °C / 30 minutes

LANXESS Deutschland GmbH
Business Unit
Inorganic Pigments
D-51369 Leverkusen