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(54) IRON-CONTAINING MICA FLAKE PIGMENTS

(71) We, MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG, of 250, Frankfurter Strasse, 61 Darmstadt, Federal Republic of Germany, a Joint-Stock Company organised under the laws of the Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with new iron-containing mica flake pigments and with the production thereof.

It is known that lustrous pigments are obtained when mica flakes are coated with titanium dioxide or zirconium dioxide and/or iron oxides. Such pigments are described, for example, in British Patent Specifications Nos. 974,874 and 1,268,177. However, these pigments are not sufficiently light-stable so that their use in many fields is very considerably restricted. The previously known iron oxide-containing mica flake pigments are also not completely satisfactory with regard to the possible colour variations.

We have now found, surprisingly, that very light-fast and temperature-stable mica flake pigments, some of which possess hitherto not achievable colours, are obtained when homogeneous iron-containing layers are applied to the substrates in the form of magnetite or of α -, β - or γ - ferric oxide hydroxide or of α - or γ - ferric oxide (Fe_2O_3).

It was not to have been foreseen that, in this way, completely new types of pigments can be produced which are characterised by outstanding light-fastness and a surprising breadth of variation of the colour nuances. Such pigments have hitherto not been produced and their properties cannot be deduced either from the known properties of mica flakes or of mica flakes coated with titanium dioxide and/or zirconium dioxide or from those of the known iron oxide and iron oxide hydroxide modifications. It could not have been foreseen that from the interplay between the mica substrate and the layers, homogeneous layers of the above-mentioned forms of iron oxide and iron oxide hydroxide would give these advantages. In principle, it cannot be foreseen which modification of a compound is formed when it is deposited on another. The influence of the substrate is usually decisive for the modification produced. For example, the behaviour of titanium dioxide aquates on mica is characteristic. Titanium dioxide occurs in several modifications. However, the mica substrate forces the titanium dioxide into the anatase form, even in those temperature ranges in which the conversion into the rutile form has normally long since taken place. Only when it is possible to weaken the influence of the mica surface in the case of coating with titanium dioxide by coprecipitation of, for example, tin dioxide, is it possible to ensure the formation of titanium dioxide in the rutile form. Therefore, in the case of the system iron oxides or iron oxide hydroxides on mica, it also cannot be predicted which modification will be formed, even when using the processes which are known for the production of particular iron oxide or iron oxide hydroxide modifications. It is also fully unforeseeable whether these known processes would even lead to a suitable coating and what properties would be obtained, in the case of a successful coating, for the layers formed.

The light fastness of the new pigments according to the present invention is sur-

prisingly great. Even the pigments based on mica flakes coated with titanium dioxide or zirconium dioxide, previously known to be very light stable, are further substantially improved in their light stability by the coating according to the present invention.

Thus, according to the present invention, there is provided an iron-containing pigment based upon mica flakes or on mica flakes provided on both sides with a coating of titanium dioxide and/or zirconium dioxide or of a hydrate thereof, said coating adhering to the mica flakes, wherein the iron-containing layers, provided on both sides of the flakes, consist homogeneously of magnetite or of α -, β - or γ -ferric oxide hydroxide or of α - or γ - Fe_2O_3 , resulting therefrom after drying and/or calcining at temperatures below 1100°C .

Furthermore, the present invention provides a process for the production of this pigment by application of a layer of magnetite or of α -, β - or γ -ferric oxide hydroxide on to mica flakes, optionally coated with titanium dioxide and/or zirconium dioxide or a hydrate thereof, optional application of a covering layer of colourless metal oxide, separation of the coated particles, washing, drying and optional calcining at temperatures below 1100°C ., wherein, for the precipitation of the layer of magnetite or of α -, β - or γ -ferric oxide hydroxide, an aqueous solution of an iron salt, preferably of a ferrous salt, is allowed to flow slowly, at constant temperature and at constant pH value, into an aqueous suspension of optionally coated mica flakes in the presence of an oxidation agent, whereby there is precipitated on the mica flakes present in suspension a homogeneous layer of α -, β - or γ -ferric oxide hydroxide or of magnetite.

Pigments of this kind are new. Admittedly, in the case of the already known pigments, layers of α - Fe_2O_3 are formed after the calcining but these pigments show, surprisingly, quite important differences in comparison with the new pigments, for example, with regard to light fastness, lustre, interference colour formation and colour nuances. This clearly shows that the chemical constitution of the coating alone is not responsible for the properties of the pigment but rather that, surprisingly, numerous other factors play a role, especially the construction and the nature of the layer, which clearly depend upon the properties of the originally precipitated layer. It is clearly important that the original precipitation provides a homogeneous layer of magnetite or of α -, β - or γ -ferric oxide hydroxide, the crystal form and structure of which remains in the calcined pigment, i.e. in the case of conversion of the precipitated layers into α - Fe_2O_3 or γ - Fe_2O_3 and, depending upon its formation, determines the various properties of appearances.

It was hitherto not known that α - FeOOH , β - FeOOH , γ - FeOOH or Fe_3O_4 can be deposited on mica. Therefore, no predictions could be made regarding the pigment properties of the coated products and regarding the properties of the pigments which are formed by the conversion of the α - FeOOH , β - FeOOH , γ - FeOOH or Fe_3O_4 layers into Fe_2O_3 layers. Surprisingly, we have found that, in the case of α - FeOOH or of the α - Fe_2O_3 obtainable therefrom, on mica optionally coated with titanium dioxide and/or zirconium dioxide, layers are formed which also show interference colours.

Furthermore, no process was hitherto known to precipitate iron-containing layers in comparatively large amounts on mica. In British Patent Specification No. 974,874, it is, for example, expressly stated that a content of iron oxide of over 30% by weight is difficult to obtain and one of over 40% by weight is practically unobtainable. However, an iron oxide content of less than 30% by weight does not suffice in order to achieve the layer thicknesses necessary for strong interference colours and lustre. Surprisingly, according to the process of the present invention, by precipitation of X-ray pure layers of, for example, α - FeOOH , it is now possible to produce pigments with iron oxide or iron oxide hydroxide layers with thicknesses which correspond to a content of up to 90% by weight of iron oxide or iron oxide hydroxide. Thus, for the first time, good lustrous pigments are obtainable which consist only of mica and iron or an iron oxide hydroxide.

The new pigments according to the present invention can be produced from all pigments based on mica flakes. Thus, as starting material there can be used not only mica flakes themselves but also those which are coated with homogeneous metal oxide layers. Such pigments are commercially available and are described, for example, in German Patent Specification No. 2,009,566. As a rule, the mica flakes used have a diameter of from 5 to 200 microns and a thickness of from 0.1 to 5 microns and preferably of about 0.5 microns. As metal oxide coatings, because of the advantageous refractive index, there is used titanium dioxide or titanium dioxide auate and/or zirconium dioxide or zirconium dioxide auate. A particularly preferred pigment is, for example, a mica flake pigment in which mica flakes with a diameter of from 5 to 50 microns and a thickness of about 0.5 microns are uniformly coated with an optionally hydrated titanium dioxide layer, the mica surface containing from 5 to 300 mg. TiO_2/m^2 . These known lustrous pigments possess, depending upon the layer thickness

of the precipitated titanium dioxide and/or zirconium dioxide layer, various colours and, therefore, are available in various types. As a rule, calcined products are used but non-calcined pigments can be employed according to the present invention. However, in principle, of course, all other pigments based on coated mica flakes can be used, especially those with other layer thicknesses of titanium dioxide and/or zirconium dioxide. The titanium dioxide layers in particular can be substantially reduced, especially in comparison with the commercial products. Furthermore, insofar as particular effects are to be achieved, in principle, as starting material to be coated, there can also be used all lustrous pigments which, in the layer present on the mica flakes, contain further additions of colouring metal oxides, for example, those of iron, nickel, cobalt, chromium or vanadium. These layers can possibly also contain non-colouring metal oxides, for example aluminium oxide or antimony oxide. These pigments are also known and are described, for example, in British Patent Specifications Nos. 974,874 and 1,268,177.

The coating of these starting materials is carried out in such a manner that the forming precipitate is immediately and quantitatively precipitated. For this purpose, it is important to avoid an excess of metal ions in the suspension. Thus, per unit time, only such an amount may be supplied to the reaction which, as sparingly soluble iron compound, can be taken up per unit time by the surface to be coated. Only by avoiding the presence of precipitated particles in the suspension which are not bound to the pigment surfaces, is it possible to obtain homogeneous layers of identical and uniform thickness, which are essential for pigments with high luminescence and good lustre. Further details of carrying out the precipitation for the achievement of such layers are given, for example, in German Patent Specifications Nos. 2,009,566 and 2,244,298.

According to the present invention, the coating of the starting material takes place in such a manner that uniformly smooth layers of magnetite or of α -, β - or γ -ferric oxide hydroxide result, the detection and testing of which is carried out with X-rays.

α -FeOOH exhibits especial advantages which extend not only to mica but also to mica coated with titanium dioxide and/or zirconium dioxide in smooth layers with interference colours. The pigments based on mica/ α -FeOOH are also characterised by an excellent light fastness. In the case of a small layer thickness of α -FeOOH, red-brown powders are formed which, in incident light, show a silver shade superimposed by the inherent colour of the pigment; with increasing layer thickness, red-brown powders are formed and the interference colours run through the known spectrum from yellow via red, blue and green in the direction of colours of higher order.

When calcined at a temperature of from 400°C to a temperature below 1100°C., the α -iron oxide hydroxide is converted into α -Fe₂O₃ which also forms smooth layers with interference colours and is light-fast and temperature stable.

The calcined products are mica/ α -Fe₂O₃ pigments with differing powder colours. In the case of a content of up to 25% by weight Fe₂O₃, they are orange-brown and show, in incident light, a silver shade superimposed by the actual colour of the pigment. In the case of higher layer thickness, a violet-red powder is obtained and the interference colours pass through the known spectrum.

In this connection, γ -FeOOH also exhibits very interesting properties. In a thin layer on mica, it forms deep orange-coloured, moderately smooth layers without interference colours. When dehydrated at temperatures of up to 350°C., this iron oxide hydroxide is converted into γ -Fe₂O₃, which shows dark brown layers and again neither interference nor lustre. When calcined at a temperature of from 400°C to a temperature below 1100°C. and preferably of from 600—1000°C., this iron oxide hydroxide is, on the other hand, converted into α -Fe₂O₃ which, however, in this case, exhibits orange-coloured layers.

Furthermore, β -FeOOH, which possesses a luminescent, orange-yellow colour shade, can also be considered. Upon calcining, it is converted into γ -Fe₂O₃ or α -Fe₂O₃ or into mixtures thereof, which possess a gold-yellow colour.

Good results can also be produced with a coating of magnetite (Fe₃O₄), whereby black and, depending upon the crystal form of the Fe₃O₄, rough layers without lustre are formed. These are stable up to 200°C. Upon heating in the air to a temperature of from 300°C to a temperature below 1100°C. and preferably of from 600 to 1000°C., from magnetite there is also formed α -Fe₂O₃ which, in this case, is obtained in a red-brown layer which, depending upon the base layer of magnetite, also does not have a smooth surface. It is temperature-stable but exhibits no interference colours and thus also no lustre.

If, instead of mica, there is used a mica pigment coated with titanium dioxide and/or zirconium dioxide, which in incident light already shows interference colours, then, after coating with α -FeOOH, there is observed, with increasing layer thickness, a further displacement of the interference colours in the direction of colours of higher

order. In the case of small layer thicknesses of α -FeOOH, such powders are beige to flesh coloured, but with increasing layer thickness, they become brown in colour. If such pigments are calcined at temperatures above 400°C. but below 1100°C., then the α -FeOOH layer is converted into an α -Fe₂O₃ layer. The resultant pigments also show strong interference colours in incident light. However, in comparison with the starting materials, the colour shades are slightly displaced. The displacement depends not only upon the calcining conditions (time and temperature) but also upon the substrate. If, after calcining, the layer thickness remains unchanged, the colours are displaced in the direction of higher order. If, after calcining, the substrate can shrink or if the refractive index of the substrate changes upon calcining, then a displacement of the interference colours in the opposite direction can also take place. Both effects can also compensate one another. In the powder colour, the calcined pigments show various nuances of a warm red-brown.

If titanium dioxide- and/or zirconium dioxide-coated mica flake pigment is coated with γ -FeOOH, then, here too, the interference colour is displaced. If, for example, a blue-reflecting mica titanium dioxide pigment is used as starting material, then a gold-olive shade is obtained. In the case of a small layer thickness of γ -FeOOH, the pigments are beige to flesh coloured, whereas with increasing layer thickness, the pigments have a chocolate-brown colour.

If such pigments are calcined at a temperature of from 400°C to a temperature below 1100°C., then the γ -FeOOH layer is converted into an α -Fe₂O₃ layer. The resultant pigments show, in incident light, strong interference colours, the colour shades being somewhat displaced in comparison with the starting materials. Thus, for example, a previously olive green pigment shows, after the calcining, a clearly gold-yellow shimmer. The calcined powders are, in the case of small layer thickness, flesh coloured, whereas, in the case of greater layer thicknesses, they are red-brown.

If pigments coated with γ -FeOOH are dehydrated by heating at temperatures below 350°C., then the γ -FeOOH layer is converted into a γ -Fe₂O₃ layer. The resultant pigments show, in incident light, strong interference colours, the colour shades, in comparison with the starting materials, being scarcely displaced but, in some cases, they are more intense.

If titanium dioxide- and/or zirconium dioxide-coated mica flake pigments are coated with magnetite, then, in the case of small layer thickness, the interference colour of the starting materials is strengthened and the originally silver-white powder itself achieves the interference colour. With increasing layer thickness, the pigments become black and lose their gloss; however, in principle, the interference colour shade is maintained.

The α -Fe₂O₃ or γ -Fe₂O₃ layers obtainable from the various primary modifications by calcining exhibit differing colours because the shape obtained of the particles precipitated on the substrate is substantially retained after calcining. Besides the modification, it determines the colour of the end product. This provides several variation possibilities of the achievable colour shades.

The fundamental conditions for the precipitation of the various iron oxide hydroxide or iron oxide modifications are described in the literature. Thus, for example, detailed instructions for the carrying out of the reactions are given in *Journal für praktische Chemie*, 4th Series, Volume 13, pages 163—176 (1961), as well as in *Farbe und Lack*, Volume 69, pages 814—819 (1963). It is known that, for the formation of the individual compounds and modifications, several interrelated factors are decisive. To these belong, in the first place, the nature of the reaction medium, its pH value, the temperature and, in many cases, also the strength of the oxygen supply. Generally, however, it can be said that the formation of a α -FeOOH from ferrous salt solutions is favoured by higher temperatures and lower pH values and that of γ -FeOOH by lower temperatures and higher pH values. The formation of magnetite from ferrous salt solutions, especially ferrous sulphate solutions, is achieved by higher temperature and relatively high pH values.

In the presence of air as oxidation agent, for the formation of α -FeOOH, a temperature range of from 25 to 100°C. and preferably of from 50 to 80°C. and a pH value range of from 4 to 8 and preferably of from 5.5 to 7.0, has proved to be favourable. On the other hand, for the precipitation of γ -FeOOH, it is preferable to operate at temperatures of from 0 to 50 and preferably of from 15 to 40°C., and at pH values of from 5 to 11 and preferably of from 6 to 9. Finally, β -FeOOH precipitates out most favourably from ferric salt solutions at temperatures above 75°C. but with the use of urea or acetamide as precipitation agent. It is preferable to use an excess of from 100 to 400% of urea. For the formation of magnetite, the possible temperature range is

from 0 to 100°C., preferably from 50 to 100°C., at a pH value above 7 and preferably of from 8 to 11.

The optimum reaction conditions, which lead to the formation of a uniform layer of a particular modification, can easily be found by routine investigations. However, as already stated, they vary somewhat, i.e. frequently also depending upon other reaction conditions, such as concentration of the solutions used, inflow rate, speed of stirring and nature of the oxidation agent used. Thus, in each case, an adjustment must take place with regard to the selected reaction conditions.

In the case of the precipitation of the iron oxide hydroxides, air is preferably used as oxidation agent, whereas in the case of the precipitation of magnetite, it is usually better not to use air as oxidation agent in order to exclude further oxidation of the Fe_3O_4 to Fe_2O_3 . Thus, Fe_3O_4 is preferably formed quantitatively as magnetite from ferrous salt solutions, with the exclusion of air, in the presence of an oxidation agent, preferably of a nitrate, for example, ammonium, sodium or potassium nitrate, or of a chlorate. Under these conditions, the oxidation stops at the desired oxidation stage when the pH value is above 7. The oxidation agent should be added, if possible, in a stoichiometric amount, whereby, for 12 mole of ferrous ions, when using a nitrate, 1 mole of oxidation agent is necessary. However, it has also already been described in the literature that, even when using an excess of oxidation agent, especially in the case of nitrates, no further oxidation takes place. Thus, in this regard, too, the reaction conditions can be varied within wide ranges. In each case, it is only necessary that the desired modification is uniformly precipitated.

Furthermore, it has proved to be important to carry out the coating of the starting material in such a manner that the coatings are precipitated from solutions of ferrous salts. With ferric ions, as a rule $\text{Fe}(\text{OH})_3$ gels are obtained which lead to agglomerations and subsidiary hydrolyses. Only in the case of the precipitation of $\beta\text{-FeOOH}$ is it normal to use ferric chloride solutions or solutions of other ferric salts.

The precipitation of the iron-containing layers to be applied according to the present invention usually takes place in such a manner that the starting material, i.e. the optionally coated mica flakes, is slurried with water to give a suspension. The pH value of this suspension is adjusted to the pH value desired for the precipitation by the addition of a mineral acid, for example sulphuric acid, or of a base, for example ammonia or sodium hydroxide. While continuously stirring, an aqueous solution of an iron salt is measured into this suspension at the desired temperature, which is preferably maintained during the whole coating procedure. The precipitation takes place under the conditions which permit the formation of a homogeneous and coherent layer. This is, for example, especially well possible when starting from solutions of ferrous salts, especially from ferrous sulphate. However, ammonium ferrous sulphate or ferrous halides can also be used. The concentration of the iron salt solutions is normally of from 5 to 500 g./litre and is preferably from 10 to 300 g./litre. During the precipitation, the pH value should be kept as constant as possible. Therefore, during the reaction, the pH value should, if necessary, be adjusted by the addition of alkali or acid. In some cases, it is also advisable to carry out the precipitation in the presence of a buffer system. Such buffer systems include, for example, borate, acetate, ammonia-ammonium chloride and/or glycocoll buffers of known composition. They can either be present in the pigment suspension or can also be added with the precipitation solution.

By variation of the coating rate and of the concentrations, in some cases, especially in the case of the precipitation of magnetite, the granulation of the coating can also be changed, which can then exert an effect on the colour.

When precipitating α - and $\gamma\text{-FeOOH}$, a strong air stream is simultaneously passed in, in order to achieve the oxidation to the desired oxidation stage. When coating with magnetite, on the other hand, it is preferable to work in an atmosphere of nitrogen or of another inert gas in order not to exceed the desired oxidation stage but to achieve it by adding an oxidation agent in stoichiometric amounts.

Furthermore, it has proved to be advantageous to add a preferably non-ionic wetting agent before coating the starting material. There can be used, for example, wetting agents based on polyalkylene glycols, polyoxyethylene fatty alcohol ethers, polyoxyethylene fatty acid esters, alkyl-phenol polyglycol ethers and hydroxyalkyl celluloses, for example hydroxypropyl-cellulose. As a rule, the wetting agents are added in amounts of from 0.01 to 10% by weight, referred to the starting suspension of mica flakes. The pigments obtained with the use of these wetting agents are characterised by an especially good gloss and, furthermore, increased colour strength.

In some cases, it is desirable additionally to provide a covering layer on the new pigments. For this purpose, in known manner, there are preferably selected layers of colourless oxides, for example titanium dioxide, zirconium dioxide, aluminium oxide,

antimony oxide, zinc oxide or tin oxide. Such a covering layer can be applied according to the usual methods on to dried or also calcined pigments or, more simply, before the separation of the pigments from the precipitation solution. In general, the covering layer is thinner than the layers applied according to the present invention. In particular, a titanium dioxide layer should not be thicker than about 15 nm in order not to impair the light fastness of the new pigments. A layer of aluminium oxide hydrate or of Al_2O_3 usually brings about an additional stabilising, not only with regard to the mechanical properties but also with regard to the light stability. The layer thickness is here not especially critical since aluminium oxide hydrates and oxides possess a comparatively low refractive index. The methods for the application of such layers are known and are described, for example, in British Patent Specification No. 974,874. In most cases, a conventional calcining after application of the covering layer is recommended.

The coated mica flakes are normally separated from the reaction mixture, well washed out with water and dried. If desired, a calcination for 10 minutes up to 4 hours at temperatures below 1100°C . can then follow. The preferred calcination temperature is from 600 to 1000°C .

Depending upon the desired colour, the iron-containing layers can have thicknesses of up to 500 nm and preferably of from 0.1 nm to 250 nm. In each case, the coating process is discontinued after reaching the desired colour shade. If, as starting material, lustrous pigments have been used and iron-containing layers are precipitated which produce no interference colours, naturally, with increase of the layer thickness, the lustre slowly decreases. Thus, a further variation possibility is here provided. The layer thicknesses are usually slightly changed by a subsequent calcining.

The new pigments can contain up to 90% by weight of iron oxide hydroxides or of iron oxides. For most fields of use, contents of up to 65% by weight are preferred. In this way, it is, for the first time, possible to produce coated pigments with smooth, homogeneous and adherent layers with such a high iron content. This is all the more surprising since, according to the previously known processes, a deposition of more than 30 to 40% by weight of iron oxides come up, in practice, against insuperable difficulties. However, the coating with iron oxides and iron oxide hydroxides according to the present invention now also permits the production of pigments with extremely high iron contents.

The new pigments according to the present invention represent an important technical advance. Thus, there is now available a whole spectrum of iron-containing pigments which are characterised by a good light fastness and light stability and by a plurality of colours and colour nuances. Furthermore, due to the nature and form of the substrate, the technical use properties can also be controlled.

When using mica flakes coated with titanium dioxide and/or zirconium dioxide as starting material, lustrous pigments are obtained in a hitherto not exceeded nuancing, with simultaneous light stability. If uncoated mica flakes are coated, pigments are obtained with outstanding transparent character. According to the present invention, the possibility also exists of producing a particular colour of iron pigments in a particular particle size. Whereas in the case of the previously known iron oxide pigments, the pigment colour is associated with a particular crystal size, in the case of the pigments according to the present invention, it is possible, due to the variation possibilities with regard to the substrate, i.e. the mica flakes, to vary the form of the particles substantially independently of the colour.

The pigments according to the present invention, which possess a layer of $\alpha\text{-FeOOH}$ on mica, show, in calcined and uncalcined state, in the case of layer thicknesses of >50 nm, outstanding interference colours. Therefore, they are outstanding lustrous pigments, some of which have a metal character, and are extremely light fast. They can, therefore, be used preferably, but not exclusively, in synthetic resins, lacquers, especially lacquers for motor vehicles, and in cosmetics and also as bronze substitute. Pigments according to the present invention which possess layers of $\alpha\text{-FeOOH}$ on mica flakes coated with titanium dioxide, are, in the calcined and uncalcined state, lustrous pigments with yellow to reddish-brown powder colours and outstanding gloss. They are more lightfast than the underlying mica/titanium dioxide pigment. They are preferably used in synthetic resins, lacquers and in cosmetics. The pigments obtainable with layers of $\gamma\text{-FeOOH}$ on mica are, in calcined and uncalcined state, transparent pigments without lustre and with orange to deep brown colour shades. They can be used for all fields for which iron oxide pigments with such colours have previously been used. Pigments according to the present invention which have $\gamma\text{-FeOOH}$ on mica flake pigments coated with titanium dioxide are, in calcined and uncalcined state, lustrous pigments which exhibit different interference colours and have a beige to dark brown powder colour. They are mainly used in the synthetic resin industry and in cosmetics.

The uncalcined pigment obtained by the precipitation of magnetite on mica is black and is, because of its particle size, more widely usable than the previously known black iron pigments. In the calcined state, this pigment is a dark brown to red-brown, transparent powder. It can be used in all fields in which iron oxide pigments with these colours have previously been used. The pigments which have magnetite on mica flakes coated with titanium dioxide and/or zirconium dioxide are, in uncalcined state, lustrous pigments with very strong interference colours with grey to black powder colour shimmering in the interference colour shade. After calcination, this pigment gives lustrous pigments with a beige to brick red powder colour. This pigment can be used, for example, in synthetic resins, in lacquers and in cosmetics. The interference colours of the lustrous pigments used as starting material are strengthened by the precipitated black layer of Fe_3O_4 , so that a still more luminescent play of colour is produced, especially in the case of relatively thin layers of magnetite. Furthermore, by the precipitation of the magnetite on the structure of the substrate provided by the mica flakes, there is also achieved an orienting of the magnetite crystals in the precipitation. Magnetic pigments are thus obtained with possibilities of variation with regard to orienting in a magnetic field. Such pigments can, for example, be embedded in synthetic resins and used as domestic magnets or also as storage magnets, for example sound recorders.

The pigments according to the present invention based upon uncoated mica flakes are also outstanding rust protection agents. Rust protection agents based on iron oxide possess an especial effectiveness when they have platelet-like particles since the atmospheric oxygen must diffuse along a very long path in order to pass from the surface to the substrate to be protected. There is here a further substantial advantage which is achieved by the alteration, according to the present invention, of the form of the iron oxide pigments.

All pigments according to the present invention can be used in the same way as the previously known pigments. They are especially suitable where light fastness is necessary, for example in lacquers for motor vehicles, or in cosmetics, where definite and highly differentiated colour nuances are desired. The concentrations in the appropriate compositions are preferably from 0.1 to 80%, depending upon the intended field of use.

In cosmetics, lustrous pigments are, as a rule, added in amounts of from 0.1 to 80%. Cosmetic compositions include, for example, powders, salves, emulsions and grease pencils, for example eyelid shadow pencils (pigment content 5—15%), eyelid shadow powder compacts (pigment content 20—70%), liquid compositions for eyelid shadows and eyelid lining (pigment content 7—85%), lipsticks (pigment content 10—20%), lip gloss creams for pencilling on (pigment content 10—15%), make-up in pencil form (pigment content 15—25%), make-up powder compacts (pigment content 10—50%), make-up emulsions (pigment content 5—10%), make-up fatty gels (pigment content 1—5%), light-protection emulsions and tanning emulsions (pigment content 5—10%), foam bath concentrates with lustrous gloss (pigment content 0.1—2%) and skin care lotions (pigment content 0.1—2%), all the above percentages being by weight. The advantage of the pigments according to the present invention when used in cosmetics is that an outstanding colour gloss is produced such as is desired for many decorative cosmetics. Furthermore, the pigments according to the present invention are characterised by their simple use as master batches since here colour and gloss components are combined in one substance which otherwise would necessitate the separate use of colour and gloss pigments. Since the coloured materials are naturally, due to the nature of their production, very finely divided, in the case of their incorporation into other materials, the otherwise conventional roundabout way via a mechanical pasting is unnecessary. Furthermore, with the pigments according to the present invention, it is possible, in a simple manner, to achieve changing colour effects in the incorporated product. Finally, there must be stressed the simple and expedient combination of the new pigments with most conventional synthetic lustrous pigments based on mica/titanium dioxide, bismuth oxychloride or guanine. By mere mixing and blending of the powdery new pigments with the known lustrous powders, colour and gloss can be varied in any desired manner adapted to the fashion requirements. The pigments obtainable according to the present invention represent a valuable technical advance due to the beige or brown skin shades achievable for the first time by means of lustrous pigments. The previously available spectrum of brown shades was extremely limited.

The following Examples are given for the purpose of illustrating the present invention:—

Example 1.

a) 15 kg. muscovite with a diameter of 10—40 μ and a thickness of about 0.5 μ (specific surface area about 3.5 m^2/g , determined from the amount of nitrogen ad-

sorbed) are suspended in 600 litres of fully desalinated water. The suspension is heated, while stirring, to 75°C. and, by the addition of sulphuric acid or ammonia, the pH value is adjusted to 6.0. A solution of 90 kg. ferrous sulphate heptahydrate and 900 ml. concentrated sulphuric acid in 300 litres water is then slowly measured in, air being simultaneously passed in, while stirring. The pH value is thereby kept constant at pH 6.0 by the addition of ammonia. The precipitated α -FeOOH deposits on the mica flakes as a smooth coating. The product obtained initially has the yellow colour of the precipitated iron oxide hydroxide but, with increasing iron oxide hydroxide content, achieves a strong lustre, the colour of the powder and the colour of the reflected light depending upon the layer thickness of the iron oxide hydroxide coating. The colour of the reflected light passes through the characteristic series of the interference colours, modified by the inherent colour of the precipitated iron oxide hydroxide; the powder colour of the pigment passes through various nuances from a reddish-yellow up to a dark red-brown.

The coating can be discontinued at any desired amount of iron oxide hydroxide. The pigment is then allowed to settle, filtered off, washed salt-free with water and dried at about 130°C. The pigment so obtained has an outstanding light fastness.

b) The pigments produced according to Example 1a) are calcined for 30 minutes at 900°C. The α -FeOOH is thereby converted into α -Fe₂O₃ and the colour changes slightly. Furthermore, the interference colour observable by reflected light thereby changes somewhat in the direction of an interference color of higher order. The pigment obtained also has an outstanding light fastness and chemical stability.

Table I summarises the relationship between the amount of iron oxide hydroxide or iron oxide, powder colour and interference colour for the noncalcined and calcined pigment.

TABLE I

consumption of FeSO ₄ solution in litres	dried pigment			calcined pigment		
	α -FeOOH % by wt.	interference colour	powder colour	α -Fe ₂ O ₃ % by wt.	interference colour	powder colour
25	13.7	silver	orange	12.6	silver	orange
100	38.9	reddish-gold	brown	36.5	reddish-gold	brown
175	52.7	orange-red	red	50.2	red	violet-red
225	58.9	red-violet	red-violet	56.4	violet	red-violet
250	61.4		brown-violet-red	59.1	green	brown-violet-red

Example 2.

a) 15 kg. muscovite with a diameter of 10–40 μ and an average thickness of about 0.5 μ (specific surface about 3.5 m²/g) are suspended in 600 litres of water. Thereafter, the pH value is adjusted to 7.5 by the addition of sulphuric acid or ammonia and, at ambient temperature, 125 litres of a solution of 90 kg. ferrous sulphate heptahydrate and 900 ml. concentrated sulphuric acid in 300 litres water is slowly measured in, air being simultaneously passed into the reaction mixture. By the measured addition of ammonia, the pH value is maintained constant at 7.5. The γ -FeOOH thereby precipitated deposits quantitatively on the mica particles and leads to the formation of an orange-coloured pigment without lustre. The colour of the pigment powder deepens with an increasing content of iron oxide hydroxide, without the colour shade altering substantially. The end product contains 44.2% by weight γ -FeOOH and is deep orange coloured.

b) The pigment obtained according to Example 2 a) is calcined for 30 minutes at about 300°C. A coffee-brown pigment is obtained, without lustre, which contains 41.7% by weight γ -FeOOH.

c) The pigment obtained according to Example 2 a) or 2 b) is calcined for 1 hour at 950°C. A pigment is obtained with an orange-red colour and without lustre, which contains 41.7% by weight α -Fe₂O₃.

Example 3.

a) 15 kg. of muscovite used in Example 2 a) are suspended in 600 litres of fully desalinated water. The suspension is heated to 75°C., while stirring, and, by the addition of a 10% by weight aqueous solution of sodium hydroxide, adjusted to a pH value of 9.5. 7.5 kg. potassium nitrate are then added thereto and subsequently 125 litres of a solution of 90 kg. ferrous sulphate heptahydrate and 900 ml. concentrated sulphuric acid in 300 litres water are slowly added thereto, while simultaneously passing in nitrogen. The pH value is maintained at 9.5 by the measured addition of a 10% by weight aqueous solution of sodium hydroxide. The precipitated magnetite (Fe₃O₄) deposits out quantitatively on the mica in the form of small crystals and gradually colours them black. The reaction temperature of 75°C. is maintained during the whole precipitation. The pigment is allowed to settle out and is then filtered off, washed with water and dried at a temperature below 250°C., preferably at about 130°C.

b) The black pigment obtained according to Example 3a) is, by calcining for one hour at 950°C., converted into a red-brown product which has a transparent character but possesses no lustre. It contains 41.7% by weight α -Fe₂O₃ on mica.

Example 4.

a) Analogously to Example 1, 20.8 kg. mica flakes coated with titanium dioxide (consisting of 72% by weight muscovite with the particle size 10—40 μ and 28% by weight titanium dioxide; silvery lustre) are coated with α -FeOOH. In this case, too, the precipitated iron oxide hydroxide deposits in a smooth layer on the pigment particles. The known interference colours are thereby passed through in quick succession; the powder colour of the preparation depends also upon the precipitated amount of α -FeOOH.

The coating can be discontinued at any desired iron oxide hydroxide amount and, consequently, at any desired interference colour. The pigment is allowed to settle out, filtered off, washed with water until salt-free and dried for 2 hours at about 130°C.

b) The pigment obtained according to Example 4 a) is calcined for 1 hour at 950°C. The colour thereby changes and the α -FeOOH layer is converted into the corresponding α -Fe₂O₃ layer.

Table II summarises the relationship between the iron oxide hydroxide content, the iron oxide content, the interference colour and the powder colour.

TABLE II

consumption of FeSO ₄ solution in litres	dried pigment			calcined pigment		
	α -FeOOH % by wt.	interference colour	powder colour	α -Fe ₂ O ₃ % by wt.	interference colour	powder colour
25	10.9	silver to yellow	beige-brown	9.35	silver to yellow	beige-brown
50	18.6	gold-yellow	pale brown	17.25	red-gold	orange-brown
75	25.6	red-gold	medium brown	23.6	deep red gold	medium brown
125	36.4	copper red	red-brown	34.1	copper red	violet-red

Example 5.

a) Analogously to Example 2, 30 kg. mica flakes coated with titanium dioxide (consisting of 50% by weight muscovite with the particle size 10—40 μ and 50% by weight titanium dioxide; blue lustre) are coated with γ -FeOOH. In this case, too, the precipitated iron oxide hydroxide is deposited quantitatively on the pigment particles, the interference colour of the lustrous pigment being initially somewhat displaced. A

larger amount of γ -FeOOH then leads to a clear reduction of the lustre and finally to a deepening of the orange-brown colour shade associated with the γ -FeOOH. The coating can be discontinued at any desired amount of γ -FeOOH and the pigment worked up as already described above.

5 Table III summarises the relationship between the precipitated amount of γ -FeOOH, the interference colour and the powder colour.

5

TABLE III

consumption of FeSO_4 solution in litres	γ -FeOOH % by wt.	interference colour	powder colour
25	7.36	sky blue	pink-beige
50	13.7	blue-green	medium brown (earth colour)
75	19.3	brownish-green	medium brown (earth colour)
100	24.2	olive green	brown
125	28.5	deep olive green	chocolate brown

b) The brown pigment obtained according to Example 5 a) with an γ -FeOOH content of 28.5% by weight is heated for 30 minutes at 300°C. A product is formed with a coffee-brown powder colour and a content of 26.5% by weight of the related γ -Fe₂O₃.

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c) The pigments obtained according to Examples 5 a) and 5 b) are calcined for 30 minutes at 900°C. The following Table IV shows the relationship between the interference colour and the powder colour:

TABLE IV

consumption of FeSO_4 solution in litres	α -Fe ₂ O ₃ % by wt.	interference colour	powder colour
25	6.7	sky blue	flesh colour
50	13.0	green	orange-brown
75	17.8	green-yellow	orange-brown
100	22.4	green-gold	deep orange-brown
125	26.5	red-gold	deep orange-brown

Example 6.

a) Analogously to Example 4, 27.3 kg. mica flakes coated with titanium dioxide (consisting of 55% by weight muscovite of the particle size 10–40 μ and 45% by weight titanium dioxide; red interference colour) are coated with α -FeOOH. The pH value is adjusted to 6.2 and the reaction temperature is 70°C. The pigment is worked up as described above.

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b) The pigments produced according to Example 6 a) are calcined for 45 minutes at 900°C. The α -FeOOH layer is thereby converted into the related α -Fe₂O₃ layer and the interference colours and the powder colours change. Table V summarises the relationship between the amount of precipitated α -FeOOH, of α -Fe₂O₃, of the powder colour and of the interference colour:

25

25

TABLE V

consumption of FeSO ₄ solution in litres	dried pigment			calcined pigment		
	α -FeOOH % by wt.	interference colour	powder colour	α -Fe ₂ O ₃ % by wt.	interference colour	powder colour
25	8.0	red	ochre	7.3	pink-red	ochre yellow
50	14.9	lilac colour	lilac-red	13.7	pale violet red	flesh colour
75	20.8	blue-green	violet-red	19.2	blue	reddish brown
100	25.9	yellow-green	dark brown	24.1	blue-green	brown
125	30.4	green-gold	medium brown	28.4	yellow-green	coffee brown

Example 7.

a) Analogously to Example 3, 22.5 kg. mica flakes coated with titanium dioxide and zirconium dioxide (consisting of 72% by weight muscovite with the particle size 10–40 μ , 26% by weight titanium dioxide and 2% by weight zirconium dioxide; silvery lustre) are coated with Fe₃O₄. In this case, too, the precipitated magnetite is quantitatively deposited on the pigment particles. The interference colour of the lustrous pigment does not change but the pigment achieves a metallic character. When coating with greater amounts of magnetite, the pigment becomes black and completely loses its lustrous character. The coating can be discontinued at any desired amount of iron oxide. The pigment is worked up as described above and dried at about 100°C. for 2 hours.

b) The pigments produced according to Example 7 a) are calcined at 900°C. The Fe₃O₄ is thereby converted into the related α -Fe₂O₃ layer and the powder colour of the pigment changes. Table VI summarises the relationship between the amount of iron oxide, the interference colour and the powder colour.

TABLE VI

consumption of FeSO ₄ solution in litres	dried pigment			calcined pigment		
	Fe ₃ O ₄ % by wt.	interference colour	powder colour	α -Fe ₂ O ₃ % by wt.	interference colour	powder colour
12.5	4.8	silver	pale mouse grey	4.9	silver	beige
25	9.1	silver	medium mouse grey	9.3	silver	medium beige
37.5	13.1	silver	medium mouse grey	13.5	silver	dark beige
50	16.7	silver	dark mouse grey	17.3	silver	flesh colour
75	23.1	silver	grey-black	23.6	silver	pale brick red
125	33.4	silver	black	34.1	silver	brick red

Example 8.

- 5 a) 15 kg. muscovite with a diameter of about 10—40 μ and an average thickness of about 0.5 μ (specific surface area about 3.5 m²/g) are suspended in 600 litres of completely desalinated water. The suspension is heated to 65°C., while stirring, and the pH value is adjusted to 5.7 by the addition of sulphuric acid. 175 litres of a solution of 90 kg. ferrous sulphate heptahydrate and 900 ml. sulphuric acid in 300 ml. water is then slowly measured in, air being simultaneously passed in, while stirring. The pH value is kept constant at 5.7 by adding ammonia. The temperature is also maintained constant. After the coating is finished, the preparation has an orange-red interference colour and contains 47.3% by weight mica and 52.7% by weight α -FeOOH. The suspension is stirred at 65°C. for 30 minutes. The pH value is then increased to 8.0 by the addition of ammonia and a solution of 4.75 kg. aluminium chloride hexahydrate in 50 litres water is slowly measured in, the pH value being kept constant at 8.0 by passing in ammonia. The temperature is adjusted to 65°C. The precipitated aluminium hydroxide deposits quantitatively on the pigment, the appearance of the preparation only changing unsubstancially. It is then stirred for about 1 hour at 65°C., whereafter the pigment is left to settle out. The product is filtered off, washed with water and dried for 1 hour at 130°C. It has a red powder colour, an orange-red interference colour and contains 45.8% by weight mica, 51.1% by weight α -FeOOH and 3.1% by weight aluminium oxide hydrate (as Al_2O_3).
- 10 b) The pigment obtained according to Example 8 a) is calcined at 850°C. for 40 minutes, a pigment being obtained which has a violet-red powder colour and a red interference colour. It contains 48.2% by weight mica, 48.6% by weight Fe_2O_3 and 3.2% by weight Al_2O_3 .

25 Use of the pigments (percentages by weight).

1. Eyelid shadow pencil with colour lustre

Pigment according to Example 1 b)

	(56.4% Fe_2O_3)	10%	
30	castor oil	15%	
	perfume	0.5%	
	wax/oil base mass	74.5%	30

Composition of the wax/oil mass:

	bees' wax	12.5%	
	carnauba wax	6.2%	
35	hard paraffin	6.2%	
	cetyl alcohol	3.7%	
	white petroleum jelly	2.5%	
	lanolin	2.5%	
	paraffin	1.2%	
40	isopropyl myristate	10.0%	
	castor oil	55.05%	40
	propyl <i>p</i> -hydroxybenzoate	0.1%	
	antioxidant	0.05%	

2. Eyelid shadow powder compact with colour lustre

45	pigment according to Example 1 b)		45
	(36.5% Fe_2O_3)	50%	
	talc	29.5%	
	kaolin	3%	
	calcium stearate	5%	
50	maize starch	3%	
	isopropyl lanolate	6%	50
	isopropyl myristate	3%	
	perfume	0.5%	

3. Eyelid shadow and eyelid liner, liquid

55	pigment according to Example 6 b)		55
	(24.1% Fe_2O_3)	12%	
	1,2-propyleneglycol	20%	
	magnesium aluminium silicate	2.5%	
	water	65.6%	

4. Lipstick with colour lustre			
	pigment according to Example 1 b)		
	(36.5% Fe_2O_3)	15%	
5	castor oil	14%	
	perfume	0.5%	5
	wax/oil base mass	70.5%	
Composition of the wax/oil base mass:			
	bees' wax	13.7%	
10	carnauba wax	7.5%	
	hard paraffin	7.5%	10
	cetyl alcohol	2.5%	
	candelilla wax	3.7%	
	lanolin	2.5%	
	paraffin	1.2%	
15	isopropyl myristate	6.2%	15
	castor oil	55.05%	
	propyl <i>p</i> -hydroxybenzoate	0.1%	
	antioxidant	0.05%	
5. Lip gloss cream, liquid, for pencilling on			
20	pigment according to Example 4 b)		20
	(23.6% Fe_2O_3)	12.5%	
	perfume	0.5%	
	oil/wax base mass	87%	
Composition of the oil/wax base mass:			
25	castor oil	82%	25
	lanolin	15%	
	cetyl alcohol	3%	
6. Make-up in pencil form			
30	pigment according to Example 7 b)		30
	(9.3% Fe_2O_3)	20%	
	castor oil	6%	
	perfume	1%	
	oil/soap/wax base mass	73%	
Composition of the base mass:			
35	bees' wax	21.5%	35
	carnauba wax	6%	
	white petroleum jelly	6%	
	castor oil	43.85%	
	propyl <i>p</i> -hydroxybenzoate	0.1%	
40	antioxidant	0.05%	40
	calcium stearate/paraffin viscous (1 + 2)	16.5%	
	talc	6.0%	
7. Make-up powder compact			
45	pigment according to Example 4 a)		45
	(18.6% $\alpha\text{-FeOOH}$)	30%	
	talc	52.5%	
	kaolin	3%	
	calcium stearate	5%	
	maize starch	3%	
50	isopropyl lanolate	5%	50
	isopropyl myristate	1%	
	perfume	0.5%	

8. Make-up emulsion				
	pigment according to Example 4 b)			
	(23.6% Fe_2O_3)	10%		
	lanolin	4%		
5	white petroleum jelly	4%		5
	isopropyl myristate	7%		
	titanium dioxide	6%		
	sorbitan monostearate	5%		
	polyoxyethylene monostearate	5%	} as emulsifiers	
	propane-1,2-diol	4%		
10	methyl 4-hydroxybenzoate	0.2%		10
	magnesium silicate, highly purified	1%		
	water, desalinated	53.5%		
	perfume	0.3%		
9. Make-up fatty gel				
15	pigment according to Example 2 b)	2%		15
	white petroleum jelly	58%		
	paraffin, liquid	20%		
	triglyceride of saturated vegetable			
	fatty acids C_8 — C_{12}	15%		
20	isopropyl myristate	5%		20
	perfume			
10. Light-protection emulsion with make-up colour gloss				
	pigment according to Example 1 b)			
	(56.4% Fe_2O_3)	7%		
25	paraffin, liquid	9%		25
	C_8 — C_{12} fatty acids triglyceride	5%		
	isopropyl myristate	3%		
	cetyl alcohol	2.5%		
	sorbitan monostearate	1.8%	} as emulsifiers	
	polyoxyethylene sorbitan			
30	monostearate	2.7%		30
	titanium dioxide	6%		
	2-phenylbenzimidazole-5-sulphonic acid	2%		
	triethanolamine	1%		
	sorbitol, liquid	3%		
35	magnesium silicate, highly purified	0.5%		35
	methyl 4-hydroxybenzoate	0.2%		
	water, desalinated	56.3%		
	perfume			
11. Tanning emulsion with make-up colour gloss				
40	pigment according to Example 5 b)			40
	(26.5% $\gamma\text{-Fe}_2\text{O}_3$)	7%		
	paraffin, liquid	17%		
	isopropyl myristate	5%		
	hard paraffin	1%		
45	bees' wax	1.0%		45
	sorbitan sesquioleate	3.0%	} emulsifiers	
	polyoxyethylene sorbitan trioleate	3.0%		
	sorbitol solution 70%	3.0%		
	propane-1,2-diol	2.0%		
	magnesium sulphate heptahydrate	0.6%		
50	dihydroxyacetone	4.0%		50
	phosphate buffer	1.0%		
	methyl 4-hydroxybenzoate	0.2%		
	water, desalinated	52.2%		

12. Lustrous foam bath concentrate
pigment according to Example 1 b)
(50.2% of α -Fe₂O₃) 0.2%
silicic acid, finely dispersed 1 + 9 10.0% 5
pasted with water 8.3%
water, completely desalinated 1.0%
citric acid 1.5%
perfume, water-soluble 15.0%
sodium lauryl ether sulphate 60.0% 10
ammonium fatty alcohol ether sulphate 4.0%
coconut fatty acid diethanolamide
13. Skin care lotion with colour lustre
pigment according to Example 5 c)
(26.5% Fe₂O₃) 0.1%
carboxyvinyl polymer 0.2% 15
water, deionised 70.4%
diisopropanolamine 0.2%
allantoin 0.1%
vitamins A, D₃, E, water-soluble 1.0%
1,2-propylene glycol 3.0% 20
ethanol 95 wt.% 25.0%
perfume, water-soluble
14. Button plate
A pigment according to Example 1 b) is pasted with double the amount of a mixture of equal parts of *n*-butyl acetate, ethylene glycol monoethyl ether and dibutyl phthalate. 2.5 g. of the so obtained suspension are mixed with 250 g. of an unsaturated polyester resin and the batch is, after the addition of 1 ml. of a 1% by weight solution of cobalt octoate and 6 ml. of a 50% by weight ketone peroxide, hardened in a centrifugal drum. After hardening, a polyester plate is obtained of uniformly lustrous character with a brown-red gloss, from which can be produced, for example, buttons. 25 30
15. Pigmenting of thermoplasts
10 kg. polystyrene are mixed with 50 g. dibutyl phthalate and intensively mixed for 15 minutes. After the addition of 100 g. of the pigment obtained according to Example 1 b) with 50.2% by weight Fe₂O₃, it is intensively shaken for a further half hour. The mixture obtained is then extruded from a screw injection moulding machine at about 200°C. to give small platelets, which possess a very good lustre and a violet colour. 35 35
16. Pigmented lacquer
30 parts by weight collodion wool (22% by weight in butyl acetate)
40 parts by weight long-chain oily alkyd resin based on synthetic fatty acids (75% by weight in white spirit) 40
10 parts by weight toluene
4 parts by weight butyl glycolate
2 parts by weight cobalt siccative
are mixed together and stirred. 2 parts by weight of a pigment produced according to Example 1 b) are moistened with 4 parts by weight butyl acetate and added to the batch. After thorough mixing, the lacquer is sprayed on to primed metal plates. Upon drying, a smooth film is obtained with a very good lustre. 45 45
- WHAT WE CLAIM IS:—
- 50 1. Iron-containing pigment based on mica flakes or on mica flakes provided on both sides with a coating of titanium dioxide and/or zirconium dioxide or of a hydrate thereof, said coating adhering to the mica flakes, wherein the iron-containing layers, provided on both sides of the flakes, consist homogeneously of magnetite or of α -, β - or γ -ferric oxide hydroxide or of α - or γ -Fe₂O₃ resulting therefrom after drying and/or calcining at temperatures below 1100°C. 55 55
2. Pigment according to claim 1, wherein the iron-containing layer consists uniformly of γ -Fe₂O₃ which has been formed by the dehydration of γ -FeOOH at a temperature below 350°C.
- 60 3. Pigment according to claim 1 or 2, wherein the iron-containing layers have a thickness of up to 500 nm. 60 60



12. Lustrous foam bath concentrate
pigment according to Example 1 b)
(50.2% of α -Fe₂O₃) 0.2%
silicic acid, finely dispersed 1 + 9 10.0%
pasted with water 8.3%
water, completely desalinated 1.0%
citric acid 1.5%
perfume, water-soluble 15.0%
sodium lauryl ether sulphate 60.0%
ammonium fatty alcohol ether sulphate 4.0%
coconut fatty acid diethanolamide
13. Skin care lotion with colour lustre
pigment according to Example 5 c)
(26.5% Fe₂O₃) 0.1%
carboxyvinyl polymer 0.2%
water, deionised 70.4%
diisopropanolamine 0.2%
allantoin 0.1%
vitamins A, D₃, E, water-soluble 1.0%
1,2-propylene glycol 3.0%
ethanol 95 wt.% 25.0%
perfume, water-soluble
14. Button plate
A pigment according to Example 1 b) is pasted with double the amount of a mixture of equal parts of *n*-butyl acetate, ethylene glycol monoethyl ether and dibutyl phthalate. 2.5 g. of the so obtained suspension are mixed with 250 g. of an unsaturated polyester resin and the batch is, after the addition of 1 ml. of a 1% by weight solution of cobalt octoate and 6 ml. of a 50% by weight ketone peroxide, hardened in a centrifugal drum. After hardening, a polyester plate is obtained of uniformly lustrous character with a brown-red gloss, from which can be produced, for example, buttons.
15. Pigmenting of thermoplasts
10 kg. polystyrene are mixed with 50 g. dibutyl phthalate and intensively mixed for 15 minutes. After the addition of 100 g. of the pigment obtained according to Example 1 b) with 50.2% by weight Fe₂O₃, it is intensively shaken for a further half hour. The mixture obtained is then extruded from a screw injection moulding machine at about 200°C. to give small platelets, which possess a very good lustre and a violet colour.
16. Pigmented lacquer
30 parts by weight collodion wool (22% by weight in butyl acetate)
40 parts by weight long-chain oily alkyd resin based on synthetic fatty acids (75% by weight in white spirit)
10 parts by weight toluene
4 parts by weight butyl glycolate
2 parts by weight cobalt siccative
are mixed together and stirred. 2 parts by weight of a pigment produced according to Example 1 b) are moistened with 4 parts by weight butyl acetate and added to the batch. After thorough mixing, the lacquer is sprayed on to primed metal plates. Upon drying, a smooth film is obtained with a very good lustre.
- WHAT WE CLAIM IS:—
1. Iron-containing pigment based on mica flakes or on mica flakes provided on both sides with a coating of titanium dioxide and/or zirconium dioxide or of a hydrate thereof, said coating adhering to the mica flakes, wherein the iron-containing layers, provided on both sides of the flakes, consist homogeneously of magnetite or of α -, β - or γ -ferric oxide hydroxide or of α - or γ -Fe₂O₃ resulting therefrom after drying and/or calcining at temperatures below 1100°C.
2. Pigment according to claim 1, wherein the iron-containing layer consists uniformly of γ -Fe₂O₃ which has been formed by the dehydration of γ -FeOOH at a temperature below 350°C.
3. Pigment according to claim 1 or 2, wherein the iron-containing layers have a thickness of up to 500 nm.

4. Pigment according to claim 3, wherein the iron-containing layers have a thickness of from 0.1 to 250 nm.
5. Pigment according to any of the preceding claims, wherein the iron oxide or iron oxide hydroxide content is up to 90% by weight.
- 5 6. Pigment according to claim 5, wherein the iron oxide or iron oxide hydroxide content is up to 65% by weight.
7. Pigment according to any of the preceding claims, wherein an additional covering layer of a colourless metal oxide is present.
- 10 8. Pigment according to any of the preceding claims, wherein the mica flakes have a diameter of from 5 to 200 microns and a thickness of from 0.1 to 5 microns.
9. Pigment according to claim 8, wherein the mica flakes have a thickness of about 0.5 microns.
10. Pigment according to any of claims 1 to 7, wherein the mica flakes have a diameter of from 5 to 50 microns and a thickness of about 0.5 microns and are uniformly coated with an optionally hydrated titanium dioxide layer, the mica surface containing from 5 to 300 mg. titanium dioxide/m².
- 15 11. Pigment according to claim 10, wherein the titanium dioxide layer contains at least one colouring and/or non-colouring metal oxide.
12. Pigments according to claim 1, substantially as hereinbefore described and exemplified.
- 20 13. Process for the production of a pigment according to claim 1, wherein an aqueous solution of an iron salt is allowed to flow slowly, at a constant temperature and pH value, into an aqueous suspension of mica flakes which are optionally coated on both sides with titanium dioxide and/or zirconium dioxide or a hydrate thereof, in the presence of an oxidation agent, whereafter the mica flakes, which are homogeneously coated on both sides with magnetite or with α -, β - or γ -ferric oxide hydroxide are separated, washed, dried and, if desired, thereafter calcined at temperatures below 1100°C.
- 25 14. Process according to claim 13, wherein the iron salt used is a ferrous salt.
- 30 15. Process according to claim 13 or 14, wherein magnetite or α - or β - or γ -FeOOH is deposited on the mica flakes.
16. Process according to any of claims 13 to 15, wherein the iron salt used is ferrous sulphate.
- 35 17. Process according to claim 15 or 16, wherein the precipitation of a uniform layer of α -FeOOH is carried out at a temperature of from 25 to 100°C. and at a pH value of from 4 to 8.
18. Process according to claim 17, wherein the precipitation is carried out at a temperature of from 50 to 80°C.
- 40 19. Process according to claim 17 or 18, wherein the precipitation is carried out at a pH value of from 5.5 to 7.0.
20. Process according to claim 15 or 16, wherein the precipitation of a uniform layer of γ -FeOOH is carried out at a temperature of from 0 to 50°C. and at a pH value of from 5 to 11.
- 45 21. Process according to claim 20, wherein the precipitation is carried out at a temperature of from 15 to 40°C.
22. Process according to claim 20 or 21, wherein the precipitation is carried out at a pH value of from 6 to 9.
23. Process according to claim 15 or 16, wherein the precipitation of a uniform layer of magnetite is carried out at a temperature of from 0 to 100°C. and at a pH value above 7.
- 50 24. Process according to claim 23, wherein the precipitation is carried out at a temperature of from 50 to 100°C.
25. Process according to claim 23 or 24, wherein the precipitation is carried out at a pH value of from 8 to 11.
- 55 26. Process according to any of claims 13 to 25, wherein the iron oxide hydroxides are precipitated with the use of air as oxidation agent.
27. Process according to any of claims 13 to 25, wherein magnetite is precipitated with the use of an oxidation agent other than air.
- 60 28. Process according to claim 27, wherein the oxidation agent used is a nitrate or chlorate.
29. Process according to any of claims 13 to 28, wherein the iron salt solution used contains from 5 to 500 g. of iron salt per litre.
30. Process according to claim 29, wherein the iron salt solution used contains from 10 to 300 g. of iron salt per litre.



31. Process according to any of claims 13 to 30, wherein the precipitation is carried out in the presence of a buffer system.
- 5 32. Process according to any of claims 13 to 31, wherein a non-ionic wetting agent is added to the aqueous suspension of mica flakes before starting the precipitation reaction. 5
33. Process according to claim 32, wherein the wetting agent is used in an amount of from 0.01 to 10% by weight, referred to the suspension of mica flakes.
- 10 34. Process according to any of claims 13 to 33, wherein a covering layer of a colourless metal oxide is applied to the mica flakes before separation thereof from the suspension or after drying or after calcining. 10
35. Process according to any of claims 13 to 34, wherein the coated mica flakes are calcined at a temperature of from 600 to 1000°C.
- 15 36. Process according to claim 13 for the production of iron-containing pigments, substantially as hereinbefore described and exemplified. 15
37. Pigments, whenever produced by the process according to any of claims 13 to 36.
38. Cosmetics, whenever containing at least one pigment according to any of claims 1 to 12 and 37.
- 20 39. Lacquers, whenever containing at least one pigment according to any of claims 1 to 12 and 37. 20
40. Synthetic resins, whenever containing at least one pigment according to any of claims 1 to 12 and 37.

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