

PATENT SPECIFICATION

(11) 1 238 440

DRAWINGS ATTACHED

- (21) Application No. 4507/71 (22) Filed 8 Sept. 1967
 (62) Divided out of 1 237 866
 (23) Complete Specification filed 6 Sept. 1968
 (45) Complete Specification published 7 July 1971
 (51) International Classification C 09 c 1/00
 (52) Index at acceptance
 C4A 6
 C4X 6



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(54) PIGMENTS

(71) We, MAY & BAKER LIMITED, a British Company of Dagenham, Essex, England, 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:—

This invention relates to pigments of a nacreous or decorative character and their production. This Application is divided out of our copending Application No. 41182/67 Serial No. 1,237,866.

One of the most satisfactory nacreous pigments (or pearling agents) is natural pearl essence, the naturally occurring form of guanine which can be obtained from fish scales. Unfortunately, however, this substance is difficult to isolate and thus very costly. Moreover, attempts to make a similar form of guanine synthetically have so far failed. Artificial nacreous pigments have in general suffered from one or other of the defects of being insufficiently pearlescent or too toxic for general use. Ideally, a nacreous pigment should not only be inherently pearlescent but, in addition, have a high refractive index, good stability to heat and light, chemical unreactivity, and lack of toxicity. Titanium dioxide satisfies these criteria, and a number of proposals have therefore been made for producing pigments from this substance.

Known titanium dioxide pigments, produced by hydrolysis of titanium esters, have suffered from a number of disadvantages. They have been costly to produce, have had poor nacreous lustre or colour, or have been unstable to light, or have had a combination of these defects. It has been proposed to improve the quality of the product by increasing the reflectance of the particles. This can be achieved by making a multi-layer product consisting of layers of a high refractive index material such as titanium dioxide, alternately with a low refractive index material such as calcium fluoride. Methods devised for making

such pigments have usually had recourse to deposition of layer material from the vapour phase at low pressures. These procedures are inherently expensive to operate.

The present invention provides new pigments based on titanium dioxide or the chemically closely related zirconium dioxide or alkaline earth metal titanates which have a decorative or highly pearlescent appearance approaching natural pearl essence in quality, and which in certain preferred embodiments can be made chemically very inert and resistant to light, and also to display different colours.

The pigment of the present invention comprises a plurality of thin, clear layers, each of which is uniform, of titanium or zirconium dioxide, or an alkaline earth metal titanate (as hereinafter defined), each such adjacent layer being separated by one, and adherent to one or two thin, clear layers, each of which is uniform, of an interleaving agent, which is an organic film-forming substance containing hydroxyl groups, carboxylic anhydride or carboxylic ester groups, or other groups capable of reacting with titanium ester, zirconium ester or alkaline earth metal titanate ester groups, the refractive index of the titanium or zirconium dioxide or alkaline earth metal titanate ester layer (hereinafter referred to as the high refractive index layer) exceeding that of the interleaving agent layer by at least 0.05. The refractive index of the titanium dioxide is preferably 1.85 to 1.95 and that of the zirconium dioxide and the alkaline earth metal titanates 1.69 to 1.75. The refractive index of the interleaving agent is usually 1.45 to 1.50, but may be as high as 1.67, provided always that it is lower than that of the titanium or zirconium dioxide or alkaline earth metal titanate layer by at least 0.05 in the final product. Preferably, the difference in refractive index between the titanium or zirconium dioxide or alkaline earth metal titanate and the interleaving agent

is greater than 0.05 and is 0.2 to 0.5. By suitable choice of layer thicknesses, as herein-after described, a range of coloured pigments can be produced. These materials owe their colour to optical interference of light to produce the coloured effect rather than to absorption phenomena.

It is to be understood that the terms "titanium dioxide" and "zirconium dioxide" are used herein to refer to the hydrolysis products of titanic and zirconic esters respectively, although such hydrolysis products are not necessarily pure dioxide, and will generally contain residual unhydrolysed ester groupings, and some hydroxyl groups. Similarly the term "alkaline earth metal titanate" refers to the hydrolysis product of an alkaline earth metal, e.g. calcium, titanic ester and does not imply that the material is necessarily a pure alkaline earth metal titanate. The terms "alkoxide" and "ester" are used interchangeably herein as it is, in many cases, difficult to determine whether a given compound is mainly ionic or mainly covalent.

In accordance with this invention, the new pigment is made by applying to a support a release layer which is wetted by the composition used to apply the first layer of (I) and which is insoluble in the compositions used to apply the layers of (I) and (II) but soluble in the solvent used to release the multi-layer product from the support, and then alternately thin layers, each of which is uniform, of (I) a hydrolysable titanic or zirconic ester or alkaline earth metal titanic ester and (II), as interleaving agent former, an organic film-forming substance containing hydroxyl, carboxylic anhydride, carboxylic ester or other groups capable of reacting with titanium ester or zirconium ester or alkaline earth metal titanic ester groups such that after hydrolysis of the hydrolysable layers (I) and, if necessary after heating the layers produced, the refractive index of layer (I) exceeds that of layer (II) by 0.05; hydrolysing each hydrolysable layer (I) immediately after application to a clear layer by contact with water vapour; and when at least two layers of the titanic or zirconic ester or alkaline earth metal titanic ester have been applied and hydrolysed, releasing the multi-layer product from the support by dissolving away the release layer and, if required, heating the layers so produced before or after release of the pigment to give a pigment wherein the refractive index of layer (I) exceeds that of layer (II) by 0.05. In order to obtain the best results, it is desirable that the surface of the support should be as smooth and uniform as possible. For example the support may be of glass, polished metal or polyethylene terephthalate film.

To obtain continuous production of the pigment, the support is preferably an inert, long or endless (i.e. looped) belt. Suitable

materials for the belt are metals, plastics and coated paper, and the material must, of course, be inert to water and the various reagents used. Not all potentially suitable belt materials will in fact allow satisfactory clear films to be laid down under equivalent conditions; for example, with polytetrafluoroethylene or cellulose acetate sheet, cloudy films are readily formed, from which only poor quality pearly material can be made. This may be the result of an absorbed layer of moisture on the sheet, or of poor heat capacity or heat conductivity. It is, however, very easy to select a suitable material by simple small-scale trial. Polyethylene terephthalate film, which is readily available, has been found to be very suitable.

So that the pigment can readily be released from the support, the latter is provided with a release layer to prevent the pigment from adhering to the support. The nature of the release layer will of course depend upon the particular conditions under which the pigment is prepared. It must, however, be insoluble in the compositions used to apply the layers of (I) and (II) but be soluble in a solvent so that it can readily be dissolved away by such a solvent to release the pigment from the support. In addition in order to ensure even coating the release layer must be wetted by the composition applied thereover to apply the first layer of (I). It is convenient for such a layer to be soluble in water, being preferably of polyethylene glycol or polyvinyl pyrrolidone so that immersion in water of the film carrying pigment on the release layer causes the pigment to separate from the film. Since layers of titanium dioxide formed by hydrolysis of the esters tend to darken on keeping, possibly due to adsorption of coloured impurities from the storage medium, a further important function of the release layer is to stabilise the pigment, possibly through chemical binding of a monolayer of release agent on the fresh titanium dioxide surface. Another function of the release layer, which probably depends on the same monolayer, is in acting as a mild surfactant which discourages coagulation of the multi-layer pigments during isolation. An especially suitable material for the release layer is polyethylene glycol in the molecular weight range 6,000 to 100,000 which may be applied in solution in methanol, but other water-soluble substances may be used. An example of another release agent is cellulose diacetate which is soluble in acetone. Cellulose diacetate bonds with the compounds of layer (I) and thus can also be used as an interleaving agent. Accordingly when it is used as a release agent the layer must be sufficiently thick to ensure that part of the layer is not bonded and thereby rendered insoluble.

The hydrolysable titanic or zirconic ester is generally a tetra-alkyl titanate or zirconate in which each alkyl group contains 1 to 8

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carbon atoms. Titanium compounds are preferred because of their ready availability and lower cost. Tetra-isopropyl titanate and tetra-n-butyl titanate are both available commercially and are preferably used in the present invention. Tetra-isopropyl titanate which hydrolyses readily to give layers of refractive index 1.85—1.95 depending on plating conditions, produces pearling agents which have superior reflectivity to those from tetra-n-butyl titanate. The latter ester, however, is easier to use because it hydrolyses less readily. The hydrolysable alkaline earth metal titanic ester is preferably calcium titanium isopropoxide, although other esters can be used, e.g. esters in which each alkyl group contains 1 to 8 carbon atoms. This ester, as well as tetra-n-propyl zirconate and tetra-n-butyl titanate, produces films of refractive index in the range 1.69 to 1.75 when deposited at temperatures below about 30°C. These refractive indices can be raised by application of the esters at higher temperature, or by heating the film or multilayer sandwich after deposition. The esters may be applied in the absence of a solvent, but are preferably applied in solution in a suitable inert volatile solvent, for example a volatile hydrocarbon, e.g. petroleum spirit, ether, or alcohol. When such a solvent is used, it is most important that it should be removed from the layer before the titanic, zirconic or alkaline earth metal titanic ester is hydrolysed. If any significant hydrolysis of the ester takes place before the solvent has been entirely removed, the titanium or zirconium dioxide or alkaline earth metal titanate separates as small, rounded particles which dry to give a chalky, non-pearly powder rather than a clear, adherent film. For dipping techniques 40—60°C. petroleum ether is a suitable solvent but for roller-coating techniques, as hereinafter described, a higher boiling solvent may be desirable. Ordinarily, the titanic, zirconic or alkaline earth metal titanic esters are hydrolysed by contact with moist air, as lower alkyl titanates, zirconates and alkaline earth metal titanic esters are rapidly hydrolysed at ambient temperatures under these conditions. The rate of hydrolysis is determined, *inter alia*, by the relative humidity of the moist air and the ambient temperature. Satisfactory results can in general be obtained at 20—50% relative humidities at temperatures in the range 20—36°C. At temperatures in the range 20—30°C., using 4—8% by weight solutions of titanic esters in petroleum ether (b.p. 40—60°C.) at speeds of dipping of 2 to 4 cm. per second, using a 0.01 inch (0.25 mm.) thick polyethylene terephthalate belt coated with a 100 μ thick layer of polyethylene glycol (M.W.=20,000), a 30% relative humidity will generally give a satisfactory rapid hydrolysis time without any danger that the hydrolysed film will not be clear and adherent. Where difficulty is en-

countered in the formation of a clear film, it is nearly always correct to assume that lower humidity conditions would give better results. The lower the concentration of the titanic ester solution, the more difficult it is to produce a clear transparent film. The lowest concentration of solution at which it is possible to obtain clear films of titanium esters by dipping followed by evaporation of the solvent, even with humidities as low as 2%, is about 0.2% by weight. Extrapolation of the measured film thicknesses obtained with more concentrated solutions to these low concentrations suggests that monolayer films would be produced at solution concentrations of 0.1% to 0.05% by weight. This is therefore the minimum possible concentration.

After the high refractive index layer has been formed, an interleaving layer is applied. As already stated, this is formed of an organic film-forming substance containing hydroxyl or other reactive groups for example a soluble cellulose derivative such as cellulose diacetate, a partially hydrolysed polyvinyl acetate, a polyvinyl acetal or butyral, gelatin, or an organo-silanol. The solvent used to dissolve such substances will, of course, depend on the precise material being used. For example, for cellulose diacetate, acetone is a suitable solvent. Because these interleaving agents have much lower refractive indices than those of titanium dioxide, zirconium dioxide or alkaline earth metal titanates, usually in the range 1.45 to 1.50, the interleaving layers contribute to the desirable pearlescent properties of the resulting product, through multilayer interference effects. It is important that the organic film-forming substances should contain groups such as hydroxyl, carboxylic ester, or carboxylic anhydride groups, which react with residual alkoxy groups in the titanium or zirconium dioxide or alkaline earth metal titanate layer to ensure good chemical bonding between the latter and the interleaving layer. This prevents delamination of the nacreous pigment in use.

After the interleaving layer, a layer of titanium or zirconium dioxide or alkaline earth metal titanate is applied in the manner already described. In this way, a multi-layer laminate can be built up consisting of alternate high refractive index layers and interleaving agent layers. The number of high refractive index layers in the laminate will not ordinarily be less than 3 and is preferably 3—8. Above about 15 layers, no further advantage is obtained and the production of the pigment becomes unnecessarily complicated.

The thickness of the high refractive index layers and the interleaving agent layers is of some importance as it determines the precise optical properties of the pigment. In general, each layer will be 0.01—1 micron in thickness, and is preferably 0.03—0.3 micron in thickness. It is advantageous, if a very white

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product is desired, for each layer to be from 0.03—0.1 micron in thickness and vary in thickness within this range as this eliminates coloured effects caused by optical interference.

- 5 If, however, a material displaying colour due to optical interference is required, then the thickness and evenness of the layers must be controlled. If n is the refractive index of a layer, and d is the thickness, then the colour displayed by a thin layer is governed by the

- 10 product $n \cdot d$ (the optical thickness). The colours observed at normal incidence in reflection on such a film are determined partly by reinforcement (constructive inter-
- 15 fference) of light of wavelength $\frac{4}{2N-1} \cdot nd$,

but mainly by destructive interference of light of wavelength $\frac{2}{N} \cdot nd$, where N is a positive

- integer. The resulting variation of colour with increasing film thickness is given by
- 20 Newton's scale of colours. For example a film 115 $m\mu$ thick of titanium dioxide of refractive index 1.94 will have an optical thickness $115 \times 1.94 = 223 \cdot m\mu$ and light of wavelength $2 \times 223 \cdot m\mu = 446 \cdot m\mu$ (blue) will
- 25 be diminished in reflection, and the resulting reflection colour will be orange. For multilayer films the constructive interference becomes more important, and where each layer in a multilayer stack is of equivalent optical thick-
- 30 ness, the reflected colour becomes more intense and saturated, and the variation of colour with angle of viewing becomes more striking. Thus by incorporation of the pigment of this invention, articles can be made which show a
- 35 coloured pearly sheen the colour of which varies with the angle of observation. For materials displaying colour due to optical interference, the thickness of the high refractive index layers and the interleaving layers is preferably 0.05—0.3 micron.

- 40 When dipping techniques are used for the production of thin layer films, solutions of about 3—6% of metal ester in petroleum spirit generally give high refractive index
- 45 layers of the correct thickness to show first order interference colours, but the precise thickness depends on the conditions of dipping used. The colour shown by a layer deposited from a solution of given concentration cannot be exactly defined, because the film thickness is dependent not only on measurable quantities such as belt speed, but also on such features as the surface perfection of the release layer, and the draught drying the solution on the
- 55 belt. For a given machine, even belt speed, even ventilation, vertical withdrawal of the belt and protection of the metal ester solution from vibration which would disturb the surface, are important to ensure uniform films of the same thickness both sides of the belt.
- 60 In general, an increase of 10%—20% in

the concentration of the metal ester, keeping all other conditions constant in a given dipping arrangement, results in a colour change of one spectral colour in the order of increasing wavelength. In practice violet, blue and green are easier to obtain from first order interference under these conditions, because the slight irregularity causing colour variation and the colour variation with angle of viewing are such as to favour cancellation of the reds and yellows. By the use of higher orders of interference (thicker layers), however, it is easy to obtain more saturated reds and yellows.

After the requisite number of layers has been built up on the support, the pigment is removed therefrom by dissolving away the release layer, for example by immersing the support in water when a water-soluble release agent, such as a polyethylene glycol release layer, is used. The pigment separates from the support either as a soft filmy material or as rather coarse particles which can be separated from the water in conventional manner, e.g. by decantation, filtration or centrifugation. The material may then be immersed in a bath of acetone or ethanol to dehydrate it and finally comminuted without crushing to small particle size, e.g. by vigorous stirring in viscous solution, by ultrasonic agitation, or by passage through a colloid mill. It is most important not to crush the product as this destroys its desirable optical properties. Ordinarily, each particle of the comminuted pigment is 1—70 microns across and preferably 5—50 microns across.

The particular conditions for comminution required depend on the strength of the particles which is dependent, *inter alia*, on the particular interleaving layer used and upon the conditions of deposition. In general satisfactory comminution can be accomplished by two passages in dibutyl phthalate through a colloid mill with a rotor speed of 10,000 revs/min. using a gap setting of 0.0015—0.002 inch (0.038—0.051 mm).

If material having a sparkling decorative appearance is required as opposed to material for strictly nacreous finishes, then larger particle sizes perhaps up to 1—2 mm. diameter are required and comminuting conditions adjusted accordingly, or the comminution omitted.

It is possible to increase the amount of pigment produced for a given area of support by forming a multi-layer laminate in the manner already described, and then coating the upper surface of this laminate with a further layer of release agent and then building up a further multi-layer laminate in the same manner. In this way, two or more layers of the pigment can be built up on a single area of support.

If desired, the pigments may be heated in order to raise the refractive index of the higher refractive index layer; the upper

temperature limit is, of course, dependent on the stability of the organic layer.

The new process readily lends itself to continuous operation. Thus, a continuous belt coated with a release layer may be fed first into a solution of a titanate or zirconate ester or alkaline earth metal titanate ester, then through a zone in which the solvent is evaporated and the ester hydrolysed to give a clear layer of titanium or zirconium dioxide or alkaline earth metal titanate, and finally into a solution of the interleaving agent, before being re-passed into the solution containing the titanate or zirconate ester or alkaline earth titanate ester. After a sufficient number of layers have been built upon the belt, the pigment is released from the belt, e.g. by immersion in water when a water-soluble release agent is used, and then worked up in the manner already indicated. Alternatively, a very long belt of a flexible support (after being coated with a water-soluble release layer) may be passed successively through alternate baths of titanate or zirconate ester or alkaline earth metal titanate ester solution and interleaving agent solution, the evaporation of the solvents and the hydrolysis of the ester taking place between the various baths. Finally, the belt is passed into an aqueous bath, in which the release layer is soluble, and which detaches the pigment from the support and the belt is then wound up (after suitable cleaning) for reuse. In this latter method, the number of high refractive index layers in the resulting pigment is clearly determined by the number of baths through which the belt is passed.

There are many techniques in the coating industry for producing thin layers of a material by some form of roller coating; but none of these processes are routinely used to coat layers as thin as those used in this invention. By experimentation it has been found that very even layers of the thicknesses required can be deposited by a commercially available roller coating machine, when a reverse roller kiss coating method is used. This is a technique which comprises coating a band or belt with a liquid composition by moving the belt in one direction over a roller wetted with the liquid composition and rotating in the opposite sense. These machines can operate with belt speeds up to 1000 feet per minute or more, and thus can give a much faster rate of production than a simple dipping procedure. By arranging several coating stations in series, all the layers can be coated in sequence in one operation. Moreover, by using a continuous belt and a washing stage in the process, continuous operation is possible.

The invention is illustrated by the accompanying drawings, in which:

Figure 1 is a cross-section, greatly enlarged,

of a pigment particle in accordance with the invention; and

Figure 2 shows diagrammatically an apparatus for producing a pigment in accordance with the invention.

In Figure 1, a pigment particle comprises three thin, clear films 11 of high refractive index material, e.g. titanium dioxide, separated by two thin, clear, adherent layers 2 of an interleaving agent, e.g. cellulose diacetate.

In Figure 2, a long belt 11 of polyethylene terephthalate film is unwound from spool 12 and passes over idler rollers 13 to drive roller 14, and is then wound up on take-up spool 15. A layer of release agent and then alternate layers of high refractive index material and interleaving agent are applied to the belt 11 by the coating roller 16, which rotates in the direction shown, i.e. in the opposite direction to the belt 11. The amount of coating solution 19 applied to the belt 11 is controlled by the gap 18 between the doctor roller 17 (which rotates in the direction shown) and the coating roller 16. The surface of the doctor roller is itself scraped free of solution 19 by doctor blade 20. The whole coating operation takes place within box 21 which provides a controlled atmosphere. After being coated, the belt 11 passes through drying oven 22 in which, after the solvent of solution 19 has evaporated and (in the case of layer (I)) the deposited layer is hydrolysed by atmospheric water vapour entering through inlet 23. The air is mainly exhausted at outlet 24, but some hot air leaves *via* outlet 25 to provide a controlled atmosphere in box 21. After leaving oven 22, the belt passes over drive roller 14 and is wound up on take-up spool 15. The operation is repeated for each layer applied to the support, and after a sufficient number of layers have been applied, the pigment is released from the support and further treated in the manner already described.

It is important to prevent premature evaporation of the solvent or hydrolysis of the esters in the solution or on the coating and doctor rollers. For this purpose, the incorporation of suitable baffles or enclosures to protect the coating and doctor rollers and the solution from currents of air is desirable. It is also desirable to keep the surface area of the solution to a minimum to reduce evaporation.

The value under equivalent conditions of the various substances available for preparing the high refractive index layers has been generally found to be in the order:—tetra-isopropyl titanate=tetra-ethyl titanate=tetra-(methyl/isopropyl) titanate > tetra-n-propyl zirconate > tetra-n-butyl zirconate, tetra-n-butyl titanate, calcium titanium isopropoxide > tetra-n-hexyl titanate, tetra(2-ethyl-n-hexyl) titanate > dibutyl polytitanate.

The organic film-forming substances used

for interleaving layers are graded in order of whiteness of product thus:— methyl vinyl ether/ethyl hydrogen maleate copolymer> methyl vinyl ether/maleic anhydride copolymer> sulphonamide/formaldehyde resin, ethyl cellulose, polyvinyl acetal> partially acetylated polyvinyl alcohol. For lustre, these materials are graded thus:— methyl vinyl ether/ethyl hydrogen maleate or maleic anhydride> ethyl cellulose $\equiv$ polyvinyl butyral> polyvinyl acetal> sulphonamide/formaldehyde resin> ethyl-hydroxyethyl cellulose. Nitro-cellulose gives high lustre but poor colour.

The performance of the water-soluble release layers tested is:— polyvinyl pyrrolidone $\equiv$ polyethylene glycol>> polyvinyl methyl ether.

The performance of the substrate materials tested is:— glass>metals> polyethylene terephthalate>>> others.

The following Examples illustrate the invention.

EXAMPLE 1

An endless belt of polyethylene terephthalate (0.01 inch [0.254 mm.] thick) is passed three times through a 4% w/v solution of polyethylene glycol 6000 in methanol, the belt being dried between coatings. This gives a film about 100 microns thick of the polyethylene glycol. The belt is then passed at a speed of 1.2 cm. per second through a 4% w/v solution of redistilled tetra isopropyl-titanate in petroleum spirit (b.p. 40–60°C.). The petroleum spirit evaporates and the tetra isopropyl-titanate then hydrolyses by contact with atmospheric moisture to produce a clear layer of titanium dioxide. The humidity of the air surrounding the belt is 25–30% at a temperature of 28°C. The belt is then passed through an 0.6% w/v solution of cellulose diacetate in acetone, and the acetone is allowed to evaporate. The belt is passed again through the titanate solution and the cellulose diacetate solution in succession until 10 layers of titanium dioxide and 9 interleaving layers of cellulose diacetate have been formed. The belt is then immersed in water to wash off the products (or alternatively another coating of the polyethylene glycol is deposited on the product and the sequence of operations repeated to provide a larger amount of material on the single support). The product washed off by the water is collected, washed well with acetone and then comminuted by ultra-sonic agitation in acetone. It has a brilliant silvery-white lustre when dispersed in acetone or a similar solvent. When the pigment is dried or is a dry lacquer film it is somewhat less lustrous with a bluish tinge. Typical particle size after comminution is 20–31 $\times$ 20–40 μ , the material containing no particles greater than 70 $\times$ 70 μ .

The product so obtained, while of relatively low heat stability because of its cellulose

diacetate content, is very suitable for use in applications where a non-toxic pearlescent pigment is required and stability to heat is not important, for example in cosmetics such as eye shadows, lipsticks and nail varnishes, or in leather finishes and printing inks.

EXAMPLE 2

A glass plate is coated by dipping it into a 24% w/v solution of polyethylene glycol 20,000 in methanol. The plate is then dipped alternately in a solution of 4% w/v tetra-isopropyl titanate in 40–60°C., petroleum spirit and a solution of 0.5% w/v ethyl-hydroxyethyl-cellulose (low viscosity grade) in 40–60°C. petroleum spirit containing enough isopropanol (10% v/v) to produce a clear solution. After dipping, each layer is dried in a current of air at 90–100°C. for 10–20 seconds, the relative humidity of the ambient air being 42% at 22°C. After four layers of titanium dioxide and three layers of interleaving agent have been laid down, the plate is immersed in water with gentle agitation. Large particles of product are collected by decantation and transferred to acetone, or are caught on a wire gauze, and immersed in acetone, and reduced in size by ultra-sonic agitation. A rather powdery white product is obtained. Typical particle size after comminution is 8–43 $\times$ 6–37 μ .

In principle any suitable organic film-forming substance may be used in the procedure of this Example in place of the ethyl-hydroxyethyl cellulose. For example:—

(a) An 0.6% w/v solution of polyvinyl acetal (Alvar 1570 of Shawinigan Ltd. "ALVAR" is a registered Trade Mark) in acetone is used. A lustrous white product is obtained. Typical particle size after comminution is 10–25 $\times$ 4–10 μ .

(b) An 0.5% w/v solution of polyvinyl butyral (S-LEC resin type BH-2 of British Traders and Shippers) in acetone is used. A white lustrous product is obtained. Typical particle size for this product after comminution is 10–39 $\times$ 8–21 μ .

(c) An 0.6% w/v solution of partially hydrolysed polyvinyl acetate (ca. 40% hydrolysis: Resin D 383 of Shawinigan Ltd.) in acetone, is used. A white product is obtained. Typical particle size for this product after comminution is 8–25 $\times$ 8–21 μ .

(d) An 0.25% w/v solution of nitro-cellulose (commercial pyroxylin, 10.5–12% nitrogen) in acetone is used. The product possesses a superior lustre but discolours rapidly on exposure to light.

(e) An 0.5% w/v solution of a commercial sulphonamide-formaldehyde resin (Santolite MHP of Monsanto Ltd. "SANTOLITE" is a registered Trade Mark) in acetone is used. The product obtained was of a silvery-white appearance with a satisfactory lustre. Typical particle size after comminution is 6–25 $\times$ 6–18 μ .

- (f) A 3% w/v solution of a silicone glycol copolymer (Silicone Surfactant 193 of Dow Corning Ltd.) in acetone is used. A white product is obtained. Typical particle size after comminution is $8-37 \times 6-31 \mu$. 5
- (g) An 0.5% w/v methyl vinyl ether-maleic anhydride copolymer (Gantrez AN 169 of Fine Dyestuffs and Chemicals Ltd., "GANTREZ" is a registered Trade Mark) solution in acetone is used. (Hydrolysis is effected at 23°C. and 25% relative humidity). The product obtained is particularly lustrous. Typical particle size after comminution is $8-25 \times 6-21 \mu$. 10
- (h) An 0.5% w/v methyl vinyl ether-ethyl hydrogen maleate copolymer (Gantrez ES 225 of Fine Dyestuffs and Chemicals Ltd.) solution in acetone is used. (Hydrolysis is effected at 23°C. and 25% relative humidity). The product obtained is substantially identical to that from the previous Example 2 (g). Typical particle size after comminution is $6-21 \times 6-16 \mu$. 15
- (i) An 0.5% w/v solution in acetone of *p*-*t*-butyl-phenol/formaldehyde novolak resin (prepared as described in Plastics Monograph C3—Phenolic Resins, page 86, published by the Plastics Institute), is used. The resulting product is pearly but dark yellow in colour. Typical particle size after comminution is $10-35 \times 6-27 \mu$. 30
- (j) An 0.5% w/v solution in acetone of a phenol/formaldehyde novolak resin prepared as described in Plastics Monograph C3—Phenolic Resins, page 86, published by the Plastics Institute (having a refractive index of 1.66—1.67) is used. The product obtained is similar to that from 2 (i) but paler yellow in colour. Typical particle size after comminution is $8-29 \times 6-21 \mu$. 35
- (k) An 0.5% w/v solution in acetone of ethyl cellulose of viscosity 7 c.p.s. and 48—49% ethoxy content, is used. A white product of good lustre is obtained. Typical particle size after comminution is $10-39 \times 8-33 \mu$. 40
- The refractive indices of the individual layers of the products of some of the preceding Examples have been measured and found to be as follows. 45 50

Example	Refractive Index of	
	High refractive index layer	Interleaving layer
1	1.84 — 1.86	1.47 — 1.49
2 (d)	1.90 — 1.94	1.48 — 1.50
2 (k)	1.90 — 1.94	1.46 — 1.48

WHAT WE CLAIM IS:—

1. A pigment comprising a plurality of thin, clear layers, each of which is uniform, of titanium or zirconium dioxide, or an alkaline earth metal titanate (as hereinbefore defined) each such adjacent layer being separated by one, and adherent to one or two thin clear layers, each of which is uniform, of an interleaving agent, which is an organic film-forming substance containing hydroxyl, carboxylic anhydride, carboxylic ester, or other groups capable of reacting with titanium ester or zirconium ester or alkaline earth metal titanate ester groups, the refractive index of the layers of titanium or zirconium dioxide or alkaline earth metal titanate exceeding that of the layers of interleaving agent by at least 0.05. 55
2. A pigment comprising a plurality of thin, clear layers, each of which is uniform, of titanium or zirconium dioxide (as hereinbefore defined) separated by, and adherent to, one or more layers of an interleaving agent which is an organic film-forming substance containing hydroxyl groups. 60
3. A pigment according to claim 2 in which the interleaving agent is cellulose diacetate. 65
4. A pigment according to claim 1 in which the interleaving agent is cellulose diacetate, ethyl cellulose, nitrocellulose, ethyl-hydroxy-ethyl-cellulose, polyvinyl acetal, polyvinyl butyral, partially hydrolysed polyvinyl acetate, a sulphonamide-formaldehyde resin, a silicone-glycol copolymer, a methyl vinyl ether-maleic anhydride copolymer, a methyl vinyl ether-ethyl hydrogen maleate copolymer, a *p*-*t*-butyl-phenol-formaldehyde novolak resin, or a phenol-formaldehyde novolak resin. 80
5. A pigment according to any of claims 1 to 4 in which the refractive index of the layers of titanium dioxide is 1.85 to 1.95 or of zirconium dioxide or alkaline earth metal titanate is 1.69 to 1.75 and the refractive index of the layers of interleaving agent is 1.45 to 1.50. 85
6. A pigment according to any of claims 1 to 5 comprising 3 to 8 thin, clear layers of titanium or zirconium dioxide or an alkaline earth metal titanate. 90
7. A pigment according to any of claims 1 to 6 comprising 3 to 8 thin, clear layers of titanium or zirconium dioxide or an alkaline earth metal titanate. 95



- (f) A 3% w/v solution of a silicone glycol copolymer (Silicone Surfactant 193 of Dow Corning Ltd.) in acetone is used. A white product is obtained. Typical particle size after comminution is 8—37×6—31 μ .
- 5 (g) An 0.5% w/v methyl vinyl ether-maleic anhydride copolymer (Gantrez AN 169 of Fine Dyestuffs and Chemicals Ltd., "GANTREZ" is a registered Trade Mark) solution in acetone is used. (Hydrolysis is effected at 23°C. and 25% relative humidity). The product obtained is particularly lustrous. Typical particle size after comminution is 8—25×6—21 μ .
- 10 (h) An 0.5% w/v methyl vinyl ether-ethyl hydrogen maleate copolymer (Gantrez ES 225 of Fine Dyestuffs and Chemicals Ltd.) solution in acetone is used. (Hydrolysis is effected at 23°C. and 25% relative humidity). The product obtained is substantially identical to that from the previous Example 2 (g). Typical particle size after comminution is 6—21×6—16 μ .
- 20 (i) An 0.5% w/v solution in acetone of *p*-*t*-butyl-phenol/formaldehyde novolak resin (prepared as described in Plastics Monograph C3—Phenolic Resins, page 86, published by the Plastics Institute), is used. The resulting product is pearly but dark yellow in colour. Typical particle size after comminution is 10—35×6—27 μ .
- 30 (j) An 0.5% w/v solution in acetone of a phenol/formaldehyde novolak resin prepared as described in Plastics Monograph C3—Phenolic Resins, page 86, published by the Plastics Institute (having a refractive index of 1.66—1.67) is used. The product obtained is similar to that from 2 (i) but paler yellow in colour. Typical particle size after comminution is 8—29×6—21 μ .
- 35 (k) An 0.5% w/v solution in acetone of ethyl cellulose of viscosity 7 c.p.s. and 48—49% ethoxy content, is used. A white product of good lustre is obtained. Typical particle size after comminution is 10—39×8—33 μ .
- 40 The refractive indices of the individual layers of the products of some of the preceding Examples have been measured and found to be as follows.
- 45
- 50

Example	Refractive Index of	
	High refractive index layer	Interleaving layer
1	1.84 — 1.86	1.47 — 1.49
2 (d)	1.90 — 1.94	1.48 — 1.50
2 (k)	1.90 — 1.94	1.46 — 1.48

WHAT WE CLAIM IS:—

1. A pigment comprising a plurality of thin, clear layers, each of which is uniform, of titanium or zirconium dioxide, or an alkaline earth metal titanate (as hereinbefore defined) each such adjacent layer being separated by one, and adherent to one or two thin clear layers, each of which is uniform, of an interleaving agent, which is an organic film-forming substance containing hydroxyl, carboxylic anhydride, carboxylic ester, or other groups capable of reacting with titanium ester or zirconium ester or alkaline earth metal titanate ester groups, the refractive index of the layers of titanium or zirconium dioxide or alkaline earth metal titanate exceeding that of the layers of interleaving agent by at least 0.05.
- 55
- 60
- 65
- 70
- 75
2. A pigment comprising a plurality of thin, clear layers, each of which is uniform, of titanium or zirconium dioxide (as hereinbefore defined) separated by, and adherent to, one or more layers of an interleaving agent which is an organic film-forming substance containing hydroxyl groups.
3. A pigment according to claim 2 in which the interleaving agent is cellulose diacetate.
4. A pigment according to claim 1 in which the interleaving agent is cellulose diacetate, ethyl cellulose, nitrocellulose, ethyl-hydroxy-ethyl-cellulose, polyvinyl acetal, polyvinyl butyral, partially hydrolysed polyvinyl acetate, a sulphonamide-formaldehyde resin, a silicone-glycol copolymer, a methyl vinyl ether-maleic anhydride copolymer, a methyl vinyl ether-ethyl hydrogen maleate copolymer, a *p*-*t*-butyl-phenol-formaldehyde novolak resin, or a phenol-formaldehyde novolak resin.
5. A pigment according to any of claims 1 to 4 in which the refractive index of the layers of titanium dioxide is 1.85 to 1.95 or of zirconium dioxide or alkaline earth metal titanate is 1.69 to 1.75 and the refractive index of the layers of interleaving agent is 1.45 to 1.50.
6. A pigment according to any of claims 1 to 5 comprising 3 to 8 thin, clear layers of titanium or zirconium dioxide or an alkaline earth metal titanate.
7. A pigment according to any of claims
- 80
- 85
- 90
- 95
- 100



1 to 6 in which the thickness of the layers of titanium or zirconium dioxide or alkaline earth metal titanate and of the interleaving layers is within the range 0.01 to 1 micron.

8. A pigment according to claim 7 in which the thickness of the layers of titanium or zirconium dioxide or alkaline earth metal titanate and of the interleaving layers is within the range 0.03 to 0.3 microns.

9. A pigment according to claim 8 in which the thickness of the layers of titanium or zirconium dioxide or alkaline earth metal titanate and of the interleaving agent is 0.03 to 0.1 micron, the layers vary in thickness within this range and the pigment is white.

10. A pigment according to claim 8, in which the thickness of the layers of titanium or zirconium dioxide or alkaline earth metal titanate and of the interleaving agent is 0.05 to 0.3 microns, the layers are of controlled thickness within this range, and the pigment is coloured.

11. A pigment according to any of claims 1 to 10 in which each pigment particle is from 1 micron to 2 mm. across.

12. A pigment according to claim 11 in which each pigment particle is 5 to 50 microns across.

13. A pigment according to claim 1 substantially as hereinbefore described.

14. A pigment according to claim 1 substantially as described in Example 1.

15. A pigment according to claim 1 substantially as described in Example 2.

16. Process for the preparation of a pigment which comprises applying to a support a release layer which is wetted by the composition used to apply the first layer of (I) and which is insoluble in the compositions

used to apply the layers of (I) and (II) but soluble in the solvent used to release the multi-layer product from the support, and then alternately thin layers, each of which is uniform, of (I) a hydrolysable titanic or zirconic ester or alkaline earth metal titanate

and (II), as interleaving agent former, an organic film-forming substance containing hydroxyl, carboxylic anhydride, carboxylic ester or other groups capable of reacting with titanium ester or zirconium ester or alkaline earth metal titanate ester groups such that after hydrolysis of the hydrolysable layers (I) and, if necessary after heating the layers produced,

the refractive index of layers (I) exceeds that of layers (II) by at least 0.05; hydrolysing each hydrolysable layer (I) immediately after application to a clear layer by contact with water vapour; and when at least two layers of the titanic or zirconic ester or alkaline earth metal titanate ester have been applied

and hydrolysed, releasing the multi-layer product from the support by dissolving away the release layer and, if required, heating the layers so produced before or after release of the pigment to give a pigment wherein the

refractive index of layers (I) exceeds that of layers (II) by at least 0.05.

17. Process for the preparation of a pigment which comprises applying to a support a release layer which is wetted by the composition used to apply the first layer of (I) and which is insoluble in the compositions used to apply the layers of (I) and (II) but soluble in the solvent used to release the multi-layers product from the support, and then alternately thin layers, each of which is uniform, of (I) a hydrolysable titanic or zirconic ester and (II), as interleaving agent former, an organic film-forming substance containing hydroxyl groups, hydrolysing each hydrolysable layer (I) immediately after application to a clear layer by contact with water vapour, and, when at least two layers of the titanic or zirconic ester have been applied and hydrolysed, releasing the multi-layer product from the support by dissolving away the release layer.

18. Process according to claim 17 in which the interleaving agent former used is cellulose diacetate.

19. Process according to claims 17 or 18 in which the hydrolysable titanic or zirconic ester used is an alkyl titanate or zirconate.

20. Process according to claim 16 in which the interleaving agent former used is cellulose diacetate, ethyl cellulose, nitro-cellulose, ethyl-hydroxyethyl-cellulose, polyvinyl acetate, polyvinyl butyral, partially hydrolysed polyvinyl acetate, a sulphonamide-formaldehyde resin, a silicone-glycol copolymer, a methyl vinyl ether-maleic anhydride copolymer, a methyl vinyl ether-ethyl hydrogen maleate copolymer, a *p*-*t*-butyl-phenol-formaldehyde novolak resin, or a phenol-formaldehyde novolak resin.

21. Process according to claim 16 or 20 in which the hydrolysable titanic or zirconic ester or alkaline earth metal titanate ester used is an alkyl titanate, zirconate, or alkaline earth metal titanate, in which each alkyl contains 1 to 8 carbon atoms.

22. Process according to claim 21 in which tetra-isopropyl titanate, tetra-*n*-butyl titanate, tetra-*n*-propyl zirconate, or calcium titanium isopropoxide is used.

23. Process according to any of claims 16 to 22 in which the support is of glass, polished metal, or polyethylene terephthalate film.

24. Process according to any of claims 16 to 23 in which the release layer is water-soluble.

25. Process according to claim 24 in which the release layer is polyethylene glycol of molecular weight 6000 to 100,000.

26. Process according to claim 24 in which the release layer is polyvinylpyrrolidone.

27. Process according to any of claims 16 to 26 in which the hydrolysable titanic or zirconic ester or alkaline earth metal titanate ester is applied as a solution in an inert volatile solvent, and the said solvent is

evaporated before the said ester is hydrolysed.

28. Process according to claim 27 in which the said solvent is a volatile hydrocarbon.

5 29. Process according to any of claims 16 to 28 in which 3 to 8 layers of hydrolysable titanic or zirconic ester or alkaline earth metal titanic ester are applied to the support and hydrolysed.

10 30. Process according to any of claims 16 to 29 in which each layer is 0.01 to 1 micron thick.

31. Process according to claim 30 in which each layer is 0.03 to 0.3 microns thick.

15 32. Process according to claim 31 in which each layer is 0.03 to 0.1 microns thick, the layers vary in thickness within this range and the pigment is white.

20 33. Process according to claim 31 in which each layer is 0.05 to 0.3 microns thick, the layers are of controlled thickness within this range, and the pigment is coloured.

25 34. Process according to any of claims 16 to 33 in which, after being released from the support, the pigment is comminuted to a particle size of from 1 micron to 2 mm.

35. Process according to claim 34 in which,

after being released from the support, the pigment is comminuted to a particle size of 5 to 50 microns.

36. Process according to any of claims 16 to 35 in which the layers are applied to the support by a reverse roller kiss-coating technique.

37. Process according to claim 36 when carried out using an apparatus substantially as shown in Figure 2 of the accompanying drawings.

38. Process according to claim 16 substantially as hereinbefore described.

39. Process for the preparation of a pigment substantially as described in Example 1.

40. Process for the preparation of a pigment substantially as described in Example 2.

41. A pigment produced by the process of any of claims 16, 20 to 38 and 40.

42. A pigment produced by the process of any of claims 17 to 19 and 39.

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114 South Square,
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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1971.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



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