

WE CLAIM

1. A process for producing flaky aluminum oxide, said process comprising steps of preparing (a) an aqueous solution of water-soluble aluminum salt and titanium salt and (b) an aqueous solution of alkali carbonate in an amount approximately equivalent to said water-soluble aluminum salt and titanium salt in said aqueous solution (a), uniformly dissolving alkali metal sulfite and phosphoric acid or a phosphate in either aqueous solution (a) or aqueous solution (b), mixing said aqueous solutions (a) and (b) to give a suspension or gel containing hydrolyzates, drying the suspension or gel by evaporation, and molten-salt treating the dried product by heating at 900-1400 °C to give a solid product, which is finished by water washing, filtering, and drying.
2. The process as claimed in claim 1, flaky aluminum oxide comprises containing therein titanium oxide.
3. The process as claimed in claim 1 wherein said flaky aluminum oxide is in the form of particles having an average particle diameter of 5-60 μm , a thickness smaller than 1 μm , and an aspect ratio (particle diameter/thickness) greater than 20.
4. The process as claimed in claim 1 flaky aluminum oxide wherein the content of titanium oxide is 0.1-4 wt % in said flaky aluminum oxide.

Dated this 10th day of SEPTEMBER 1996.

Banerjee
(I. BANERJEE)
OF L S DAVAR & CO
APPLICANTS' AGENT

FLAKY ALUMINUM OXIDE AND PEARLESCENT PIGMENT, AND
PRODUCTION THEREOF

The present invention relates to a new grade of flaky aluminum oxide which is composed of aluminum oxide and titanium oxide and also to a process for producing the same. The flaky aluminum oxide containing titanium oxide is characterized by its great aspect ratio (particle diameter/thickness) and very little tendency toward crystal twinning and aggregation. The present invention also relates to a pearlescent pigment formed from such flaky aluminum oxide by coating with metal oxide. The pearlescent pigment will find use as a raw material for paint, plastic, ink, cosmetic, and glaze.

[Prior art]

There is known a pearlescent pigment which is formed by coating a flaky substrate (such as mica flakes) with a metal oxide (such as titanium oxide) having a high refractive index. A substrate desirable for this kind of pigment is a qualitywise stable synthetic substance, such as flaky iron oxide, flaky titanium oxide, and aluminum doped flaky iron oxide, which has been developed and put on the market recently.

For better pearlescence, the substrate is required to be uniformly thin flakes with a large aspect ratio (or with a large diameter for thickness), which are extremely

colorless and transparent and have good heat resistant and high mechanical strength in the flaky state.

Aluminum oxide with high hardness finds use as wear-resistant material, ceramic material, paint pigment, abrasive, etc. Attempts have been made to produce simple aluminum oxide in a flaky form which would have improved characteristic properties. Typical examples proposed so far are given below.

- α -Aluminum oxide in the form of hexagonal flake, having a particle diameter greater than 10 μm and an aspect ratio (particle diameter/thickness) of 5-10. (Japanese Patent Laid-open No. 111239/1982)
- α -Aluminum oxide in the form of flake, having an average particle diameter of 0.5-3 μm . (Japanese Patent Publication No. 72527/1991)
- α -a-Aluminum oxide in the form of hexagonal small plate single crystal, 0.1-2 μm thick and 2-20 μm in diameter, with the aspect ratio being 5-40. (Japanese Patent Laid-open No. 131517/1991)
- Aluminum oxide in the form of fine platy particle of hexagonal crystal system, with the plane perpendicular to the c axis grown into a plate. (Japanese Patent Laid-open No. 39362/1992)

It turned out, however, that these kinds of aluminum oxide are not suitable for use as the flaky substrate for

pearlescent pigments because of excessively small particle diameters, small aspect ratios, strong tendency toward crystal twinning and aggregation, and poor dispersion in water. In addition, such aluminum oxide particles are difficult to coat with a metal oxide because they are poor in dispersion in water and are composed of aluminum oxide alone. Even if coating is possible, the resulting coated particles are nonuniform in particle of a metal oxide diameter and liable to aggregation and merely assume a dull pearlescence. Consequently, they are not suitable for use as a substrate for pearlescent pigments. Moreover, the above-mentioned aluminum oxide particles have a disadvantage that they are usually produced by the hydrothermal process (as disclosed in Japanese Patent Laid-open No. 39362/1992) which needs an expensive high-pressure reactor.

The present invention is intended to address problems associated with the prior art technology mentioned above. It is an object of the present invention to provide flaky aluminum oxide (to be used as a substrate) which is characterized by a greater aspect ratio than the conventional one, uniform small thickness, smooth surface, almost complete colorlessness, and very little tendency toward crystal twinning and aggregation. It is another object of the present invention to provide a pearlescent pigment prepared by coating said flaky substrate with a

metal oxide. It is further another object of the present invention to provide a simple process for producing said flaky aluminum oxide.

[Disclosure of the invention]

The present invention discloses a new grade of flaky aluminum oxide having outstanding characteristic properties required of the substrate for pearlescent pigments. The flaky aluminum oxide is composed of aluminum oxide (as a major constituent) and titanium oxide (as a minor constituent). It is prepared from a uniform aqueous solution of water-soluble aluminum salt and titanium salt by hydrolysis with an alkali carbonate aqueous solution, under co-existence of an aqueous solution containing alkali metal sulfate and phosphoric acid (or phosphate), drying by evaporation (dehydration by heating), and molten-salt treatment.

The first aspect of the present invention resides in flaky aluminum oxide which comprises containing therein titanium oxide.

The second aspect of the present invention resides in a process for producing flaky aluminum oxide, said process comprising steps of preparing (a) an aqueous solution of water-soluble aluminum salt and titanium salt and (b) an aqueous solution of alkali carbonate in an amount approximately chemical equivalent to said water-soluble

aluminum salt and titanium salt in said aqueous solution (a), uniformly dissolving alkali metal sulfate and phosphoric acid or a phosphate in either aqueous solution (a) or aqueous solution (b), mixing said aqueous solutions (a) and (b) to give a suspension or gel containing hydrolyzates, drying the suspension or gel by evaporation, and molten-salt treating the dried product by heating at 900-1400°C to give a solid product, which is finished by water washing, filtering, and drying.

The third aspect of the present invention resides in a process for producing flaky aluminum oxide, said process comprising steps of adding dropwise a solution of water-soluble aluminum salt and a solution of alkali carbonate simultaneously to water in such a way that the former is approximately chemical equivalent to the latter, thereby forming a suspension of hydrated aluminum hydroxide, adding this suspension (or solids filtered out from this suspension) to an aqueous solution of alkali metal sulfate, adding to the resulting solution a titanium salt and phosphoric acid or a phosphate to give a suspension or gel containing hydrolyzates, drying the suspension or gel by evaporation, and molten-salt treating the dried product by heating at 900-1400°C to give a solid product, which is finished by water washing, filtering, and drying.

The fourth aspect of the present invention resides in

a pearlescent pigment which comprises particles of said flaky aluminum oxide and metal oxide coating formed on the surface of said particles.

The fifth aspect of the present invention resides in a paint, plastic, ink, cosmetic, or glaze composition which comprises containing therein said flaky aluminum oxide or said pearlescent pigment.

The present invention is embodied in flaky aluminum oxide containing titanium oxide. As compared with conventional aluminum oxide composed of aluminum oxide alone, it has a larger particle diameter, a uniform smaller thickness, and a greater aspect ratio. In addition, it has a smooth surface and very little tendency toward crystal twinning and aggregation, which are outstanding characteristic properties required of the substrate. It may be coated with a metal oxide having a high refractive index to give a pearlescent pigment which takes on a good pearlescent gloss. This pearlescent pigment is suitable for plastic, paint, ink, cosmetic, and glaze.

The flaky aluminum oxide of the present invention is produced by the process explained in detail in the following.

The first process as defined in Claim 4.

This process starts with preparation of two aqueous solutions (a) and (b). The aqueous solution (a) is prepared

from water-soluble aluminum salt and titanium salt. The former may be selected from a variety of aluminum salts, of which aluminum sulfate and aluminum nitrate are desirable because of their availability and handling properties. The titanium salt may be selected from titanium tetrachloride, titanium trichloride, titanium oxysulfate, and titanyl sulfate. The amount of titanium salt varies depending on the shape (particle diameter, thickness, and aspect ratio) of the desired product. It is usually 0.1-4.0 wt%, preferably 0.5-3.0 wt% (in terms of oxide) of the amount of aluminum oxide. It seems that the titanium salt prevents crystal twinning and aggregation during crystal growth in the molten-salt treatment. In addition, it seems that titanium facilitates adhesion of metal oxide to the flaky aluminum oxide (as a substrate) in the process of preparing a pearlescent pigment by coating the substrate with a metal oxide. Titanium salt in an amount less than 0.1 wt% is not enough to prevent crystal twinning and aggregation. Conversely, titanium salt in an amount more than 4.0 wt% prevents the formation of flaky shaped aluminum oxide. In preparing the solution (a), heating will promote the dissolution of the components.

The aqueous solution (b) is prepared from alkali carbonate in an amount approximately chemical equivalent for neutralization and hydrolysis to the water-soluble aluminum

salt and titanium salt in the aqueous solution (a). A desirable alkali carbonate is sodium carbonate and potassium carbonate.

To the aqueous solution (a) or (b) is added alkali metal sulfate (as a mineralizer) and phosphoric acid or a phosphate (collectively referred to as phosphoric compound hereinafter). It is possible to add the two components together to either (a) or (b) or to add each of them to (a) and (b) separately. It is important to ensure complete dissolution in the solutions (a) and (b).

Examples of the alkali metal sulfate (as a mineralizer) include sodium sulfate, potassium sulfate, and lithium sulfate. The first two are desirable because of availability. They may be used in combination with one another. The amount (in mol) of the mineralizer should be 1 to 5 times the amount of the water-soluble aluminum salt. With an amount less than specified above, the mineralizer will not fully produce the effect of molten-salt heat treatment and flaking. With an amount more than specified above, the mineralizer will be wasted without added effect of flaking and need a large amount of water for removal by washing in the subsequent steps.

The phosphoric compound may be any water-soluble compound selected from phosphoric acid, phosphates, condensed phosphoric acid, and condensed phosphates.

Examples include phosphoric acid, sodium secondary phosphate, sodium primary phosphate, potassium secondary phosphate, potassium primary phosphate, ammonium phosphate, sodium pyrophosphate, potassium pyrophosphate, sodium tripolyphosphate, potassium tripolyphosphate, and ammonium tripolyphosphate. The phosphoric compound makes crystals flaky during molten-salt treatment by heating. With an amount less than 0.1 wt%, it will not produce thin flaky aluminum oxide as desired. With an amount more than 2.0 wt%, it will not produce added effect in reducing the thickness of flaky aluminum oxide. In preparing the solution (b), heating will promote the dissolution of the components.

The aqueous solutions (a) and (b) prepared as mentioned above are mixed together by stirring to effect hydrolysis. The mixing may be accomplished in the following manner (1) or (2).

(1) Simultaneous dropping. This method consists of adding dropwise the aqueous solutions (a) and (b) simultaneously to water such that the former is approximately equivalent to the latter.

(2) Simple addition. This method consists of adding the solution (a) to the solution (b) or vice versa with stirring. The resulting product is a suspension or gel containing a hydrolyzate.

Mixing by the method (1) or (2) gives rise to a suspension or gel containing hydrated aluminum oxide (in the form of fine particles), mineralizer, hydrated titanium oxide, and phosphoric compound, which are uniformly dispersed in the aqueous medium. The suspension or gel is subsequently dehydrated and dried by evaporation. In order to save the amount of heat for drying, it is desirable that the aqueous solutions (a) and (b) be prepared from a minimum of water which is enough for the solutions to be nearly saturated. Another way of achieving this objective is by heating the aqueous solutions (a) and (b), thereby concentrating the salts, before starting the above-mentioned method (1) or (2). In any way, the aqueous solutions (a) and (b) should contain a certain amount of water that ensures complete dissolution. If either or both of the two solutions contain undissolved matter, their mixing results in incomplete hydrolysis which leads to a product which is not flaky and uniform due to twinning and aggregation. In other words, the aqueous solutions (a) and (b) should be uniformly dissolved ones. The thoroughly dehydrated product is subsequently heat-treated at 900-1400°C. The resulting product is washed with water to remove free compounds (mainly sulfates) sticking to it. The washed product is finally dried. In this way there is obtained the desired flaky aluminum oxide.

The second process as defined in Claim 5.

This process employs as a raw material aluminum hydroxide which has previously been prepared from the same materials as used in the first process mentioned above. The aluminum hydroxide is prepared by adding dropwise a solution of water-soluble aluminum salt and a solution of alkali carbonate simultaneously to water such that the alkali carbonate is approximately equivalent to the aluminum salt. The resulting suspension containing hydrated aluminum oxide (or the solid separated from the suspension by washing and filtration) is added to an aqueous solution of alkali metal sulfate as a mineralizer. (The amount of alkali metal sulfate should preferably be 1 to 5 times (in mol) the amount of water-soluble aluminum salt.) To the resulting solution are further added titanium salt and phosphate. (The amount of titanium salt should preferably be 0.1-4.0 wt%, in terms of titanium oxide, of the amount of aluminum oxide. The amount of phosphate should preferably be 0.1-2.0 wt%, in terms of P_2O_5 , of the amount of aluminum oxide.) The resulting suspension is thoroughly dehydrated by evaporation in the same manner as used in the first process mentioned above. During the dehydration step, titanium salt remaining unhydrolyzed is thermally hydrolyzed. The dehydrated product is molten-salt heat-treated at 900-

1400°C. The resulting product is washed with water to remove free compounds (mainly sulfates) sticking to it. The washed product is finally dried. In this way there is obtained the desired flaky aluminum oxide. Incidentally, the hydrated aluminum oxide used in this process may be replaced by commercially available alumina sol or aluminum oxide in the form of fine particles.

For investigation of its physical properties, the sample of flaky aluminum oxide prepared as mentioned above according to the present invention was examined by a scanning electron microscope. It was found to have an average particle diameter of 5-60 μm , a thickness smaller than 1 μm , and an aspect ratio greater than 20. It was also found to be free from crystal twinning and aggregation and readily dispersible in water.

The good dispersibility was proved by the fact that the sample of flaky aluminum oxide gave a streamline when it was dispersed and stirred in water. (A streamline is a lamellar streaky pattern produced by reflected rays from the surface of flaky particles suspending and flowing in a liquid.)

Chemical analysis of the flaky aluminum oxide suggests that it contains nearly as much titanium as the starting material contains and that it contains only a trace amount of phosphorus. Presumably, the phosphorus compound used in

the process of the present invention produces the effect of rendering the aluminum oxide flaky but it is finally released and removed from the system. The phosphoric compound helps the metal oxide to adhere to the aluminum oxide particles in the subsequent step. A probable reason for this is that a trace amount of phosphorus modifies the surface properties of the aluminum oxide particles in the step of heat treatment.

Thus, the flaky aluminum oxide defined in the present invention is composed of aluminum oxide (as a major component) and titanium oxide (as a minor component).

The pearlescent pigment pertaining to the present invention is prepared by coating said flaky aluminum oxide (as a substrate) with a metal oxide (such as titanium oxide and zirconium oxide) having a high refractive index. The coating layer produces a silvery color tone or an interference color depending on the coating thickness. If the coating material is replaced by a colored metal oxide, such as iron oxide, the resulting pearlescent pigment will take on a reddish or blackish color.

Coating with a metal oxide may be accomplished by any known method, such as hydrolysis of a metal salt by heating or alkali, which deposits hydrated metal oxide, followed by calcination. If this calcination is carried out in a reducing atmosphere, the resulting pearlescent pigment takes

on a blackish color due to titanium oxide or iron oxide in a lower oxidation state.

Coating with a metal oxide is difficult to perform on the conventional substrate, which is flaky aluminum oxide composed of aluminum oxide alone. By contrast, the flaky aluminum oxide pertaining to the present invention is highly receptive to a metal oxide. The resulting metal oxide coating is very thin and uniform and hence produces an excellent pearlescent gloss.

The flaky aluminum oxide pertaining to the present invention or the pearlescent pigment derived therefrom may be used as such as a raw material of ceramics or as a pigment for paint, plastics, ink, cosmetics, and glaze. Depending on its use, it will undergo treatment which imparts water resistance, weather resistance, chemical resistance, discoloration resistance, or high dispersibility.

To further illustrate the present invention, and not by way of limitation, the following examples are given.

[Examples]

(Preparation of flaky aluminum oxide)

Example 1

In 450 ml of deionized water were dissolved 223.8 g of aluminum sulfate 18-hydrate, 114.5 g of anhydrous sodium sulfate, and 93.7 g of potassium sulfate, by heating up to

about 75°C. To the resulting solution was added 2.0 g of 34.4% solution of titanyl sulfate. The resulting solution is designated as the aqueous solution (a).

In 250 ml of deionized water were dissolved 0.9 g of sodium tertiary phosphate 12-hydrate and 107.9 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b).

The aqueous solutions (a) and (b) were added simultaneously to 200 ml of deionized water with stirring at a constant rate over about 15 minutes, in such a manner that the solutes in the solution (a) are approximately equivalent to the solutes in the solution (b). Stirring was continued for additional 15 minutes. The resulting solution was evaporated to dryness. The resulting solids were heated at approximately 1200°C for 5 hours. Water was added to the heat-treated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained the desired flaky aluminum oxide.

The thus obtained flaky aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). It was found by chemical analysis that the flaky aluminum oxide contains titanium oxide in an amount of 0.9%. Observation by an optical microscope and an electron microscope revealed

that the flaky aluminum oxide has a particle diameter of 3-16 μm and a thickness of about 0.2 μm and is free from crystal twinning. When dispersed into water by stirring, the flaky aluminum oxide produced a smooth streamline which is a sign of good dispersibility.

Example 2

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate, by heating to above 60°C. To the resulting solution was added 1.0 g of 34.4% solution of titanyl sulfate. The resulting solution is designated as the aqueous solution (a).

In 150 ml of deionized water were dissolved 0.45 g of sodium tertiary phosphate 12-hydrate and 54.0 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b).

The aqueous solution (b) was added with stirring to the aqueous solution (a), which had been heated to about 60°C. Stirring was continued for 15 minutes. The resulting mixture of the two solutions was a gel. This gel was evaporated to dryness. The resulting solids were heated at approximately 1200°C for 5 hours. Water was added to the heat-treated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained the desired flaky aluminum

oxide.

The thus obtained flaky aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). It was found by chemical analysis that the flaky aluminum oxide contains titanium oxide in an amount of 0.9%. Observation by an optical microscope and an electron microscope revealed that the flaky aluminum oxide has a particle diameter of 4-21 μm and a thickness of about 0.2 μm and is free from crystal twinning. When dispersed into water by stirring, the flaky aluminum oxide produced a smooth streamline which is a sign of good dispersibility.

Example 3

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate, by heating to above 60°C. To the resulting solution was added 3.0 g of 34.4% solution of titanyl sulfate. The resulting solution is designated as the aqueous solution (a).

In 150 ml of deionized water were dissolved 0.45 g of sodium tertiary phosphate 12-hydrate and 55.0 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b).

The aqueous solution (b) was added with stirring to the aqueous solution (a), which had been heated to about

60°C. Stirring was continued for 15 minutes. The resulting mixture of the two solutions was a gel. This gel was evaporated to dryness. The resulting solids were heated at 1200°C for 5 hours. Water was added to the heat-treated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained the desired flaky aluminum oxide.

The thus obtained flaky aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). It was found by chemical analysis that the flaky aluminum oxide contains titanium oxide in an amount of 2.6%. Observation by an optical microscope and an electron microscope revealed that the flaky aluminum oxide has a particle diameter of 5-22 μm and a thickness of about 0.2 μm and is free from crystal twinning. When dispersed into water by stirring, the flaky aluminum oxide produced a smooth streamline which is a sign of good dispersibility.

Example 4

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate, by heating to above 60°C. To the resulting solution was added 1.0 g of 34.4% solution of titanyl sulfate. The resulting solution is designated as the aqueous solution (a).

In 150 ml of deionized water were dissolved 1.35 g of sodium tertiary phosphate 12-hydrate and 54.0 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b).

The aqueous solution (b) was added with stirring to the aqueous solution (a), which had been heated to about 60°C. Stirring was continued for 15 minutes. The resulting mixture of the two solutions was a gel. This gel was evaporated to dryness. The resulting solids were heated at 1200°C for 5 hours. Water was added to the heat-treated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained the desired flaky aluminum oxide.

The thus obtained flaky aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). It was found by chemical analysis that the flaky aluminum oxide contains titanium oxide in an amount of 0.8%. Observation by an optical microscope and an electron microscope revealed that the flaky aluminum oxide has a particle diameter of 5-20 μm and a thickness of about 0.2 μm and is free from crystal twinning. When dispersed into water by stirring, the flaky aluminum oxide produced a smooth streamline which is a sign of good dispersibility.

Example 5

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate, by heating to above 60°C. To the resulting solution was added 0.5 g of 34.4% solution of titanyl sulfate. The resulting solution is designated as the aqueous solution (a).

In 150 ml of deionized water were dissolved 0.45 g of sodium tertiary phosphate 12-hydrate and 53.7 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b).

The aqueous solution (b) was added with stirring to the aqueous solution (a), which had been heated to about 60°C. Stirring was continued for 15 minutes. The resulting mixture of the two solutions was a gel. This gel was evaporated to dryness. The resulting solids were heated at 1100°C for 5 hours. Water was added to the heat-treated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained the desired flaky aluminum oxide.

The thus obtained flaky aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). It was found by chemical analysis that the flaky aluminum oxide contains titanium oxide in an amount of 0.4%. Observation by an optical microscope and an electron microscope revealed

that the flaky aluminum oxide has a particle diameter of 4-18 μm and a thickness of about 0.2 μm and is free from crystal twinning. When dispersed into water by stirring, the flaky aluminum oxide produced a smooth streamline which is a sign of good dispersibility.

Example 6

In 500 ml of deionized water was dissolved 223.8 g of aluminum sulfate 18-hydrate by heating. In 250 ml of deionized water was dissolved 106.8 g of sodium carbonate. The two aqueous solutions were added simultaneously to 200 ml of deionized water with stirring at a constant rate over about 15 minutes, in such a manner that the solute in the first solution was always approximately equivalent to the solute in the second solution. Stirring was continued for additional 15 minutes. There was obtained a dispersion. The dispersion was filtered off and the solids were washed with water. Thus there was obtained hydrated aluminum oxide.

In 500 ml of deionized water were dissolved 57.3 g of anhydrous sodium sulfate and 46.9 g of potassium sulfate by heating. To the resulting solution was added the above-mentioned hydrated aluminum oxide and then were added 2.0 g of 34.4% solution of titanium sulfate and 0.9 g of sodium tertiary phosphate 12-hydrate. The resulting solution was stirred for 10 minutes. The solution was evaporated to

dryness. The resulting solids were heated at 1200°C for 5 hours. Water was added to the heat-treated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained the desired flaky aluminum oxide.

The thus obtained flaky aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). It was found by chemical analysis that the flaky aluminum oxide contains titanium oxide in an amount of 0.9%. Observation by an optical microscope and an electron microscope revealed that the flaky aluminum oxide has a particle diameter of 3-16 μm and a thickness of about 0.2 μm and is free from crystal twinning. When dispersed into water by stirring, the flaky aluminum oxide produced a smooth streamline which is a sign of good dispersibility.

[Comparative Examples]

Comparative Example 1

A powder mixture was prepared by milling for 30 minutes from 111.9 g of aluminum sulfate 18-hydrate, 71.6 g of anhydrous sodium sulfate, and 53.4 g of sodium carbonate. The powder mixture was heated at 1000°C for 1 hour. Water was added to the heated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained aluminum oxide

powder.

The thus obtained aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only one peak attributable to aluminum oxide (corundum). Observation by an optical microscope and an electron microscope revealed that the aluminum oxide has a particle diameter smaller than 5 μm and a thickness of about 0.3 μm , with the aspect ratio being small. When dispersed into water by stirring, the aluminum oxide powder did not produce any streamline. In addition, crystal twinning and aggregation were noticed by observation by an optical microscope and an electron microscope.

Comparative Example 2

A powder mixture was prepared by milling for 30 minutes from 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, 46.9 g of potassium sulfate, 0.34 g of titanium oxysulfate pentahydrate, 0.45 g of sodium tertiary phosphate 12-hydrate, and 53.4 g of sodium carbonate. The powder mixture was heated at approximately 1200°C for 5 hours. Water was added to the heated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained aluminum oxide powder.

The thus obtained aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only one peak attributable to aluminum oxide (corundum). Observation by an

optical microscope and an electron microscope revealed that the aluminum oxide greatly fluctuates in diameter and thickness and contains many aggregates. In addition, it was poor in dispersibility.

Comparative Example 3

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate by heating above 60°C. The resulting solution is designated as the aqueous solution (a').

In 150 ml of deionized water was dissolved 53.4 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b').

The aqueous solution (b') was added with stirring to the aqueous solution (a') kept at about 60°C. Stirring was continued for 15 minutes. The resulting gel was evaporated to dryness, and the dried product was heated at 1200°C for 5 hours. Water was added to the heated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained aluminum oxide powder.

The thus obtained aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). Observation by an optical microscope and an electron microscope revealed that

the aluminum oxide is in the form of platy particle, having a diameter of 5-30 μm and a thickness of about 1 μm and contains crystal twinning and aggregation remarkably. When dispersed into water by stirring, the aluminum oxide powder did not produce any streamline because of poor dispersibility.

Comparative Example 4

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate by heating above 60°C. To the resulting solution was added 1.0 g of 34.4% solution of titanyl sulfate without heating. The resulting solution is designated as the aqueous solution (a').

In 150 ml of deionized water was dissolved 54.0 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b').

The aqueous solution (b') was added with stirring to the aqueous solution (a') kept at about 60°C. Stirring was continued for 15 minutes. The resulting gel was evaporated to dryness, and the dried product was heated at 1200°C for 5 hours. Water was added to the heated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained aluminum oxide powder.

The thus obtained aluminum oxide was examined by X-ray

diffraction pattern had only one peak attributable to aluminum oxide (corundum). It was found by chemical analysis that the aluminum oxide contains titanium oxide in an amount of 0.9%. Observation by an optical microscope and an electron microscope revealed that the aluminum oxide has a particle diameter of 5-20 μm and a thickness of about 1.0 μm . This thickness is much greater than that of the aluminum oxide prepared by adding a phosphoric compound.

Comparative Example 5

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate by heating above 60°C. The resulting solution is designated as the aqueous solution (a').

In 150 ml of deionized water were dissolved 0.45 g of sodium tertiary phosphate 12-hydrate and 53.4 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b').

The aqueous solution (b') was added with stirring to the aqueous solution (a') kept at about 60°C. Stirring was continued for 15 minutes. The resulting gel was evaporated to dryness, and the dried product was heated at 1200°C for 5 hours. Water was added to the heated product to dissolve free sulfate. Insoluble solids were filtered off, washed

with water, and finally dried. Thus there was obtained aluminum oxide powder.

The thus obtained aluminum oxide was examined by X-ray diffractometry. The diffraction pattern had only peaks attributable to aluminum oxide (corundum). Observation by an optical microscope and an electron microscope revealed that the aluminum oxide has a particle diameter of 5-20 μm and a thickness of about 0.2 μm and contains crystal twinning and aggregation remarkably. When dispersed into water by stirring, the aluminum oxide powder did not produce any streamline because of poor dispersibility.

Comparative Example 6

In 300 ml of deionized water were dissolved 111.9 g of aluminum sulfate 18-hydrate, 57.3 g of anhydrous sodium sulfate, and 46.9 g of potassium sulfate by heating above 60°C. To the resulting solution was added 2.25 g of 34.4% solution of titanyl sulfate. The resulting solution is designated as the aqueous solution (a').

In 150 ml of deionized water were dissolved 4.5 g of sodium tertiary phosphate 12-hydrate and 53.7 g of sodium carbonate. The resulting solution is designated as the aqueous solution (b').

The aqueous solution (b') was added with stirring to the aqueous solution (a') kept at about 60°C. Stirring was continued for 15 minutes. The resulting gel was evaporated

to dryness, and the dried product was heated at 1200°C for 5 hours. Water was added to the heated product to dissolve free sulfate. Insoluble solids were filtered off, washed with water, and finally dried. Thus there was obtained aluminum oxide powder.

The thus obtained aluminum oxide was found by chemical analysis to contain 4.5% of titanium oxide. Observation by an optical microscope and an electron microscope revealed that the aluminum oxide contains no flaky particles.

[Table showing the conditions of preparation]

Table 1 shows the conditions under which the process was carried out in Examples 1 to 6 and Comparative Examples 1 to 6.

Table 1

Example (Comparative Example)	Conditions of preparation				
	Method	Mineralizer/ Aluminum salt (molar ratio)	TiO ₂ /Al ₂ O ₃ (wt%)	P ₂ O ₅ /Al ₂ O ₃ (wt%)	Type of reaction
1	Simultaneous dropping	4.0	1.0	0.5	wet process
2	Simple addition	4.0	1.0	0.5	wet process
3	Simple addition	4.0	3.0	0.5	wet process
4	Simple addition	4.0	1.0	1.5	wet process
5	Simple addition	4.0	0.5	0.5	wet process
6	Hydrolysis	2.0	1.0	0.5	wet process
(1)	—	3.0	0	0	dry process
(2)	—	4.0	0.6	0.5	dry process
(3)	Addition	4.0	0	0	wet process
(4)	Addition	4.0	1.0	0	wet process
(5)	Addition	4.0	0	0.5	wet process
(6)	Addition	4.0	5.0	2.5	wet process

[Shape and dispersibility]

Table 2 shows the shape and dispersibility of the samples of flaky aluminum oxide obtained in Examples 1 to 6 and Comparative Examples 1 to 6.

Table 2

Example (Comparative Example)	Particle diameter (μm)	Thickness (μm)	Aspect ratio	Twinning and aggregation	Duration of streamline (sec) ^{*1}
1	3-16	0.2	45	No	85
2	4-21	0.2	60	No	80
3	5-22	0.2	65	No	71
4	5-20	0.2	60	No	75
5	4-18	0.2	55	No	70
6	3-16	0.2	50	No	77
(1)	≤ 5	0.3	x	Yes	0
(2)	x	x	x	yes	16
(3)	5-30	1.0	x	Yes	21
(4)	5-20	1.0	13	Yes	23
(5)	5-20	0.2	x	Yes	25
(6)	≤ 4	x	x	Yes	0

*1 : The sample is dispersed and stirred in water, and time required for the streamline of the sample to disappear is measured. The longer the duration, the better the dispersibility of the sample, with particles remaining dispersed in water without aggregation.

x : not measurable.

[Production of pearlescent pigment]

Example 7

The flaky aluminum oxide (20 g) obtained in Example 1 was suspended in 400 ml of deionized water. To the resulting suspension (kept at about 65°C) was added a solution containing 125 g of TiCl_4 per liter at a rate of 0.6 ml/min. Simultaneously a 10% solution of NaOH was added to keep the pH at 2.5. The addition of the TiCl_4 solution was stopped when the resulting product took on a silvery color. The

suspending solids were filtered off, washed with water, and dried. Finally, the dried solids were calcined at 850°C to give a highly whitish and glossy pearlescent pigment.

Example 8

The flaky aluminum oxide (20 g) obtained in Example 2 was suspended in 400 ml of deionized water. To the resulting suspension (kept at about 75°C) was added a 10% solution of NaOH to adjust the suspension to pH 9.0. After 10 minutes, 40 ml of a solution containing 36 g of SnCl₄ per liter was added at a rate of 0.6 ml/min. Simultaneously a 10% solution of NaOH was added to keep the pH at 1.9. After 15 minutes, a solution containing 125 g of TiCl₄ per liter was added at a rate of 0.6 ml/min. Simultaneously a 10% solution of NaOH was added to keep the pH at 1.9. The addition of the TiCl₄ solution was stopped when the resulting product took on a silvery color. The suspending solids were filtered off, washed with water, and dried. Finally, the dried solids were calcined at 850°C to give a highly whitish and glossy pearlescent pigment. Examination by X-ray diffractometry revealed that all the titanium oxide in this pigment is of rutile type.

Example 9

The flaky aluminum oxide (20 g) obtained in Example 5 was suspended in 400 ml of deionized water. To the resulting suspension (kept at about 75°C) was added 220 ml

of a 20% solution of iron nitrate 9-hydrate at a rate of 1.0 ml/min. Simultaneously a 10% solution of NaOH was added to keep the pH at 3.0. The suspending solids were filtered off, washed with water, and dried. Finally, the dried solids were calcined at 850°C to give a reddish brown pearlescent pigment having a golden interference color.

The following examples demonstrate the application of the pearlescent pigment to paint, plastic composition, and printing ink.

Example 10

A base coat paint for automobiles was prepared according to the following formulation.

<Base coat system> Acrylic-melamine resin system	
"Acrydic 47-712" *	70 pbw
"Superbakkamine G821-60" **	30 pbw
Toluene	30 pbw
Ethyl acetate	50 pbw
n-Butano	110 pbw
Solvesso #150	40 pbw

* Acrylic resin from Dainippon Ink & Chemicals, Inc.

** Melamine resin from Dainippon Ink & Chemicals, Inc.

The above acrylic-melamine resin system (100 pbw) was incorporated with 20 pbw of the flaky aluminum oxide or pearlescent pigment obtained in Examples 1 to 9. The resulting compound was diluted with a thinner so that the

resulting paint has an adequate consistency for spraying. (12-15 seconds, Ford cup #4) This paint was applied to a substrate by spraying to form a base coat layer.

The base coated layer was coated further with a colorless top clear coat paint, which was prepared according to the following formulation.

<top clear coat system>

"Acrylic 44-179"	14 pbw
"Superbakkamine L117-60"	6 pbw
Toluene	4 pbw
MIBK	4 pbw
Butyl cellosolve	3 pbw

The top coating was exposed to air at 40°C for 30 minutes and then cured at 135°C for 30 minutes.

Example 11

A base coat paint for automobiles was prepared according to the following formulation.

<Base coat system>

"Dynapol H-700" *1	25.2 g
"Mapranal MF-650" *2	2.7 g
"Cellulose acetobutyrate 531.1" *3	15.5 g
"Irgarol TZ-6"	1.1 g
Ethyl acetate	23.3 g
Xylene	11.6 g
Solvesso 150	11.6 g

C.I. Pigment Red 177 4.5 g

Flaky aluminum oxide or pearlescent pigment obtained in
Examples 1 to 9 4.5 g

*1 A 60% solution of polyester resin in Solvesso 150, from Dynanit
Nobel.

*2 A 55% solution of melamine resin in butanol, from Hoechst.

*3 A 25% solution in a 1:2 mixture of xylene and butyl acetate, from
Eastman Chemical International.

*4 A catalyst based on mineral oil and carboxylate, from Ciba-Geigy.

The above-listed components were mixed for 96 hours using a ball mill, so that the pigments were thoroughly dispersed into the lacquer vehicle. The resulting composition was diluted with a mixed solvent of butyl acetate, xylene, and solvesso 150 to give a paint having a consistency of about 18 seconds (at 20°C) according to DIN4. The paint was applied to a metal plate. After exposure to air at about 40°C for 2 minutes, the base coat was further coated with a colorless top coat paint, which was prepared according to the following formulation.

<Top clear coat system>

"Viacryl VC-373" *1 58.3 g

"Maprenal MF-590" *2 27.3 g

Silicone oil *3 1.0 g

"Tinuvin 900" *4 1.0 g

Xylenel.0 g

"Solvesso 150" 5.4 g

Ethylene glycol acetate 3.0 g

- *1 A 60% solution of acrylic resin in xylene, from Vianora.
- *2 A 55% solution of melamine resin in butanol, from Hoechst.
- *3 A 1% solution in xylene, from Bayer.
- *4 A benzotriazole derivative, from Ciba-Geigy

The top coating was exposed to air at 40°C for 30 minutes and then cured at 135°C for 30 minutes.

Example 12

This example demonstrates the application of the pearlescent pigment to the coloring of plastics. An injection molding compound (in pellet form) was prepared by dry blending according to the following formulation.

Polyethylene resin (pellets)	100 pbw
Flaky aluminum oxide or pearlescent pigment obtained in Examples 1 to 9	1 pbw
Zinc stearate	0.2 pbw
liquid paraffin	0.1 pbw

Example 13

This example demonstrates the application of the pearlescent pigment to a gravure printing ink, which was prepared according to the following formulation.

CCST medium *1	10 pbw
Flaky aluminum oxide or pearlescent pigment obtained in Examples 1 to 9	8 pbw

*1 Nitrocellulose resin, from Toyo Ink.

The thus obtained ink was diluted with a solvent ("NC102" from Toyo Ink) so that the resulting ink had a consistency of 20 sec, Zahn cup No. 3.

ABSTRACT

A process for producing flaky aluminum oxide, said process comprising steps of preparing (a) an aqueous solution of water-soluble aluminum salt and titanium salt and (b) an aqueous solution of alkali carbonate in an amount approximately equivalent to said water-soluble aluminum salt and titanium salt in said aqueous solution (a), uniformly dissolving alkali metal sulfate and phosphoric acid or a phosphate in either aqueous solution (a) or aqueous solution (b), mixing said aqueous solutions (a) and (b) to give a suspension or gel containing hydrolyzates, drying the suspension or gel by evaporation, and molten-salt treating the dried product by heating at 900-1400 °C to give a solid product, which is finished by water washing, filtering, and drying.

19554:1

10 SEP 1996