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(57) Abstract

The present invention provides a process for the production of hydrophobic inorganic oxide products which comprises reacting the inorganic oxide particles with organohalosilanes, preferably organochlorosilanes, to produce hydrophobic organosilane coated inorganic oxides. It is preferred that the organohalosilane compounds be reacted with the inorganic oxide particles in an aqueous slurry and subjected to intense mixing. The inorganic oxide pigments prepared by the processes of this invention have essentially quantitative retention of the organosilanes and contain no adsorbed aldehydes on their surface. The by-products produced in the preferred embodiments of the invention are innocuous salts, which are environmentally safe and readily disposable.

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Silane Treated Inorganic Pigments

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application U.S. Application Serial No. 08/565,852, filed December 1, 1995, the contents of which are hereby incorporated by reference into the present disclosure.

BACKGROUND OF THE INVENTION

The present invention relates to hydrophobic, surface modified, inorganic metal oxide pigments, such as titanium dioxide (TiO_2) pigments, which are substantially free of aldehydes and other potentially volatile organic compounds on their surface. The invention also relates to an improved, environmentally safer method for the preparation of such pigments and to polymers containing such pigments.

Titanium dioxide is the premier white pigment used for whitening, brightening and opacifying paper, paints and plastics. As normally produced, TiO_2 is a hydrophilic pigment, meaning that it is readily wet by water and not wet by hydrophobic materials like organic polymers. In order to permit TiO_2 pigments to be wet-out by and dispersed in organic polymers, the surface of the pigment must be modified, or made hydrophobic, so that the polymer will spread over the pigment's surface and good adhesion between the pigment and polymer will occur.

Prior art references teach the preparation of hydrophobic TiO_2 pigments by treatment with "non-reactive" organic substances, such as polydimethylsiloxanes (see e.g., Noll, Chemie und Technologie der Silicon, 2nd ed.,1968, page 386 et seq.), polyorganosiloxanes (see e.g., U.S. Patent No. 4,810,305) and

phosphorylated fatty acid derivatives (see e.g., U.S. Patent No. 4,209,430). These prior art, non-reactive organic substances interact with the metal oxide's surface partially or completely through Van Der Waals forces and/or electrostatic interactions. Since these forces are comparatively weak, pigments treated with these organic substances may lose the coatings in later processing stages or the organic substances may be extracted from the pigments during use.

The use of "reactive" organic compounds to modify the surface of metal oxide pigments is also well known. U.S. Patent Nos. 4,061,503 and 4,151,154 (both assigned to Union Carbide) disclose reactions of organosilanes with TiO_2 to produce hydrophobic TiO_2 pigments which enhance dispersibility in polymer matrices such as paints and plastics. In these patents the TiO_2 surface is treated with a silane possessing at least two hydrolyzable groups bonded to the silicon and an organic group containing a polyalkylene oxide group. The hydrolyzable groups are described as alkoxys, such as methoxy and ethoxy. More specifically, U.S. Patent No. 4,061,503 (which issued December 6, 1977) describes the use of a polyethyl substituted silicon compound having alkoxy-containing hydrolyzable groups with from about 1 to about 4 carbon atoms. U.S. Patent No. 4,151,154 (which issued April 24, 1979) also discloses the treatment of titanium dioxide pigments with organosilicon compounds to improve dispersibility in polymers, similar to the '503 Patent, except its claims are directed to inorganic oxide particles generally and not just titanium dioxide.

European Patent Application No. 492,223 (published July 1, 1992) discloses the treatment of TiO_2 pigment with an organosilicon compound having the formula $R^1R^2R^3R^4Si$ wherein R^1 is a halogen or an alkoxy radical with 1 to 10 carbon atoms, R^2 is an alkyl group with 1 to 30 carbons (preferably more than 8), and R^3 and R^4 are the same as either R^1 or R^2.

Great Britain Patent No. 1,154,835 (published June 11, 1969) discloses a process

for the treatment of finely divided materials, including titanium dioxide pigment. The patent indicates that inorganic powders may be rendered hydrophobic by treatment with organosilicon compounds. Specifically, the silicon compound has the formula R_nSiX_{4-n} wherein X is a halogen atom or a hydrolyzable alkoxy radical and R is a monovalent hydrocarbon radical (including an octyl [8 carbons] or an octadecyl [18 carbons] radical) and n has the value of either 0 or 1.

Suzuki, et al., "Chemical Surface Treatment of Alumina, Titania, and Talc and Their Respective Surface Properties," *Shikizai*, [J. Jap. Soc. Col. Mat.], Vol. 65, No. 2, pp. 59-67, 1992, describes the surface treatment of titania (large titanium dioxide crystals). As a comparison, the article refers to titanium dioxide particles that have been treated with octadecyltriethoxysilane - [the nonhydrolyzable group is octadecyl (18 carbons); the hydrolyzable groups are ethoxy] - to improve the particles' dispersibility properties in organic solutions and solvents.

Union Carbide's A-137 Product Information brochure (copyrighted 1991) cites to a organosilane compound wherein the nonhydrolyzable group has 8 carbons and the hydrolyzable group is ethoxy.

Great Britain Patent 785,393 discloses the treatment of TiO_2 pigment with organosilanes to improve uniformity of coloration and to reduce streaking in polymer matrices. Table 1 discloses the use of nonyltriethoxysilane (the nonhydrolyzable group has 9 carbon atoms; the hydrolyzable group is ethoxy) and the use of ethyltrichlorosilane (the nonhydrolyzable group is ethyl; the hydrolyzable group is chloro).

Great Britain Patent 825,404 discloses a treatment of TiO_2 pigment to improve dispersibility in organic solvents, including paint. In the patent, the organosilanes are represented by the formula $R_{4-n}Si(OR^1)_n$ wherein R and R^1 represent alkyl, aryl, or a hydrogen group. The preferred compounds include dimethyl-diethoxysilane,

methyltriethoxysilane, ethyltriethoxysilane, and phenyltriethoxysilane.

U.S. Patent No. 4,141,751 discloses the treatment of TiO_2 pigment with one of three different agents to improve the pigment's dispersion properties in various polymers. In one embodiment, the agent is R-Si-X_3 wherein R can be an aliphatic or cycloaliphatic and X is a halogen or an alkoxy group. Preferably, the treating agent is a methyltrimethoxysilane.

Recently, several PCT patent applications by DuPont have published in which organosilanes, similar to those disclosed in the above cited references, are used for surface treatment of TiO_2 pigment. For example, PCT patent publication WO 95/23192, published August 31, 1995, discloses polymer matrices containing silanized TiO_2 pigments in which a coating on the pigments contains an organosilicon compound having the formula:

$$R_xSi(R^1)_{4-x}$$

wherein R is a nonhydrolyzable aliphatic, cycloaliphatic or aromatic group having 8 to 20 carbon atoms; R^1 is a group selected from alkoxy, halogen, acetoxy or hydroxy or mixtures thereof; and x = 1 to 3. Although halogens are mentioned as suitable hydrolyzable groups, all examples and preferred embodiments specify alkoxy groups. Specifically, the publication discusses the use of octyltriethoxysilane - [the nonhydrolyzable group is octyl or 8 carbons; the hydrolyzable group is ethoxy]. As obvious from the above discussion of the prior art, the DuPont patent application repeats various teachings already disclosed in the Union Carbide patents and the other documents cited above.

DuPont's application WO 95/23194 discloses a process for preparing silanized titanium dioxide pigments by media milling in which an aqueous slurry of the pigment is adjusted to pH 7.5 to 11, then treated with an organosilicon reagent. The reagent is essentially the same as that specified in WO 95/23192, and preferably one which contains an alkoxy hydrolyzable group, such as methoxy or

ethoxy.

DuPont's application WO 95/23195 discloses titanium dioxide pigments which are treated with organosilicon compounds and boric acid or boron oxide. The boron ingredient can be dissolved in the organosilicon compound and the admixture applied to the pigments by dry mixing or in an aqueous slurry. The organosilicon compound again preferably contains an hydrolyzable alkoxy group.

As can be seen from the above discussion, organoalkoxysilanes have been traditionally used in the prior art for hydrophobizing inorganic pigments, such as TiO_2. A major deficiency of procedures that use alkoxy silanes is the generation of volatile organic compounds (VOC's), such as methanol or ethanol, during hydrolysis of the silanes, according to the equation:

$$R - Si(OCH_2CH_3)_3 + 3H_2O \rightarrow R - Si(OH)_3 + 3CH_3CH_2OH$$

Producers of minerals treated with organoalkoxysilanes are obligated to protect their workers and the environment by collecting and disposing of these volatile organic compounds, which can often be expensive and time-consuming. A further deficiency of utilizing alkoxyorganosilanes is that under conditions encountered during processing and finishing the treated pigments, a portion of the volatile alcohol can be converted to noxious aldehydes. For example, ethanol can be oxidized to acetaldehyde which can remain on the surface of the inorganic oxide and be subject to evolution during further processing of the inorganic oxide by the inorganic oxide producer or customer. Further, alkoxyorganosilanes are among the most expensive organic materials known for hydrophobizing pigment surfaces.

Organohalosilanes are alternatives to organoalkoxysilanes for the treatment of inorganic oxide pigments. However, since these compounds, particularly the organohalosilanes, react vigorously with moisture and water, it would be expected that these reagents would have to be applied to the inorganic oxides dry or using

nonaqueous, organic media. One would expect that if an organohalosilane was applied to an inorganic oxide in an aqueous system, the organohaosilane would rapidly hydrolyze and form oligomers and polymers rather than react with the hydroxyl groups of the inorganic oxide.

SUMMARY OF THE INVENTION

The present invention provides an environmentally safer process for the production of hydrophobic inorganic oxide products which comprises reacting the inorganic oxide particles with organohalosilanes, preferably organochlorosilanes, to produce hydrophobic organosilane coated inorganic oxides. It is preferred that the organohalosilane compounds be reacted with the inorganic oxide particles in an aqueous slurry under pH and mixing conditions sufficient to cause the desired reaction to take place but inhibit reaction between the organohalosilane and water of the slurry.

The inorganic oxide pigments prepared by the processes of this invention have essentially quantitative retention of the organosilanes and contain no adsorbed aldehydes on their surface, unlike pigments produced by prior art methods using organoalkoxysilanes, which are later released as volatile organic compounds (VOC) in later stages of pigment processing or use. The by-products produced in the preferred embodiments of the invention are innocuous salts, which are environmentally safe and readily disposable.

DETAILED DESCRIPTION OF THE INVENTION

This invention provides hydrophobic inorganic oxide products which are free of adsorbed aldehydes and other potentially volatile organic compounds. The products of the present invention are produced by a process which overcomes the environmental deficiencies of prior art processes while, unexpectedly, maintaining or improving upon the processibility characteristics (e.g., dispersibility properties and lacing resistance) of such products in paints, plastics and other materials.

This section details the preferred embodiments of the subject invention. These embodiments are set forth to illustrate the invention, but are not to be construed as limiting. Since this disclosure is not a primer on the manufacture of inorganic oxide products or pigments or their treatment with organosilane compounds, basic concepts known to those skilled in the art have not been set forth in detail. Concepts such as choosing proper solvents or reaction conditions are readily determinable by those skilled in the art. Attention is directed to the appropriate texts and references known to those in the art for details regarding acceptable temperatures, solvents, curing agents, etc.

Inorganic oxides appropriate for use in the present invention include those which have surface hydroxyls capable of condensing with reactive organohalosilanes or hydrolyzed organohalosilanes. Such inorganic oxides are represented by the rutile and anatase forms of titanium dioxide, kaolin and other clays, alumina, silica, aluminum trihydrate, zirconium oxide, zinc oxide, iron oxide, cadmium pigments, chromate pigments, chromium oxide pigments, glass fibers, glass flake, wollastonite and the like. Preferred are standard pigment-grade titanium dioxides, regardless of whether they have been obtained from titanium tetrachloride or from titanium sulfate.

The inorganic oxide being coated with the organohalosilane can be an untreated

inorganic oxide or an inorganic oxide whose surface has been treated by deposition thereon of phosphate, alumina, silica, zirconia and the like, using procedures well known to practitioners in the field of inorganic oxide surface treatment.

Suitable organohalosilanes for use in the present invention are represented by the formula

$$R_nSiX_{4-n}$$

where R represents a nonhydrolyzable aliphatic, cycloaliphatic or aromatic group (including saturated or unsaturated, branched or unbranched alkyl, aryl, cycloalkyl or alkylaryl groups) having from 1 to 20 carbon atoms or a polyalkylene oxide group; X represents a halogen and n = 1, 2 or 3.

For example, organochlorosilanes useful in this invention include butyltrichlorosilane, hexyltrichlorosilane, octyltrichlorosilane, octylmethyldichlorosilane, decyltrichlorosilane, dodecyltrichlorosilane, tridecyltrichlorosilane, dihexyldichlorosilane, dioctyldichlorosilane, octadecyltrichlorosilane and tributylchlorosilane. Preferred organochlorosilanes have R groups with 4 to 10 carbons; most preferred are those with 6 to 8 carbons. Hexyltrichlorosilane and octyltrichlorosilane are commercially and economically available and result in organosilane-coated inorganic oxide pigments that have excellent dispersibility properties in plastics, and (particularly in the case of hexyltrichlorosilane) produce pigmented plastics with excellent lacing resistance.

The organohalosilanes can be employed in the invention individually or as mixtures of two or more species. The organohalosilane weight content, based upon the weight of the silanized inorganic oxide, is typically about 0.1 to about 5.0%. For organochlorosilanes, the preferred weight content is about 0.1 to about 2% and most preferably about 0.5 to about 1.5%.

The reacting of the inorganic oxide particles with the organohalosilanes in

accordance with the invention may be accomplished by any suitable method by which surface treatment agents, coupling agents and the like are supplied to particulate surfaces. Suitable methods include those known to practitioners in the field of surface treatment of inorganic oxides, including the methods described in the prior art with respect to the treatment of titanium dioxide pigment with organoalkoxysilanes (e.g., spraying the organohalosilanes onto the pigment or grinding the organohalosilanes and pigment in a fluid energy mill). Suitable methods also include those utilized for the treatment of materials such as silicic fillers with organohalosilicon compounds.

However, it is preferred that the organohalosilanes are reacted with the inorganic oxide pigments in an aqueous medium under acidic conditions. It has been surprisingly discovered that organohalosilanes can be made to react with inorganic oxides in aqueous environments if the admixture of the organohalosilanes and the inorganic oxide particles are subjected to intense mixing under acidic conditions.

The fact that organohalosilanes can be made to react with inorganic oxides in an aqueous slurry is surprising since organohalosilanes, particularly organochlorosilanes, react vigorously with moisture and water. Accordingly, it would have been expected that these substances must be applied to the inorganic oxides dry or using nonaqueous, organic media. Conventional wisdom would predict that if the organohalosilane was applied to inorganic oxides in an aqueous system, the organohalosilane would rapidly hydrolyze and form oligomers and polymers rather than react with hydroxyl groups on the inorganic oxide's surface. See, e.g., Smith, A.L., Analytic History of Silicones, Wiley & Sons, 1991, pages 10-11, 29-30 and 256-257; Elvers, B. et al., Ullman's Encyclopedia Of Industrial Chemistry, 5th Ed., Vol. A 24 (1993), pp. 30-31; and Goldschmidt et al., Silicones: Chemistry and Technology, CRC Press, Boca Raton, FL, 1991, pp. 98-99.

Unexpectedly, it has been found that organohalosilanes can be made to react with the surface of inorganic oxides in aqueous suspension by providing an acidic environment and sufficient mixing and curing. Although not wishing to be bound by a particular theory or mechanism of operation, the inventors present the following explanation to aid in an understanding of the invention.

When the titanium dioxide / organohalosilane reaction is conducted in an aqueous medium, the organohalosilane, e.g., octyltrichorosilane, is added to a treatment vessel containing a slurry composed of predominately water with a small volume percentage of titanium dioxide particles. If octyltrichorosilane is added to pure water or to a neutral (non-acidic) water dispersion or slurry of titanium dioxide, there is an extremely fast reaction of octyltrichorosilane forming hydrochloric acid and a sticky resin from the polymerization of the silane portion of the octyltrichorosilane molecule. As noted in Smith, The Analytical Chemistry of Silicones, "One's first encounter with chlorosilanes is usually sufficient to instill a respect for their reactivity. The briefest exposure to atmospheric moisture when loading a syringe and injecting a specimen into a chromatograph results in the evolution of hydrogen chloride [hydrochloric acid] and the appearance of siloxanes in the chromatogram." p. 256.

Even though the titanium dioxide may be treated at solids levels of 500 grams per liter of slurry or higher, the system is mostly water as the volume occupied by the titanium dioxide particles is only about 8% of the system and that of water is about 92%. Consequently, as octyltrichorosilane is added to the treatment vessel, the probability of reacting with water is extremely high and quite low with respect to the titanium dioxide. The main problem is control of the octyltrichorosilane's reactivity so that the silane can be directed to and be in a position to react with the surface of the titanium dioxide before hydrolysis with the water that surrounds the TiO_2 particles in the aqueous slurry.

Fortunately, most chemical reactions are reversible, i.e. the products of a reaction may usually be made to react with each other by suitable choice of conditions to produce the original substances. In the case of the reaction of interest, octyltrichorosilane plus water produces hydrochloric acid (HCl) and a siloxane-like polymer; the reaction may be written as:

$$C_8H_{17}SiCl_3 + H_2O \leftrightarrows HCl + Polymer$$

The arrows pointing in each direction indicate reversibility. When the reaction has proceeded and a state of equilibrium exists, it is possible to disturb (or shift) this state by changing the relative speeds of the two opposing reactions. One way the rates may be affected is by changing the concentration of the substances involved.

If the concentration of one of the reacting substances (on either side of the arrows) is increased, there are then more molecules of that substance present in a given space and their ability to find and react with the other corresponding molecules is increased. This will cause a temporary gain in the rate of the reaction using up this kind of molecule, until more of the products of this reaction, represented on the other side of the equation, are produced, so as to equalize again the rates of the two reactions. The net result is that the reaction proceeds to some extent in the direction which will use up the substances whose concentration is increased.

To control the reaction of octyltrichorosilane with water and direct it to the titanium dioxide particles, the reaction is conducted in dilute hydrochloric acid solution; i.e., the forward reaction is slowed (by increasing concentration of one of the products) and the reverse reaction is increased, thus increasing the probability of reaction of octyltrichorosilane with the pigment. In fact it was found that any strong acid (in particular, phosphoric acid) can accomplish the same phenomenon. This happens because of a further reaction that occurs when hydrochloric acid itself reacts with water in solution forming ionized substances, namely,

$$HCl + H_2O \leftrightarrows H_3O^+ + Cl^-$$

Other strong acids also form the hydronium ion (H_3O^+) and therefore can function to reverse the ionization of HCl and subsequently slow the reaction of octyltrichorosilane.

Once a more homogeneous distribution of octyltrichorosilane is achieved in the system (owing to the acid environment and good mixing), the octyltrichorosilane can be made to react with the titanium dioxide by raising the pH of the system (preferably by adding alkali) as is described in the examples.

It is contemplated that this aspect of the invention regarding the reaction of organohalosilanes with inorganic oxides in an aqueous system may be useful in fields outside of the treatment of inorganic oxides. Materials (besides inorganic oxides) that are presently treated with organohalosilanes in nonaqueous, organic media may be suitable for treatment in aqueous systems in accordance with this disclosure. Such treatment procedures may provide environmental and/or cost benefits such as the easy disposal of by-products, as discussed above with respect to inorganic oxide treatment.

In a preferred embodiment of the invention, the organohalosilane is added to a stirred, aqueous slurry of the inorganic oxide at a solids level of about 50 to 500 grams inorganic oxide per liter of water, preferably at a solids level of 300 to 400 grams per liter, at an initial pH less than about 11, preferably less than about 7, most preferably between 2 and 6. The pH can be allowed to drift downward as the organohalosilane is added or can be maintained at a desired value by adding base concurrently with the organohalosilane. The organohalosilane can be added dropwise into the stirred slurry, pumped into the slurry or pumped into a slurry recirculation line or added by any other suitable method. The rate of

organohalosilane addition is such that all of the organohalosilane is added in about 1 minute to about 3 hours or longer, with a preferred addition time of 5 minutes to 1 hour and a most preferred addition time of about 10 minutes to about 45 minutes. The temperature of the organohalosilane treatment can be any suitable treatment temperature up to approximately the boiling point of the water. Preferably the treatment temperature is between 25 and 90 °C, and most preferably between 60 to 80 °C.

Following treatment of the inorganic oxide, the slurry pH is adjusted to a desired value, typically between 2.0 and 8.0, more typically between 4.0 and 6.0, preferably using sodium hydroxide, and the slurry is allowed to age with mixing for the time, preferably up to about 1 hour, required to assure equilibrium distribution of the components of the slurry.

Following aging, the pH of the slurry is adjusted to about 6.0 or greater, preferably between about 6.0 to 9.0, and the organosilane coated inorganic oxide is collected using filtration, centrifugation or any other suitable technique, washed to remove soluble impurities (such as by-product salt), dried and further processed into a finished product using techniques suitable for the specific inorganic oxide being processed.

The use of organohalosilanes avoids formation of volatile organic compounds, such as methanol and ethanol, which arise from the hydrolysis of traditional organoalkoxysilanes. The innocuous salts, such as sodium chloride, which result from treatment of inorganic oxides with organohalosilanes followed by neutralization, are easily disposed of and do not pose a threat to the environment and health as do the volatile alcohols. In addition, the use of organohalosilanes eliminates the formation of noxious aldehydes which can form during inorganic oxide pigment processing. The noxious aldehydes can present an environmental hazard during pigment preparation and residues can present a threat during

silanized pigment use in plastics applications.

The inorganic metal oxide pigments of this invention are unique in that they are not contaminated by measurable amounts of potentially hazardous oxidized by-products of prior art processes, e.g., aldehydes. The hydrophobic inorganic oxide products of this invention offer processibility in polymer composites as least as good as pigments prepared according to prior art procedures; that is, the dispersibility of the products of the present invention in polymers is at least as good as prior art inorganic oxide pigments and the lacing resistance of the resulting polymer composites containing the products of the present invention is as good as prior art polymer composites. Representative polymers in which the products of the present invention may be used include, but are not limited to, polymers of ethylenically unsubstituted monomers, including polyethylene, polypropylene, polybutylene and copolymers of ethylene with alpha-olefins containing 4 to 12 carbon atoms or vinyl acetate; vinyl homopolymers, acrylic homopolymers and copolymers, polyamides, polycarbonates, polystyrenes, acrylonitrile-butadiene-styrenes, polyethers and the like.

The following examples set forth preferred embodiments of the invention. These embodiments are merely illustrative and are not intended to, and should not be construed to, limit the claimed invention in any way.

EXAMPLES

Comparative examples 1-4 demonstrate that metal oxide pigments treated with organotriethoxysilanes of the prior art contain associated aldehydes while the pigments of the present invention do not.

Comparative Example 1

800 grams of neutral tone, chloride process, TiO_2 product containing about 1.3% Al_2O_3 and about 0.15% P_2O_5 were slurried with 800 grams deionized water using a Rockwell Drill Press equipped with a 3 inch Cowles blade, mixing at 2000 rpm. The slurry was transferred to a 2000 ml glass beaker, heated to 80-85 °C, and the slurry pH was adjusted from an initial pH of 5.9 to 4.5. While maintaining the slurry at about 80 °C and with rapid stirring, 8.0 grams of octyltriethoxysilane (Prosil 9206 from PCR, Incorporated) was added. The treated slurry was aged with rapid stirring for 30 minutes at 80 - 85 °C followed by oven drying at 110 °C and micronization at 500 °F. The micronized pigment was analyzed for acetaldehyde using gas chromatography/mass spectroscopy head space analysis at 150 °C. The acetaldehyde evolved from the pigment is shown in Table 1.

Comparative Example 2

An octyltriethoxysilane treated pigment was prepared according to the method of example 1 except the pH of the slurry during silane treatment and aging was adjusted to 6.0. The micronized pigment was analyzed for acetaldehyde using gas chromatography/mass spectroscopy head space analysis at 150 °C. The acetaldehyde evolved from the pigment is shown in Table 1.

Comparative Example 3

An octyltriethoxysilane treated pigment was prepared according to the method of example 1 except the pH of the slurry during silane treatment and aging was adjusted to 7.0. The micronized pigment was analyzed for acetaldehyde using gas chromatography/mass spectroscopy head space analysis at 150 °C. The acetaldehyde evolved from the pigment is shown in Table 1.

Comparative Example 4

197.9 kilograms of a blue base chloride process TiO_2 rutile product was mixed with deionized water so that the final volume of the slurried product was 568.8 liters. The TiO_2 slurry was heated with continuous stirring to 60°C. Sufficient phosphoric acid was added to make the system acidic with a pH of 2.1. After a brief aging of 10 minutes, the pH of the slurry was adjusted with caustic to a pH of 5.0. Over a period of 6 minutes 2,137 grams of octyltrichlorosilane was added to the slurry and the pH of the system was adjusted to 6.0 with caustic. After approximately 90 minutes, the slurry was filtered, washed and dried in an oven. The dried octytrichlorosilane-treated TiO_2 was deagglomerated in a fluid energy mill with superheated steam at 240°C. The milled pigment was analyzed for acetaldehyde using gas chromatography/mass spectroscopy head space analysis at 150 °C. No acetaldehyde evolved from a sample of this pigment as shown in Table 1.

Table 1

Micrograms of Acetaldehyde Evolved at 150 °C per Gram of TiO_2 Pigment

Example 1 (Prior Art)	1.2
Example 2 (Prior Art)	1.5
Example 3 (Prior Art)	2.4
Example 4 (This Invention)	0.0

The data in Table 1 show that the hydrophobic TiO_2 pigment product of this

invention is clearly improved compared to pigments prepared using organotriethoxysilanes of the prior art. The pigment prepared according to this invention evolves no noxious acetaldehyde.

Preparation of Polyethylene Concentrates/Master Batches

50% TiO_2:50% polyethylene concentrates were prepared using a Haake Rheocord 9000 Computer Controlled Torque Rheometer. 125 g of TiO_2 and 125 g of LDPE 722 manufactured by Dow Chemical Company were dry blended and added to the 75 °C preheated chamber with rotors running at 50 rpm. One minute after addition of the TiO_2/LDPE mixture, the chamber temperature was raised to 105 °C. Frictional heat generated by the mixing process was allowed to drive the rate of incorporation of the TiO_2 into the LDPE until a steady state mixture was achieved.

75% TiO_2:25% polyethylene concentrates were prepared using a BR Banbury Mixer. The mixer was preheated to 150 °C. While the rotors were turning, 313 grams of LDPE NA 209, manufactured by The Quantum Chemical Company, were added followed by 939 grams of TiO_2 which, in turn, was followed by the remaining 313 grams of LDPE NA 209. The ram was lowered and set to 50 psi. The point at which the two materials mix together and flux could be recognized by the ram bouncing up and down and an audible cracking sound. The material was allowed to mix for an additional 3 minutes after flux before opening the mixer and allowing the material to discharge. This material was then cut into ~1 inch pieces while hot. These pieces were then placed into a Cumberland Crusher to obtain finely granulated 75% concentrate samples.

The processibility of inorganic oxides into polymer composites can be judged by evaluating the performance of the inorganic oxide under four test conditions, namely, extruder screen dispersion, melt flow, energy to achieve steady state flux and high temperature stability or lacing performance. Each of these tests requires

the use of a TiO_2/polymer concentrate of one of the types described above.

The extruder screen dispersion test measures how readily the TiO_2 disperses in a polymer, *e.g.* low density polyethylene. 400 grams of a 75% TiO_2 concentrate, prepared as described above, is extruded through a Killion 1" extruder, followed by 1500 grams of LDPE, manufactured by The Chevron Chemical Company. The extruder temperatures are set at 350 °F (zone 1), 350 °F (zone 2), 390 °F (zone 3), and a screen pack configuration of 100/400/200/100 mesh screens (from tip of extruder screw to exit point for extrudate) is used. After all of the material has extruded, the screen pack is removed, and the screens are stapled onto an extrusion card. The screens are visually examined under a low power microscope (15x) and assigned screen ratings using standards. A rating of 1 signifies "Best" and 5 "Worst."

The fusion energy, or total torque required to achieve a steady state mixture of TiO_2 and polymer, under fixed process conditions, is also a good indicator of processibility. Fusion energy measurements tabulated in Table 2 were obtained during production of 50 weight percent TiO_2 concentrates in low density polyethylene using the procedure described above. The total torque required to achieve the steady state mixture is readily obtainable during the production of the concentrates using the software supplied with the Torque Rheometer. Lower fusion energy values indicate that the TiO_2 is more readily incorporated into the polymer matrix.

The melt index is another measure, albeit rather rough, indicator of processibility. Melt flows were measured according to ASTM method D1238-90b using 50% concentrates prepared according to the method described above. Higher melt indices imply easier processing.

Lacing is a measure of concentrate volatility at specific weight % pigment loadings and processing temperatures. Lacing tests were conducted on 50% TiO_2 concentrate samples prepared according to the method described above. The concentrates were conditioned for 48 hours at 23 °C and 50% relative humidity. The concentrates were then let down into LDPE 722 to achieve a 20% loading of TiO_2 in the final film.

Lacing evaluations were run on a 1" Killion extruder equipped with a slot die for fabricating cast films. A temperature profile of 343 °C/die, 288 °C/adaptor, 232 °C/zone 3, 190 °C/zone 2, 148 °C/zone 1 was used. The screw speed was set at 90 rpm. A Killion 25.4 cm polished chrome chill roll was used to cool and transport the films and was set to maintain a 75 μm film thickness. The chill roll distance from the die lips was 22 mm and the temperature was ~27 °C.

After the TiO_2/LDPE mix was placed in the hopper, the material was allowed to run until the appearance of white in the clear film was first noted. To ensure the concentration of TiO_2 in the film had stabilized, a two minute time interval was allowed before observations were recorded and a film sample taken. The extruder was then purged with LDPE until the film returned to clear.

Lacing performance was ranked by visual observations. Film samples were laid out on a dark surface and ranked according to the relative size and number of holes. A 1.0 - 3.0 rating system was used. A rating of 1 was given to films with no lacing, 2 was given to films showing the onset of lacing, and 3 was given to films with extreme lacing. Increments of 0.1 were used to give some indication of relative performance between the samples.

Comparative examples 5-8 demonstrate that pigments prepared according to the teachings of this invention maintain equal or improved processibility in

polyethylene compared to prior art pigments. This is accomplished in conjunction with the reduced environmental threats of the present inventive process. The pigments of examples 5-8 were prepared in full scale production facilities. Comparisons are made realizing that many factors can influence variability in production processes. Statistical process control techniques were used to minimize variability in the production processes.

Comparative Example 5

Optimized, state-of-the-art production technology was used to prepare a hydrophobic TiO_2 pigment using polydimethysiloxane as a treatment for hydrophobizing the TiO_2. The pigment was tested in polyethylene for screen dispersion, energy required to mix with polyethylene, melt flow and lacing performance. The results are summarized in Table 2.

Comparative Example 6

Optimized, state-of-the-art production technology was used to prepare a hydrophobic TiO_2 pigment using Sylvacote K, a phosphorylated fatty acid derivative, as a treatment for hydrophobizing the TiO_2. The pigment was tested in polyethylene for screen dispersion, energy required to mix with polyethylene, melt flow and lacing performance. The results are summarized in Table 2.

Comparative Example 7

Optimized, state-of-the-art production technology was used to prepare a hydrophobic TiO_2 pigment using octyltriethoxysilane as a treatment for hydrophobizing the TiO_2. The pigment was tested in polyethylene for screen dispersion, energy required to mix with polyethylene, melt flow and lacing performance. The results are summarized in Table 2.

Comparative Example 8

Optimized, state-of-the-art production technology was used to prepare a hydrophobic TiO_2 pigment using octyltrichlorosilane as a treatment for hydrophobizing the TiO_2. The pigment was tested in polyethylene for screen dispersion, energy required to mix with polyethylene, melt flow and lacing performance. The results are summarized in Table 2.

Comparative Example 9

Optimized, state-of-the-art production technology was used to prepare a hydrophobic TiO_2 pigment using hexyltrichlorosilane as a treatment for hydrophobizing the TiO_2. The pigment was tested in polyethylene for screen dispersion, energy required to mix with polyethylene, melt flow and lacing performance. The results are summarized in Table 2.

Table 2

Processibility Parameters of Hydrophobic TiO_2 Pigments

	Screen Dispersion	Fusion Energy (m.Kg.M)	Melt Flow (g/10min)	Lacing
Example 5 (prior art)	2	15.4	5.5	2.0
Example 6 (prior art)	1	10.7	5.3	1.7
Example 7 (prior art)	1	14.3	5.2	1.6
Example 8 (this invention)	1	10.2	5.7	1.6
Example 9 (this invention)	1	14.0	5.7	1.1

The data in Table 2 show that a TiO_2 pigment of this invention provides for processing in polyethylene at least as well as optimized TiO_2 pigments made according to prior art. This is accomplished in conjunction with the reduced environmental threats of the present inventive process.

Upon reading the subject application, various alternative constructions and embodiments will become obvious to those skilled in the art. These variations are to be considered within the scope and spirit of the subject invention. The subject invention is only to be limited by the claims which follow and their equivalents.

We claim:

1. A silanized inorganic oxide pigment which does not release aldehydes or other volatile organics from its surface during processing or use.

2. The pigment of claim 1 in which the silanized inorganic oxide pigment is a titanium dioxide pigment.

3. A process for producing a silanized inorganic oxide pigment which comprises reacting an inorganic oxide with an organohalosilane represented by the formula

$$R_nSiX_{4-n}$$

where R represents a nonhydrolyzable aliphatic, cycloaliphatic or aromatic group having from 1 to 20 carbon atoms or a polyalkylene oxide group; X represents a halogen and n = 1, 2 or 3.

4. The process of claim 3 in which the organohalosilane is an organochlorosilane.

5. The process of claim 3 in which R has 4 to 10 carbon atoms.

6. The process of claim 5 in which R has 6 to 8 carbon atoms.

7. The process of claim 4 in which the organochlorosilane is octyltrichlorosilane or hexyltrichlorosilane or mixtures thereof.

8. The process of claim 3 in which the inorganic oxide is titanium dioxide.

9. The process of claim 7 in which the inorganic oxide is titanium dioxide.

10. The process of claim 3 in which the inorganic oxide is selected from the group consisting of zinc oxide, aluminum oxide, silicon dioxide, zirconium oxide, lithipone, lead oxide, chromium oxide pigments, iron oxide pigments and cadmium pigments.

11. The process of claim 3 wherein the reacting step is effected by adding the organohalosilane to a stirred aqueous slurry of the inorganic oxide and subjecting the admixture to intense mixing.

12.. The process of claim 11 wherein said intense mixing is at a level sufficient to achieve equilibrium distribution of the organohalosilane throughout the slurry.

13. The process of claim 11 which further comprises adjusting the pH to acidic conditions during the reacting step, aging the slurry, neutralizing any acid that may evolve, and recovering the reacted inorganic oxide.

14. The process according to claim 11 in which the pH of the slurry is initially between 2 and 6.

15. The process according to claim 11 in which the organohalosilane is added over a time period between about 10 minutes and about 45 minutes.

16. The process according to claim 11 in which the temperature of the slurry is between 60 and 80 °C.

17. The process according to claim 13 in which the pH during the aging of the slurry is between about 2 and about 7.

18. The process according to claim 13 in which the aging time is sufficient to assure equilibrium distribution of the components of the slurry.

19. The process according to claim 13 in which the slurry is neutralized to a pH of between about 6.0 to about 9.0.

20. The process according to claim 13 in which the oxide is wet ground or dry ground to a desired particle size following recovery.

21. A silanized inorganic oxide pigment produced by the process of claim 3.

22. A silanized inorganic oxide pigment produced by reacting an organochlorosilane with an inorganic oxide in an aqueous slurry.

23. A silanized inorganic oxide pigment produced by the process of claim 13.

24. The process of claim 13, wherein the inorganic oxide is reacted with an organohalosilane or a mixture of two or more organohalosilanes independently represented by the formula R_nSiX_{4-n} where R represents a nonhydrolyzable aliphatic, cycloaliphatic or aromatic group having 5-10 carbon atoms or a polyalkylene oxide group.

25. A silanized inorganic oxide pigment produced by the process of claim 24.

26. A polymer composite containing the pigment of claim 1.

27. A polymer composite containing the pigment of claim 22.

28. A pigment as claimed in claim 1 or claim 22, substantially as herein

described and illustrated.

29. A process as claimed in claim 3, substantially as herein described and illustrated.

30. A polymer composite as claimed in claim 26 or claim 27, substantially as herein described and illustrated.

31. A new pigment, new polymer composite, or new process for producing a pigment, substantially as herein described.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18941

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09C 1/36
US CL :106/442, 444, 445, 446, 490
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/442, 444, 445, 446, 490

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,501,732 A (NIEDENZU ET AL) 26 MARCH 1996, COL. 2, LINE 52-COL. 3, LINE 11	1-27
Y	US 4,375,989 A (MAKINEN) 08 MARCH 1983, COL. 2, LINES 44-47 AND COL. 4, LINES 1-16	1-27
Y	EP 492,223 A2 (DIETZ ET AL) 01 JULY 1992, ABSTRACT, PAGE 3, LINES 1-16 AND PAGE 5, LINES 7-16	1-27
Y	UK 594,802 A (THE BRITISH THOMSON-HOUSTON COMPANY LIMITED) 11 NOVEMBER 1947, COL. 1, LINE 41 - COL. 2, LINE 66	1-27
A	UK 785,393 A (GROFF ET AL) 30 OCTOBER 1957	
A	UK 825,404 A (NATIONAL LEAD COMPANY) 16 DECEMBER 1959	

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
03 APRIL 1997	11 APR 1997
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18941

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	UK 1,154,835 A (LEWIS ET AL) 11 JUNE 1969, COL. 3, LINES 7-59	1-27
A	UK 1,204,323 A (BRIGGS ET AL) 03 SEPTEMBER 1970	
A	WO 95/23192 A (TOOLEY ET AL) 31 AUGUST 1995	
A	WO 95/23193 A (TOOLEY ET AL) 31 AUGUST 1995	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18941

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS and STN
search on claim 1 (i.e. silanized inorganic pigment containing no aldehydes on its surface) and on inventors names (i.e. L. Weber, R.J. Kostelnik, and C. Wheddon).