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(54) Titre : PIGMENTS TRAITES AVEC DES ACIDES ORGANOPHOSPHORIQUES ET LEURS SELS
(54) Title: PIGMENTS TREATED WITH ORGANO-PHOSPHORIC ACIDS AND THEIR SALTS

(57) Abrégé/Abstract:
A unique treatment for pigments is provided. This treatment, which uses certain organo-phosphoric acids and/or their salts, imparts improved physical and chemical qualities including lacing resistance, improved dispersion and decreased chemical reactivity when these treated pigments are incorporated into polymeric matrices.

ABSTRACT

A unique treatment for pigments is provided. This treatment, which uses certain organo-phosphoric acids and/or their salts, imparts improved physical and chemical qualities including lacing resistance, improved dispersion and decreased chemical reactivity when these treated pigments are incorporated into polymeric matrices.

PIGMENTS TREATED WITH ORGANO-PHOSPHORIC ACIDS AND THEIR SALTS

BACKGROUND OF THE INVENTION

The present invention relates to novel pigments, and in particular, pigments that have been treated with certain organo-phosphoric acid compounds and/or their salts.

The incorporation of pigments into polymer matrices has been performed for many years, and over the years, pigments have been and continue to be incorporated into polymer matrices for many reasons. For example, pigments may be used as fillers. They may also be used to impart better physical and chemical attributes to polymer matrices, including improved thermal stability, especially lacing resistance in extruded polymer film applications, and decreased chemical activity. In order to obtain different benefits, pigments may be treated in different ways, including by adding surface treatments.

Commonly used pigments include titanium dioxide, kaolin and calcium carbonate. Commonly known surface treatments that have been applied to pigments include silanes, alkylphosphonic acids and phosphorylated polyenes.

The precise attributes that one wants in a treated pigment will depend in part on the application in which it will be used. Often one wants to provide a hydrophobic pigment that is stable, easy to prepare, cost effective, can be dispersed to a high degree in polymers, and does not react in the presence of other additives such as lithopone. However, despite the numerous known surface treatments, for various reasons, including cost and desired properties, no known surface treatments are ideal

for all applications. Thus, there is always a need to develop new and better treatments for pigments.

One under-explored option for treating pigments is the use of organo-phosphoric acids, including the esters of phosphoric acids and their corresponding salts. These compounds have been suggested as useful when mixed in relatively large amounts with pigments and to form suspensions in, for example, aqueous coatings applications. However, such a use produces a unique product that may be used only in a limited application. Thus, the teachings for the use of relatively large amounts of esters of phosphoric acids in aqueous coatings applications do not suggest the treatment of pigments with low levels of the organo-phosphoric acids of this invention or that the pigments treated with the low levels of the organo-phosphoric acids of this invention would have utility in plastics.

The present invention provides economical and easily prepared novel pigments that possess resistance to lacing when incorporated into polymeric articles (such as films), do not produce objectionable side reactions when mixed with common plastics additives such as lithopone, which contains zinc sulfide, and are stable such that they possess low levels of extractable organics. Further, durable plastics products that incorporate the treated pigments of the present invention are likely to resist yellowing when phenolic-type antioxidants are used.

SUMMARY OF THE INVENTION

The present invention provides novel treated pigments for use in polymer matrices. According to the present invention, pigmentary bases are treated with one or more organo-phosphoric acid compounds and/or their salts in order to form treated pigments.

In one embodiment, the treated pigment comprises a pigmentary base that may be treated with the reaction products of: (1) at least one organic alcohol; and (2) P_2O_5 and/or phosphoric acid. The phrases "at least one organic alcohol" and "organic alcohols" mean one or more types of organic alcohols, for example, a solution of hexanol or octanol or a mixture of hexanol and octanol. The organic alcohols, P_2O_5

and phosphoric acid are selected such that their reaction products include an organo-acid phosphate that may be represented by the formula:

Formula 1: $(R\text{-}O)_xPO(OH)_y$

wherein x = 1 or 2;
y = 3 – x; and
R is an organic group having from 2 to 22 carbon atoms.

Alternatively, one may start with the organo-acid phosphate or its corresponding salt directly if it is available, rather than produce it from the reactants described above.

In another embodiment, the present invention provides for a pigment treated with an organopyrophosphate or an organopolyphosphate and/or their corresponding salts. The organopyrophosphate and organopolyphosphate compounds may be represented by the formula:

Formula 2: $R'_n\text{-}P_{(n-2)}\ O_{4+[3(n-3)]}$

wherein n = 4 - 14; and
each R' is an organic group having from 2 to 22 carbon atoms or hydrogen and within any one molecule, any two or more R' groups may be the same provided that at least one of the R' groups is not hydrogen.

In still another embodiment, the present invention provides for a treated pigment comprised of a pigmentary base that has been treated with an organometaphosphate compound and/or its corresponding salt wherein the organometaphosphate compound may be represented by the formula:

Formula 3: $(R''PO_3)_m$

wherein m = 1 -14, and each R" is an organic group having from 2 to 22 carbon atoms or hydrogen and within any one molecule, any two or more R" groups may be the same provided that at least one of the R" groups is not hydrogen.

Collectively, the group of compounds represented by Formulas 1 -3, *i.e.*, the organo-acid phosphate, the organopolyphosphate, the organopyrophosphate and the organometaphosphate are referred to herein as "organo-phosphoric acids."

The treated pigments of the present invention may be combined with and readily dispersed into polymers to form polymer matrices. For example, the pigments of the present invention may be incorporated into a polymer matrix containing up to about 85% of organo-phosphoric acid treated titanium dioxide pigment, based on the weight of the polymer matrix to be produced. The polymer matrix may be an end-product in and of itself or a product that will be further processed such as in a masterbatch, which can be let down into a polymeric film. These polymer matrices have improved physical properties such as impact strength, tensile strength and flexural characteristics.

The treated pigments of the present invention may also be used to prepare highly loaded polymer masterbatches. These highly loaded masterbatches are especially useful in applications in which dispersion and thermal stability, especially resistance to lacing, are critical.

The treated pigments of the present invention have the advantages of being pigments that are stable, easy to prepare, cost effective, can be dispersed to a high degree in polymers, and do not react in the presence of other additives such as lithopone. Such treated pigments may be useful in the manufacture of plastics and other products.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides novel pigments for use in connection with polymers and offers several benefits over currently used pigments. According to the present invention, pigmentary bases are treated with an organo-phosphoric acid that may be an organo-acid phosphate, an organopyrophosphate, an organopolyphosphate or an organometaphosphate; or a salt of any of the aforementioned compounds. The pigmentary bases may also be treated with mixtures of any of the aforementioned compounds and/or their salts. The resulting treated pigments may then be combined with polymers to form novel polymer matrices.

The present disclosure is not intended to be a treatise on either pigments or the production of polymer matrices. Readers are referred to appropriate, available texts and other materials in the field for additional and detailed information on any aspect of practicing this invention.

Suitable pigmentary bases for use in the present invention include titanium dioxide, kaolin, talc, mica and calcium carbonate. The phrase "pigmentary base" as used herein refers to the pigment that has not been treated with an organo-phosphoric acid compound. Preferably, titanium dioxide is the chosen pigmentary base. When the pigmentary base is titanium dioxide, the titanium dioxide may be either rutile or anatase, both of which may be produced by processes that are well known to those skilled in the art. For certain applications, it may be desirable to pre-treat the pigmentary base with inorganic oxides or other compounds prior to the addition of the organo-phosphoric acid compound in order to alter the attributes of the final product or to facilitate production.

Under the first embodiment, one treats the pigmentary base with an organo-acid phosphate, which may be formed from the reaction of organic alcohols, and P_2O_5 and/or phosphoric acid. The organic alcohols useful in the present invention may have hydrocarbon groups from about 2 to about 22 carbon atoms. These hydrocarbons may be linear or branched, substituted or unsubstituted, and saturated or unsaturated. Some examples of the organic alcohols suitable for use in the present invention include, ethanol, propanol, butanol, isobutanol, tertiary butanol, pentanol, hexanol, heptanol, octanol, isooctanol, 2-ethylhexanol, decanol, dodecanol and the like. Preferably, the alcohol is a linear hexanol, a linear octanol, isooctanol or 2-ethylhexanol. The alcohol may be combined with either or both P_2O_5 and phosphoric acid. The conditions under which to react these materials in order to form the organo-acid phosphate are generally known or knowable to those skilled in the art.

Rather than beginning with the organic alcohols and P_2O_5 and/or phosphoric acid, one may start directly with the organo-acid phosphate of the below formula:

Formula 1: $(R\text{-}O)_xPO(OH)_y$

wherein $x = 1$ or 2;
$y = 3 - x$; and
R is an organic group having from 2 to 22 carbon atoms.

The phrase "organo-acid phosphate" as used herein refers to a compound that may be represented by Formula 1. In the organo-acid phosphate of Formula 1, the organic groups may be linear or branched, substituted or unsubstituted, and saturated or unsaturated. Preferably R is a linear hexyl- or octyl- aliphatic group or a branched hexyl- or octyl- aliphatic group. The use of hexyl-, octyl- or ethylhexyl- aliphatic groups will result in excellent pigmentary performance.

In a second embodiment, the present invention provides for a treated pigment that comprises a pigmentary base that has been treated with an organo-phosphoric acid compound that is either an organopyrophosphate or organopolyphosphate. These compounds may be represented by the formula:

Formula 2: $R'_n\text{-}P_{(n-2)}\ O_{4+[3(n-3)]}$

wherein $n = 4 - 14$; and
each R' is an organic group having from 2 to 22 carbon atoms or hydrogen and within any one molecule, any two or more R' groups may be the same provided that at least one of the R' groups is not hydrogen.

The symbol R' as used in Formula 2 denotes any organic group that contains from 2 to 22 carbon atoms or hydrogen. Within any molecule the R' groups may all be the same moiety or they may be different moieties. These organic groups may be linear or branched, substituted or unsubstituted, and saturated or unsaturated. If the R' groups are all the same moieties, then they cannot be hydrogen. Preferably at least one of the R' groups is hydrogen and at least one of the R' groups will be linear hexyl or octyl aliphatic groups or branched hexyl or octyl aliphatic groups. Examples of organopyrophosphate acid compounds and organopolyphosphate acid compounds include caprylpyrophosphate, 2-ethylhexylpyrophosphate, dihexylpyrophosphate, dihexylammoniumpyrophosphate, dioctylpyrophosphate, diisooctylpyrophosphate, dioctyltriethanolaminepyrophosphate, bis(2-ethylhexyl)pyrophosphate, bis(2-ethylhexyl) sodium pyrophosphate, tetraethylpyrophosphate, tetrabuytlpyrophosphate,

tetrahexylpyrophosphate, tetraoctylpyrophosphate, pentahexyltripolyphosphate, pentaoctyltripolyphosphate, tetrahexyl sodium tripolyphosphate, tetrahexylammoniumtripolyphosphate, pentahexyl sodium tetrapolyphosphate, trioctyl sodium tetrapolyphosphate, trioctyl potassium tetrapolyphosphate, hexabutyltetrapolyphosphate, hexahexyltetrapolyphosphate and hexaoctyltetrapolyphosphate.

In a third embodiment, the present invention provides for a treated pigment comprised of a pigmentary based that has been treated with an organometaphosphate compound wherein the organometaphosphate compound may be represented by the formula:

Formula 3: $(R"PO_3)_m$

wherein m = 1 -14, and each R" is an organic group having from 2 to 22 carbon atoms or hydrogen and within any one molecule, any two or more R" groups may be the same provided that at least one of the R" groups is not hydrogen.

The symbol R" as used in Formula 3 denotes any organic group that contains from 2 to 22 carbon atoms or hydrogen. These organic groups may be linear or branched, substituted or unsubstituted, and saturated or unsaturated. "m" may be from about 1 to about 14, and preferably "m" is from about 4 to about 14. Within any molecule, the R" groups may all be the same moiety or they may be different moieties. If the R" groups are all the same moieties, then they cannot be hydrogen. Preferably at least one of the R" groups will be a linear hexyl or octyl aliphatic group or a branched hexyl or octyl aliphatic group. Examples of organometaphosphates include ethylmetaphosphate, propylmetaphosphate, butylmetaphosphate, hexylmetaphosphate and octylmetaphosphate.

The organo-phosphoric acids of the present invention may be utilized in their acidic or salt forms. Examples of salts useful with the present invention are the potassium, sodium, ammonium and aluminum salts and salts formed with

alkanolamines such as triethanolamine of the substances identified by Formula 1, Formula 2 or Formula 3.

Organo-acid phosphates are available commercially through, for example, Albright & Wilson Americas of Glen Allen, Virginia or may be prepared by procedures known or knowable to those skilled in the art such as those procedures disclosed in U. S. Pat. No. 4,350,645, issued on September 21, 1982 to Kurosaki *et al.*

Organopyrophosphates and organopolyphosphates may be purchased from Akzo Nobel or produced according to the procedures that are known or easily knowable to persons skilled in the art. Organometaphosphates may also be produced according to the procedures that are known or easily knowable to persons skilled in the art. Examples of these procedures for synthesizing organopyrophosphates, organopolyphosphates and organometaphosphates are described in Alder, Howard and Woodstock, Willard Chem, Indus., 1942, 51: 516.

The aforementioned organo-phosphoric acids, which are the surface treatments of the present invention will be used to treat the pigmentary bases and to form treated pigments. The phrase "treated pigment" refers to any pigmentary base that has been surface treated or modified. The phrase "organo-phosphoric acid treated pigment" refers to a pigmentary base that has been treated with the reaction products of organic alcohols and P_2O_5 and/or phosphoric acid; an organo-acid phosphate that may be represented by the above Formula 1; an organopyrophosphate or organopolyphosphate of Formula 2; an organometaphosphate of Formula 3; or a mixture or any of the aforementioned substances. Preferably, the level of organo-phosphoric acid or corresponding salt that is used to treat the pigmentary base ranges from about 0.01 percent to about 5 percent by weight, based on the weight of the pigmentary base; more preferably from about 0.3 percent to about 2.0 percent; and most preferably from about 0.7 percent to about 1.2 percent.

In the organo-phosphoric acid treated pigment, the organo-phosphoric acid may interact with the pigment in a number of manners such as through hydrogen bonding and/or covalent attachments such that the surface treatment resists extraction

from the treated pigment. The organo-phosphoric acids that are the reaction products of the organic alcohols, and P_2O_5 and/or phosphoric acid are generally mixtures of mono- and di-substituted esters in combination with orthophosphoric acid.

The process for making an organo-phosphoric acid treated pigment is easily and flexibly incorporated into existing pigment production processes. Preferably the combining of the pigmentary base and the surface treatment of the invention will occur at a temperature of from about 10°C to about 270°C. The specific temperature at which the pigmentary base and the surface treatment are combined is dependent on the step during the pigment production process in which the surface treatment is added.

When an organo-phosphoric acid is used to treat a pigment according to the present invention, a by-product is thought to be water. Because water is the by-product, the organo-phosphoric acid may be added at any one of, or several of, the operations in the pigment production process. For example, the organo-phosphoric acid may be added to a washed filter cake prior to spray drying, to a high intensity milling device or to a micronizer feed prior to or concurrent with micronization. It is not as effective to add the organo-phosphoric acid to a pigment slurry prior to filtration and washing since a portion of the organo-phosphoric acid will be lost upon washing of the pigment depending on the pH. The organo-phosphoric acid can be added to a washed filter cake at normal process operating temperatures. If the organo-phosphoric acid is a solid substance, it may be dissolved in an appropriate solvent, such as water, alcohol, tetrahydrofurn, *etc.*, before being added to the pigmentary base. It is desirable to add the organo-phosphoric acid to a fluidized, washed filter cake with agitation in order to assure uniform mixing of the organo-phosphoric acid among the pigment particles. The pH of the fluidized filter cake prior to addition of the organo-phosphoric acid is not critical, and normal operating pH values are acceptable. These values are known or readily knowable to those skilled in the art. If the organo-phosphoric acid is added to a dry pigment such as a spray drier product or micronizer feed, care must be taken to ensure uniform mixing of the organo-phosphoric acid with the pigment powder.

Devices such as a V-shell blender equipped with an intensifier bar for application of the liquid organic or other suitable mixing devices known to those in the art may be used. Alternatively, the organo-phosphoric acid may be metered into the micronizer along with the pigment powder to be ground. Air or steam micronization techniques may be used at temperatures from room temperature up to 250 °C or higher as is known or easily knowable to those skilled in the art.

If one adds the organo-phosphoric acid of the present invention to the filter cake or to the micronizer feed, one will minimize the loss of the organic portion of the surface treatment and thereby improve manufacturing efficiency. The treated pigment may be fluid energy milled using steam or air to produce finished pigments that retain high levels of the organo-phosphoric acid compound, which would reduce the overall cost of producing the treated pigment.

When, for example, the pigment is titanium dioxide, organo-phosphoric acid may be added to the untreated titanium dioxide obtained from a production process such as the chloride or sulfate processes. Alternatively, the pigmentary base titanium dioxide may be further treated with additional metal oxides, such as aluminum oxide, silicon dioxide, zirconium oxide and the like, using any process known to those skilled in the art, prior to treatment with the organo-phosphoric acid of the present invention. Additionally, the untreated pigmentary base or the treated pigment may be secondarily treated with polyalcohols such as trimethylolethane and trimethylolpropane or alkanolamines such as triethanolamine.

Once the organo-phosphoric acid treated pigment is formed, it may then be combined with a polymer. The nature of the surface treatment of the present invention allows the treated pigments to be easily incorporated into a polymer matrix. The phrase "polymer matrix" refers to the substance comprising the polymer and the treated pigment. Polymers that may be of use in the present invention include polymers of unsubstituted ethylene 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, polystyrene, acrylonitrile-butadiene-styrenes and polyethers. Other suitable polymer types also

include polyvinylchloride, polyurethanes, polysulfones, polyimides, polyesters and chlorinated polyesters, polyoxyethylenes, phenolics, alkyds, amino resins, epoxy resins, phenoxy resins and acetal resins.

The treated pigment may be combined with the polymer and have a loading of up to about 85% by weight, based on the weight of the polymer matrix. Preferably a loading of treated pigment of about 50% to about 85% by weight based on the weight of the polymer matrix is used. This loading may be used as a masterbatch. A "masterbatch" is meant to refer to a mixture of two or more substances that are blended together and then blended with one or more other ingredients that may be the same or different as either of the first two substances. The methods for creating a masterbatch with the treated pigment are known or easily knowable to those skilled in the art. For example, the masterbatch may be created by combining the treated pigment and the polymer using a BR Banbury Mixer.

It has been found, surprisingly and unexpectedly, that the treated pigments of this invention do not generate potentially hazardous or noxious gases when used in combination with the polymeric filler lithopone, which contains combinations of zinc sulfide and barium sulfate. Lithopone, a composition containing zinc sulfide is used as a filler and extender in various polymer compositions. When a TiO_2 pigment treated with a phosphorylated polyene is contacted with zinc sulfide at temperatures greater than about 20 to 25°C, noxious odors are generated. In contrast, no odors are generated when pigments of the present invention are contacted with zinc sulfide under the same conditions.

It has also been found, surprisingly and unexpectedly that the treated pigments of this invention impart greater lacing resistance to polymers into which they are incorporated. Lacing, which is a believed to be a measure of volatility at specific weight percent pigment loadings and processing temperatures, may manifest as a void or hole in a plastic film.

Examples

The following examples set forth preferred embodiments of the invention. These embodiments are merely illustrative and are not intended and should not be

construed to limit the claimed invention in any way. Among the parameters described in the examples below are lacing evaluations and dispersion testing. The methods used to describe these parameters are set forth prior the specific examples.

Lacing Evaluations

The high temperature stability of polymers containing pigments is an important property of commercial polymer films, especially polyethylene film applications. Voiding or "lacing" accompanies the failure of films. Lacing is believed to be a measure of volatility at specific weight percent pigment loadings and processing temperatures.

For the present invention, lacing tests were conducted on 50% TiO_2 concentrate samples prepared using a Haake Rheocord 9000 Computer Controlled Torque Rheometer. Thus, 125g of TiO_2 and 125g 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. The concentrate was removed from the mixing chamber and placed into a Cumberland Crusher to obtain finely granulated 50% concentrate samples. The granulated samples were then pelletized on a Killion 25 mm single screw extruder with a 20:1 L/D ratio, equipped with a strand die, water bath and pelletizer. A flat temperature profile of 180°C was used to extrude the masterbatch pellets. The granulated concentrates were conditioned for 48 hours at 23°C and 50% relative humidity. These concentrates were then let down into Dow Chemical 722 LDPE to achieve a 20% loading of TiO_2 in the final film.

Lacing evaluations were run on a 1" extruder equipped with a cast film slot die. A temperature profile of 625°F die, 515 °F clamp ring, 415 °F zone 3, 350 °F zone 2, and 300 °F zone 1 was used. The screw speed was set at about 90 rpm. A 25.4 cm polished chrome chill roll, set in conjunction with the extruder was used to maintain a 75-μm-film thickness, and to cool and transport the films. The chill roll distance from the die lips was about 22 mm and the temperature was about 27 °C.

After the TiO_2/LDPE mix was placed in the hopper, the material was allowed to purge until the appearance of a white tint in the film was first noted. To ensure the concentration of TiO_2 in the film had stabilized, a time interval of two minutes was allowed before lacing observations were recorded and a film sample obtained. The extruder was then purged with LDPE until the film turned clear. Lacing performance was determined by counting the relative size and number of holes generated in a film sample laid out on a dark surface. 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 an indication of the relative performance between the samples.

Dispersion Testing

Using a small-scale laboratory extrusion apparatus, a measure of pigment dispersion into organic polymers was obtained by measuring the relative amount of pigment trapped onto screens of extruder screen packs. Tests were made using 75% TiO_2 concentrates in low density polyethylene prepared using a Haake 3000 Rheomix mixer. The mixer was controlled and monitored with a Haake 9000 Rheocord Torque Rheometer. 337.7 grams of micronized TiO_2 and 112.6 grams of NA209 LDPE manufactured by Equistar were dry blended and added to the 75°C mixing chamber with rotors operating at 50 rpm. The mixer temperature was programmed to increase to 120°C one minute after the dry blend was introduced to the mixing chamber. After a steady state mixture was achieved, the compound was mixed for an additional 3 minutes. The compound was removed from the chamber and granulated using a Cumberland crusher.

Dispersion tests were conducted using a Killion single screw extruder, model KL-100 equipped with a 20:1 length to diameter screw. The extruder was preheated at 330, 350, 390 and 380 °F from zone 1 to the die, respectively, and operated at 70 rpm. A purge of 1000 grams of NA952 LDPE manufactured by Equistar was run through the system, and a new screen pack was installed. The screen pack consisted of 40/500/200/100 mesh screens from the die towards the extruder throat. After temperature stabilization, 133.33 grams of granulated 75% TiO_2 concentrate was fed into the extruder. This was followed with 1500 grams of NA952 purge as the feed

hopper emptied. After the LDPE purge was extruded, the screens were removed, separated and tested using a relative count technique from the measurements from an X-ray fluorescence spectrometer. The number of TiO_2 counts per second was obtained for the 100, 200 and 500 mesh screens in the pack and totaled to obtain the dispersion result. A count result of less than 5000 is considered to represent excellent dispersion.

Example 1- Octyl Acid Phosphate Prepared in Accordance with U.S. Patent No. 4,350,645

To 65.12 g of 1-octanol (0.5 mol) and 9.0 g of water (0.5 mol), phosphorous pentoxide (70.96 g, 0.5 mol) was added gradually with vigorous stirring while maintaining the temperature below 80^{0}C. The reaction mixture was stirred for 3 hours at 80^{0}C. Subsequently, another 65.12 g of 1-octanol (0.5 mol) was added. The mixture continued to stir for another 10 hours at 80^{0}C. This method is more fully described in U.S. Pat. No. 4,350,645.

The resulting mixture was analyzed via titration methods, following the teachings of U.S. Patent No. 6,407,277, and found to yield 63-68% mono octyl acid phosphate, ~21% dioctyl acid phosphate and ~7% phosphoric acid.

Example 2 – Hexyl Acid Phosphate

Example 1 was repeated using 1-hexanol in place of the 1-octanol. The final product contains the presence of 60% monohexyl acid phosphate, 18% dihexyl acid phosphate, and ~12% phosphoric acid.

Example 3 – Polymer Matrices From Octyl Acid Phosphate Treated TiO_2 (Chloride Process)

51.8 mls of a 386.4 grams Al_2O_3/liter solution of sodium aluminate were added to 5000 grams of the TiO_2 in a 350 grams/liter slurry with mixing at 70°C. The pH was adjusted to 7.0 using a 50% sodium hydroxide solution, and the slurry was allowed to age for 30 minutes.

The aged slurry was filtered and washed three times with 5000 ml aliquots of 80°C deionized water, and then dried overnight at 115 °C in a drying oven.

The dried filter cake was forced through an 8-mesh sieve prior to treatment with octyl acid phosphate. 8.4 grams of the reaction product of octanol, P_2O_5 and phosphoric acid from Example 1 were added drop-wise to 1200 grams of the dry, 8 meshed, alumina coated TiO_2, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into a low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 1 below.

Example 4 - Polymer Matrices From Octyl Acid Phosphate Treated TiO_2 (Sulfate Process)

51.8 ml of a 386.4 grams Al_2O_3/liter solution of sodium aluminate were added to 5000 grams of fine particle sulfate process rutile TiO_2 in a 350 grams/liter slurry with mixing at 70°C. The slurry pH was adjusted to 7.0 using a 50% sodium hydroxide solution, and the slurry was allowed to age for 30 minutes. The aged slurry was filtered and washed three times with 5000 ml aliquots of 80°C deionized water and dried overnight at 115°C.

The dried filter cake was forced through an 8-mesh sieve in preparation for treatment with octyl acid phosphate. 8.4 grams of the octyl acid phosphate product were added dropwise from a syringe to 1200 grams of the dry, 8 meshed, alumina coated TiO_2 spread to a 1 cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed bottle and agitated for 10 minutes on a roller mill. The raw pigment was steam micronized to produce the finished pigment.

The finished pigment was incorporated into 75% and 50% TiO_2 based masterbatches containing low-density polyethylene for dispersion and lacing evaluations. Results are given in Table 1 below.

Comparative Example 1

Rutile TiO_2, prepared by the chloride process, coated with hydrous alumina as described in Example 3 was treated with 0.60% by weight triethanolamine based on the weight of dry pigment. The triethanolamine treated pigment was steam micronized to produce the finished pigment.

The finished pigment was incorporated into 75% and 50% TiO_2 containing low-density polyethylene masterbatches for dispersion and lacing evaluations. Results are given in Table 1 below.

Comparative Example 2

A sulfate process rutile TiO_2 base was coated with alumina as described in Example 4. The organic treatment applied to the dry, 8-meshed alumina coated, sulfate process TiO_2 was 0.60% by weight triethanolamine based upon the weight of the dry pigment. The triethanolamine treated pigment was steam micronized to produce the finished pigment. The finished pigment was incorporated into 75% and 50% TiO_2 masterbatches for dispersion and lacing evaluations. Results are given in Table 1 below.

TABLE 1

	Dispersion (Counts/Second)	Lacing
Example 3	1,750	1.7
Example 4	5,140	1.5
Comparative Example 1	13,700	1.4
Comparative Example 2	24,000	1.2

The data illustrate that dispersion performance of both chloride and sulfate process-based pigments, treated with the octyl acid phosphate reaction product (Examples 3 and 4), is dramatically improved over like pigmentary bases treated with a conventional, commercially used organic treatment, triethanolamine (comparative Examples 1 and 2). Further, the excellent dispersion performance is obtained with no

significant decay in resistance to lacing. The standard error for the lacing measurement is about 0.1 to 0.2.

Examples 5 –21: Dispersion and Lacing

In the following examples (Examples 5-21), the organo-acid phosphate was added to a dry, chloride process base rutile TiO_2 further treated with 0.20% by weight of alumina, prior to micronization. The organo-acid phosphate ester was added as a neat liquid or in solution if the organo-acid phosphate was a solid material. The general preparation method used for producing the organo-acid phosphate, alumina treated pigmentary base was as follows:

25.9 mls of a 386.4 grams Al_2O_3/liter solution of sodium aluminate were added with mixing to 5000 grams of the TiO_2 in a 350 grams/liter slurry at 70°C. The pH was adjusted to 7.0 using a 50% sodium hydroxide solution, and the slurry was allowed to age for 30 minutes.

The aged slurry was filtered and washed three times with 5000 ml aliquots of 80°C deionized water, and then dried overnight at 115 °C in a drying oven. The dried filter cake was forced through an 8-mesh sieve prior to treatment with the organo-acid phosphate. The desired amount of organo-acid phosphate was added dropwise to 1200 grams of the dry, 8 meshed, alumina coated TiO_2, which was spread to a 1-cm thickness on polyethylene film. If the organo–acid phosphate was a solid material, it was dissolved in tetrahydrofuran (THF) prior to application to the dry pigment, and the THF was allowed to evaporate. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

Example 5 – 0.9% Octyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% octyl acid phosphate prepared according to Example 1 and steam micronized to produce the final product. The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Dispersion results were 780 XRF counts of TiO_2/sec and lacing was rated a 1.5.

Example 6 – 1.1% Octyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 1.1% octyl acid phosphate prepared according to Example 1 and steam micronized to produce the final product. The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Dispersion results were 1,080 XRF counts of TiO_2/sec and lacing was rated 1.3.

Example 7 – 0.9% Hexyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% hexyl acid phosphate prepared according to the method of Example 2 and steam micronized to produce the final product. The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Dispersion results were 1,260 XRF counts of TiO_2/sec and lacing was rated 1.3.

Example 8 – 1.1% Hexyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 1.1% hexyl acid phosphate prepared according to the method of Example 2 and steam micronized to produce the final product. The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Dispersion results were 1,310 XRF counts of TiO_2/sec and lacing was rated 1.2.

Example 9 – 0.5% Butyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.5% butyl acid phosphate obtained from Albright and Wilson Americas and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 12,720 XRF counts of TiO_2/sec.

Example 10 – 0.7% Butyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.7% butyl acid phosphate obtained from Albright and Wilson Americas and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 2,180 XRF counts of TiO_2/sec.

Example 11 – 0.9% Butyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% butyl acid phosphate obtained from Albright and Wilson Americas and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 1,030 XRF counts of TiO_2/sec.

Example 12 – 0.9% 2-Ethylhexyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% 2-ethylhexyl acid phosphate, which was commercially available from Specialty Industrial Products, Inc. under the tradename Sipophos 2EHP, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 790 XRF counts of TiO_2/sec.

Example 13 1.1% 2-Ethylhexyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 1.1% 2-ethylhexyl acid phosphate, which was commercially available from Specialty Industrial Products, Inc. under the tradename Sipophos 2EHP, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 280 XRF counts of TiO_2/sec.

Example 14 - 0.9% Cetyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% cetyl acid phosphate, which was commercially available from Colonial Chemical Company under the tradename Colafax CPE, and steam

micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 15,140 XRF counts of TiO_2/sec.

Example 15 - 1.1% Cetyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 1.1% cetyl acid phosphate, which was commercially available from Colonial Chemical Company under the tradename Colafax CPE, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 2,970 XRF counts of TiO_2/sec.

Example 16 - 0.7% Oleyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.7% oleyl acid phosphate, which was commercially available from Albright & Wilson Americas under the tradename DURAPHOS APO-128, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 25,730 XRF counts of TiO_2/sec.

Example 17 - 0.9% Oleyl Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% oleyl acid phosphate, which was commercially available from Albright & Wilson Americas under the tradename DURAPHOS APO-128, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 20,720 XRF counts of TiO_2/sec.

Example 18 - 0.5% Bis(2-ethylhexyl) Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.5% bis(2-ethylhexyl) acid phosphate, which was commercially available from Albright & Wilson Americas, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-

density polyethylene masterbatch for dispersion evaluation. The dispersion result was 5,610 XRF counts of TiO_2/sec.

Example 19 - 0.7% Bis(2-ethylhexyl) Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.7% bis(2-ethylhexyl) acid phosphate, which was commercially available from Albright & Wilson Americas, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 1,120 XRF counts of TiO_2/sec.

Example 20 - 0.9% Bis(2-ethylhexyl) Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 0.9% bis(2-ethylhexyl) acid phosphate, which was commercially available from Albright & Wilson Americas, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 1,530 XRF counts of TiO_2/sec.

Example 21 - 1.1% Bis(2-ethylhexyl) Acid Phosphate Treated TiO_2

The pigmentary base prepared according to the above-described method was treated with 1.1% bis(2-ethylhexyl) acid phosphate, which was commercially available from Albright & Wilson Americas, and steam micronized to produce the final product. The finished pigment was incorporated into a 75% by weight low-density polyethylene masterbatch for dispersion evaluation. The dispersion result was 1,070 XRF counts of TiO_2/sec.

Zinc Sulfide Reactivity

Example 22 - Zinc Sulfide and Phosphorylated Polyenes

5 grams of a pigment product comprising titanium dioxide and a phosphorylated polyene were placed in a sealed vial with 1g of zinc sulfide. The vial was heated to 195 ^{0}C for 10 minutes. Noxious vapors emanating from the vial were

injected in to a Hewlett-Packard GC-MS and dimethyl disulfide and dimethyl trisulfide were detected.

Example 23 - Zinc Sulfide and Octyl Acid Phosphate Treated TiO_2

5 grams of the pigment as prepared in Example 3 were placed in a sealed vial with 1 g of zinc sulfide. The vial was heated to 195°C for 10 minutes. No noxious odors were detected nor were sulfur components detected via GC-MS.

EXTRACTION OF FINISHED PIGMENTS

Samples of finished pigments from Examples 3 and 4 were extracted using Soxhlet extraction procedures with hexane, tetrahydrofuran and a 10%:90% ethanol:water (W/W) mixture as extraction solvents. The carbon contents of the dried pigments were determined both before and after extraction. Results are shown below in Table 2.

TABLE 2

	Example 3	Example 4
% Carbon		
theoretical	*0.31*	*0.31*
before extraction	0.28	0.28
after hexane extraction	0.28	0.27
after THF extraction	0.29	0.27
after EtOH: H_2O extraction	0.28	0.25

Based on the extraction results, the organo-acid phosphate is apparently strongly bonded to the TiO_2 pigment since carbons levels of the treated pigment are not significantly affected by extraction. Further, the octyl-acid phosphate appears not to be appreciably hydrolyzed during the high temperature steam micronization process since over 90% of the added carbon remains attached to the pigment after micronization. It would be expected that hydrolysis of the acid phosphate would liberate octanol, which is volatile and would evaporate during micronization.

Example 24: Acid form of Caprylpyrophosphate

The acid form of caprylpyrophosphate was prepared from its corresponding sodium salt (purchased from Chem Service, Inc. P.O.Box 599, West Chester, Pa, 19381; Catalog # S-481) according to the following procedure: A portion of the sodium salt (~37gm) was dissolved in water and acidified with concentrated HCl until pH < 2. The resulting reaction mixture was then extracted with 3x200mL of diethyl ether. The combined organic layers were washed with 5x200mL of water and then dried over anhydrous $MgSO_4$. The ether layer was decanted, and the remaining drying agent was washed with 50mL of diethyl ether, and the ether was decanted. The combined ether extracts were evaporated on a rotary evaporator at room temperature. The remaining residue was used for TiO_2 surface treatment.

Example 25: Acid form of Caprylpyrophosphate

51.8 mls of a 386.4 grams Al_2O_3/liter solution of sodium aluminate were added to 5000 grams of oxidizer product TiO_2 in a 350 grams/liter slurry with mixing at 70°C. The pH was adjusted to 7.0 using a 50% sodium hydroxide solution, and the slurry was allowed to age for 30 minutes.

The aged slurry was filtered and washed three times with 5000 ml aliquots of 80°C deionized water, and then dried overnight at 115 °C in a drying oven. The dried filter cake was forced through an 8-mesh sieve prior to treatment with caprylpolyphosphate.

10.75g of the acid form of caprylpyrophosphate prepared according to the method of example 24 were added drop-wise to 980 grams of the dry, 8 meshed, alumina coated TiO_2, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given Table 3.

Example 26: Acid form of 2-Ethylhexylpyrophosphate

The acid form of 2-ethylhexyl-pyrophosphate was prepared from its corresponding sodium salt (purchased from Chem Service, Inc. P.O.Box 599, West Chester, Pa, 19381; Catalog # S-480) according to the following procedure: A portion of the sodium salt (~37gm) was dissolved in water and acidified with concentrated HCl until pH < 2. The resulting reaction mixture was then extracted with 3x200mL of diethyl ether. The combined organic layers were washed with 5x200mL of water and then dried over anhydrous $MgSO_4$. The ether layer was decanted, and the remaining drying agent was washed with 50mL of diethyl ether, and the ether was decanted. The combined ether extracts were evaporated on a rotary evaporator at room temperature. The remaining residue was used for TiO_2 surface treatment.

Example 27: Acid form of 2-Ethylhexylpyrophosphate

11.20 grams of the acid form of 2-ethylhexyl-pyrophosphate prepared in example 26 were added drop-wise to 1000 grams of the dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 28: Sodium Salt of Caprylpyrophosphate

15.08 grams of the sodium salt of caprylpyrophosphate obtained from Chem Service Inc, catalogue # S-481, were dissolved in 30.9 grams of deionized water. The aqueous solution was added drop-wise to 1000 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in the Table 3w.

Example 29: Sodium Salt of Caprylpyrophosphate

18.38 grams of the sodium salt of caprylpyrophosphate obtained from Chem Service Inc, catalogue # S-481, were dissolved in 33.1 grams of deionized water. The aqueous solution was added drop-wise to 1000 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 30: Sodium Salt of 2- Ethylhexyl Polyphosphate

15.05 grams of the sodium salt of 2-ethylhexyl polyphosphate obtained from Chem Service Inc, catalogue # S-480, were dissolved in 26.9 grams of deionized water. The aqueous solution was added drop-wise to 1000 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 31: Acid form of Dihexylpyrophosphate

The acid form of dihexylpyrophosphate, acid form was prepared in accordance to Alder, Howard and Woodstock, Willard. Chem. Industries, 1942, 51, 516 with the following considerations: 28.4 grams of P_2O_5 were adding to 40.8 grams of 1-hexanol

with stirring using a stir bar or a mechanical stirrer. No cooling was employed during the reaction. The temperature reached as high as ~125-145 ^{0}C during the mixing of the P_2O_5 with the alcohol, and the reaction was considered complete when the temperature declined to room temperature.

10.89 grams of the acid form of dihexylpyrophosphate prepared according to the above method were dissolved in 16.6 grams of tetrahydrofuran. The tetrahydrofuran solution of dihexylpyrophosphate was added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 32: Acid form of Dihexylpyrophosphate

14.52 grams of the acid form of dihexylpyrophosphate prepared according to the method described in example 31 were dissolved in 21.7 grams of tetrahydrofuran. The tetrahydrofuran solution of dihexylpyrophosphate was added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 33: Acid form of Dioctylpyrophosphate

The acid form of dioctylpyrophosphate, was prepared in accordance to Alder, Howard and Woodstock, Willard. Chem. Industries, 1942, 51, 516 with the following considerations:

28.4 grams of P_2O_5 were added to 52.0 grams of 1-octanol with stirring using a stir bar or a mechanical stirrer. No cooling was employed during the reaction. The temperature reached as high as ~125-145 ^{0}C during the mixing of the P_2O_5 with the alcohol, and the reaction was considered complete when the temperature declined to room temperature.

10.80 grams of the acid form of dioctylpyrophosphate prepared according to the above method were added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 34: Acid form of Dioctylpyrophosphate

14.54 grams of the acid form of dioctylpyrophosphate prepared according to the method described in example 10 were added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 35: Potassium Salt of Dihexylpyrophosphate

The potassium salt of the dihexylpyrophosphate was prepared by dissolving portions of the acid form of dihexylpyrophosphate prepared according to the method described in example 31 in ethanol which contained phenolphthalein. Approximately 0.5M ethanolic KOH solution was added dropwise to the solution of dihexylpyrophosphate until the reaction mixture turned slightly pink. The resulting solution was then dried on a rotary evaporator at room temperature. The remaining residue was used for surface treatment of TiO_2 pigment.

11.17 grams of the potassium salt of dihexylpyrophosphate prepared according the above described method was dissolved in 78.0 grams of tetrahydrofuran. The tetrahydrofuran solution of the potassium salt of dihexylpyrophosphate was added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into low-density polyethylene in 75% and 50% masterbatches for dispersion and lacing evaluations. Results are given in Table 3.

Example 36: Acid form of Pentaoctyltripolyphosphate

The acid form of pentaoctyltripolyphosphate was prepared in accordance to Alder, Howard and Woodstock, Willard. Chem. Industries, 1942, 51, 516 with the following considerations: 17.0 grams of P_2O_5 were added to 26.0 grams of 1-octanol with stirring using a stir bar or a mechanical stirrer. No cooling was employed during the reaction. The temperature reached as high as ~125-145 ^{0}C during the mixing of the P_2O_5 with the alcohol, and the reaction was considered complete when the temperature declined to room temperature.

10.85 grams of the acid form of pentaoctyltripolyphosphate prepared according to the above method were dissolved in 43.9 grams of tetrahydrofuran. The tetrahydrofuran solution of pentaoctyltripolyphosphate was added drop-wise to 1200

grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into a 75% low-density polyethylene masterbatch for dispersion evaluation. Results are given in the Table 3.

Example 37: Acid form of Pentaoctyltripolyphosphate

13.27 grams of the acid form of pentaoctyltripolyphosphate prepared according to the above method were dissolved in 40.2 grams of tetrahydrofuran. The tetrahydrofuran solution of pentaoctyltripolyphosphate was added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into a 75% low-density polyethylene masterbatch for dispersion evaluation. Results are given in the Table 3.

Example 38: Acid form of Trioctyltetrapolyphosphate

The acid form of trioctyltetrapolyphosphate, was prepared in accordance to Alder, Howard and Woodstock, Willard. Chem. Industries, 1942, 51, 516 with the following considerations: 28.4 grams of P_2O_5 were added to 39.0 grams of 1-octanol with stirring using a stir bar or a mechanical stirrer. No cooling was employed during the reaction. The temperature reached as high as ~125-145 ^{0}C during the mixing of the P_2O_5 with the alcohol, and the reaction was considered complete when the temperature declined to room temperature.

10.80 grams of the acid form of trioctyltetrapolyphosphate prepared according to the above method were dissolved in 47.1 grams of tetrahydrofuran. The tetrahydrofuran solution of trioctyltetrapolyphosphate was added drop-wise to 1200

grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into a 75% low-density polyethylene masterbatch for dispersion evaluation. Results are given in Table 3.

Example 39: Acid form of Trioctyltetrapolyphosphate

13.28 grams of the acid form of trioctyltetrapolyphosphate prepared according to the method described in example 15 were dissolved in 41.3 grams of tetrahydrofuran. The tetrahydrofuran solution of trioctyltetrapolyphosphate was added drop-wise to 1200 grams of dry, 8 meshed, alumina coated TiO_2 prepared according to example 25, which was spread to a 1-cm thickness on polyethylene film. The pigment was mixed and transferred to a one gallon wide-mouthed plastic bottle and agitated for 10 minutes on a roller mill. The resulting material was steam micronized to produce the finished pigment.

The finished pigment was incorporated into a 75% low-density polyethylene masterbatch for dispersion evaluation. Results are given in Table 3.

Table 3

	Dispersion	Lacing
Example 25	570	1.4
Example 27	840	1.2
Example 28	690	1.6
Example 29	550	1.4
Example 30	870	1.7
Example 31	1,570	1.5
Example 32	860	1.2
Example 33	230	1.2
Example 34	1,560	1.3
Example 35	1,760	1.5
Example 36	1,890	not measured
Example 37	3,860	not measured
Example 38	2.240	not measured
Example 39	4,860	not measured
Comparative Example 3	13,700	1.4

The data in the table illustrate that dispersion performance of TiO_2 pigments, treated with the organo acid pyrophosphates and organo acid polyphosphates, is dramatically improved over like pigmentary bases treated with a conventional, commercially used organic treatment, triethanolamine (comparative Example 3). Further, the excellent dispersion performance is obtained with no significant decay in resistance to lacing. The standard error for the lacing measurement is about 0.1 to 0.2.

Having thus described and exemplified the invention with a certain degree of particularity, it should be appreciated that the following claims are not to be so limited but are to be afforded a scope commensurate with the wording of each element of the claim and equivalents thereof.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A pigment comprising a pigmentary base that has been treated with an organo-phosphoric acid compound having the formula:

$R'_n-P_{(n-2)}O_{4+[3(n-3)]}$

wherein n = 4 - 14; and each R' is an organic group having from 2 to 22 carbon atoms or hydrogen and within any one molecule, any two or more R' groups may be the same provided that at least one of the R' groups is not hydrogen; and

wherein the organo-phosphoric acid compound is present in an amount from about 0.01 percent to about 5 percent by weight based on the weight of the pigmentary base.

2. A pigment according to claim 1, wherein the pigmentary base is selected from the group consisting of titanium dioxide, kaolin, talc, mica and calcium carbonate.

3. A pigment according to claim 2, wherein the pigmentary base is titanium dioxide.

4. A pigment according to claim 1, wherein the pigmentary base is treated with a compound selected from the group consisting of polyalcohols, alkanolamines, aluminum oxide, silicon dioxide and zirconium oxide.

5. A pigment according to claim 1, wherein the pigmentary base is treated with trimethylolpropane or triethanolamine.

6. A pigment comprising a pigmentary base that has been treated with a salt of the organo-phosphoric acid compound as defined in claim 1.

7. A polymer matrix comprised of a polymer and the pigment of claim 1.

8. A polymer matrix according to claim 7, wherein the polymer is polyethylene.

9. A polymer matrix according to claim 8, wherein the amount of the pigment is from about 50 percent to about 85 percent by weight of the polymer matrix, based on the weight of the polymer matrix.

10. A method for preparing a pigment, comprising combining a pigmentary base and an organo-phosphoric acid compound, wherein the organo-phosphoric acid compound has the formula:

$$R'_n\text{-}P_{(n-2)}O_{4+[3\,(n-3)]}$$

wherein n = 4 - 14; and each R' is an organic group having from 2 to 22 carbon atoms or hydrogen and within any one molecule ; any two or more R' groups may be the same provided that at least one of the R' groups is not hydrogen; and

wherein the organo-phosphoric acid compound is present in an amount from about 0.01 percent to about 5 percent by weight of the pigmentary base, based on the weight of the pigmentary base.

11. A method for preparing a pigment comprising combining a pigmentary base with a salt of the organo-phosphoric acid compound as defined in claim 10.