COSMETIC COMPOSITIONS
ORGANOPHOSPHONIC ACID COATED
PARTICULATES AND METHODS FOR
PRODUCING THE SAME

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References Cited
U.S. PATENT DOCUMENTS
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4,877,604 A 10/1989 Schlossman
5,106,736 A 4/1992 Schlossman
5,346,760 A 9/1994 Parker
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5,599,530 A 2/1997 Paol et al.
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ABSTRACT

The invention provides cosmetic compositions containing
powders that are surface treated with organophosphonic acid
compounds, where the surface treated particulates are simul-
taneously hydrophobic and lipophilic. The invention also
provides (a) methods for preparing cosmetic compositions con-
taining said powders, and (b) methods for preparing cosmetic
compositions containing said powders where the powders
have been treated via a volatile organic solvent-free manufac-
turing process.

13 Claims, No Drawings
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COSMETIC COMPOSITIONS
ORGANOPHOSPHONIC ACID COATED
PARTICULATES AND METHODS FOR
PRODUCING THE SAME

RELATED APPLICATION

This application is claiming the benefit, under 35 U.S.C. § 119(e), of the provisional application filed Jun. 5, 2003 under 35 U.S.C. § 111(b), which was granted Ser. No. 60/475,960. This provisional application is hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

Cosmetic compositions are provided which contain organophosphonic acid surface treated particulates. The powders are characterized as being pigments or fillers for said compositions. When surface treated, the powders are essentially hydrophobic in the sense that they repel water (i.e., they do not disperse in water), whereas in the absence of surface treatment, the same powders are observed to disperse in water. Simultaneously, the surface treated powders are essentially lipophilic, and hence exhibit improved dispersion characteristics in oily media commonly used in cosmetics, including silicones, hydrocarbons, natural esters, and synthetic esters.

The advantages of cosmetics compositions that contain pigments with such characteristics have been described in the prior art by several inventors. For example, Schlossman in U.S. Pat. No. 4,877,604 used tituanated treated powders to achieve cosmetic compositions with (a) improved dispersion characteristics, (b) with the capacity for higher inorganic loadings, (c) with less settling and improved shelf stability, (d) with increased "smoothness" upon application, (e) with improved skin adhesion, and (f) with improved moisture resistance in the final skin application. Hollenberg, et al. in U.S. Pat. No. 5,413,722 disclosed similar improvements that were achieved via reactive polysiloxane or organosilane surface-treated pigments. In addition, fluorosilane surface treatment were used for the achievement of simultaneous hydrophobicity and lipophilicity by Farer, et al. in U.S. Pat. No. 5,315,990. Similarly, organometalic zincium compounds have been used to achieve improved cosmetic compositions as taught by Patil, et al. in U.S. Pat. No. 5,399,530.

Although the prior-art cosmetics compositions share many advantages, they also share common shortcomings. For example, undesirable byproducts such as volatile organic compounds (VOC's), hydrochloric acid, or hydrogen are often evolved during the process of manufacturing the surface treated powders that are used in such compositions. When solvent-based carriers are used, environmental concerns can sometimes arise since the solvents must be volatilized during the later stages of manufacturing (i.e., during the drying process). In certain cases, and depending on the chemical nature and quantity of the solvent carrier, some of these volatile organic compounds can remain adsorbed on the particle surfaces together with unwanted by-products of oxidation. Also, even in the absence of organic solvent carriers, the nature of the hydrolysis and condensation reactions of many neat prior-art compounds leads to the inevitable evolution of volatile organic compounds, or other potentially deleterious reaction by-products. For example, when a surface treatment is performed by mixing and reacting polyhydrogenasiloxanes with dry powders (as described by Hallenberg et al. in U.S. Pat. No. 5,413,722), or by dry blending n-octyltriethoxysilane with inorganic powders as taught by Horn et al. in U.S. Pat.

No. 5,543,173; incomplete hydrolysis can lead to the slow release of either hydrogen or VOC's over time (i.e., during the storage of the treated powders, or during the storage of finished products that contain the treated powders). When an alternative surface treatment is used such as an organosilicon as taught by Weber, et al. in U.S. Pat. No. 6,214,106, the by-products include halogen salts such as hydrogen chloride, which can also be deleterious in many end-use applications.

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BRIEF SUMMARY OF THE INVENTION

In contrast to the prior art, the current invention provides for cosmetic compositions comprising surface treated particulates, wherein either all or a portion of said particulates are partially or completely surface treated with an organophosphonic acid compound. Preferably, the surface treatment compounds and preparation methods are chosen so as to reduce or eliminate the possibility of producing and retaining residual hazardous byproducts. Furthermore, the current invention makes use of surface treated powders that retain their hydrophobic characteristics and are stable in the presence of water for long periods of time, and as such there are no storage restrictions for cosmetics compositions that are prepared with them.

Specifically, the cosmetic compositions of the present invention make use of alkylphosphonic acid treated powders, whereby the powders by definition are devoid of the deleterious reaction by-products that are otherwise characteristic of the prior art surface treatments. The alkylphosphonic acid treated powders also exhibit unexpected combinations of hydrophobic and lipophilic characteristics. The term "lipophilic" in this context means that the powder particle surfaces are easily wetted and dispersed within the liquid oils that are commonly used in cosmetic compositions. The term "hydrophobic" is used in this context means that the powders have the ability to completely repel water (as evidenced by the formation of a segregated partition between the pigment and the water-phase; such that the water-phase remains clear, but which does not become cloudy when the two are mixed). It is to be appreciated that although many powders of the prior-art are lipophilic, not all of them are simultaneously hydrophobic; i.e., not all lipophilic powders have the ability to repel water. The simultaneous achievement of these characteristics is an important aspect of this invention, especially since these simultaneous characteristics are highly desirable for producing many types of cosmetics compositions (as noted by Hallenberg et al. in U.S. Pat. No. 5,413,722), including those provided by the present invention.

The cosmetic compositions of the present invention can be prepared with pigments that have been surface treated with an alkylphosphonic acid, where the alkylphosphonic acid may be applied by means of either an organic solvent or a water-based carrier. Surprisingly, each type of carrier can be equivalently employed for the purposes of achieving the unique hydrophobic and lipophilic characteristics that are desirable for producing the cosmetic compositions of the present invention. Given the relatively poor solubility of alkylphosphonic acids in water, it is surprising to note that hydrophobic characteristics are achieved from powders that are treated with solely water based mixtures. In fact, it is plausible to anticipate that heterogeneous mixtures such as these might lead to heterogeneous surface coverage, where the resultant properties of the heterogeneously treated powders would be inferior to those treated with otherwise homogeneous surface treatment solutions. However, this is surprisingly not the case. For example, in spite of the partial solubility of n-octylphosphonic acid in water (an opaque, viscous,
emulsion-like mixture forms when α-octylphosphonic acid is added to water at concentrations of greater than about 10% by weight, the resultant surface coverage is unexpectedly efficient. In fact, the resultant powders are completely hydrophobic, and dispersible in oil. Moreover, similar results are achieved when a completely soluble solution of α-octylphosphonic acid in isopropyl alcohol is used in place of a water-based mixture. Thus, partially soluble mixtures of alkylphosphonic acid in water yield surface treated pigments that are unexpectedly on par with those obtained through the use of completely miscible treatment solutions.

It is equally surprising to note that when the treatment is applied through a water medium, the resultant treated powders tend to repel and not disperse in water, and the treatment remains intact even when the treated powders are exposed to water for long periods of time. Moreover, in cases where the neat alkylphosphonic acid is itself soluble in a hydrophilic solvent medium, the successfully treated powders remain unexpectedly dispersible in the same medium even after several attempts have been made to remove the surface treatment (through repeated washing with virgin aliquots of the same hydrophobic solvent). Thus, once the treated powders are formed, the treatment is unexpectedly stable and resistant to removal by both water and oil. It is to be appreciated that pigments with these attributes are paramount to the achievement of stable water-in-oil and oil-in-water cosmetics compositions (as taught by Hollenberg et al. in U.S. Pat. Nos. 5,143,722). Consequently, alkylphosphonic acid treated particulates with these attributes are important components for use in the cosmetic compositions as defined by the present invention.

A neat alkylphosphonic acid compound can also be used to prepare the powders for use in this invention; and in such cases, it is preferable to heat the neat compound above its melt point and to mix it with the powder while the compound is in its molten state. Similarly, when water-based mixtures are used, the mixtures can be heated to improve solubility and to reduce viscosity. In such cases, heated mixtures can be mixed directly with the powder either at ambient or at elevated temperatures.

The combined hydrophobic/lipophilic characteristics that are imparted by alkylphosphonic acid treated pigments are surprisingly unique and cannot be anticipated from the behavior of pigments that have been surface treated with analogous compounds. Although organophosphonic acids have been shown to chemically adsorb onto certain inorganic materials (i.e., onto aluminum as shown by Webers et al., U.S. Pat. No. 5,059,258; and onto titanium dioxide as shown by Watson, et al. in U.S. Pat. No. 5,837,049), the comparative examples provided herein demonstrate that chemical adsorption alone and/or surface polymerization are not predictors of, nor are they prerequisites for the simultaneous achievement of the hydrophobicity and lipophilicity that are paramount to this invention. For example, monomeric alkylcarboxylic acids are known from the prior-art to adsorb onto pigment surfaces, and to impart lipophilicity, but the hydrophobic characteristics of such treated pigments are surprisingly inferior to those treated with analogous monomeric alkylphosphonic acids. By contrast, the hydrophobic and lipophilic characteristics imparted by alkylphosphonic acids are surprisingly similar to those imparted by alkyltrialkoxysilanes; but unlike the alkylphosphonic acids, the alkyltrialkoxysilanes are known to hydrolyze and polymerize on the surfaces of inorganic pigments. Thus, there is no known mechanism by which one can predict the simultaneous achievement of hydrophobicity and lipophilicity as has been surprisingly achieved through the use of alkylphosphonic acid modified pigments.

Thus, in one aspect the invention provides cosmetics compositions that contain organophosphonic acid surface treated particulates, where the particulates possess lipophilic, or simultaneously hydrophobic and lipophilic characteristics. Methods of producing such compositions are also provided.

In another aspect of this invention, cosmetics compositions are provided that comprise organophosphonic acid surface treated particulates, whereby the organophosphonic acid treated particulates are produced via a volatile organic solvent-free process, and where the surface treated particulates possess simultaneous hydrophobic and lipophilic characteristics.

In a further aspect of the invention, cosmetic compositions are provided having particulates, where at least some of which, if not all of which, are coated with an organophosphonic acid.

**DETAILED DESCRIPTION OF THE INVENTION**

The cosmetic compositions of this invention are prepared with pigments that have been surface treated with organophosphonic acids. The organophosphonic acid surface treatments may be monomeric, oligomeric, or polymeric as described by the general formulas:

\[ \text{R}_x\text{PO(OH)}_y \]

where \( R \) is an organic group containing 1 to 50 carbon atoms, \( x \) is the number of organic groups (about 1-30), and \( y \) is the number of phosphonic acid groups (about 1-20). Examples of suitable monomeric organophosphonic acid compounds (where \( x = y + 1 \)) include methylphosphonic acid, ethylphosphonic acid, butylphosphonic acid, octylphosphonic acid, dodecylphosphonic acid, and octadecylphosphonic acid.

The \( R \) group can be generally comprised of long or short chain aliphatic hydrocarbons, aromatic hydrocarbons, styrenic, vinyl, carboxylic acids, aldehydes, ketones, amines, amides, imides, lactams, carboxylates, esters, lactones, ethers, alcohols, amines, ureas, organosilicones, perfluorinated groups, silanes, and others as well as combinations of these groups. In addition, the \( R \) group can be a polymeric structure that contains \( y \) phosphonic acid groups. Examples of representative structures include products of monomeric phosphonic acid homopolymerization such as polyvinylphosphonic acid, poly(vinylbenzyl)phosphonic acid, products of copolymerization of such monomers with other types of monomers; and polymeric molecules that have been functionalized with phosphonic acid moieties through post polymerization processes.

The surface treatments can also include organophosphonic acids of the general formula:

\[ \text{R}_x\text{PO(OH)}_y \]

where \( R \) is an organic group like that described above.

In addition, pigments can be optionally pre-treated with appropriate acidic or basic solutions prior to treatment with an organophosphonic acid compound; wherein such pre-treatments may improve the performance of the final treated pigment for the purposes of this invention. Furthermore, the pigments can be optionally co-treated with other compounds for the purpose of imparting additional functionality or utility to the resultant particle surfaces. Such co-treatments can include but are not limited to organosilanes, carboxylic acids and their salts, titanates, zirconates, organoaluminum com-
phosphonic acids such as \(\text{H}-\text{octylphosphonic acid}\) are only partially soluble in water. In such cases, the organophosphonic acid can be mixed with water over any range of concentrations to yield completely soluble solutions in the dilute extreme, and to yield opaque and partially soluble slurries in the concentrated extreme. Concentrated slurries can be optionally heated to temperatures ranging from about 50-90° C. to improve solubility and to reduce viscosity. After heating, the mixtures can be cooled to room temperature before they are applied to the pigment, or they can be applied to the pigment while hot. The pigment itself can also be conditioned at ambient or at elevated temperatures prior to being mixed with the treatment slurry.

The desirable concentration of the treatment slurry (or solution) depends upon the treatment process that is to be employed. In one extreme, a wet process can be used where sufficient carrier solvent can be employed so as to completely disperse the pigment. Mixing and drying procedures can be followed as described in the prior art through the sequential use of ball mills, shear mixers, drying ovens, and the like.

However, in keeping with the advantages of this invention, it is most preferable to use dry-blending processes such as those that are known in the art; including, but not limited to those described by Hollenberg, et al. in U.S. Pat. No. 5,143,722, by Horn et al. in U.S. Pat. No. 5,943,173, and by Parker et al. in U.S. Pat. No. 5,348,750, wherein sufficient dry-blending treatments are achieved through the use of tumbling blenders, ball mills, high shear mixers, hammer mills, and combinations thereof, and where the use of carrier solvents is minimized.

In one preferred dry-blend process, the carrier is water, and the organophosphonic acid/water slurry is as concentrated as is practical for the purposes of achieving both a homogeneous mixture and a homogeneous surface treated product. In such a process, the concentrated slurry is added to the dry powder while the mixture is tumbled, ball milled, shear mixed, or the like for a sufficient time so as to achieve adequate surface coverage. "Adequate surface coverage" for the purposes of this invention can be determined via "hydrophobicity" and "lipophilicity" tests as described herein. Once sufficient blending is achieved, the powder is dried (for example in a gravity or forced air oven) at a temperature between about 50° and 105° C. for a time that is both sufficient to remove excess water, and sufficient to achieve the desired levels of hydrophobicity and lipophilicity; where the desired level of hydrophobicity is determined by the pigment's tendency to repel from water (as evidenced by the formation of a segregated partition between the pigment and the water-phase; such that the water-phase remains clear, and not cloudy when the two are mixed); and the desired level of lipophilicity is determined by the sedimentation density of the pigment in a lipophilic dispersion medium of choice (using the sedimentation methods as described by Parker in The Journal of Adhesion Science and Technology, 16, 2002, pp.679-701; and by Parker et al. in Material Research Society Symposium Proceedings, 249, 1992, pp.273-278).

In another variant of the dry-blend process, the carrier for the alkylphosphonic acid may be an alcohol such as isopropyl alcohol, or an isopropanol/water solution. The preferred processes for preparing powders with such carriers are completely analogous to the preferred processes that are employed when water is used as the carrier. However, if a solvent carrier is employed, it is most desirable to use a treatment solution where the alkylphosphonic acid concentration is as high as possible so as to minimize the level of organic solvent that must otherwise be removed during the drying process.
The concentration for the alkylphosphonic acid treatment solution or mixture must also be practical from the standpoint of achieving adequate bleeding efficiency and surface coverage in a dry-blend process. For example, at higher concentrations in water (i.e., at higher ratios of alkylphosphonic acid to water), the viscosity of the mixture could make it more difficult to achieve a homogenous dry-blend, and the process may require longer periods of time. On the other hand, the viscosity of an alkylphosphonic acid/water mixture can be reduced by raising the temperature of the slurry, by increasing the temperature of the powder, or by doing both in combination. Although higher concentrations could be employed, the preferred slurry concentration for ambient or elevated temperature blending is 5% in 50% by weight n-octylphosphonic acid in water, or preferably 5% to 25% by weight, and most preferably about 15-20% by weight n-octylphosphonic acid in water. The preferred slurry concentrate can either be added at once to the dry powder, or it can be metered into the blending apparatus over time. Turning again to the case of titanium dioxide as an example, adequate hydrophobicity and lipophilicity are achieved when a 16.7% by weight slurry of n-octylphosphonic acid (NOPA) in water is added at a level sufficient so as to achieve between 1% and 2% residual NOPA by weight powder after drying (this equates to approximately 6-12 g of concentrated slurry per 100 g of titanium dioxide).

For cases where the alkylphosphonic acid forms a miscible solution with the solvent carrier (as is the case with isopropanol and NOPA), higher surface treatment solutions can be employed during the dry-blend process. For example, when a 70/30 (v/v) blend of isopropyl alcohol and water is used as the carrier, a completely miscible solution containing about 25% by weight NOPA may be successfully used as the treatment solution. It can be appreciated that even higher concentrations could be employed, as long as adequate surface coverage is achieved (as measured by the hydrophobicity and lipophilicity tests that are described herein).

The surface treatments of this invention can be optionally dry-blended with pigments in the absence of a carrier, as long as sufficient surface coverage is achieved in the process. In such cases, the efficiency of surface coverage can be improved by increasing either the temperature of the phosphonic acid compound, the temperature of the powder, or the temperature of both in combination; where the preferred temperature is near or above the crystalline melt point of the organophosphonic acid compound.

In addition, treatments can optionally be performed through spray methods, or through integral blend methods. An integral blend method of preparing the cosmetic compositions of the present invention may include several steps, where for example in a first step 1) the particulates are mixed, blended, or dispersed together with all or a portion of the ingredients of the cosmetic composition, and in a second step 2) an organophosphonic acid compound is integrally blended with all or a portion of the premixed ingredients from step 1, and whereby if portions are premixed in either steps 1 and 2, then an optional third step is employed 3) where the finished premixed portions from steps 1 and 2 are mixed, blended, or dispersed together to achieve the final cosmetic composition.

The cosmetic compositions of the present invention are useful in a variety of products, including foundations, eyeshadows, blushes, mascaras, eyeliners, skin treatment products, sunscreens, nail enamels, powder compacts, and so on. Powders are prepared whereby the filler pigments and/or the pigments are pre-treated with alkyl phosphonic acid, rendering them lipophilic and optionally hydrophobic. Dispersed systems are comprised of organophosphonic acid treated pigments that are distributed in the appropriate cosmetically acceptable carrier, where the dispersion medium of such carriers can include various oils, solvents, wax/oil blends, and combinations leading to water-in-oil, or oil-in-water emulsions.

In one preferred embodiment, the treated pigments are lipophilic, and in another particularly preferred embodiment, the treated pigments are simultaneously lipophilic and hydrophobic. Either way, the treated pigments are preferably dispersed in the oil phase of a water-in-oil emulsion at a level of 2% to 50% by weight of the oil phase, and more preferably at about 30% by weight. The oil phase may also contain oil soluble components as are common to personal care products, including for example: preservatives (e.g. up to 0.5 weight percent of the oil phase of paraben such as propyl paraben), up to 1% percent by weight of the oil phase of any conventional cosmetically acceptable fragrance; and one or more of other components well-known to cosmetic chemists, such as those that are intended for cosmetic purposes, or for skin-soothing and/or for physiological purposes (e.g. for treating skin conditions, like dry skin or chapped skin).

The oil phase may contain one or more polyethoxylates (either linear or cyclic, volatile or non-volatile, or in any combination). Additionally, the oil phase may contain volatile or non-volatile hydrocarbons of vegetable origin, and/or of mineral or synthetic origin, such as mineral oil, polyethylene, polybutene, polypropylene glycol, polyethylene glycol, hydrogenated polybutene, hydrogenated polyethylene, isoparaffins, etc.; and hydrocarbon waxes such as petrolatum, ozokerite, microcrystalline types, polyethylene, and paraffin wax. Other examples of oil-soluble personal-care components that are useful in the compositions of this invention include, but are not limited to: ester waxes, oils and fats of animal or vegetable origin, such as stearic acid; beeswax, carnauba wax, lanolin wax, avocado oil, coconut oil, castor oil and lanolin oil; fatty alcohols such as cetyl alcohol, isostearic acid, octyldecyl alcohol, stearyl alcohol and lauryl alcohol; fatty acids such as sebacic acid, isostearic acid, and palmitic acid; short and long chain alkyl esters of fatty acids such as the isopropyl, ethylhexyl, octyldecyl esters of said fatty acids; and sunscreens such as octyl dimethoxy pentyl acrylate, octyl methoxy cinnamate, benzophenone, octyl salicylate, homomentyl salicylate, etc.

The compositions preferably contain surfactants for the purpose of maintaining emulsion stability. For the case of a water-in-oil composition, the surfactant must be capable of maintaining a stable water-in-oil emulsion both during the manufacturing process, and during end-use. A silicone-based surfactant with an HLB value of about 2.5 to about 6 may suffice (examples of which are given in U.S. Pat. No. 5,143,722); or non-silicone surfactants (with typical HLB values ranging from 2 to 12) may be used either alone or in combination with such silicone-based surfactants. Preferred silicone surfactants are polyhydroxypropylhydroxyalkoxyalkyl ethers, having International Cosmetic Nomenclature names such as PEG-3/PPG-18/18 Dimethicone, bis-PEG-PPG-14/14 Dimethicone, Cetyl PEG/PPG-10/1 Dimethicone, Lauril PEG/PPG-18/18, Lauril PEG/PPG-18/18, Dimethicone/Polysilicone-12, Dimethicone/Vinylsiloxane Crosspolymer, etc.

Examples of non-silicone surfactants can include those known to the art, provided that the overall effective HLB value still permits formation of the desired water-in-oil emulsion. The amount should be about 0.25 to 5.0 weight percent of the composition, and preferably 0.5 to 2.0 weight percent thereof. As is well known to those of ordinary skill in this art, the HLB value is determined by a standardized technique for measuring the solubility of a surfactant. Such surfactants may be anionic, cationic or non-ionic with respect to its hydrophilic portion. Satisfactory surfactants useful in this invention
include ethoxylated polyhydroxystearate esters, low mole
cule ethoxylated alkylene ethers, glyceryl monostearate, polyglyc-
eeryl esters, and sorbitan esters. Other examples of suitable
organic surfactants having an HLB value of from 2 to 12 may
be found by reference to publications such as McCutcheon’s Detergents and Emulsifiers, MC Publishing (2002).

The water phase of the composition of the present
invention may be simply water, or may contain water-soluble
cosmetically acceptable components. Provided that the emulsion
is not destabilized or inverted therein. Examples include
humectants, including propylene glycol, butylene glycol,
pentylene glycol, glycerin, sodium pyrophosphate, carboxylic
acids, citric acid, lactic acid and derivatives thereof; vitamins;
preservatives, such as methyl paraben; electrolytes, such as
NaCl and magnesium sulfate; and sunscreens, such as the
phenylbenzimidazoles sulfonic acid. The water phase comprises
up to about 80 weight percent, and preferably up to about 60
weight percent of the composition, and at least about 5 weight
percent of the composition.

The composition can also contain effective amounts of
optionally cosmetically acceptable thickeners or other com-
ponents such as cellulose derivatives, organically modified
clay, and organic thickeners to achieve desired properties
such as viscosity, stability or after-feel. Specific examples of
such components are well known to cosmetic chemists. Some
examples of water phase components include: magnesium
aluminum silicate, hydroxyethyl cellulose, xanthan gum,
cationic or cationic colloidal resins. Non-limiting examples of oil
phase thickeners include: quaternium-18 octenyl, glyceryl trihy-
doxy stearate, aluminum stearate, dextrin palmitate, dimeth-
icone copolymers, and polyisilicone resins.

To make the emulsified cosmetic compositions of the
present invention, one simply (1) stirs thoroughly together all
the components of the oil phase and the surfactant(s), (2)
disperses the hydrophobic alkylphosphonic acid treated pig-
ments in the oil phase utilizing a high speed disperser or high
shear mill and then (3) stirs in the water phase including any
components dissolved in the water phase. Any standard high-
speed stirring or homogenizing apparatus known to the art
can be used to carry out the emulsification operation.

In another preferred embodiment, lipopholic alkylphos-
phonic acid treated pigments and fillers, or more preferably,
simultaneously hydrophobic and lipopholic alkylphosphonic
acid-treated pigments and fillers are dispersed in an anhydrous
powder-cream composition. As known to cosmetic chemists,
anhydrous powder-cream products are typically formulated
with a combination of ingredients including: pigments (at
levels >35%); light, dry-drying oils having good pigment
wetting properties; non-tacky waxes; and optional spherical
filler particles to aid in slip characteristics. The resulting
foundation, blush, or eyeshadow composition is prepared by
first mixing the ingredients at temperatures that are suffi-
ciently high so as to melt the waxes, and then by pouring the
molten formula as a fluid to form a creamy mass, cake, or
stick. The resultant product is applied to the skin like a cream,
but it is characterized as having the non-greasy feel of a
powder.

U.S. Pat. No. 4,578,266 describes powder-cream com-
opositions where hydrophobic polysiloxane treated pig-
ments are utilized in a product containing at least 10% of dimethylpol-
siloxane (optionally in combination with organically modi-
cied or cyclic polysiloxanes) to improve the dispersability of
said pigment. Although polysiloxane coatings improve pig-
ment wetting and dispersion in the claimed dimethylpolytri-
siloxane containing composition, they do not optimize wetting
in many of the other vehicles that are commonly utilized in
anhydrous cosmetic cakes, creams, and sticks (such as hydro-
carbons, fatty alcohols, fatty esters, sterols and sterol esters).
U.S. Pat. Nos. 4,877,604 and 5,108,736 similarly describe the
use of titanate-coatings to aid in the dispersion of organic
pigments, but loadings in excess of 5% by weight (as is
desirable for anhydrous powder-cream products) are not
achieved.

The current invention overcomes the deficiencies of
the prior art through the use of silicon-free and titanate-free alkyl-
phosphonic acid coated pigments, where the treated pig-
ments are preferably lipophilic; and even more preferably,
where the treated pigments are simultaneously lipophilic and
hydrophobic. In either case, the alkylphosphonic acid treated
pigments and fillers are dispersed in a combination of cos-
metically acceptable waxes and oils at a level of 35% to 75%
by weight of the formula, and preferably from 50% to 60% by
weight to form a powder-cream product; that is, a product
which is applied to the skin as a cream but has the non-greasy
feel of a powder. Surprisingly, certain metal oxide pigments
(red iron oxide is a specific example) that are treated with an
alkylphosphonic acid are observed to wet more easily than
those treated with an analogous alkylsilane compound.

Non-limiting examples of suitable oils for use in the
powder-cream compositions of the present invention include:
liquid esters of C3-22 fatty alcohols and acids, such as isopropyl
palmitate, isopropyl isostearate, ethylhexyl palmitate, iso-
stearyl octanoate, cetyl octanoate, isostearate, etc.; liquid glycerol esters of C3-22 fatty acids, such as glyceryl tri-
ethoxystearate or glycerol trioleate; liquid propylene glycol
esters, such as propylene glycol dicaprylate/dicaprate; liquid
nonylphenyl glycol dicaprylate/dicaprate; liquid pentaerythritol
esters, such as pentaerythrityl
dicaprylate/dicaprate; liquid fatty alcohols; organically
modified siloxanes, such as cetyl dimethicone, phytol tri-
ethicone, or caprylyl trimethicone; dimethyldimethylsiloxanes,
cyelic polysiloxanes, cyclic polysiloxanes, such as cyclopentasiloxane, cyclotetra-
siloxane; and hydrocarbons, such as mineral oil, squalane,
synthetics (e.g. hydrogenated polydecene, hydrogenated
dioleoresins), mixed isoparaffins, isocenocane, isodecane,
and isohexadecane.

Waxes are used in the claimed powder-cream compositions
at a level of 5-25% and preferably 10-15% to provide
structure, form, and stability to the product. Suitable waxes
include those known to cosmetic chemists such as carnauba
wax, candelilla wax, Japan wax, beeswax, rice bran wax,
montan wax, paraffin, ceresin, ozokerite, microcrystalline
wax, polyethylene/propylene, polyethylene/propylene acetate
copolymer, polyethylene/polyacrylic acid copolymer, C12-24 glyc-
erol esters, &gt;C2 fatty alcohols, lanolin and lanolin waxes.
Organically modified silicone waxes such as C16-24 Allyl
Methicone, C20-24 Alkyl Methicone, C30-40 Alkyl Methicone,
Stearyl Dimethicone, Biphenyl Dimethicone, Stearyloxy Dimethicone, C 20-24 Alkyl Dimethicone, or C24-28
Allyl Dimethicone may also be used.

The composition may also contain oil soluble wetting
agents to further enhance the compatibility of the pigments
and fillers with the oily vehicle. Cosmetically suitable wetting
agents include: sorbitan esters, such as sorbitan sesquioleate,
sorbitan trioleate, sorbitan trioleate; polyglyceryl esters,
such as polyglyceryl-1 diisostearate, polyglyceryl-10 decsi-
ostearate, polyglyceryl-10 decostearate, polyglyceryl-3 ric-
oleate, etc.; and polyhydroxystearic acid and its esters.

Fillers used in powder-cream compositions to enhance
texture and provide the sensation of a dry feel are optionally
treated with alkylphosphonic acid and include talc, zinc stearate,
sericite, kaolin, calcium carbonate, magnesium carbonate,
silica, magnesium silicate, calcium silicate, spherical nylon, spherical polyethylene, spherical polyurethane, or equivalent materials.

Other anhydrous products, well known to cosmetic chemists, include lipsticks, lip glosses, and lip liners. Lipsticks are based on a wax/oil matrix formulated to be poured into molds to form a stick that is inserted into a swirl-up case. The lipstick product must have sufficient rigidity to resist breakage during use, yet it must provide easy payoff permitting deposit of the product on the lips. Pigment is generally added as a dispersion in one of the formula oils, preground by techniques known to those skilled in the art, such as milling using a three roll mill or ball mill. Lip glosses are similar but softer formulas, containing less wax, packaged in pots or vials. Lip liners are harder products, containing higher percentages of waxy materials than lipsticks, packaged as pens, formed by extrusion or hot pour techniques or as sticks filled hot into molds by gravity or injection molding. Traditional lipsticks generally contain higher viscosity, better wetting oils, combined with far lower (approximately 0-30%) pigment levels than do the powered products. Consequently, optimization of pigment wetting, although relevant, is less critical an issue in the composition of lipsticks than in the composition of powered products. Difficulty in obtaining uniform wetting and color development of the range of pigments utilized in lip products is, however, encountered, due to the differences in physical properties among the various pigments utilized to achieve all the shades required by fashion. Pigments permitted for general cosmetic use in the Code of Federal Regulations Title 21 Parts 73 and 74 are utilized. Part 73 contains the colorants not subject to certification by FDA, the naturals and inorganic pigments. Generally the inorganic pigments are more hydrophilic and less lipophilic due to their oxide nature. In contrast, the synthetic organic pigments listed in 21 CFR Part 74 (colorants subject to certification) are more lipophilic and less hydrophilic due to their organic nature. Consequently, the organic pigments wet more easily in the oil based lipstick compositions than do the inorganic pigments, resulting in easier, more complete color development. The task of the cosmetic chemist is to achieve uniform wetting of all colorants, so that the mass tone of the cosmetic seen by the customer at point of purchase is equivalent to the write off observed during use.

In another preferred embodiment of the present invention, the treated inorganic pigments for lipstick products are hydrophilic, and in another particularly preferred embodiment, the treated pigments are simultaneously lipophilic and hydrophilic. In either case, the alkyl phosphoric acid treated inorganic pigments and fillers are dispersed alone or in combination with certified organic colorants in a combination of cosmetically acceptable waxes and oils at a level of 0-35% by weight, to achieve the desired makeup, blush, and eyeshadow. Pressed powders are formed of cosmetically acceptable filler pigments, coloring pigments, dry binders, wet binders (generally oily in nature); and optionally, preservatives, fragrance, or active ingredients. Pressed powders are manufactured by combining the dry ingredients and subjecting the pigments to sufficient agitation to achieve adequate particle size reduction, then spraying on the wet binders while continuing agitation to insure a uniform distribution of the wet binder. The finished product is pressed into pans using suitable equipment such as powder presses supplied by Kenwall, Inc. of Brooklyn, N.Y. or Cavalla, Inc. of Hackensack, N.J. The task of the cosmetic chemist is to create a finished product that provides sufficient payoff when rubbed by finger, sponge applicator, or powder puff to deposit a sufficient amount of color on the desired part of the face, yet one that...
also withstands the mechanical stress of shipping and transport in women's handbags without breakage. Composition techniques known to those skilled in the art consist of balancing amounts of conventional fillers, pigments, specialty fillers, pigments, and wet and dry binders to achieve the required performance.

The most common fillers used in pressed powders are talc and mica. Examples of others include but are not limited to sericite, bismuth oxychloride, boron nitride, starches and derivatives, spherical nylon, polyethylene/ethylene, polyurethane, polyethylene/polystyrene copolymers, lauryl lysine, spherical silica, polyvinylidene copolymer.

Dry binders include metallic soaps of fatty acids, such as zinc stearate, magnesium stearate, lithium stearate, magnesium myristate, and zinc myristate, kaolin, calcium silicate, porous acrylate copolymers, calcium carbonate, magnesium carbonate, magnesium trisilicate, and powdered polyethylene.

Pigments used in pressed powders depend on the specific application and can include inorganic pigments, such as titanium oxide, zinc oxide, iron oxides, manganese violet, chromium oxide, chromium hydroxide, ferric ferrocyanide, natural pigments, such as carmine, organic lake pigments, such as FD&C Blue #1, FD&C Yellow #5, FD&C Yellow #6, FD&C Red #40, FD&C Red #33 Lakes, D&C Red #29 Lakes, D&C Red #33 Lakes organic toners, such as D&C Red #6, D&C Red #7, D&C Red #9, D&C Red #10, and pearlescent pigments such as bismuth oxychloride, metal oxide coated mica pigments, and other composite flake pigments, and mixtures thereof.

In another preferred embodiment of the present invention, one or more of the fillers and/or pigments are treated with an alkyl phosphonic acid compound, rendering them hydrophobic and lipophilic. The skin feel of powders formulated with alkyl phosphonic acid treated pigments and fillers is notably smoother and more moist feeling than untreated pigments. The hydrophobic nature of alkyl phosphonic acid treated pigments and fillers can be utilized to formulate wet/dry foundations, that is, products that can be applied to the skin either with a dry or wet applicator without adversely affecting the integrity of the cake. Compression of powders containing fillers and pigments, but not particularly fillers, coated with alkyl phosphonic acid is greatly enhanced.

Wet binders that can be utilized in the subject powders include but are not limited to mineral oil, polyethylene, hydrocarbonate polyethylene, oleurope, synthetic esters, such as isopropyl myristate, isopropyl palmitate, ethylhexyl palmitate, cetearyl ethylhexanoate, isopropyl isostearate, octadecyl myristate, dioctylphosphine dimethylstearate, octadecyl stearate, hexadecyl stearate, octyldodecyl stearoyl stearate, hexadecyl stearoyl stearate, isostearyl stearyl stearate, dioctyl palmitate, dioctyl stearate, dioleostearate, dioleostearate, dimyristyl ether adipate, propylene glycol dicaprylate/dicaprate, coco triglycerides, caprylic/capric triglycerides, and silicone oils, such as dimethicone, phenyl trimethicone, capryly trimethicone, cetyl dimethicone, fatty alcohol, such as hexadecyl alcohol, isostearyl alcohol, and octylglycol, and natural oils, such as jojoba oil, avocado oil, apricot kernel oil, and sesame oil.

Small amounts of waxes, such as ceresin, candelilla, lanolin alcohol, or silicone wax may be added to the wet binder to enhance compression, as may small amounts of oil soluble wetting agents, such as sorbitan oleate, sorbitan isostearate, polyglyceryl-3 dioleostearate, polyglyceryl-10 decaoleate, polyglyceryl-3 ricinoleate, dimethicone copolyols, and alkyl dimethicone copolyols.

The invention will be described further in the following examples, which should be interpreted as illustrative rather than limiting. Amounts identified are by weight percent unless otherwise indicated.

**EXAMPLE 1**

Example 1 relates to the preparation of simultaneously hydrophobic and lipophilic n-octylphosphonic acid treated titanium dioxide powders for use in cosmetic compositions: n-octylphosphonic acid vs. comparative compounds. Pigmentary grade titanium dioxide powder (AHP-328 from Whittaker, Clark, and Daniels, Inc.; 9 m²/g surface area, CAS# 13463-67-7) was surface treated with various levels of n-octylphosphonic acid (NPA; 98% from Alfa-Aesar, CAS# 4724-48-5), and the resultant powders were tested for hydrophobicity and lipophilicity.

The powders were dry-blended with slurries containing 16.67% NPA by weight in distilled water, and with solutions containing 24.86% by weight NPA in 70/30 (v/v) isopropyl alcohol/water (IPA). Comparative powders were also prepared with n-octanoic acid (Aldrich Chemical Company; CAS# 124-07-2), and with n-octyltriethoxysilane (NOS; Aldrich Chemical Company; CAS# 2943-75-1).

The NPA/water slurry was prepared by dispersing NPA crystals in water under ambient conditions, and by over-aging the slurry in a closed container at a temperature of 70°C for a time sufficient so as to yield a pourable, translucent, partial-solution of NPA in water. NPA was similarly mixed with IPA to yield a completely soluble solution at room temperature. The octanoic acid and NOS compounds were used as received in their neat liquid forms.

Various levels of each liquid were separately dispersed over pre-weighed aliquots of powder (5 g). The aliquots were dry-mixed with a hand-held spatula under ambient conditions in separate glass jars. The spatula was used to agitate and press the powder against the side of the glass jar to achieve complete wetting. With the exception of the water-based slurry, the liquids were dispersed under ambient conditions. The water-based slurry was pre-heated to 70°C as described above, and was applied while hot (over the ambient powder) to facilitate mixing. After blending, most of the powders were oven-dried in open containers for 24 hours at a temperature of 80°C. The only exceptions were the powders that were treated with water-based NPA slurries—they were dried at 102°C for 24 hours. The surface treated powders were removed from the oven, and were stored in closed containers under ambient conditions for later use.

The following procedure was used to determine relative hydrophobicity: 0.05 g of each powder was weighed into separate glass jars together with 10 g of distilled water. The mixtures were then vigorously shaken by hand, and the closed containers were set on a horizontal surface for visual observation. The most hydrophobic powders were observed to climb the walls of the glass jar and to float on the surface of the water. The least hydrophobic samples were observed either to coalesce and sink to the bottom of the container, or to disperse in the water phase.

The following procedure was used to determine the relative lipophilicity: approximately 2.0 g aliquots of each powder were weighed into separate glass jars together with an appropriate level of a liquid carrier to yield slurreries containing 14.26% solids by weight. The liquid carriers included two oils that are commonly used in cosmetic compositions: dimethicone/cyclopentasiloxane (DC245 from Dow Corning Corporation, CAS# 541-02-6), and ethoxylated stearate (EHS from Beloit, Inc., CAS# 2980-75-3). The slurreries were vigor-
ously shaken by hand, and then were allowed to equilibrate under ambient conditions at room temperature for a period of 4 to 6 hours. After equilibration, the slurries were again vigorously shaken, and while dispersed, aliquots of the slurries were pipetted and weighed into 10 ml graduated cylinders that were pre-tared on an analytical balance. The cylinders were filled with 10 ml aliquots, which equated to approximately 10 g of slurry in each case. The graduated cylinders were then set on a horizontal surface under ambient conditions, and the volumes of the sediments were monitored over time. The final sediment volumes were reported once no change was observed for one week (the duration of the entire settling process was typically two to three weeks).

Settling volume is a measure of the relative dispersability of a powder in a liquid medium. Higher sediment volumes (lower sediment densities) are representative of poor dispersions, whereas lower sediment volumes (higher sediment densities) are representative of better dispersions. Generally, the better dispersions are less likely to agglomerate, and thus they are able to settle into tighter compacts with less interstitial space. Thus, the sediment volume is a relative measure of the degree to which the powder particles are deagglomerated and effectively wetted by the dispersing media. In these cases, the media were hydrophobic oils, so the more lipophilic powders produced the best dispersions (least agglomeration), and the lowest sediment volumes.

Table 1 provides the surface treatment concentrations together with qualitative rankings of hydrophobicity, and final sediment volumes (representing lipophilicity).

<table>
<thead>
<tr>
<th>Surface Treatment &amp; Concentration</th>
<th>Relative Hydrophobicity</th>
<th>Final Sediment Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 = hydrophobic (repels)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 = partially hydrophobic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3 = coalesces and sinks</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4 = dispersed</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface Treatment &amp; Concentration</th>
<th>Relative Hydrophobicity</th>
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<td></td>
</tr>
<tr>
<td></td>
<td>4 = dispersed</td>
<td></td>
</tr>
</tbody>
</table>

The NOPA treated titanium dioxide powders were also examined after one month of aging in the presence of water. Samples having surface treatment concentrations of 0%, 0.5%, 1%, 2%, and 4% NOPA by weight were prepared from water based NOPA slurries (16.67% by weight), and were dried for 24 hours at 102°C. The hydrophobicity of each sample was evaluated as previously described (using 0.05 g powder), the hydrophobic characteristics are surprisingly different. Thus, lipophilicity and molecular structure cannot be used as predictors of hydrophobicity. Also, given that NOPA is not known to polymerize (as NOS does), it is even more surprising to observe that NOPA displays these simultaneous characteristics. Moreover, this also means that polymerizability is neither a predictor, nor is it a prerequisite for hydropho-
bicity. Thus, given that the best pigments for this invention are those that are simultaneously hydrophobic and lipophilic, and given that n-octylphosphonic acid treated pigments perform surprisingly well in both respects, it appears that NOPA treated pigments are surprisingly well suited for use in the cosmetics compositions of this invention.

It is equally surprising to note that the NOPA treated pigments exhibit similar hydrophobic and lipophilic characteristics, independent of the vehicle that was used during their preparation. For example, even though NOPA is only partially soluble in water, the powders treated with water-based vehicles behave the same as those treated with IPA vehicles (where the NOPA is completely soluble).

Thus, the pigments as employed in the present invention are preferably simultaneously hydrophobic and lipophilic independent of whether they have been treated from solvent based or water based media (as long as the surface coverage is within the range as defined herein); as such, pigments prepared by either method are ideal for use in the cosmetics compositions of this invention. Moreover, unlike the surface treated pigments of the prior art, the simultaneously hydrophobic/lipophilic pigments as employed in the present invention can be prepared (if so desired) from water based media whereby the resulting powders (and the cosmetics compositions that contain them) by the definition devoid of the deleterious VOC's and reaction by-products that otherwise may tint the surfaces of prior-art treated powders (as well as the cosmetics compositions that contain them).

EXAMPLE 2

Example 2 relates to volatility comparisons between NOPA, NOS, and pre-hydrized NOS. An experiment was performed for the purpose of determining the relative volatility of NOPA, neat NOS, and a pre-hydrized version of NOS. The NOPA was prepared as a 16.67% by weight slurry in water as described in Example 1. The pre-hydrized version of NOPA was prepared according to procedures outlined in U.S. Pat. No. 5,348,760, where NOPA was mixed with ethanol, water, and acetic acid at a weight ratio of 50/50/5/1 to yield the hydrolyzed oligomeric species (47.17% active). Quantities of each liquid were weighed into pre-weighted aluminum pans, using an analytical balance with accuracy to four decimal places. The pans were then placed into a forced air oven at 80°C for a period of approximately 24 hours to simulate drying conditions that could be used during a surface treatment production process (this temperature also falls within the range of temperatures that could be used in preparing the oil phase of the present invention—where the surface treated particulates dispersed therein).

TABLE 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting Weight</th>
<th>Residual Weight</th>
<th>Theoretical Residual Weight</th>
<th>Residual Weight as a percentage of Theoretical</th>
<th>% actual weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOS (neat)</td>
<td>0.3343 g</td>
<td>0.0100 g</td>
<td>0.1928 g</td>
<td>5.3%</td>
<td>96.8%</td>
</tr>
<tr>
<td>Prehydrized</td>
<td>0.5728 g</td>
<td>0.1280 g</td>
<td>0.1615 g</td>
<td>79.25%</td>
<td>77.6%</td>
</tr>
<tr>
<td>NOPA (47.17% active)</td>
<td>0.6839 g</td>
<td>0.1025 g</td>
<td>0.1139 g</td>
<td>89.99%</td>
<td>85.0%</td>
</tr>
</tbody>
</table>

When compared to NOS and prehydrized NOS, these results demonstrate that the NOPA/water slurry retains a higher level of residual weight (89.99% of theoretical) after vaporization of its liquid carrier. Moreover, unlike the other treatments (where ethanol is evaporated as a VOC), water is theoretically the only component that is volatilized from the NOS/water slurry. In addition, the actual residual weight from neat NOS is far less than its theoretical value, which indicates that besides the evolution of ethanol as a VOC, the NOS molecule itself is volatile under these conditions. The prehydrized NOS exhibits much less volatility than neat NOS, but its volatile component is still comprised of ethanol from both the condensation reaction, and from the excess ethanol that was used as a carrier. Thus, when compared to other surface treatments, NOPA has the advantages of being relatively non-volatile, of being applicable in a VOC-free water-based medium, and of being free of VOC reaction by-products. The absence of VOC's (particularly alcohols and especially primary alcohols) is advantageous for the preparation of contaminant-free pigments, which are desirable components for use in the cosmetics compositions of the present invention.

EXAMPLE 3

Example 3 relates to the durability of NOPA treated inorganic pigments. The titanium dioxide of Example 1 was treated with 2% by weight NOPA from a 16.67% NOPA/water slurry via procedures outlined in Example 1. Following the procedures of Example 1, the resulting hydrophobic powder was dispersed in EHP (a common oil that is used in cosmetics compositions), and the dispersion was weighed into a 10 ml graduated cylinder for the purpose of conducting a sedimentation experiment. The graduated cylinder was sealed with a glass stopper, and the dispersion was initially allowed to settle to its final sediment volume under ambient conditions. The clear supernatant then pipeted from the cylinder, and fresh EHP was added. The cylinder was ressealed, and vigorously shaken by hand for the purpose of
redispersing the sediment. This “first wash” sediment was then allowed to resettle to its final sediment volume. The process was then repeated in a “second wash” (the supernatant was removed, fresh EHP was added, and the sediment was re-dispersed), but this time the sealed graduated cylinder was placed in an oven at 80° C, where the slurry was allowed to settle for a period of 24 hours.

This temperature was chosen because it falls within the range of temperatures that could be employed during the process of mixing the ingredients that comprise the oil phase of an oil-in-water emulsion, a water-in-oil emulsion, or an anhydrous cosmetic composition, where one or more of the ingredients could include a surface treated particulate of the type defined by this invention. Consequently, it is important for the surface treatment to remain intact and adsorbed on the particle surfaces, otherwise the dispersion stability of the final cosmetic composition may be compromised. Thus, in order to test the durability of the NOPA treated pigment, the washing and settling processes were repeated at 80° C for two additional cycles, and then once more under ambient conditions.

Using the ratio of NOPA-treated powder to liquid in this experiment, the effective level of NOPA equates to 0.33% by weight EHP. In a separate test, neat NOPA was determined to be soluble in EHP at the 0.33% level (both at 80° C and under ambient conditions). Similar experiments on other inorganic powders have shown solvent washing will not remove a strongly adsorbed surface treatment, even when the surface treatment itself is highly soluble in the dispersion medium (Parker et al. in Material Research Society Symposium Proceedings, 249, 1992, pp. 273-278). On the other hand, when the adsorbed molecules are weakly bound, solvent washing will readily remove the surface treatment from the powder, and the resultant sediment volume will increase with each successive solvent wash.

In this experiment, the durability of the NOPA treatment was tested by solvent washing NOPA treated powder with an otherwise good solvent for NOPA under both ambient conditions, and at 80° C. The results are presented in Table 3.

### TABLE 3

<table>
<thead>
<tr>
<th>Solvent Wash Cycle</th>
<th>Temperature During Sedimentation Experiment</th>
<th>Final Sediment Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (ambient)</td>
<td>Ambient</td>
<td>3.5</td>
</tr>
<tr>
<td>1</td>
<td>Ambient</td>
<td>3.2</td>
</tr>
<tr>
<td>2</td>
<td>80° C.</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>80° C.</td>
<td>2.6</td>
</tr>
<tr>
<td>4</td>
<td>Ambient</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>Ambient</td>
<td>2.6</td>
</tr>
</tbody>
</table>

These results show that the sediment volume actually decreases with successive washing cycles (up to cycle 2), beyond which there is no change in sediment volume. Thus, the NOPA is strongly adsorbed on the inorganic pigment, and it cannot be readily solvated, even when the treated powder is extracted with an otherwise good solvent for the neat compound. This shows that NOPA treated pigments can be surprisingly durable, and as such they can withstand the conditions that are likely to be encountered during the preparation of, and during the storage of a cosmetic composition. Thus the cosmetic compositions of the present invention (with alkylphosphonic acid treated particulates incorporated therein) are anticipated to be both process and storage stable.

### EXAMPLE 4

Example 4 relates to alkylphosphonic acid surface treated pigments with simultaneous hydrophobic and lipophilic characteristics for incorporation into cosmetic compositions. Additional inorganic pigments were treated with NOPA, and several were tested for hydrophobicity and lipophilicity via the methods and procedures as outlined in Example 1. The pigments for this example include black iron oxide (Fe₂O₃, c33-134 from Sun Chemical), and red iron oxide (Fe₂O₃, A-1206 from Color Techniques, Inc., CAS# 1332-37-2). The pigments were treated with 2% by weight NOPA from a 16.67% by weight slurry of NOPA in distilled water via procedures similar to those described in Example 1. The NOPA slurry for this example was pre-heated to 80° C, and the treated powders were oven dried at 80° C for 24 hours. Untreated powders were also tested for relative comparisons.

The results of lipophilicity (sedimentation) and hydrophobicity experiments are presented in Table 4.

### TABLE 4

<table>
<thead>
<tr>
<th>Powder</th>
<th>Treatment</th>
<th>Relative Hydrophobicity</th>
<th>Lipophilic Dispersion</th>
<th>Final Sediment Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red iron oxide</td>
<td>none</td>
<td>1 - hydrophobic</td>
<td>EHP</td>
<td>3.8</td>
</tr>
<tr>
<td>Red iron oxide</td>
<td>2% NOPA</td>
<td>1 - hydrophobic</td>
<td>DC245</td>
<td>2.4</td>
</tr>
<tr>
<td>Red iron oxide</td>
<td>None</td>
<td>2 - partially hydrophobic</td>
<td>EHP</td>
<td>5.4</td>
</tr>
<tr>
<td>Black iron oxide</td>
<td>2% NOPA</td>
<td>3 - coalesces and sinks</td>
<td>DC245</td>
<td>2.1</td>
</tr>
<tr>
<td>Black iron oxide</td>
<td>None</td>
<td>3 - coalesces and sinks</td>
<td>EHP</td>
<td>7.6</td>
</tr>
<tr>
<td>Black iron oxide</td>
<td>2% NOPA</td>
<td>3 - coalesces and sinks</td>
<td>DC245</td>
<td>2.2</td>
</tr>
<tr>
<td>Black iron oxide</td>
<td>None</td>
<td>3 - coalesces and sinks</td>
<td>DC245</td>
<td>8.4</td>
</tr>
<tr>
<td>Black iron oxide</td>
<td>2% NOPA</td>
<td>3 - coalesces and sinks</td>
<td>DC245</td>
<td>2.1</td>
</tr>
</tbody>
</table>

These results show that NOPA surface treated pigments can be surprisingly hydrophobic and lipophilic—even when they have been treated from water-based media. Moreover, the hydrophobic and lipophilic characteristics occur simultaneously. Hence, NOPA treated pigments such as these (with simultaneous characteristics of hydrophobicity and lipophilicity) are useful for incorporation into the cosmetic compositions of the present invention.

### EXAMPLE 5

This example relates to cosmetic compositions containing organophosphonic acid coated particulates, and describes the preparation of a water-in-oil foundation that contains simultaneously hydrophobic and lipophilic alkylphosphonic acid surface treated pigment particles. The pigments for this example were surface treated with 2% NOPA from a water-based vehicle as described in Example 1. Note that the pigments could be equivalently prepared from a solvent-based vehicle (such as IPA) if so desired.
The above composition was prepared as follows: The components of Phase A (the emulsifier phase) were combined with stirring. The components of Phase B (the pigment grind) were combined with high shear mixing until all of the pigment particles were dispersed, and then Phase B was added to Phase A with stirring. Phase C (the viscosity stabilizer) was added to the combined Phases A and B with stirring. The methylparaben of Phase D was pre-dissolved in butylene glycol, and then it was added along with the other Phase D ingredients to the deionized water (while stirring until all components were dissolved). Phase D (the water phase) was then slowly added to the combined Phases A, B, and C (the oil phase) while homogenizing. Homogenization was continued for 15 minutes to form the finished product, which was then filled into suitable storage containers.

It can be appreciated that this example is only illustrative, and that modified procedures and compositions as described within this invention could conceivably be used to form a variety of similar products with a broad range of end-use characteristics for use in a broad range of cosmetic applications.

**EXAMPLE 6**

This example describes the preparation of a powder-cream foundation containing pigments that are lipophilic, or simultaneously lipophilic and hydrophobic. The composition ingredients for this example are given as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylhexyl palmitate</td>
<td>35.05</td>
</tr>
<tr>
<td>Tribesilane</td>
<td>5.50</td>
</tr>
<tr>
<td>C8-20 Alkyl Methicone</td>
<td>5.50</td>
</tr>
<tr>
<td>C20-40 Alcohols</td>
<td>1.10</td>
</tr>
</tbody>
</table>

**EXAMPLE 7**

Example 7 relates to powder-cream foundation containing lipophilic pigments, and describes the preparation of a powder-cream foundation containing pigments that are lipophilic. The composition was prepared according to the procedures of example 6. The composition ingredients for this example are given as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polylactyl-83 Diocistearate</td>
<td>0.50</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>0.20</td>
</tr>
<tr>
<td>Propylparaben</td>
<td>0.10</td>
</tr>
<tr>
<td>IUR</td>
<td>0.05</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated titanium dioxide</td>
<td>15.00</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated yellow iron oxide</td>
<td>1.40</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated red iron oxide</td>
<td>0.65</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated black iron oxide</td>
<td>0.90</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated talc</td>
<td>14.90</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated zirconite</td>
<td>15.00</td>
</tr>
<tr>
<td>Spherical nylon</td>
<td>3.00</td>
</tr>
</tbody>
</table>

**EXAMPLE 8 (COMPARATIVE)**

Comparative example 8 relates to powder-cream foundation containing lipophilic pigments. This example describes the preparation of a powder-cream foundation containing pigments that are lipophilic. The composition was prepared according to the procedures of example 6. The composition ingredients for this example are given as follows:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprylyl Triethicone</td>
<td>24.25</td>
</tr>
<tr>
<td>Dimethicone/10 cs</td>
<td>11.00</td>
</tr>
<tr>
<td>Tribesilane</td>
<td>6.00</td>
</tr>
<tr>
<td>C8-20 Alkyl Dimethicone</td>
<td>6.00</td>
</tr>
<tr>
<td>Polylactyl-83 Diocistearate</td>
<td>0.75</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>0.20</td>
</tr>
<tr>
<td>Propylparaben</td>
<td>0.10</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated titanium dioxide</td>
<td>15.00</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated yellow iron oxide</td>
<td>2.80</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated red iron oxide</td>
<td>1.20</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated black iron oxide</td>
<td>0.20</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated talc</td>
<td>12.50</td>
</tr>
<tr>
<td>2% n-octyl phosphonic acid treated zirconite</td>
<td>15.00</td>
</tr>
<tr>
<td>Aluminum Starch Octenyl Succinate</td>
<td>5.00</td>
</tr>
</tbody>
</table>

**EXHIBIT**

The pigments were dispersed in a portion of the oil (a portion which was sufficient for wetting-out the pigment), and the dispersion was milled using a three-roll mill (a high-speed disperser, or a media mill could also have been used). The waxes and preservatives were separately dissolved in the remaining oil and heated to 95°C until clear, and the solution was cooled to 75-80°C. The pigment dispersion was then added to the solution together with fillers, talc, serecite, and nylon; and the combination was mixed with a high-speed agitator until no agglomerates remained. The product was then stirred under vacuum to facilitate de-aerating, and the resultant mixture was subsequently filled into suitable compacts at 70-72°C.
and pearl pigment were added and stirred until dispersed. The ascorbyl palmitate was added, and the bulk was filled into suitable molds at 70-72°C. The resulting sticks exhibited the same color as does the lipstick when applied to the lips.

EXAMPLE 10

This example describes pressed powder eyeshadow having the following ingredients.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% a-octylyphosphonic acid treated talc</td>
<td>20.00</td>
</tr>
<tr>
<td>Iron Oxides</td>
<td>6.50</td>
</tr>
<tr>
<td>Zinc Stearate</td>
<td>5.00</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>0.20</td>
</tr>
<tr>
<td>Propy/paraben</td>
<td>0.10</td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated oxide</td>
<td>50.00</td>
</tr>
<tr>
<td>treated iron oxide coated</td>
<td></td>
</tr>
<tr>
<td>mica pearlescent pigment</td>
<td>8.00</td>
</tr>
<tr>
<td>(Colora &amp; Copper)</td>
<td></td>
</tr>
<tr>
<td>Isopropyl Isostearate</td>
<td>8.00</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

The treated talc, pigments, zinc stearate, and preservatives were combined in a ribbon blender and pulverized with a hammer mill through a 0.027" screen. The pearlescent pigment was added to the pulverized phase in the ribbon blender, and the oil was sprayed on with agitation. The batch was passed through the hammer mill through a jump gap then pressed into suitable pans.

The resulting eyeshadow applied smoothly to the lids and exhibited good adhesion. Cake strength was surprisingly good, in spite of the high level of pearl.

EXAMPLE 11

Example 11 describes wet/dry pressed powder foundation with hydrophilic/lipophilic pigments. The foundation is made with the following ingredients.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% a-octylyphosphonic acid treated talc</td>
<td>61.10</td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated seicite</td>
<td>20.00</td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>8.00</td>
</tr>
<tr>
<td>titanium dioxide</td>
<td></td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>2.00</td>
</tr>
<tr>
<td>yellow iron oxide</td>
<td></td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>1.25</td>
</tr>
<tr>
<td>treated red iron oxide</td>
<td></td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>0.35</td>
</tr>
<tr>
<td>black iron oxide</td>
<td></td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>3.00</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>0.20</td>
</tr>
<tr>
<td>Propy/paraben</td>
<td>0.10</td>
</tr>
<tr>
<td>Squalane</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

The treated pigments and fillers were combined with the zinc stearate and preservatives in a twin shell blender equipped with an intensifier bar and mixed with intensifier bar agitation until homogenous. The squalane was added through the intensifier bar while agitating to insure even distribution. The batch was pulverized using a hammer mill (with a 0.027" screen), and was pressed into suitable pans.

The resulting pressed powder applied smoothly with good adhesion to the skin. Repeated use either with a wet or dry sponge was possible without deterioration of application properties.

The pretreatment in comparative example 8 was observed to render the pigments and fillers hydrophobic and lipophile, and to enhance their wetting and dispersion characteristics when compared to untreated pigments (as did the claimed n-octylyphosphonic acid pre-treatment illustrated in example 7). Surprisingly however, the pigments in example 7 were observed to wet more easily than those of example 8. Of equal importance, all of the n-octylyphosphonic acid pigments unexpectedly exhibited color development prior to the high-shear agitator phase, as evidenced by the mass tone of the bulk mixture. Consequently, the time required for the milling step in example 7 was surprisingly reduced by a factor of 33% when compared to the time required for milling in example 8.

EXAMPLE 9.

Example 9 relates to lipstick containing lipophile inorganic pigments and having the following ingredients.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor Oil</td>
<td>30.00</td>
</tr>
<tr>
<td>Candelilla</td>
<td>7.00</td>
</tr>
<tr>
<td>Carnuba</td>
<td>1.50</td>
</tr>
<tr>
<td>Ceresin</td>
<td>2.50</td>
</tr>
<tr>
<td>Microcrystalline Wax</td>
<td>3.50</td>
</tr>
<tr>
<td>Octyldodeyl Stearate</td>
<td>15.00</td>
</tr>
<tr>
<td>Tricosylnl Oxide</td>
<td>20.00</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>0.20</td>
</tr>
<tr>
<td>Propy/paraben</td>
<td>0.19</td>
</tr>
<tr>
<td>Ascorbyl Palmitate</td>
<td>0.05</td>
</tr>
<tr>
<td>Pigment Grind</td>
<td></td>
</tr>
<tr>
<td>Castor Oil</td>
<td>5.00</td>
</tr>
<tr>
<td>DCC Red #7 Lake</td>
<td>0.03</td>
</tr>
<tr>
<td>DCC Red #8 Lake</td>
<td>0.17</td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>2.00</td>
</tr>
<tr>
<td>treated red iron oxide</td>
<td></td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>2.00</td>
</tr>
<tr>
<td>treated titanium dioxide</td>
<td></td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>0.03</td>
</tr>
<tr>
<td>treated black iron oxide</td>
<td></td>
</tr>
<tr>
<td>Pear Pigment</td>
<td></td>
</tr>
<tr>
<td>2% a-octylyphosphonic acid treated</td>
<td>10.00</td>
</tr>
<tr>
<td>treated mica (red) oxide</td>
<td></td>
</tr>
<tr>
<td>titanium dioxide</td>
<td></td>
</tr>
</tbody>
</table>

The pigment grind was prepared by dispersing the pigments in castor oil and milling to a particle size of <10 microns. The waxes, oils and preservatives were combined and heated to 85-90°C with propeller agitation until clear. The temperature was lowered to 80°C, and the pigment grind
The present invention has been described with particular reference to the preferred embodiments therein. It is to be appreciated that variations and modifications can be made without departing from the spirit and scope of the present invention as defined by the following claims. All U.S. patents referred to herein are incorporated by reference in their entirety.

We claim:

1. A method of preparing a cosmetic composition comprising a plurality of particulates, the method comprising:
a) at least partially surface treating at least some of the plurality of particulates with one or more organophosphonic acids such that the organophosphonic acid on said particulates is present at a level of 2-20 μmol/cm² and the surface treated particulates are simultaneously lipophilic and hydrophobic; and
b) mixing, blending, or dispersing the particulates together with any remaining ingredients of the cosmetic composition.

2. The method of claim 1 wherein said organophosphonic acid surface treated particulates from a) are dispersed during b) into the oil phase of a water-in-oil or oil-in-water cosmetic composition, and where said oil phase dispersion is then mixed, blended, or dispersed together with the remaining ingredients of the cosmetic composition.

3. The method of claim 1 wherein said organophosphonic acid surface treated particulates are surface treated in a) through the use of either a water based vehicle, an alcohol based vehicle, an alcohol/water blend, or a neat organophosphonic acid.

4. A method of preparing a cosmetic composition comprising surface treated particulates where at least some of said particulates are at least partially surface treated with one or more organophosphonic acids, the method comprising an integral blend method comprising a) mixing, blending, or dispersing the particulates together with at least a portion of any remaining ingredients of the cosmetic composition to form a mixture, blend, or dispersion, and b) integral blending an organophosphonic acid with at least a portion of the mixture, blend, or dispersion.

5. A method or preparing a cosmetic composition utilizing a plurality of particulates that have been at least partially surface treated with an organophosphonic acid.

6. The method of claim 5 wherein the organophosphonic acid is of the general formula

$$ R_y[P(O)(OR)]_x $$

where R is an organic group containing 1 to 50 carbon atoms, x is the number of organic groups and is in the range of 1-30, and y is the number of phosphonic acid groups and is in the range of 1-20.

7. A sunscreen composition comprising an amount of one or more sunscreens and a plurality of particulates surface treated with an organophosphonic acid.

8. The sunscreen composition of claim 7 wherein the one or more sunscreens are selected from the group consisting of octyldimethyl-PABA, octylmethoxycinnamate, benzophenones, octyl salicylate, homomenthyl salicylate, and phenylbenzimidazole sulfonic acid.

9. The sunscreen composition of claim 7, being a water-in-oil or oil-in-water emulsion.

10. The sunscreen composition of claim 9 having an oil phase comprised of one or more sunscreens selected from the group consisting of octyldimethyl-PABA, octylmethoxycinnamate, benzophenones, octyl salicylate, and homomenthyl salicylate.

11. The sunscreen composition of claim 9 having a water phase comprised of phenylbenzimidazole sulfonic acid.

12. A cosmetic composition comprising a water-in-oil emulsion having an oil phase, with a plurality of particulates surface treated with an organophosphonic acid dispersed within the oil phase.

13. A cosmetic composition comprising a plurality of particulates surface treated with an organophosphonic acid, the particulates being dispersed in a mixture of one or more cosmetically acceptable waxes and one or more cosmetically acceptable oils, the particulates being present at a level of 35% to 75% by weight of the cosmetic composition.