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2,995,456

COMPLEX ZINC SOAPS

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The present invention relates to novel metallic soap products. More particularly, the present invention relates to metallic soap products that have great utility in compositions such as sanding sealers, lacquers, varnishes and the like.

Use of metallic soaps in sanding sealers, lacquers and varnish compositions is well known and has been practiced by the art for many years. Sanding sealers are lacquer type coatings which are primarily employed to seal porous surfaces such as wood and are designed to prevent raising of wood grain. Zinc stearate is usually added to sanding sealer compositions in order to permit clean and easy sanding by acting as a lubricant and by retarding the gumming of the sandpaper during the sanding step.

Lacquer and varnish compositions when applied to surfaces result in a glossy finish. In many instances, a dull or matte finish is preferred. Such dull finishes are provided for by incorporating into the lacquer or varnish composition finely divided microscopic particles. Materials which are added for the purpose of bringing about dull or matte finishes are known as flatting agents. Well known flatting agents are, for instance, metallic soaps such as zinc stearate, zinc palmitate, calcium stearate and magnesium stearate.

However, in order to use these various metallic soaps as additives to sanding sealers, lacquers and varnishes, it is necessary to first grind them in order to disintegrate or break down the clusters of the soap into their individual particles. Generally, the soaps are ground in the presence of a hydrocarbon solvent or in the presence of the vehicle to which they are to be added. Pebble mills may be employed for grinding which involves grinding periods for up to twenty hours. Such grinding procedures involve unavoidably long periods of time as well as involving the extra manipulative step plus the necessary grinding equipment. Also, in many instances, heat generated during grinding procedures may cause discoloration of the various soaps. It has also been found in the case of zinc soaps, particularly due to their extreme fineness and large surface area, that they contain a large volume of air which in many instances during grinding becomes emulsified. This produces very rigid foams which cannot be poured out of the pebble mills.

Additionally, metallic soaps as presently employed bring about undesirable thickening of the vehicle when too high a concentration of soap is employed. Hence, the solids concentration is usually kept low to avoid this thickening, but, in many instances this results in films having poor weathering qualities because of the small amount of metallic soap present. These metallic soaps are, of course, known for their water-proofing properties.

Accordingly, it is an object of the present invention to obtain improved compositions of metallic soaps.

It is a further object to obtain improved metallic soaps in finely divided form which are useful in sanding sealers, lacquers, varnishes and the like.

It is another object to obtain improved metallic soaps in finely divided form that are useful as flatting agents.

It is a still further object to prepare finely divided metallic soaps useful as additives to the aforementioned vehicles without the necessity of grinding the soaps in order to obtain them in finely divided particles.

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A further object is to obtain improved compositions of metallic soaps that may be used in increased quantities in organic vehicles such as varnishes and lacquers, without detracting from the stability, color or freely flowing properties of such vehicles and which may be added to such vehicles by simple mixing.

Further objects will become apparent from the detailed description given hereinafter. It is intended, however, that the detailed description and the specific examples do not limit the invention, but merely indicate the preferred embodiments of the invention since various changes and modifications within the scope of the invention will become apparent to those skilled in the art.

The above and other objects are accomplished in the following manner. It has been unexpectedly discovered that when a water-soluble soap and a wetting agent which is the water-soluble salt or acid form of a phosphorous-containing compound having straight chain, branched chain, aryl and alkaryl hydrocarbon substituents in which the straight or branched chain hydrocarbon substituents have from about 8 to 22 carbon atoms are coprecipitated with a water-soluble zinc salt, a product results which has the following unexpected characteristics. The product is in a finely divided state and requires no mechanical grinding to bring about further subdivision after an initial grinding through a $\frac{1}{32}$ inch screen. Thus, the product may be added directly to a vehicle without further mechanical grinding. It may be added to these vehicles in increased quantities than heretofore done. It may be added in increased quantities to such vehicles without in any manner decreasing or affecting the fluidity or freely flowing properties of the mixture which may be a sanding sealer, lacquer or varnish composition. These compositions are of good color and stable and moreover, because increased quantities of metallic soap may be incorporated therein, they have improved waterproofing characteristics as well.

To prepare the novel products of the present invention, a fatty acid is first saponified with a water-soluble base thereby forming a water-soluble soap. To this water-soluble soap, a water-soluble salt or acid form of the aforementioned phosphorous-containing wetting agent is added. Then, by employing a water-soluble zinc salt, both the water-soluble soap and water-soluble wetting agent in admixture with each other are coprecipitated. The precipitate is then filtered, washed, dried and ground through a $\frac{1}{32}$ inch screen. Thereafter it may be added to an organic solvent without need of further grinding to form a freely flowing composition which may be, e.g., a sanding sealer, varnish or lacquer.

Any suitable saturated fatty acid may be employed as a starting material, e.g., saturated aliphatic monocarboxylic acids containing from about 8 to 22 carbon atoms, or mixtures thereof, a glyceride containing as a major constituent thereof saturated fatty acids having a carbon chain length of from about 8 to 22 carbon atoms, or their mixtures, or mixtures of the aforesaid fatty acids with said glycerides. Thus, for example, palmitic, stearic, arachidic, behenic, or ethylhexoic acids or their mixtures can be used. When saponified with sodium, potassium or ammonium hydroxide, the respective water-soluble soaps of the aforementioned acids and glycerides result. Also, sodium, potassium or ammonium soaps of the type produced from glycerides containing major quantities of such acids, as, for example, hydrogenated tallow, hydrogenated soybean oil, hydrogenated cottonseed oil, hydrogenated coconut oil, etc., or mixtures thereof can be employed.

Processes for the conversion of fatty acids or glycerides into their water-soluble soaps using an alkali are well known in the art. Generally, saponification is accomplished by reacting the fatty acid or glyceride with a

base in the presence of a small quantity of water. Since water-soluble soaps produced by any of the prior art processes are fully suited for use in the present invention, nothing herein should be construed as limiting the present invention to the use of soaps by any one particular method.

To an aqueous solution or dispersion of any one or more of the above water-soluble soaps, preferably dilute, there is added a water-soluble salt or acid form of one of the aforementioned wetting agents which results in an aqueous solution or dispersion of the two constituents.

The resulting solution containing both the water-soluble soap and a water-soluble salt or acid form of the wetting agent is then treated with a water-soluble zinc salt such as zinc sulfate. This brings about coprecipitation of the water-soluble soap and water-soluble salt of the wetting agent.

Coprecipitation is accomplished by gradually adding a heated aqueous solution of the water-soluble zinc salt to the above solution. If desired, however, this sequence can be reversed. The invention, however, is not limited to zinc sulfate as the precipitating agent. Other zinc salts can be employed provided they are soluble in water at the temperature at which it is to be used and, provided further that they will form water-insoluble compounds with the water-soluble soap and water-soluble wetting agents present in the aqueous solution such as zinc chloride. Generally, the solution of the zinc salt precipitant contains about 20% by weight of water-soluble salt. However, the concentration of the salt solution employed to accomplish the precipitation has little effect, if any, upon the production of the precipitated composition of the invention or the properties thereof. Thus, if desired, aqueous solutions containing more or less than 20% by weight of water-soluble salt can be employed. In the preferred embodiment of the invention, the precipitation step is accomplished by adding an aqueous solution of zinc sulfate, heated to a temperature of from about 50° C. to about 95° C., to the heated solution containing the water-soluble soap and salt mixture. However, the invention is not to be construed as limited to compositions precipitated at temperatures within that specific range. In some instances, the zinc salts of the wetting agents employed herein may be water-soluble at elevated temperatures. In such cases it is only necessary to lower the temperature of the solution to bring about the proper precipitation from solution.

The quantity of salt employed to accomplish the precipitation should be at least sufficient to react with all of the water-soluble soap and salts present in the solution. While the use of a stoichiometrically equivalent quantity of zinc salt solution should obviate the possibility that any water-soluble soap or salt of the wetting agent will be occluded in the precipitated product, an excess quantity can be, and is, at times, preferably employed.

After the desired composition has been precipitated, it can be separated from the aqueous solution in which it is dispersed by any convenient means. Usually, this step is accomplished by passing the dispersion through a suitable filter. The filtered product is subsequently washed several times in water to remove residual water-soluble salts present. The washing step is ordinarily carried out in water heated to a temperature of from about 40° C. to about 70° C. After washing, the product is dried, generally in an oven heated to a temperature of from about 100° F. to 180° F., and, subsequently, ground, by appropriate means, to a fine powder.

The resulting solid product, although insoluble and not dispersible in water, is highly dispersible in organic solvents and other organic vehicles used in e.g., sanding sealer, lacquer or varnish compositions.

As aforesaid, the addition of the novel products of the present invention to these solvents is accomplished without grinding and these products may be present in amounts not heretofore possible to employ.

An alternative procedure for obtaining the novel metallic soaps is as follows. This procedure employs the direct method for obtaining the soap of the fatty acid with the zinc. In this procedure the saturated fatty acid is reacted with a zinc carbonate, oxide or hydroxide. When such procedure is applied to the present invention, the wetting agent is first admixed with the fatty acid. Thereafter, the zinc carbonate, oxide or hydroxide is added to the resulting mixture. This results in the formation of a novel composition which is also useful in sanding sealer, lacquer and varnish compositions. The reaction temperature may vary from 50° C. to 100° C. Since higher temperatures may be employed in this procedure as compared to the aforementioned procedure in which zinc salt is added to a soap and wetting agent, care must be used in selecting a wetting agent that remains stable under the conditions of reaction. Also, it should be noted that if the direct method is used, the wetting agent, whether the salt or its acid form thereof is used, need not be water-soluble, but only water-dispersible.

Whether the novel soap compositions described herein are prepared by coprecipitating the soap of a fatty acid with the wetting agent or by having present the wetting agent while carrying out the direct method for obtaining a zinc soap from the fatty acid, it is believed that the resulting soaps are truly new compounds. These compounds are believed to contain a zinc cation attached to the anionic portions of both the fatty acid and wetting agent. The above theory is substantiated by the fact that these novel soap compositions cannot be separated into their respective zinc soaps and zinc salts of the wetting agent. Even though the composition cannot be separated, it is further believed that there may be present in minute amounts and in intimate admixture with the above, zinc soaps and zinc salts of the wetting agent. Hence, the novel soap compositions may be referred to as a complex of a zinc soap and a zinc salt of a wetting agent.

As examples of the phosphorous-containing wetting agents which may be employed herein are the water-soluble salts of the following materials. In these salts, the cation may be an alkali metal such as sodium or potassium or it may be the ammonium ion. As indicated previously, the water-soluble wetting agent may be used in its acid form as well. Mixtures of the various water-soluble wetting agents are also encompassed herein. These compounds contain straight chain, branched chain and aryl substituents. The straight and branched chain substituents may contain from about 8 to 22 carbon atoms. The aryl substituents may be derived from benzene or naphthalene or may be derived from substituted aryl substituents such as toluene, xylene, isopropyl naphthalene, dodecyl benzene, etc. The chain length should not exceed about 22 carbon atoms in length. Examples of such phosphorous-containing compounds are mono-dialkyl acid orthophosphates e.g., mono-dimethyl orthophosphate, alkyl aryl phosphonates e.g., phenyl octyl phosphonate, benzene phosphonic acid and benzene phosphinic acid.

Of particular value are alkyl polyphosphoric acid ester salts having the empirical formula $\text{Na}_5\text{R}_5(\text{P}_3\text{O}_{10})_2$ in which R is a straight or branched chain hydrocarbon radical having from about 8 to 22 carbon atoms in the chain. These materials are best identified and described by reference to a particularly well known and commercially available member of this class. This member is a product of Victor Chemical Co., Chicago, Illinois, sold under the trade name, Victawet 35-B. It is the 2-ethylhexyl ester of pentasodium tripolyphosphate. It is obtained as a 70% paste and has a light tan to white color. While this product is employed in the preferred embodiment of the invention, it must be understood that the invention is not limited solely to its use. Any similar or comparable polyphosphoric acid ester, as for example, the potassium or amine salts thereof can be used instead. Also, the

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water-soluble compounds in which the ester group is a straight or branched chain radical having from 8 to 22 carbon atoms in its chain may be used, e.g., capryl, 2-ethylhexyl. The acid forms which are water-soluble may be used.

The quantity of wetting agent may vary widely and may be from ½% to 50% by weight based upon the dry weight of the water-soluble soap. Preferably 1.0% by weight, based upon the dry weight of the water-soluble soap is used. Additionally, the solid composition may contain in minor amounts other solid constituents such as plasticizers, softeners, dyes, pigments and the like. If the alternative procedure, i.e., forming the zinc soap by the direct method, is employed, the quantity of wetting agent may conveniently be based upon the quantity of fatty acid equivalent to the water-soluble soap of the coprecipitation procedure. For a fuller understanding of the nature and objects of this invention, reference is made to the following examples which are given merely to illustrate the invention and are not to be construed in a limiting sense.

The first example is included to point out that the procedure for obtaining these novel soap compositions is important. When a zinc salt of a wetting agent is admixed with a zinc soap, there is obtained a material that is inferior for use in sanding sealer, lacquer and varnish compositions, when compared with the novel compositions described herein.

Example I

A solution was prepared containing 100 grams of Victawet 35-B (containing approximately 30% moisture and 900 grams of water. A second solution containing 28.4 grams of zinc sulfate dissolved in 114 grams of water was also prepared. The two solutions were admixed at 30° C. in order to precipitate the zinc salt of Victawet 35-B. In this manner a sticky white gray solid was obtained. It was washed once and dried at 100° C. Thereafter 0.1 gram of the zinc salt of Victawet 35-B was dissolved in 10 grams of benzene. 9.9 grams of zinc stearate were added to the solution. The benzene was evaporated and a fine powder resulted which contained, in intimate admixture, 1% by weight of the zinc salt of Victawet 35-B and 99% by weight of zinc stearate. The solution of these two materials in benzene and the subsequent evaporation of the benzene was carried out in order to insure a thorough and intimate admixture of these materials, because the zinc salt of Victawet 35-B is a sticky material and therefore resistant to uniform mechanical admixture with other solids. Thereafter, 1.6 grams of the above mixture, in the form of a fine powder were stirred into 100 grams of C.M.L. Lacquer (composition and method of preparation described in Example VI) without grinding. This dispersion was found to be inferior to dispersions containing the novel products described herein. There was observed very rapid sedimentation as well as coarse particles. When this dispersion was applied to a base, a film considerably more coarse than those obtained by employing the products of the present invention was obtained on drying.

Example II

95 grams of a commercial stearic acid were saponified with 14.9 grams of sodium hydroxide. The resulting sodium stearate was dissolved in 2000 grams of water thereby forming a 5% aqueous solution of the soap. Thereafter, 7.15 grams of Victawet 35-B (containing approximately 30% moisture) which is the 2-ethylhexyl ester of pentasodium tripolyphosphate were added to the above solution and dissolved therein. To the resulting solution, 41.1 grams of zinc sulfate were added in order to bring about coprecipitation of the sodium stearate soap and Victawet 35-B. This was accomplished at a temperature of 65° C. Thereafter the precipitate was filtered off from the mother liquor and washed three times, each time with 1600 grams of water at 40° C., in order to remove

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any water-soluble salts that may have been present. The precipitate was thereafter dried and ground. The material was found to be very easy to filter, wash and grind. The following data were determined upon analysis of the composition of Example II. The procedures used may be found in "Metasap Metallic Soaps," copyright 1940, revised 1953, pages 20 to 22, published by the Metasap Chemical Company of Harrison, New Jersey.

Percent moisture	0.2
Percent total ash	15.8
Percent washed ash	15.7
Percent soluble ash	0.1
Percent retained on a 325 mesh screen	0.0

Example III

The product of Example II was added without grinding to a lacquer solvent mixture which contained one-third by weight butyl acetate, one-third by weight isopropanol and one-third by weight toluene, thereby forming a coating composition. The product of Example II formed 5% by weight of the total coating composition, the lacquer solvent mix forming the remainder. A very fine dispersion was obtained. When applied to surfaces, an excellent film resulted which was found to be superior to that obtained using conventional zinc soaps.

Example IV

99 grams of a commercial stearic acid were saponified with 15.5 grams of sodium hydroxide. The resulting sodium stearate was dissolved in 2000 grams of water thereby forming a 5% aqueous solution of the soap. Thereafter 1.43 grams of Victawet 35-B (containing approximately 30% moisture) which is the 2-ethylhexyl ester of pentasodium tripolyphosphate were added to the above solution and dissolved therein. To this resulting solution 41.1 grams of zinc sulfate were added in order to bring about coprecipitation of the sodium stearate and Victawet 35-B. This was done at a temperature of about 65° C. Thereafter the precipitate was filtered off, washed, dried and then ground. The final product was analyzed as follows:

Percent moisture	0.4
Percent total ash	14.0
Percent washed ash	13.8
Percent soluble ash	0.2
Percent retained on a screen 325 mesh screen	0.0

Example V

A coating composition was prepared similar to Example III. In this instance, the soap composition of Example IV was directly added to a solution of a lacquer solvent mix containing one-third by weight butyl acetate, one-third by weight isopropanol and one-third by weight of toluene. In this manner, a 5% dispersion of the soap of Example IV was obtained which was both stable and very fine.

Example VI

To show the superiority of the novel soap products of the present invention, a mixture was prepared containing a zinc stearate having the following analysis:

Percent moisture	0.1
Percent total ash	14.5
Percent washed ash	14.0
Percent soluble ash	0.5
Percent retained on a 325 mesh screen	0.0

The mixture was prepared by adding the zinc stearate, without grinding to a lacquer solvent mix containing one-third by weight butyl acetate, one-third by weight isopropanol and one-third by weight of toluene. In this manner a 5% (by weight) dispersion of zinc stearate in the lacquer mix was obtained. The dispersion was found to be a coarse dispersion and it was the least stable when compared with the dispersions of Examples III and V.

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As indicated previously, the novel soap products described herein are admirably suited for use in lacquer and sanding sealer compositions without the necessity of grinding. A commercial lacquer base referred to as C.M.L. Lacquer, a product of the Coating Materials Laboratory, Belleville, New Jersey, was used as the vehicle and was prepared as follows:

First, two mixes were prepared. Mix A contained 100 parts by weight of one-half second nitrocellulose and 60 parts by weight of maleic resin. Mix B contained 15 parts by weight ethanol, 50 parts by weight toluene and 35 parts by weight butyl acetate. Then the final vehicle composition was made by mixing together 20 parts by weight of Mix A with 80 parts by weight of Mix B. This formulation is an example of a typical sanding sealer lacquer. The following examples were prepared by stirring together the soaps and the lacquer to insure proper admixture, i.e., no grinding of the soap was carried out.

	Percent By Weight of Soap	Percent By Weight of Lacquer	Rate of Sedimen- tation	Resulting Film applied to a base
Product of Example IV.	1.6	98.4	Slowest...	Smooth, clean.
Product of Example IV.	1.6	98.4	Slower....	Smooth, hazy.
Zinc Stearate of Example VI.	1.6	98.4	Fastest....	Coarse, slightly cloudy.

Generally, when the novel products described herein are employed as flattening agents, they may be present in a lacquer in an amount of from ½% to 10% by weight of the total. If they are to be employed in sanding sealers, they may be also present in an amount of from ½% to 10% by weight of the total composition. If desired, however, up to 25% of these novel soaps may be satisfactorily employed in the various vehicles.

From the foregoing, it can be seen that novel soap compositions having great utility in various coating compositions have been discovered. It will be appreciated that various modifications can be made in this invention without in any way deviating from the scope thereof as defined in the appended claims.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A composition of matter consisting essentially of a complex of a zinc soap of a saturated fatty acid having a carbon chain length of from about 8 to 22 carbon atoms and a zinc salt obtained from an alkyl polyphosphoric acid ester having the empirical formula



wherein R is selected from the group consisting of straight and branched chain hydrocarbon radicals containing eight carbon atoms, said complex having been obtained by coprecipitating a water-soluble soap of said

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fatty acid and from ½% to 50% by weight based on the dry weight of said water-soluble soap, of said water-soluble alkyl polyphosphoric acid ester with a water soluble zinc salt.

2. The composition of claim 1 in which said proportions are from about 1.0% to 5% by weight of the alkyl polyphosphoric acid ester from which said zinc salt is obtained based upon the dry weight of the water-soluble soap from which said zinc soap is obtained.

3. The composition of claim 2 in which said zinc soap is zinc stearate.

4. The composition of claim 2 in which said alkyl polyphosphoric acid ester is the 2-ethylhexyl ester of pentasodium tripolyphosphate.

5. The composition of claim 4 in which the proportions thereof are about 1% by weight of the 2-ethylhexyl ester of pentasodium tripolyphosphate from which said zinc salt is obtained based upon the dry weight of said water-soluble soap.

6. A composition of matter consisting essentially of a complex of zinc stearate and a zinc salt obtained from an alkyl polyphosphoric acid ester having the empirical formula $\text{Na}_5\text{R}_5(\text{P}_3\text{O}_{10})_2$ wherein R is selected from the group consisting of straight and branched chain hydrocarbon radicals containing eight carbon atoms, said complex having been obtained by coprecipitating a water-soluble soap of said stearate and from ½% to 50% by weight based on the dry weight of said water-soluble stearate soap, of said water-soluble alkyl polyphosphoric acid ester with a water-soluble zinc salt.

7. The composition of claim 6 wherein said water-soluble alkyl polyphosphoric acid ester is present in an amount of 1.0% by weight based on the dry weight of said water-soluble stearate soap.

8. The composition of claim 6 wherein said water-soluble alkyl polyphosphoric acid ester is the 2-ethylhexyl ester of pentasodium tripolyphosphate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,995,456

August 8, 1961

Joseph Cunder et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, in the table, column 5, line 1 thereof, for "clean" read -- clear --; same table, column 1, line 2 thereof, for "Example IV" read -- Example II --.

Signed and sealed this 5th day of December 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

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