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ZIRCONIUM SALTS OF WATER-INSOLUBLE FATTY ACIDS AND METHODS OF MAKING SAME

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Our invention relates to the preparation of novel zirconium salts of the higher fatty acids and mixtures thereof.

The raw materials which we use are any water soluble inorganic salt of zirconium and the desired fatty acid, or sodium salt of the fatty acid, or mixtures thereof. The fatty acid, or sodium salt of the fatty acid, is made by well known procedures; for example, by treatment of the fat or oil with superheated steam followed by distillation to recover free fatty acid, or the saponification of the fat or oil with caustic soda, and the subsequent separation of the sodium derivative by the addition of salt in common with general soap making procedures.

Fatty acids as employed in our present invention are stearic, palmitic, oleic, the acids of tung oil as well as of linseed oil. In other words, such fatty acids as are derived from animal and vegetable fats and oils are utilized.

The zirconium salts as finally prepared according to our invention are designed for use in producing opalescent or flat finish in fibers, films, varnishes, lacquers, paints, resins, inks, and the like without developing the cheesy or spongy appearance obtained by use of other metallic soaps, but still producing the same or a better measure of flattening. Incorporation of such derivatives further increases the water-proofness of the final product.

Derivatives such as the oleate, or the mixture hereinafter described as linoleate, which are essentially very viscous greases, have, in addition to the flattening properties noted above desired usefulness as an addition to heavy lubricating greases in which considerable friction work is to be done.

The zirconium soaps are water-proof materials whose physical characteristics are dependent on the type of fatty acid used as the starting material, and are derivatives of bivalent zirconyl radical (ZrO^{++}) groupings as set forth in the hereinafter enumerated examples.

Our invention, broadly stated, consists not only in the discovery of our new zirconium salts of water-insoluble fatty acids, but also in the discovery that by the novel methods as fully described in the following examples zirconium soaps may be prepared for use as flattening agents as well as constituents for lubricating greases, all as hereinbefore described.

Methods of Procedure

The following examples will serve to show the nature of our new products and also our improved methods of making same.

Example 1.—To a concentrated water solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate containing the equivalent of 108 grams of zirconium oxide are added 1 liter of water and 520 grams of stearic acid; the solution is then heated until the acid-melts completely. 140 cc. of a 50% caustic soda solution are added slowly with stirring together with sufficient cold water to allow the stiffening mass to be easily stirred. Such alkaline mix is stirred violently for several minutes at 50–75° C. and is then cooled to room temperature with continued stirring. The longer and more violent the stirring this slightly alkaline mix receives at this stage of our procedure, the more finely divided the final product.

After cooling to room temperature, the stirred mix is then neutralized with acid, drop by drop, until the supernatant liquor is, and permanently remains, just acid to litmus paper. Violent stirring at this stage also aids in a finer end product. If the acid neutralization is carried out above the softening point of final compound at 65–70° C., complete agglomeration of the metallic soap to a very viscous grease takes place, thereby making subsequent handling very difficult in case a fine powder is desired.

After the acid neutralization, the supernatant liquor is decanted off, and the solid is washed and dewatered completely in a high speed centrifuge until soluble ions are practically all removed. The centrifuge discharge is a brilliant-white, partially dry powdered material which air-dries rapidly when placed in flat trays in a current of cool air. Precipitation of anhydrous zirconyl stearate is quantitative, producing 617 grams of product having the formula

$$ZrO(CH_3(CH_2)_{16}COO)_2$$

thereby showing the presence of the bivalent zirconyl radical ZrO^{++}.

Example 2.—Saponify 520 grams of stearic acid with 140 cc. of a 50% caustic soda solution; dissolve the resultant mixture in warm water; add with stirring at 50–75° C. a concentrated solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate, in an amount equivalent to 108 grams of zirconium oxide. Then cool to room temperature with stirring, and thereafter proceed as set forth in Example 1.

Example 3.—To a concentrated water solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate containing the equivalent of 108 grams of zirconium oxide, 1 liter of water is added together with 2 liters of a warm solu-

tion of 560 grams of sodium stearate. Heat to 50–75° C. with stirring, and add 50 cc. of a 50% caustic soda solution, and then proceed as set forth in Example 1, after cooling to room temperature.

Example 4.—To a concentrated water solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate containing the equivalent of 108 grams of zirconium oxide is added 1 liter of water together with 470 grams of palmitic acid; the solution is heated until the acid melts completely. 140 cc. of a 50% caustic soda solution are added slowly with stirring together with sufficient cold water to allow the stiffening mass to be easily stirred. The alkaline mix is stirred violently at 50–75° C. for several minutes, and is then cooled to 15° C. with continued stirring. The stirred mix is neutralized with acid, drop by drop, until the supernatant liquor is, and permanently remains, just acid to litmus paper. Violent stirring at this stage aids in a more complete comminution of the final product. If acid neutralization is carried out above the softening point of final compound, for example 35–40° C., complete agglomeration of the metallic soap to a very viscous grease takes place, thereby making subsequent handling difficult in case a finely divided product is desired.

After the acid neutralization, the supernatant liquor is decanted off, and the solid is washed and dewatered completely on a high speed centrifuge until soluble ions are practically removed. The centrifuge discharge is a pale tan, slightly tacky, partially dry material, which air dries rapidly in a current of cool air. Precipitation of anhydrous zirconyl palmitate is quantitative, 567 grams of final product obtained having the formula $ZrO(CH_3(CH_2)_{14}COO)_2$, thereby showing the presence of the bivalent zirconyl radical ZrO^{++}.

Example 5.—Saponify 470 grams of palmitic acid with 140 cc. of a 50% caustic soda solution; then dissolve the resultant mix in warm water and add with stirring at 50–75° C. a concentrated solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate, which contains the equivalent of 108 grams of zirconium oxide. Then cool to 15° C. with stirring, and proceed as set forth in Example 4.

Example 6.—To a concentrated water solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate containing the equivalent of 108 grams of zirconium oxide, 1 liter of water is added together with 2 liters of a warm solution of 513 grams of sodium palmitate. This mix is then heated to 50–75° C. with stirring, and then we add 50 cc. of a 50% caustic soda solution, and proceed as set forth in Example 4, after cooling to 15° C.

Example 7.—To a concentrated water solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate, containing the equivalent of 61.5 grams of zirconium oxide, are added 500 cc. of water and 282.3 grams of oleic acid. This mix is heated to 50° C. and then 70 cc. of a 50% caustic soda solution are added slowly with stirring. This alkaline mix is cooled to 5° C. while stirring. This mix is then neutralized with acid, drop by drop, until the supernatant liquor is, and permanently remains, just acid to litmus, while being stirred vigorously. We filter and wash the slightly tacky solid on the centrifuge until all soluble salts are removed, but not allowing the temperature to rise above 5° C. On warming to room temperature, the white tacky solid takes on the consistency of a very viscous grease weighing 330 grams having the formula $ZrO(C_8H_{17}CH{:}CH(CH_2)_7COO)_2.XH_2O$.

If the acid neutralization is carried out at room temperature, the product forms a very permanent and stiff emulsion with water having the properties of a very viscous grease. The weight of such a product obtained in this example is 830 grams. The permanency of this water emulsion is attested to by the facts that the material (1) is miscible with oils, (2) does not give up water on violent crutching, (3) does not lose weight appreciably on standing in the open air, (4) does not give up water on long standing.

Example 8.—Saponify 282.3 grams of oleic acid with 70 cc. of a 50% caustic soda solution; the resultant mix is then dissolved in a liter of warm water, while adding with stirring a concentrated solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate, equivalent to 61.5 grams of zirconium oxide. We then cool with stirring to 5° C. and proceed as in Example 7.

Example 9.—To a concentrated water solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate equivalent to 61.5 grams of zirconium oxide, are added 304 grams of sodium oleate previously dissolved in 2 liters of warm water. This mix is then heated to 50° C. to which are added 16 cc. of a 50% caustic soda solution and then cooled to 5° C., we then proceed as set forth in Example 7.

Example 10.—221.2 grams of tung oil are completely saponified with 70 cc. of a 50% caustic soda solution; the resultant mix is then dissolved in two liters of warm water. To the stirred solution at 50–75° C. is added a concentrated solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate containing the equivalent of 42.7 grams of zirconium oxide. Sufficient cold water is added to allow the stiffening mixture to be easily stirred. The mixture is then cooled with stirring to room temperature and is neutralized with acid; it is then filtered and washed with water at 15° C. on the centrifuge until all soluble salts and glycerine are removed. The centrifuge discharge is a pale tan, soft, fluffy powder which air dries easily to a faintly tacky solid at room temperatures. The yield equals 340 grams. Tung oil is a mixture of olein and oleomargarin. Zirconyl tungate is a mixture of zirconyl oleate

$$ZrO(C_8H_{17}CH{:}CH(CH_2)_7COO)_2.XH_2O$$

and zirconyl eleomargarate $ZrO(C_{18}H_{31}O_2)$ having an average empirical formula

$$ZrO(C_{18}H_{31}O_2)_2.XH_2O$$

Example 11.—205.9 grams of raw linseed oil are completely saponified with 70 cc. of a 50% caustic soda solution; the resultant mix is then dissolved in 2 liters of warm water. To the stirred solution at 50° C. is added a concentrated solution of zirconium oxychloride, or zirconium sulphate, or zirconium nitrate containing the equivalent of 42.7 grams of zirconium oxide. Sufficient cold water is added to allow the stiffening mixture to be easily stirred. The mix is then cooled with stirring to 5° C. and neutralized with acid until the supernatant liquor is, and remains, just acid; it is then filtered and washed on the centrifuge with water at 5° C. until all soluble salts and glycerine are removed. The centrifuge discharge is a tacky pale yellow solid which becomes a very viscous grease at room temperature weighing 325 grams.

Linseed oil is a mixture of isolinolein, linolin, linolein, olein, stearin, palmitin.

The zirconium soaps prepared therefrom are mixtures of the following formulae:

$ZrO(CH_3(CH_2)_{16}COO)_2$=zirconyl stearate
$ZrO(CH_3(CH_2)_{14}COO)_2$=zirconyl palmitate
$ZrO(C_8H_{17}CH:CH(CH_2)_7COO)_2.XH_2O$=zirconyl oleate
$ZrO(C_{18}H_{31}O_2)_2.XH_2O$=zirconyl linolate
$ZrO(C_{17}H_{29}O_2)_2.XH_2O$=zirconyl linolenate
$ZrO(C_{17}H_{29}O_2)_2.XH_2O$=zirconyl isolinolenate

Each of the above formulae shows the presence of the zirconyl radical ZrO^{++}.

According to some authorities linseed oil also contains acids of following empirical composition after saponification

$C_{16}H_{25}.COOH$
$C_{16}H_{27}.COOH$

which will form zirconium soaps of formula

$ZrO(C_{16}H_{25}COO)_2$ and
$ZrO(C_{16}H_{27}COO)_2$

The average empirical formula for the total mixture used is $ZrO(C_{17}H_{31}O_2)_2.XH_2O$).

If the acid neutralization is carried out at room temperatures, a permanent and stiff emulsion of the consistency of heavy rubbery grease is formed, having a pale yellow color, weighing 835 grams. That this emulsion is permanent is shown from what we have set forth in Example 7.

Usage

As flattening agents, the zirconium stearate, zirconium palmitate, zirconium oleate, zirconium tungate or zirconium linoleate above described or any suitable mixture of these metallic soaps are mixed by milling, crutching, or similar suitable procedure in accordance with the end in view, in a dosage of 1.5 to 10 oz. per gallon of the paint, varnish, lacquer, ink, raw fiber solution, etc. A flat, deglossed, more waterproof finish is obtained, free from the cheesy or spongy appearance given by other commercially used metallic soaps.

As a constituent of lubricating grease, from ten to seventy percent of the anhydrous soaps may be incorporated in the grease to increase its lubricating life under heavy load.

We claim as our invention:

1. The method of preparing a zirconium salt of water-insoluble fatty acids, which comprises mixing an aqueous solution of a water-soluble inorganic salt of zirconium and the fatty acid in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures sufficient to melt the fatty acid, then adding an alkali solution with stirring, cooling the resulting alkaline mix and neutralizing same to acid with precipitation of solid material, and finally washing and dewatering the resulting solid material.

2. The method of preparing anhydrous zirconyl stearate, which comprises mixing an aqueous solution of a water-soluble inorganic salt of zirconium and stearic acid in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures sufficient to melt said acid, then adding an alkali solution with stirring, cooling the resulting alkaline mix and neutralizing same to acid with precipitation of solid material, and finally washing and dewatering said solid material to form the anhydrous zirconyl stearate.

3. The method of preparing anhydrous zirconyl palmitate which comprises mixing an aqueous solution of a water-soluble inorganic salt of zirconium and palmitic acid in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures sufficient to melt said acid, then adding an alkali solution with stirring, cooling the resulting alkaline mix and neutralizing same to acid with precipitation of solid material, and finally washing and dewatering said solid material to form the anhydrous zirconyl palmitate.

4. The method of preparing zirconyl oleate which comprises mixing an aqueous solution of a water-soluble inorganic salt of zirconium and oleic acid in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures sufficient to melt said acid, then adding an alkali solution with stirring, cooling the resulting alkaline mix and neutralizing same to acid with precipitation of solid material, and finally washing and dewatering said solid material to form the anhydrous zirconyl oleate.

5. In the production of zirconium salt of a water-insoluble fatty acid, the step which consists in mixing an aqueous saponified solution of said acid with a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures between 50° C. and 75° C.

6. In the production of a zirconyl stearate, the step which consists in mixing an aqueous saponified solution of stearic acid with a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures between 50° C. and 75° C.

7. In the production of a zirconyl palmitate, the step which consists in mixing an aqueous saponified solution of palmitic acid with a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures between 50° C. and 75° C.

8. In the production of a zirconyl oleate, the step which consists in mixing an aqueous saponified solution of oleic acid with a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid at temperatures between 50° C. and 75° C.

9. In the production of a zirconyl stearate from a mixture of an aqueous saponified solution of stearic acid and a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid, the step which consists in neutralizing to acid said mixture to precipitate therefrom the zirconyl stearate.

10. In the production of a zirconyl palmitate from a mixture of an aqueous saponified solution of palmitic acid and a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid, the step which consists in neutralizing to acid said mixture to precipitate therefrom the zirconyl palmitate.

11. In the production of a zirconyl oleate from a mixture of an aqueous saponified solution of oleic acid and a water-soluble inorganic salt of zirconium in the ratio of 1 mol of ZrO_2 to 2 mols of said acid, the step which consists in neutralizing to acid said mixture to precipitate therefrom the zirconyl oleate.

12. As a new composition of matter, a waterproof fatty acid soap of zirconium of the formula $ZrO(RCOO)_2$ substantially free of RCOOH and water soluble compounds, wherein R represents a higher alkyl radical.

13. As a new composition of matter, a waterproof zirconyl stearate of the formula

$ZrO(CH_3(CH_2)_{16}COO)_2$

substantially free of stearic acid and water soluble compounds.

14. As a new composition of matter, a waterproof zirconyl oleate of the formula

$$ZrO(CH_3(CH_2)_7CH{:}CH(CH_2)_7COO)_2$$

substantially free of oleic acid and water soluble compounds.

15. As a new composition of matter, a waterproof zirconyl palmitate of the formula

$$ZrO(CH_3(CH_2)_{14}COO)_2$$

substantially free of palmitic acid and water soluble compounds.

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