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PREPARATION OF FATTY ACID SALTS

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This invention relates to compounds of fatty acids and more particularly lead salts of long chain fatty acids and to a novel process by which these salts may be manufactured. This application is a continuation of application Serial No. 729,402, filed February 18, 1947, now abandoned, and is related thereto through copending application Serial No. 396,790, filed December 7, 1953, now abandoned, which is in part a continuation of said application Serial No. 729,402.

Fatty acids are considered to be the group of saturated, aliphatic organic acids represented by the general formula $C_nH_{2n+1}COOH$. The lower members of this series, formic, acetic and propionic acids, are readily soluble in water. However, as the length of the chain and the number of carbon atoms increases, the solubility becomes less and less. Thus, caproic (6 carbon atoms) and octoic (8 carbon atoms) acids are sparingly soluble, nonylic and capric are very slightly soluble and all members of the series having ten or more carbon atoms are substantially water insoluble.

Manufacture of lead salts of the lower readily soluble members of the fatty acid series presents no problem, since lead oxide will readily combine with the acid in aqueous media. In the case of the longer chain members, however, as the solubility decreases, the direct combination with the metal oxide becomes increasingly more difficult. For this reason, normal lead salts of the higher members of the series have been made heretofore by either mixing a water soluble salt of the fatty acid with a suitable soluble lead salt to precipitate the insoluble metal fatty acid compound; or by adding lead oxide to molten fatty acid whereupon combination is effected in the fused state.

An example of the lead fatty acid compound under consideration is lead stearate, which is used in various types of compositions designed for water proofing, electrical insulation and the like, and recently has been used in the formulation of synthetic rubber and polyvinyl type plastic resins. For use in these applications, the lead stearate should be of good color and contain a minimum of water soluble stalts and impurities. These criteria are extremely difficult to meet, however, when using either of the methods of manufacture described above. If lead acetate is reacted with sodium stearate, soluble sodium salts are invariably occluded in the product in spite of intensive washing. If lead oxide is reacted with molten stearic acid all the impurities in the raw materials are retained in the product resulting in generally poor color; and often undesirable side reaction products are formed at the necessary high temperature.

Another disadvantage of the prior art methods for manufacture of lead salts of long chain fatty acids is that only normal salts of the general type,

$$Pb(C_nH_{2n+1}COO)_2$$

can be prepared; the degree of reactivity obtainable is not sufficient to enable compounds containing more than the normal content of the metal or metal oxide to be produced, and the existance of corresponding basic compounds has not therefore been heretofore indicated or postulated.

A principal object of this invention is therefore, to

provide a novel process by which normal or basic compounds of lead and long chain fatty acids may be produced. Another object is to provide a process for making lead salts of long chain fatty acids which is simpler and more economical than hitherto known methods, and by which purer and more commercially valuable products may be obtained. A still further object is to provide a series of previously unknown chemical compounds comprising basic long chain fatty acid salts of lead. It is a still further object to provide a series of lead fatty acid compounds free from soluble salts and impurities and of good white color.

This invention in its broadest aspects contemplates the manufacture of lead salts of fatty acids by a process which comprises the chemical combination of lead oxide and the fatty acid in aqueous media and in the presence of a catalyst. More specifically, the process comprises reacting lead monoxide with the fatty acid in a water slurry together with a catalyst which has the characteristics of being an oxygenated, polar, soluble, aliphatic compound. By oxygenated is meant containing combined oxygen; by polar is meant capable of rotational movement; by soluble is meant water soluble at least to a limited extent; and by aliphatic is meant a chain as distinguished from a ring type compound. It will be understood by those skilled in the art that a very large number of organic compounds will fall into the above category and will function as catalysts, however best results will be obtained from those forming the group of saturated alcohols and ethers containing from 2 to 8 carbon atoms. Monohydric alcohols such as iso-butanol, or glycol ethers such as ethylene glycol monobutyl ether or diethylene glycol monobutyl ether are efficient and practical from a commercial point of view.

The fatty acids used in the process of this invention will include generally those of larger chain length in the series, that is from caproic ($C_5H_{11}COOH$) up to and including melissic ($C_{29}H_{59}COOH$). The proportions of fatty acid and lead oxide for manufacture of the normal salts will be stoichiometric amounts to form compounds having the general formula $Pb(C_nH_{2n+1}COO)_2$. For formation of compounds of this type it will be apparent that for each mol of lead monoxide there should be taken substantially 2 moles of fatty acid.

It has further been found, and is one of the unique features of this invention, that by using ingredients in proportions of 3 mols of PbO to 2 mols of fatty acid in this process, a hitherto unknown series of basic lead fatty acid compounds may be produced corresponding to the general formula $2PbO.Pb(C_nH_{2n+1}COO)_2$. If desired, as will be apparent, mixtures or combinations of these compounds may be produced by using amounts of PbO intermediate between 1 and 3 mols for each 2 mols of fatty acid.

The fatty acid, lead oxide and catalyst are mixed with sufficient water to form a slurry. This will involve the use of from about 3 to about 16 parts of water by weight for each part of lead oxide. The catalyst is preferably used in amounts from about 2% to about 15% of the weight of water, and it has been found that while the lower ranges of the catalyst proportion, that is from about 2% to about 5%, give adequate reaction speed when normal salts are being formed, the higher ranges, that is from about 5% to about 15%, are necessary for rapid formation of basic compounds.

Suitable amounts of reactants having been taken as explained above, the slurry is then thoroughly and intensively mixed for a suitable period of time. This is advantageously accomplished in a ball mill or similar device. It is necessary that intensive agitation be used to insure adequate contact and reaction between the raw materials, and while the process is herein described using a ball mill,

other types of mixing or grinding devices may be employed to give comparable results. The ball milling or mixing is continued until the reaction is complete. This may take at room temperature about 12 to 20 hours, and may be speeded up considerably by employing elevated temperatures for instance, from 25° C. to 65° C. Employing a temperature of about 40° C., most lead fatty acid compounds may be completely formed in 10 hours or less. After reaction is complete, the product which is in the form of a white, finely divided solid, is separated from the mother liquor, as by filtration, and then dried. The liquor, which will be found to contain the original catalyst, may be reused in successive batches if desired, thus contributing to the economy of the operation.

The following examples illustrate the formation of typical normal lead fatty acid compounds according to various modifications of the process of this invention.

EXAMPLE I

Normal lead stearate $Pb(C_{17}H_{35}COO)_2$

A charge consisting of 22.3 g. lead oxide, 56.8 g. pure stearic acid, 300 ml. water and 10 ml. of ethylene glycol monobutyl ether was ground in a 1 pint ball mill containing 1 lb. flint pebbles. The reaction was conducted for 16 hours at room temperature at a mill speed of 83 r.p.m. The white slurry was filtered and the solids dried at 80° C. The pH value of the filtrate was found to be 5.86 and the yield was 76.8 g. The dried product contained 28.5% lead monoxide and its specific gravity was 1.42. Refractive indices of 1.576; 1.604 were found. The melting point was found to be 115.5° C.

EXAMPLE II

Normal lead pelargonate $Pb(C_8H_{17}COO)_2$

A charge consisting of 22.3 g. lead oxide, 31.6 g. C.P. pelargonic acid, 300 ml. water and 10 ml. diethylene glycol monobutyl ether was ground in a 1 pint ball mill containing 1 lb. flint pebbles. The reaction was conducted for 16 hours at room temperature at a mill speed of 83 r.p.m. The white slurry was filtered, and the solids dried at 80° C. The pH value of the filtrate was 4.49 and the yield was 51.0 g. The dried product contained 42.9% lead monoxide and its specific gravity was 1.74. Refractive indices of 1.562; 1.587 were found. The melting point was found to be 96.0° C.

EXAMPLE III

Normal lead myristate $Pb(C_{13}H_{27}COO)_2$

A charge consisting of 22.3 g. lead oxide, 45.6 g. C.P. myristic acid, 300 ml. water and 8 ml. iso-butanol was ground in a 1 pint ball mill containing 1 lb. flint pebbles. The reaction was conducted for 10 hours at a temperature of 40° C. at a mill speed of 83 r.p.m. The white slurry was filtered and the solids dried at 80° C. The pH value of the filtrate was 5.0 and the yield was 67.0 g. the lead monoxide content of the dried product was 31.2% and its specific gravity 1.49. Refractive indices of 1.576; 1.590 were found. The melting point was found to be 105.2° C.

The following examples illustrate the formation of novel basic lead fatty acid compounds according to various modifications of the process of this invention.

EXAMPLE IV

Dibasic lead stearate $2PbO.Pb(C_{17}H_{35}COO)_2$

A charge consisting of 66.9 g. lead oxide, 53.5 g. U.S.P. triple pressed stearic acid (acid number 209.8), 300 ml. water and 25 ml. N-butanol was ground in a 1 pint ball mill containing 1 lb. flint pebbles. The operation was continued for 16 hours at room temperature, mill speed being 83 r.p.m. The white solid phase was separated by filtration and dried at 80° C. The yield was substantially complete. The lead monoxide content of the dried product was 56.1% and its specific gravity 2.02.

EXAMPLE V

Dibasic lead caproate $2PbO.Pb(C_5H_{11}COO)_2$

66.9 grams of lead monoxide were placed in a pebble mill having a capacity of 77 ml. and containing 1 lb. of flint pebbles. A solution containing 300 ml. water and 25 ml. ethylene glycol monobutyl ether was added, followed by 23.27 g. pure n-caproic acid. The mill was then sealed and rotated at 83 r.p.m. for 16 hours at room temperature. The resulting white slurry was filtered, and the solid phase dried at 75° C. The actual yield was 86.0 g. or 97.5% of the theoretical yield. The pH value of the filtrate was 8.3. The lead monoxide content of the product was found to be 75.7% and its specific gravity, 3.41. The indices of refraction were found to be 1.6568; 1.6798.

EXAMPLE VI

Dibasic lead laurate $2PbO.Pb(C_{11}H_{23}COO)_2$

A charge consisting of 22.3 g. lead oxide, 13.3 g. C.P. lauric acid, 300 ml. water and 20 ml. diethylene glycol monobutyl ether was ground in a 1 pint ball mill containing 1 lb. of flint pebbles. The operation was conducted for 10 hours at 40° C. temperature; mill speed, 83 r.p.m. The white slurry was filtered, and the solids dried at 80° C. The pH value of the filtrate was 6.33. Yield was 33.4 g., or 95.4% of the theoretical yield. The lead monoxide content of the dried product was 63.0% and its specific gravity, 2.25. Refractive indices of 1.6040; 1.6100 were found.

It is to be understood that the scope of this invention is not limited to compounds formed by the use of pure raw materials. In Example IV above, the stearic acid used was a commercial grade known as "triple pressed" which consists actually of a mixture of stearic acid and other fatty acids, particularly palmitic and a minor amount of oleic acid. Thus while the product is termed basic lead stearate, it may contain lead compounds of other fatty acids to the extent that they are present in the original fatty acid raw material.

The precise action of the catalyst in the novel process of this invention is not clearly understood. It is postulated that it may act as an intermediate chemical reactant; or may influence the wetting or surface tension effects on the surfaces of the ingredients; or may affect the water miscibility of the fatty acid phase.

Whatever the nature of its action, however it does surprisingly promote the speed of reaction so that normal and basic compounds may be formed in aqueous media from PbO and the fatty acid. Inasmuch as this reagent is used in this capacity and is recoverable intact after the reaction is complete, justification exists for the use of the term "catalyst" as herein employed.

In general a larger proportion of the catalyst, within the limits hereinbefore noted, will result in increased reaction speed and in addition, when elevated temperatures are employed less catalyst may be necessary. The effect of temperature is not critical and it may, if desired, be raised to the boiling point of water or higher, if suitable arrangements for replacing lost vapor are employed. However, for simple, practical operation, using a conventional ball mill, a temperature of 25° C. to 65° C. is preferred.

The process of this invention provides a simple and economical method for manufacturing compounds of the class described. It provides for direct combination of lead monoxide with the fatty acid which obviates the use of relatively expensive lead salts and soluble fatty acid compounds. It has the advantage over the fusion method described above of producing a more desirable product and does not involve the high temperatures necessary for this type of process, and in addition produces a finely divided product instead of a fused mass which must generally be further processed.

The products of this invention have improved charac-

teristics compared to prior art products. They will be found to be of attractive white color making them valuable as ingredients in light colored compositions. Since no inorganic radicals are employed in the raw materials, no salts can be present as impurities in the finished product. Any residual catalyst occluded after filtration may be removed by vaporization in the drying stage or may remain in the product without deleterious effect. The normal lead fatty acid compounds may be substituted for prior art similar products with improved results while the basic lead fatty acid compounds are particularly useful where a higher proportion of lead is desired than exists in the normal compound. Such applications may include those in which a high specific gravity is desirable or where a product containing a higher content of available lead oxide is advantageous. Basic lead stearate is particularly useful as a stabilizer for vinyl type plastics and synthetic rubber. Those artificial resins known collectively as vinyl resins have attained wide recognition in the field of plastics. Of this class, the resins which include a vinyl halide, usually vinyl chloride, in their constitution are probably most widely known, particularly the resins such as are formed by conjoint polymerization of vinyl chloride with vinyl esters of aliphatic acids or with other unsaturated polymerizable compounds. See U.S. Patent No. 2,394,418, Quattlebaum et al., February 5, 1946.

It is to be understood that the examples shown have been given for the purpose of illustration and it is not intended to limit the scope of the invention particularly thereto. Various modifications and variations of the catalytic process as hereinbefore described may be employed and various products manufactured as limited by the following claims.

I claim:

1. A process for the manufacture of lead fatty acid compounds which comprises mixing lead monoxide and a saturated fatty acid containing at least 6 carbon atoms in amounts so that for each 2 mols of fatty acid there are present from 1 to 3 mols of lead monoxide, with water in amount of 3 to 16 parts by weight of the lead monoxide and from 2% to 15% of the weight of water of a compound selected from the group consisting of aliphatic alcohols and ethers containing from 2 to 8 carbon atoms, and mixing the same until the lead monoxide and the fatty acid are chemically combined.

2. A process for the manufacture of lead fatty acid compounds which comprises mixing lead monoxide and a saturated fatty acid containing at least 6 carbon atoms in amounts so that for each 2 mols of fatty acid there are present from 1 to 3 mols of lead monoxide, with water in amount of 3 to 16 parts by weight of the lead monoxide and from 2% to 15% of the weight of water of a compound selected from the group consisting of aliphatic alcohols and ethers containing from 2 to 8 carbon atoms and mixing at a temperature of between about 25° C. and about 65° C. until the lead monoxide and the fatty acid are chemically combined.

3. A process for the manufacture of lead fatty acid compounds which comprises mixing lead monoxide and a saturated fatty acid containing at least 6 carbon atoms in amounts so that for each 2 mols of fatty acid there are present from 1 to 3 mols of lead monoxide, with water in amount of 3 to 16 parts by weight of the lead monoxide and from 2% to 15% of the weight of water of isobutanol, and mixing the same until the lead monoxide and the fatty acid are chemically combined.

4. A process for the manufacture of lead fatty acid compounds which comprises mixing lead monoxide and a saturated fatty acid containing at least 6 carbon atoms in amounts so that for each 2 mols of fatty acid there are present from 1 to 3 mols of lead monoxide and from 2% to 15% of the weight of water of ethylene glycol monobutyl ether, and mixing the same until the lead monoxide and the fatty acid are chemically combined.

5. A process for the manufacture of lead fatty acid compounds which comprises mixing lead monoxide and a saturated fatty acid containing at least 6 carbon atoms in amounts so that for each 2 mols of fatty acid there are present from 1 to 3 mols of lead monoxide, with water in amounts of 3 to 16 parts by weight of the lead monoxide and from 2% to 15% of the weight of diethylene glycol monobutyl ether.

6. As a new chemical compound, basic lead palmitate, corresponding to the formula $2PbO.Pb(C_{15}H_{31}COO)_2$.

7. As a new chemical compound, basic lead oleate, corresponding to the formula $2PbO.Pb(C_{17}H_{33}COO)_2$.

8. As a new chemical compound, basic lead caprate, corresponding to the formula $2PbO.Pb(C_9H_{19}COO)_2$.

9. As a new chemical compound, a basic lead soap selected from the group consisting of basic lead palmitate, basic lead caprate, and basic lead oleate.

10. A mixture of at least two basic lead soaps suitable as a stabilizer in resin compositions containing vinyl chloride, the fatty acid radicals in said mixture being selected from the group consisting of the fatty acid radicals of stearic acid, palmitic acid and oleic acid, and said soaps containing in excess of one mol of lead calculated as PbO for each two mols of said fatty acid radicals calculated as the fatty acids.

11. As a new chemical composition suitable for use as a stabilizer in resin compositions containing vinyl chloride, a mixture of basic lead soaps corresponding to the general formula $2PbO \cdot Pb(X)_2$ in which X consists of the fatty acid radicals of stearic acid, palmitic acid and oleic acid, each of which radical is present in said mixture, the proportions of said radicals approximating those found in commercial triple pressed stearic acid.

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