

- [54] **MANUFACTURE OF METALLIC SOAPS**
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- [58] **Field of Search** ..... **260/414, 429 R, 435 R, 260/429.9, 439 R**

- [56] **References Cited**  
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[57] **ABSTRACT**

Metallic soaps, particularly zinc soaps are produced from a reaction mixture initially comprising a metal oxide or hydroxide, for example, zinc oxide, water and a glyceryl ester, particularly a triglyceride, the ester and said metal oxide or hydroxide being present in at least approximately stoichiometric amounts; the reaction mixture is agitated and the reactants are reacted in the agitated mixture to produce a metallic soap and glycerine, at a temperature at which the metallic soap is molten, in the presence of an excess of water effective to dissolve the glycerine formed in the reaction mixture such that reaction between by-product glycerine and the product metallic soap is substantially hindered, eventually the reaction mixture is allowed to separate into an aqueous layer and a molten layer of product metallic soap under a pressure such that the aqueous layer is essentially quiescent, and the molten metallic soap layer is dissociated from the aqueous layer; in this way metallic soaps of high purity can be obtained.

19 Claims, No Drawings

## MANUFACTURE OF METALLIC SOAPS

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to the manufacture of water-insoluble heavy metal soaps or metallic soaps and, more particularly, it relates to the manufacture of those metallic soaps which, in their molten state, are pourable liquids. It is therefore chiefly concerned with the soaps of cadmium, cobalt, lead, manganese, copper and zinc.

#### 2. Description of the Prior Art

Metallic soaps have found wide application in industry, for example, as waterproofing agents, thickening and suspending agents, and as lubricants; they are also employed in cosmetics, lacquers, plastics, in powder metallurgy, as mold release agents, flattening agents, fillers, anti-foaming agents and driers in paints, and in tablet manufacture. They are also used as heat and light stabilizers for plastics, especially polyvinyl chloride. The most common metallic soaps are those prepared from calcium, zinc, magnesium, barium and aluminum.

The heavy metal or metallic soaps have conventionally been prepared from the metal oxides or metal salts and aliphatic carboxylic acids, particularly the higher fatty acids containing from about 12 to 22 carbon atoms, which acids are known and sold to the industry as commercial fatty acids. The commercial fatty acids as commonly used are usually mixtures of higher fatty acids in which the name attached to them may be only the dominant acid of the mixture. In some grades of commercial stearic acid, however, the dominant fatty acid is not stearic acid but another fatty acid, for example, palmitic acid.

The three basic methods conventionally employed for the manufacture of metallic soaps are described in U.S. Pat. No. 2,890,232, Russell H. Rogers, Jr. et al, issued June 9, 1959 and U.S. Pat. No. 3,803,188, Leonard Frank Scott et al, issued Apr. 9, 1974. The manufacture of metallic soaps is also described in U.S. Pat. Nos. 2,945,051, Gerald M. Davis, issued July 12, 1960 and 2,650,932, Leonard M. Kebrich et al, issued Sept. 1, 1953.

Metallic soaps of the higher fatty acids, the most common of which are the metallic stearates derived from commercial grades of stearic acid, are prepared by two principal methods:

#### (i) DOUBLE DECOMPOSITION PROCESS

This is the oldest process and probably still the one most commonly used. A hot aqueous solution of the sodium salt of the fatty acid is first prepared by the addition of aqueous caustic soda to a mixture of the fatty acid in hot water. The sodium salt is then reacted with a hot aqueous solution of an appropriate metal salt. The insoluble precipitate of the fatty acid metallic soap is filtered, washed free of the soluble sodium salt, dried, and ground to a fine powder. By proper control of the reaction conditions, including temperature, rate of addition of reactants, and degree of dilution, a product with a fine particle size and of high purity can be obtained. The production cost, however, is high, especially because of the filtration, washing, and drying operations required. The process also has the drawback that frequently it creates a water pollution problem.

Zinc stearate is manufactured commercially employing this process by the action of sodium stearate on a solution of zinc sulphate.

#### (ii) REACTION OF METALS, METAL OXIDES OR METAL HYDROXIDES WITH MOLTEN FATTY ACIDS

##### (a) Fusion Process

Only certain metallic soaps can be formed by this method. The metallic soap is formed by reacting the molten fatty acid with the appropriate metal oxide or hydroxide at a temperature above the melting point of the metallic soap to be formed, and generally at a temperature considerably above this, because, during the reaction, water is formed and this must be driven off. Generally, the reaction requires in the neighbourhood of 5 hours for completion. This process can only be used for making metallic soaps which are pourable in their molten state. It, therefore, cannot be used for such metallic soaps as calcium or barium stearate, but it is suitable for zinc and lead stearates. The final product is in the form of flakes or lumps and a considerable energy must be expended in grinding it to the required very fine particle size. This process does have the advantage of not requiring the use of caustic soda, and no filtering or drying is required. It also does not lead to any water pollution or the consumption of any water.

##### (b) Modified Fusion Process

This is much like the fusion process (a), except that a small amount of water is added to the mixture of molten fatty acid and metal oxide or hydroxide. The water acts as a catalyst and allows the reaction to be carried out at a somewhat lower temperature, and more quickly. The final product produced is very much like, if not identical to, that resulting from the fusion process (a).

##### (c) Fusion in an Aqueous Slurry

In this process, the molten fatty acid is first emulsified in water using an appropriate emulsifying agent. To this aqueous emulsion, is added an aqueous slurry of the metal oxide or hydroxide. The metallic oxide or hydroxide reacts with the fatty acid to form the metallic soap. This is then removed by filtration, during which it is washed, and then it is dried and ground. The product is considerably easier to grind because it is produced in the form of coarse particles. These particles, however, are much coarser than those produced in the double decomposition process.

##### (d) Miscellaneous Fusion Methods

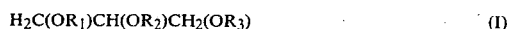
Occasionally, it is possible and of commercial value to react certain metals directly with molten fatty acid. For example, iron stearate may be prepared by this method; however, hydrogen rather than water is actually a by-product of reaction and, because the reaction generally has to be carried out at an unusually high temperature, the colour of the resulting metallic soap is poor.

### SUMMARY OF THE INVENTION

The present invention provides a new and improved method for the manufacture of metallic soaps that are pourable in their molten state, utilizing oxides or hydroxides of divalent metals and appropriate fats or oils rather than the fatty acids derived from such fats and oils.

The method of the invention permits the production of metallic soaps in good yield and purity with low free fatty acid content.

According to the invention there is provided a process for producing a metallic soap having a viscosity such that it is a pourable liquid when molten, of a monocarboxylic acid of the formula R-COOH wherein R is a linear or branched, saturated or unsaturated, unsubstituted or substituted by one or more hydroxy groups, aliphatic hydrocarbon radical of 5 to 21 carbon atoms, which comprises: (i) forming a reaction mixture initially comprising a metal component comprising a metal oxide selected from the group consisting of oxides of cadmium, lead and zinc or a metal hydroxide selected from the group consisting of hydroxides of cobalt, manganese, and zinc, water and a glyceryl ester of formula (I):



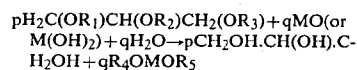
wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, which may be the same or different are selected from the group consisting of hydrogen and linear or branched, unsubstituted or substituted by one or more hydroxyl groups, saturated or unsaturated aliphatic hydrocarbon acyl radicals of 6 to 22 carbon atoms, provided that at least one of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> is an acyl radical, said ester and said metal oxide or hydroxide being present in at least approximately stoichiometric amounts; (ii) agitating said reaction mixture; (iii) reacting the reactants in the agitated mixture to produce a metallic soap of the carboxylic acid and glycerine, at a temperature at which the metallic soap is molten, in the presence of an excess of water effective to dissolve the glycerine formed in the reaction mixture such that reaction between the reactants proceeds in favour of metallic soap production and the reaction between glycerine and the product metallic soap is substantially hindered; (iv) continuing the reacting in (iii) until substantially no more metallic soap is formed; (v) allowing the reaction mixture to separate into an aqueous layer and a molten layer of product metallic soap substantially free of metallic oxide or metallic hydroxide, carboxylic acid and glyceryl ester, under a pressure such that said aqueous layer is essentially quiescent, and (vi) dissociating the molten metallic soap layer from the aqueous layer.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the invention employs a reaction between a metal oxide or hydroxide, a glyceryl ester, particularly a mono-, di or triglyceride, preferably a triglyceride, for example, unhydrogenated or hydrogenated, naturally occurring, vegetable oil or animal fat, and, in the case of the oxide, water. A particular advantage of the method of the invention, which employs a glyceryl ester, particularly a triglyceride, instead of a fatty acid or mixture of fatty acids derived from the corresponding triglyceride, is that it is unnecessary to carry out the procedure of first deriving the acid or acids from the corresponding glyceryl ester prior to forming the metallic soap by reacting the metal oxide or hydroxide with the fatty acid; instead, the metallic soaps are formed directly from the glyceryl esters. Furthermore, unlike the double decomposition process, no caustic soda is required, and it is not necessary to carry out any filtering, washing or drying.

In one embodiment of the process of the invention an oxide of a heavy metal, particularly a divalent metal, is

reacted with the glyceryl ester of formula (I), which may be a mono-, di- or triglyceride, and water, with elimination of glycerine. The reaction proceeds in accordance with equation (I)—



wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are as defined above in formula (I), M is the metal, R<sub>4</sub> and R<sub>5</sub>, which may be the same or different, are acyl radicals selected from R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>, p is an integer of 1 or 2 and q is an integer of 1 or 3. When the glyceryl ester is a monoglyceride, p is 2 and q is 1; when the glyceryl ester is a diglyceride, p and q are both 1; and when the glyceryl ester is a triglyceride, p is 2 and q is 3.

In another embodiment a heavy metal hydroxide is employed in place of the oxide and no water is required in the chemical reaction with the glyceryl ester although water is still required in the reaction mixture to dissolve the glycerine; the values for p and q are as indicated in equation (I) except that for the water as reactant q is 0.

The heavy metal of the metal oxide may be cadmium, lead or zinc; the heavy metal of the metal hydroxide may be cobalt, manganese, copper or zinc. The preferred metal oxide is zinc oxide; the preferred metal hydroxide is cobaltous hydroxide. Although oxides and hydroxides of some of the alkaline earth and other heavy metals will react with glyceryl esters, the resulting metallic soaps do not form pourable liquids when heated above their melting points and, consequently, the separation of the resulting metallic soaps from the solution of by-product glycerine and water is difficult and not commercially practical. The present invention is concerned only with those metallic soaps which are pourable liquids at temperatures exceeding their melting points. For the purposes of this invention, a pourable liquid is defined as one having a viscosity of less than 1,000,000 and preferably less than 500,000 cps.

In a preferred embodiment of the process of this invention, the glyceryl ester is a triglyceride selected from the triglycerides which are derived from, or contained in, animal or vegetable fats or oils, since these are more readily available commercially. Such triglycerides include those in which the aliphatic hydrocarbon radical is saturated or unsaturated.

Triglycerides in which one or more of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> has less than 6 carbon atoms or more than 22 carbon atoms will produce metallic soaps by the process of the invention, however, such triglycerides are rare and not generally commercially available.

A large number of triglycerides, which are derived from or contained in animal or vegetable fats or oils, may be used in the invention. The degree of unsaturation of a triglyceride is indicated by the iodine value. The higher the iodine value, the higher the degree of unsaturation. Frequently, it is desirable to reduce the degree of unsaturation of a triglyceride and this can be accomplished by reacting the triglyceride with hydrogen, the process being called hydrogenation. The degree to which the unsaturation is reduced is determined by the amount of hydrogen which is allowed to react with the triglyceride.

Occasionally, complete saturation or hydrogenation is desired and, in this case, the iodine value is reduced to

essentially zero. In other instances, it may be sufficient to merely reduce the iodine value from, say, 40 to 15.

The triglycerides which occur naturally differ widely in iodine value and also in composition. This is demonstrated in Table I below.

colour of the metallic soap produced is whiter and the colour stability on heating is greater.

The melting point of the metallic soap depends on the degree of unsaturation in the aliphatic hydrocarbon radicals, or in other words it depends on the iodine

TABLE I

Unhydrogenated Fat or Oil	Iodine Value	APPROX. NATURE AND AMOUNTS (IN WT. %) OF DERIVABLE SATURATED FATTY ACIDS							APPROX. NATURE AND AMOUNTS (IN WT. %) OF DERIVABLE UNSATURATED FATTY ACIDS				
		caprylic	capric	lauric	myristic	palmitic	stearic	oleic	erucic	ricino-leic	lino-leic	lino-leic	
		Castor	85	—	—	—	—	—	0.3	8.2	—	87.6	3.6
Coconut	10	8.0	7.0	48.2	17.3	8.8	2.0	6.0	—	—	2.5	—	
Cottonseed	110	—	—	—	0.5	22.9	2.2	24.7	—	—	49.7	—	
Lard	55	—	—	—	1.0	26.0	11.0	48.7	—	—	12.2	0.7	
Linseed	180	—	—	—	—	6.4	4.5	21.0	—	—	17.4	50.6	
Palm	50	—	—	—	1.0	42.5	4.0	43.0	—	—	9.5	—	
Peanut	90	—	—	—	—	7.0	5.0	60.0	—	—	21.0	—	
Rape-seed	100	—	—	—	1.0	1.0	1.0	29.0	50.0	—	15.0	1.0	
Soya-bean	135	—	—	—	—	6.5	4.2	28.0	—	—	52.6	8.0	
Beef Tallow	40	—	—	—	2.2	35.0	15.7	44.4	—	—	2.2	0.4	

During hydrogenation, the double bonds in the unsaturated aliphatic hydrocarbon radicals of the triglyceride molecules are gradually replaced with single bonds and, in this way, the chemical composition is significantly changed. For example, when the unsaturated hydrocarbon radical of oleic acid radical is hydrogenated, the oleic acid is converted to stearic acid. The typical composition of the naturally occurring triglycerides of Table I after hydrogenation is shown in Table II below.

value of the triglyceride employed. The lower the iodine value, i.e., the higher the saturation of the aliphatic hydrocarbon radicals, the higher the melting point of the metallic salt. For a given chain length or number of carbon atoms in a fatty acid aliphatic hydrocarbon radical, the greater the number of carbon-carbon double bonds in the chain, the lower will be the melting point; for example zinc stearate melts at 120° C. and zinc oleate melts at 70° C.

In carrying out the process of the invention on a

TABLE II

Hydrogenated Fat or Oil	Iodine Value	APPROX. NATURE AND AMOUNTS (IN WT. %) OF DERIVABLE SATURATED FATTY ACIDS							APPROX. NATURE AND AMOUNTS (IN WT. %) OF DERIVABLE UNSATURATED FATTY ACIDS		
		caprylic	capric	lauric	myristic	palmitic	stearic	12-hydroxystearic	other	oleic	
Castor	2	—	—	—	—	2	10	88	—	—	
Coconut	1	4	6	49	21	10	10	—	—	—	
Cottonseed	5	—	—	—	1	23	70	—	—	6	
Lard	3	—	—	—	1	26	69	—	—	4	
Linseed	2	—	—	—	—	6	92	—	—	2	
Palm	1	—	—	—	1	43	55	—	—	1	
Peanut	4	—	—	—	—	7	81	—	—	5	
Rape-seed	6	—	—	—	1	1	39	—	51 Behenic	7	
Soya-bean	7	—	—	—	—	7	85	—	—	8	
Beef Tallow	2	—	—	—	3	28	65	—	—	2	

It is especially preferred to employ a triglyceride having an iodine value of less than 50, and preferably less than 10. Some of the naturally occurring triglycerides have an iodine value of this order, but others must be hydrogenated to convert them into triglycerides having a low iodine value. The advantage in employing triglycerides having a lower iodine value is that the

commercial scale, commercially available materials are utilized. It will be appreciated that commercially available materials are of varying grades of composition.

In the specification, identification of materials by the chemical name is intended to embrace both the chemically pure material and the commercially available product. For example, the "zinc stearate" produced in

the examples illustrating this invention will be a commercial grade of zinc stearate, similar to the product derived commercially by reacting zinc oxide with "stearic acid", which term covers such products as single-pressed, double-pressed and triple-pressed stearic acid and also mixtures of fatty acids derived from the complete or incomplete hydrogenation and subsequent hydrolysis of certain animal and vegetable fats and oils, for example, tallow fat and soybean oil.

The triglycerides employed in the invention have mixtures of aliphatic hydrocarbon radicals similar to those in the fatty acids derived from them, so that the composition of the metallic soaps produced in this invention from a particular fat or oil will be similar to that produced by the conventional method from a mixture of fatty acids derived from that fat or oil.

Thus it will be recognized that the nature of the commercially available reactants employed in the invention results in metallic soap products which, essentially, are mixtures of different metallic soaps rather than a single metallic soap. Of course, the process of the invention can be utilized to produce particular metallic soaps which are not mixtures by appropriate selection of triglycerides in which all the aliphatic hydrocarbon radicals are the same, but for most purposes such selection is unnecessary as the different metallic soaps in a metallic soap product have sufficiently similar properties and characteristics for most industrial uses.

As illustrative of the novel process of the invention, zinc stearate can be prepared by heating together under conditions of agitation in an enclosed reactor (for example, an autoclave) zinc oxide, hydrogenated tallow, and

of the aqueous glycerine at the temperature in the autoclave. Under these conditions of temperature and pressure and in the absence of agitation, the molten zinc soap forms a discrete layer above an aqueous layer of glycerine. Having obtained this layer separation, it is a simple matter to drain off the lower aqueous layer before draining off the molten zinc soap into a separate container.

It is an important aspect of this invention that the reaction conditions be such that a thorough separation of the metallic soap from the aqueous glycerine is achieved. Table III below shows the dependence of specific gravity on temperature for several metallic soaps and on both temperature and glycerine content for several different solutions of glycerine in water. These results show that when certain metallic soaps are in the presence of certain glycerine in water solutions at a particular temperature, the specific gravity of the molten metallic soap and that of the aqueous glycerine solution are equal and it is therefore impossible to achieve the formation of the two distinct layers of immiscible materials. If the specific gravity of the molten metallic soap is only slightly less or slightly greater than that of the aqueous solution, it is very difficult, and frequently impossible, to obtain a complete separation.

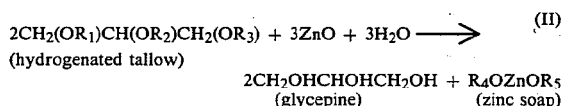
It is therefore appropriate to control the process conditions such that there is an adequate difference in the specific gravities of the molten metallic soap and the aqueous glycerine to permit complete separation to form distinct layers. The specific gravities may suitably be altered by varying the temperature or by diluting the reaction mixture with further quantities of water.

TABLE III

SPECIFIC GRAVITY FOR VARIOUS METALLIC SOAPS AND FOR VARIOUS AQUEOUS GLYCERINE SOLUTIONS

MATERIAL	TEMPERATURE IN °C.						
	20	50	100	130	150	185	200
10% glycerine in water	1.025	1.012	0.983	0.960	0.943	0.908	0.891
20% glycerine in water	1.051	1.038	1.008	0.986	0.969	0.934	0.918
30% glycerine in water	1.077	1.063	1.033	1.011	0.994	0.961	0.945
40% glycerine in water	1.104	1.089	1.058	1.036	1.019	0.987	0.972
cadmium stearate	1.21			1.00	0.99	0.95	
copper stearate	1.10						
cobalt stearate	1.13						
lead stearate	1.37			1.17	1.15	1.11	
manganese stearate	1.22						
zinc stearate	1.09			0.92	0.91	0.89	
zinc palmitate	1.12						

water according to the following equation (II):



where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are acyl radicals as defined previously and are the same or different for each molecule of hydrogenated tallow, and are present in amounts corresponding approximately to the composition given in Table I, and R<sub>4</sub> and R<sub>5</sub>, which may be the same or different, are acyl radicals selected from R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub>.

When the reaction is complete, the agitation is stopped and the temperature is maintained above the melting point of the product zinc soap. In a preferred embodiment the pressure is increased by the introduction of an inert gas, for example, air or nitrogen, so that the pressure is substantially above the vapour pressure

An important feature of the invention is that during the process step leading to the separation of the two layers, one layer composed of molten metallic soap and the other of an aqueous solution of glycerine, the pressure in the reactor should exceed the vapour pressure of the aqueous solution of glycerine at the temperature within the reactor; otherwise the aqueous solution will continue to boil and this boiling action will effect an agitation that will make it impossible to achieve a complete separation of the metallic soap from the glycerine in water solution. At this stage of the process the pressure is controlled so that the solution forms an essentially quiescent layer.

If the reactor is air-tight and the air initially present in the reactor is not expelled then the pressure will remain above the vapour pressure of the aqueous glycerine solution at all times during the course of the reaction and, therefore, it will be possible to obtain a phase separation once the reaction has been completed and the

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