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OIL SOLUBLE SOAP OF POLYCARBOXYLIC ACIDS 5

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No Drawing. Application December 19, 1949, Serial No. 133,957

14 Claims. (Cl. 252—35)

This invention relates to oil soluble soaps comprising polycarboxylic acids.

The new soaps are primarily useful in the manufacture of greases. In the past greases have been composed of a lubricating material such as an oil and a soap. The soaps have been metallic soaps of monocarboxylic acids, and particularly the fatty acids, having from eight to twenty-two carbon atoms in the chain. Of recent years the aluminum soaps have been highly favored, although calcium soap greases were probably the first known, and soaps of other metals, such as sodium, calcium, barium, magnesium, zinc, lead and lithium, were also recognized. Soaps of these metals may be produced hereunder.

Present greases are deficient in a number of respects. Of these the most important is the lack of ability of the greases to withstand working. While an oil does not wear out under use, greases hitherto known did. Standard working tests are known for greases, and a grease which stood up for 5000 strokes of the testing machine without breakdown was considered a good grease. By means of the present invention greases may be produced which show no substantial breakdown or deterioration between 5000 strokes and 100,000 strokes.

Another defect of present greases is that they do not set well at high temperatures. Thus, on a warm day it may be impossible to produce a satisfactory grease, and even after production of a grease at a low temperature, it tends to bleed or break down at a higher temperature. Greases may be produced with soaps of the present invention which will set at temperatures markedly above those heretofore possible, and which are stable at higher temperatures.

Another defect of greases up to the present time has been the inability to procure a very stiff grease without also making it grainy. The present soaps make it possible to produce stiffer greases without spoiling the structure of the grease.

It is also possible with the present soaps to produce greases with less soap than was heretofore required.

Dicarboxylic acid soaps of metals such as aluminum are not ordinarily oil soluble. By "soluble" it is not necessarily meant that the soap goes into a true solution, but simply that it have the ability to form a gel structure characteristic of a soap. It has been found, in accordance with this invention, that oil soluble soaps of polycarboxylic acids may be produced, provided such formation is carried out in conjunction with a reaction with a monocarboxylic fatty acid in which the monocarboxylic acid is in considerable excess. Suitable results have been obtained with dicarboxylic acids present in an amount of 0.5% to 25% of the total acid by weight. Normally, however, the ratio will be from 5% to 20% polycarboxylic acid by weight and 80 to 95% of monocarboxylic acid by weight.

The exact chemical basis for the solubility of the present product when the directly formed materials would not be soluble, is not known. It is postulated, however, that cross linkages are produced within the molecules so that highly linked structures of three dimensional characteristics soluble in oils are produced, solubility depending upon the preponderance of two dimensional chains in the molecules. Mere mixtures of separately formed polycarboxylic acid soaps and monocarboxylic acid soaps do not produce solubility in the polycarboxylic acid portions thereof.

The soaps of the present invention are preferably produced by saponifying the mixed acids with a strong base

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such as caustic soda, or some other alkali metal hydroxide, and then forming the final soap, if it is other than an alkali metal soap, by double decomposition. For example, in forming an aluminum soap the acids may be reacted with caustic soda in aqueous solution, then alum added until the pH of the solution is about 5. The aluminum soap is precipitated and may be filtered, dried and ground. The soap may then be mixed with oil to form a grease.

10 On the other hand, the entire grease forming operation may be carried out in one operation, the oil being present during the saponification.

The monocarboxylic acids employed may be varied widely. Conventionally almost all commercial acids are designated as "stearic" acid, even though much of the acid content may be other acids such as palmitic, myristic, behenic or other saturated or unsaturated fatty acids, usually between 8 and 22 carbon atoms to the molecule. The proportions of these acids do affect the ultimate soap and its grease forming properties. However, the commercial mixtures are varied, and it is usually impossible to duplicate exactly the fatty acid distribution even from a single source. Therefore the grease forming ability of any soap is usually somewhat subject to test and adjustment in combination with the oil with which it is used. Likewise the oil itself will vary in composition, although usually oils from a particular source have a reasonably fixed group of properties.

20 One of the advantages of the present soaps, however, is that they work equally well with oils of all origins. Past soaps were quite selective, some of them working well with paraffin base oils and others with Gulf Coast oils which have a higher asphaltic content.

The various soaps are not limited to the completely reacted materials. For example, aluminum is a trivalent metal, and it is, thus, possible to make mono, di or tri salts. Hitherto the aluminum di-stearate has been that usually employed. The present invention extends to the various salts.

30 In the past it has been suggested to use other monocarboxylic acids besides the stearic acid in order to improve gelling strength. These acids have some value and some defects, and they may be eliminated by the use of the present invention, or they may be included if desired.

The preferred dibasic acid of the present invention is sebacic. Another acid giving particularly good results is the dimer of linoleic acid, which is known commercially as Emery M461-R. Other acids are adipic, pimelic and suberic.

40 The monocarboxylic acid, of course, is not limited to the saturated acids. Unsaturated acids such as oleic or ricinoleic may be employed. Likewise hydroxy acids, such as hydroxy stearic acids, may be utilized.

50 The following examples illustrate the preparation of soaps:

Example 1

A mixture of 84 parts of hydrated lime with 1000 parts of 300 S. U. V. @ 100 oil was added to 640 parts of a 40:40:20 of stearic, oleic and sebacic acids. This mixture was then heated to 250° F. until saponification was complete. The mixture was then cut back to a 10.0% soap content with more oil. The grease was then run through a homogenizer. The worked penetration of the grease was 260-270.

A similar grease made without the dicarboxylic acid gave a penetration of 370 at the same soap content.

Example 2

70 95 parts of hydrogenated herring acids and 5 parts of sebacic acid were saponified with 22 parts of caustic soda in aqueous solution. Aluminum sulphate was added in excess until the solution had a pH of 5. The solid precipitate was filtered, washed, dried and ground. (Aluminum soap "A.") 6% of this product was dissolved in a mid-Continent oil (300 S. S. U. at 100° F.) at 300° F. to form a stiff gel. For comparative purposes a similar sample was made using 100 grams hydrogenated herring acid and no sebacic acid. (Aluminum soap "B.")

80 Comparative penetration results of greases (at 77° F.)

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containing 6% of soap "A" and "B" are shown in the following table:

	Soap "A"	Soap "B"
Unworked.....	177	210
60 Strokes.....	284	350
5,000 Strokes.....	305	430

Example 3

One part of lithium hydroxide and 6 parts of water were stirred together at 180° F. and then caused to react with 6.5 parts of 12-hydroxy stearate and 0.5 part of sebatic acid in 15 parts of a 100 S. S. U. @ 100° F. oil. At the end of the reaction the temperature was raised to 300° F. to eliminate the water from the mixture. Seventeen parts of oil were then added and the temperature was raised to 380° F. for 2 hours. The temperature was decreased to 200° F. by adding enough oil to give a lithium soap content of 12% and the entire composition was pumped through a 60 mesh screen. The worked penetration of the resultant mixture was 305. A similar run without the sebatic acid gave a grease that was too thin to take penetrations on.

Example 4

An aluminum soap was prepared in the same manner as described in Example 2, except that 90 grams of hydrogenated herring acid and 10 grams of sebatic acid were used (aluminum soap "C"). 6% of this material dissolved in the oil described in Example 2 by heating to 300° F. and then cooled to form a gel gave penetrations as follows:

Unworked	Worked	5,000
146	230	260

Example 5

A stearate was prepared in exactly the same manner as Example 2, using 95 grams of hydrogenated herring acid and 5 grams of Emery's 461R dimer acid (chemically the dimer of linoleic acid) (aluminum soap "D"). When 6% of this material was dissolved in the mid-Continent oil as described previously, penetrations obtained were as follows:

Unworked	60 Strokes	5,000 Strokes
175	285	335

Example 6

A soap made and treated as Example 2 except that raw materials were 90 grams of hydrogenated herring acid and 10 grams of Emery's 461R dimer acid (aluminum soap "E"). A grease made as in Example 2 containing 6% of this soap gave penetrations as follows:

Unworked	60 Strokes	5,000 Strokes
150	250	280

Example 7

In order to check the effect of higher concentrations of dicarboxylic acids a soap was made up using 85 grams of hydrogenated herring acid and 15 grams of Emery's 461R dimer acid. A grease made as in Example 2 containing 6% of this soap gave the following penetrations:

Unworked	60 Strokes	5,000 Strokes
165	255	290

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Aluminum stearate greases prepared by dissolving six parts of aluminum stearate with 94 parts of oil using the material described in Example 6 gave excellent results with all the different types of oils tried. Results with the various oils are shown in the following table.

In every instance it will be noted that the penetration or yield of the grease was superior for the soap prepared in Example 6, and in addition the change in penetration on working (delta value) was smaller in every instance than for soaps not containing the dicarboxylic acid.

As further evidence of the efficiency of the stearate prepared in Example 6, greases were made up using a lower percentage of stearate. The following tables show that products with contents as low as 3½% of aluminum stearate make greases of exceptionally good worked stability:

	Penetrations	
	60 Stroke	5,000 Stroke
Midcontinent Stock, 300 SSU @ 100° F.:		
4.0% Aluminum Soap "E".....	335	365
4.5% Aluminum Soap "E".....	310	345
5.0% Aluminum Soap "E".....	290	320
5.5% Aluminum Soap "E".....	270	300
6.0% Aluminum Soap "E".....	250	280
Gulf Coastal Stock, 65 SSU @ 210° F.:		
3.5% Aluminum Soap "E".....	335	365
4.5% Aluminum Soap "E".....	295	325
5.0% Aluminum Soap "E".....	270	300
6.0% Aluminum Soap "E".....	230	260

In order to determine the effect of oxidation resistance upon the finished grease, greases made up from the stearate described in Example 2 were subjected to test in a Norma Hoffman bomb. Oxygen pressure drop after 100 hours at 210° F. was three pounds or less for all greases made with Pennsylvania base structure. This showed that the stearates have no effect upon the oxidation resistance of the finished grease.

The monocarboxylic acids employed may be hydrogenated vegetable fatty acids, hydrogenated fish acids, hydrogenated animal fatty acids, or naturally occurring fatty acids. Among the latter may be listed stearic, palmitic, myristic, 12-hydroxystearic, 9,10-dihydroxystearic, oleic, lauric, behenic and ricinoleic.

The foregoing detailed description is given for clearness of understanding only and no unnecessary limitations should be understood therefrom as modifications will be obvious to those skilled in the art.

We claim:

1. A polyvalent metal soap characterized by solubility in oil to form a grease, said soap comprising soap molecules co-formed by reaction of the polyvalent metal ions with mixed mono and polycarboxylic acids, the proportion of the polycarboxylic acid being from 0.5% to 25% of the total carboxylic acid by weight and the monocarboxylic acid being predominantly a fatty acid having from 8 to 22 carbon atoms.

2. A soap as set forth in claim 1 in which the polycarboxylic acid is a dicarboxylic acid in a proportion of from 0.5% to 25% of the total of mono and dicarboxylic acids by weight.

3. A soap as set forth in claim 1 in which the polycarboxylic acid is a dicarboxylic acid in a proportion of from about 5 to 20% of the total of mono and dicarboxylic acids by weight.

4. An aluminum soap characterized by solubility in oil to form a grease, said soap comprising soap molecules co-formed by reaction of the aluminum ions with mixed mono and polycarboxylic acids the proportion of the polycarboxylic acid being from 0.5% to 25% of the total carboxylic acid by weight, and the monocarboxylic acid being of the class consisting of the fatty acids containing from 8 to 22 carbon atoms.

5. A soap as set forth in claim 4 in which the monocarboxylic acid is predominantly hydrogenated herring oil.

6. A soap as set forth in claim 4 in which the polycarboxylic acid is a dibasic acid.

7. A soap as set forth in claim 4 in which the polycarboxylic acid is sebatic acid.

8. A soap as set forth in claim 4 in which the polycarboxylic acid is the dimer of linoleic acid.

9. A calcium soap characterized by solubility in oil

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to form a grease, said soap comprising soap molecules co-formed by reaction of the calcium ions with mixed mono and polycarboxylic acid the proportion of the polycarboxylic acid being from 0.5% to 25% of the total carboxylic acid by weight, and the monocarboxylic acid being of the class consisting of the fatty acids containing from 8 to 22 carbon atoms.

10. A polyvalent soap comprising a polyvalent metal salt characterized by solubility in oil to form a grease, said soap comprising soap molecules co-formed by reaction of the polyvalent metal ions with mixed mono and polycarboxylic acids, the proportion of the polycarboxylic acid being from 0.5% to 25% of the total carboxylic acid by weight, and the monocarboxylic acid being of the class consisting of the fatty acids containing from 8 to 22 carbon atoms.

11. A soap as set forth in claim 10 in which the monocarboxylic acid comprises largely stearic acid.

12. The method which comprises saponifying a fatty acid having from 8 to 22 carbon atoms with an alkali metal hydroxide in the presence of 0.5% to 25% of a

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polycarboxylic acid, and then forming an aluminum soap by double decomposition.

13. A soap as set forth in claim 10 in which the monocarboxylic acid is 12-hydroxystearic acid.

14. A soap composition consisting essentially of aluminum salt of a mixture of about 1% to 20% by weight of dimerized polyunsaturated fatty acids of 18 carbon atoms and about 99% to 80% of monomeric fatty acid of 12-22 carbon atoms.

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