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ALUMINUM SOAP HYDROCARBON THICKENER WITH INCREASED SOLVATION

Rudolph R. Leverberg, Metuchen, and Frederick Neil Baumgartner, Plainfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention relates to the production of improved basic metal soaps of aliphatic carboxylic acids for use as thickeners of hydrocarbon oils. It relates more particularly to the improvement of basic aluminum disoaps formed from relatively lower molecular weight aliphatic or fatty acids by addition of minor or small amounts of less water-soluble higher aliphatic and fatty acids after the precipitation or dispersion of the soaps but before filtration and washing.

In a conventional preparation of the soaps useful for hydrocarbon thickening purposes, a water-soluble salt of the metal to be used in the soap is added to an aqueous solution of an alkali metal salt of an aliphatic or fatty acid, or mixtures thereof, such aqueous solution having about 50% excess caustic. The preferred metal to be used in the thickening soap is aluminum; accordingly, a water-soluble aluminum salt, generally referred to as alm, such as aluminum sulfate, aluminum chloride, etc. is added for precipitating the aluminum soap from the alkaline aqueous solution of an alkali metal salt. After precipitation, the soap precipitate is filtered, washed, then dried. It has been found that in using aliphatic or fatty acids of relatively low molecular weight, e.g. the C₈ acids, such as 2-ethyl hexoic acid or other such acids in the range of C₂ to C₁₀, the thickening soap product formed does not gel a hydrocarbon liquid without prolonged mixing and thus is unsatisfactory.

A significant product evaluation test for determining the rate of gel formation of the thickening soaps is known as the vortex time. The vortex time is a measure of time in minutes for thickening a given hydrocarbon liquid to a point where settling of the thickening soap will not occur. In this test the thickening soap is added rapidly to the organic solvent (e.g. gasoline) which is to be thickened while the mixture is stirred at a controlled speed and temperature. Short vortex times are generally desirable. For example, thickening soaps which give vortex times up to 10 minutes are acceptable, although soap products which give vortex times less than 10 minutes are much more desirable. Many commercially produced soap thickeners on the same basis have been found to possess vortex times of 30 minutes or longer and are thus unsuitable. Many thickeners on aging have been found to have their vortex times increased to well over 10 minutes and thus become quite unsuitable.

By analysis of thickening soap products found to give long vortex times or to show poor solvation in hydrocarbon liquids, it was discovered that such products possessed a low free fatty acid and a high excess hydroxide content, which for analytical purposes is expressed in terms of Al(OH)₃. In other words, the mole ratio of the free acid (FA, to said excess hydroxide content, Al(OH)₃ is low, and at the same time, the excess hydroxide content of the soap is high. There are indications from the studies of the soaps, that those formed from aliphatic or fatty acids having appreciable solubility in water have the free organic acids removed in the washing step, leaving unreacted hydroxide to render the soap particles more impervious to the action of solvents which

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are to be gelled. The soap particles left more impervious to the action of the solvents on contact with the hydrocarbon or other organic solvents have a lower rate of solvation which shows up in lengthened vortex time.

The foregoing difficulties are overcome by adding to the precipitated soap product formed from an aliphatic or fatty acid of lower molecular weight and appreciable water-solubility a small quantity of aliphatic or fatty acid having a higher molecular weight and less water-solubility.

Examples of aliphatic or fatty acids of higher molecular weight and less water-solubility useful for improving the thickening soaps formed from the lower molecular weight organic acids are such as obtained from the naturally occurring coconut oil, which include principally acids having above 8 carbon atoms per molecule, e.g. capric, lauric, myristic, palmitic, stearic, oleic, linoleic, dimerized linoleic, etc. Other high molecular weight fatty acids, like those in coconut fatty acids, are obtainable from plant and animal sources, e.g. palm kernel oil, and animal fats. The higher molecular weight aliphatic carboxylic acids may also be produced synthetically as by oxidation of hydrocarbons, aldehydes, etc. and may be obtained from petroleum oils, e.g. naphthenic acids.

For the sake of brevity, all of the organic acids that are of use, including fatty acids and aliphatic carboxylic acids, straight chain, branched chain, cyclic, saturated and unsaturated, will be referred to as aliphatic acids.

Since the higher acids may be added to the soaps of the lower aliphatic acids for their improvements after the lower aliphatic acid soaps have been precipitated, the higher acids need not react to form the soaps themselves. The higher acids are advantageously added after the precipitation, but before filtering, and before washing, and are not removed by the washing to any substantial extent.

The quantity of higher organic acids added to the precipitated thickening soaps formed from the lower acids can be economically kept to a minimum depending on the excess hydroxide content of the soap to be improved. In general, sufficient amount of the higher acid is preferably added to give an FA/Al(OH)₃ molar ratio of from 0.1 to 1.0. At the same time, the quantity of excess hydroxide present will determine at which point in this range the ratio of the free acid to the excess hydroxide in the product should lie. For example, normal soap products which contain small amounts of excess hydroxide, are improved by adding the higher acid to make the FA/AL(OH)₃ mole ratio be in the range of 0.1 to 0.5 approximately; while the soap products having a somewhat higher amount of excess hydroxide, e.g. more than 1% by wt. calculated as Al(OH)₃, are improved in their solvation rate (decreased vortex time) by adding sufficient higher acid to give the soap an FA/Al(OH)₃ mole ratio in the range of approximately 0.5 to 1.0.

An illustration of the foregoing method of improving the soap products follows:

TABLE I

| Soap Thickener | Excess Hydroxide as Percent Al(OH) ₃ | Mole Ratio, FA/Al(OH) ₃ | Vortex Time, Min. | Gel Strength 2%, 150° F. |
|----------------|---|------------------------------------|-------------------|--------------------------|
| Soap A..... | 1.7 | 0.05 | 20 | 230 |
| Soap B..... | 0.9 | 0.70 | 10 | 200 |

Soap A—Aluminum ethyl hexoate soap by normal preparation.
Soap B—Aluminum ethyl hexoate soap by normal preparation plus 0.8 wt. percent coconut acids added prior to filtration and washing.

It is to be observed that the addition of the small amount of coconut acids for obtaining the improved Soap B brought the percent of excess hydroxide down below approximately 1.0% as $\text{Al}(\text{OH})_3$ and increased the $\text{FA}/\text{Al}(\text{OH})_3$ mole ratio to above 0.1, thereby reducing the vortex time by 50% to an acceptable 10 minutes without appreciable change in the gel strength or consistency. In any event, the gel strength or consistency remained at a satisfactory level so long as the amount of added acid was not excessive.

It is to be understood that various components of the coconut oil acids or similar fatty acids from other sources and their mixtures may be used. The best amounts of the coconut acids to be added similarly should be determined for each soap which is to be improved in accordance with the present invention.

To estimate the free fatty acid in the soap, the soap is extracted with a suitable selective extraction solvent. Isooctane has been used at low temperatures, but a better solvent is anhydrous dimethylformamide which extracts the free fatty acid at ordinary temperatures in the range of 15° to 40° C. without dissolving the thickener even on prolonged standing. One or more extractions may be made with the solvent to remove all the free fatty acid from a given sample. Two extractions with anhydrous dimethylformamide are sufficient to remove all free fatty acid since subsequent extractions showing no titratable acid indicate a complete removal of the free acid with no decomposition of the thickener. Of course, the soaking in the solvent could be excessive; therefore, it was found best to use four successive extractions. The extractions are carried out rapidly to insure a minimum of decomposition. The extraction may be carried out by placing a weighed amount of the soap thickener on a sintered support in a glass funnel fitted into the upper part of a filter flask. Using a 2 gram sample, 25 ml. anhydrous dimethylformamide is added to the funnel to pass through the soap in finely divided and wet condition. Vacuum may be applied to expedite passage of the solvent through the sample. Additional similar amounts of the solvent are added for repeating the above step three more times, although for some soaps two extractions are sufficient. 10 ml. distilled water is added for each extraction and 3 to 4 drops of phenolphthalein are added. The diluted combined extracts containing the indicator are then titrated with 0.1 NaOH to an end point stable for 15-20 seconds. A blank, similar solution of the solvent containing no extract is titrated. The percent free fatty acid (FA) is then found by the following calculation:

$$\frac{(\text{Ml. NaOH for samples} - \text{ml. NaOH for blank}) \times 14.42 \times N \text{ NaOH}}{\text{Sample weight}}$$

=percent free fatty acid (FA) (as eaprylic acid)

The total fatty acid content of the soaps is determined by decomposing a soap with HCl of determined amount and the liberated fatty acid extracted is titrated with a standardized sodium hydroxide solution in a well-known manner.

The use of anhydrous dimethylformamide as a selective solvent for removing the free organic acids from the thickening soaps is described and claimed in an application, Serial Number 617,663, filed October 22, 1956, now U.S. Patent No. 2,884,430, for F. N. Baumgartner.

The percentage of excess hydroxide as $\text{Al}(\text{OH})_3$ can be determined by analyzing for the total aluminum in the soap, then subtracting from the equivalent total $\text{Al}(\text{OH})_3$ the amount of the aluminum combined with the fatty acid as in a disoap. The total aluminum content of the soap can be determined by the classical hydroxide precipitation and ignition method. In this analysis an addition of an ashless white mineral oil to the precipitate prior to ignition prevents loss of powder. All organic material is burned to leave the aluminum oxide residue by heating the ignition residue for 4 to 6 hours

in a muffle furnace at 1600° F. The calculation of the percentage $\text{Al}(\text{OH})_3$ is given as follows:

$$\text{Percent Al}(\text{OH})_3 = \frac{\text{Percent Al}}{27} - \frac{\text{Percent Al}(\text{OH})(\text{RCO}_2)_2}{\text{Molecular wt. Al}(\text{OH})(\text{RCO}_2)_2} \times 78$$

In the above formula (RCO_2) represents the radical of the fatty acid combined with the aluminum which is also combined with the hydroxide group (OH) .

The aluminum soaps can be prepared by the addition of aqueous solutions of aluminum salts to solutions of sodium or potassium soaps of the fatty acids in the presence of excess alkali. The term excess alkali refers to the amount of alkali hydroxide used over that required for saponification. The aluminum soaps can be prepared in nonaqueous solvents by reaction between fatty acids and aluminum alkoxides. Soaps have been prepared in this way from acetic acid and higher fatty acids, both saturated and unsaturated, acyclic and cyclic. There are other variations in the preparation of the soaps, but the present invention is not concerned with the steps of making the soap except with regard to the improvement of increasing the $\text{FA}/\text{Al}(\text{OH})_3$ mole ratio.

For the purpose of comparison preparation of soaps from lower fatty acids were made in accordance with the following example:

Example

To a measured amount of distilled water, 4243 grams, in the reaction vessel was added a calculated amount of sodium hydroxide (4.5 moles for 3.0 moles of 2-ethyl hexoic acid). When all the caustic had dissolved, the required amount of 2-ethyl hexoic acid, i.e. 3.0 moles, was added. The resulting soap solution was stirred for 10 to 15 minutes and brought to the desired temperature of 35° C. The alum solution (2.18%) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was then added at a controlled rate. The alum solution was made up of 0.86 mole of the aluminum salt and 1560 grams water. The reaction mixture was stirred for about 10 minutes following completion of the alum addition. The mixture was then transferred to a filter and washed. The wet filter cake product was dried in an oven at elevated temperatures in the range of 47° to 82° C., and the dried product was pulverized, then ready for packaging or use as a thickener of hydrocarbon oil.

The resulting product was compared with a commercial soap product which had been prepared in conventional manner. The comparison is shown in the following table:

TABLE II

| Soap Thickener | Percent $\text{Al}(\text{OH})_3$ | $\text{FA}/\text{Al}(\text{OH})_3$ | Vortex Time, Min. |
|--------------------------|----------------------------------|------------------------------------|-------------------|
| Commercial Soap—C..... | 2.5 | 0.081 | 55 |
| Experimental Soap—D..... | 1.7 | 0.045 | 20 |

The comparison in Table II shows that the low $\text{FA}/\text{Al}(\text{OH})_3$ ratio and high percentage of $\text{Al}(\text{OH})_3$ gave the commercial product the undesirable high vortex time of 55 minutes. Even the freshly prepared Soap-D by the conventional procedure could be improved in accordance with the present invention.

The variations and deficiencies of the different commercial products may be due to a number of factors. The high excess hydroxide and low free fatty acid contents may be originally due to incomplete reaction during precipitation followed by overwashing. Incomplete reaction may be caused by a multitude of factors, including inadequate mixing, incorrect addition of the alum, and prolonged hydrolysis. As stated, with aging for several months the condition of the thickener becomes

worse and vortex times of one hour or more are commonly found.

As pointed out in the foregoing parts, the soaps having poor solvation properties are improved by a treatment with an aliphatic carboxylic or fatty acid of relatively low-water solubility and thereby are made to meet specific requirements without altering or damaging other desirable properties appreciably. The fatty acid treatment of the soaps involves the following steps:

- (1) Dispersion of the poor soap thickener in suitable medium, preferably water.
- (2) Addition of the aliphatic acid having a relatively low water solubility, preferably of higher molecular weight than the acid used in forming the soap.
- (3) Filtration, preferably by centrifuge.
- (4) Redrying to the desired moisture content.

It is apparent that the method of dispersing the soap to be improved in water is immaterial as long as adequate dispersion is obtained. When the freshly prepared soap is being improved, the addition of the higher molecular weight fatty acid is made to the precipitated soap prior to filtering. Any satisfactory filtering and drying technique may be used without deviating from the objects of the invention.

The quantity of fatty acid which is added depends largely on the following factors:

- (a) The molecular weight and water-solubility of the acid saponified:
- (b) The excess (OH) content of the soap:
- (c) The free acid content of the soap.

The last two quantities may be determined from the total aluminum analysis, total fatty acid, and free fatty acid analysis, as previously described. In general, it is desirable to make the soap contain a total free fatty acid (including aliphatic acid added) to excess hydroxide mole ratio in the range of 0.05 to 1.0. However, the exact amount of fatty acid to be added and the exact ratio of FA/Al(OH)₃ is readily determined by experiment so that the quantity of the fatty acid added is changed until the product gives the desired vortex time.

The following examples additionally show how the invention has been demonstrated and applied.

A variety of commercial soaps showing poor solvation properties, i.e. high vortex times, were treated with coconut acids in amounts of 0.87% to 1% by weight based on the dry soap samples. The soap samples were first dispersed in water, a 150 gram sample being mixed with 1800 ml. H₂O using a dispersator. To the dispersion mixtures 1.3 g. of coconut acids were added and mixing was continued. The mixture was then filtered by centrifuging and the soap product separated from liquid was dried at 49° C. for 2½ hours in a forced draft oven.

The following comparative data is representative of the improvement made by adding the coconut fatty acids:

TABLE III

| Sample | Vortex Time | Gel Strength, 2% at 150° F. |
|----------------------|-------------|-----------------------------|
| Commercial Soap..... | 50 | 260 |
| Treated Soap..... | 7 | 280 |

In the above table the treated commercial soap was made by adding 0.87% coconut fatty acids. The treated soap was given a very satisfactory lowered vortex time of 7 minutes. This treated soap had unimpaired gel strength. Similar tests were made using an added wetting agent and the improvement by the added fatty acid was of similar order. It is to be understood that the examples given are for the purpose of illustration, and are not intended to limit the scope of the invention.

The hydrocarbon oil thickening soaps, methods for their preparation, and the uses are well known and the present invention is not concerned therewith except for the improvement which is described and claimed herein.

- 5 The thickening soaps are used as thickeners or gelation agents in various hydrocarbon liquids, e.g. gasoline, naphtha, kerosene, heat oil, lubricating oils, other distillates, and mixtures of such distillates, which also may contain other dissolved or dispersed materials. The soaps are considered to be polymeric in structure, both in the solid state and in hydrocarbon solution. They are characterized by their ability to form with hydrocarbon oil, gels of high viscosity.

- 15 Usually the aluminum disoaps requiring solvation improvement have been found to contain less than 1 wt. percent and even less than 0.5 wt. percent free aliphatic acids corresponding to the aliphatic acids combined in the soap. These soaps have been well improved in solvation properties by adding 0.5 to about 1 wt. percent of an aliphatic acid, preferably an aliphatic acid more difficult to wash out.

In the solvation improved disoap products, the basic aluminum disoap units may be represented by the formula:



- wherein (RCO₂) is a carboxylic radical of an aliphatic acid, RCOOH, having appreciable water-solubility, e.g. 2-ethylhexoic acid or isoocotic acids, R thus being an aliphatic hydrocarbon group of 7 carbon atoms. Associated with the disoap units are units containing more than one (OH) group for each aluminum atom and these are the excess hydroxide groups. A small amount of the aliphatic acid, RCOOH, having appreciable water-solubility will tend to be present as free acid, e.g. occluded by the disoap units. To achieve improved solvation, the total free acids present is made to include another aliphatic carboxylic acid of still lower water-solubility, and thus generally, of higher molecular weight than the acid combined in the disoap. Moreover, frequently the acid of lower water-solubility added to increase the total free acid content of the disoap product will be present in higher proportion of the total free acid than the aliphatic acid indicated to be mainly combined in the disoap.

What is claimed is:

- 45 1. The method of improving a hydrocarbon oil soap thickener in solvation properties, said soap being a basic aluminum disoap of an aliphatic carboxylic acid having 8 to 10 carbon atoms per molecule which comprises dispersing said soap thickener in a liquid medium in which the soap is not soluble, adding to the thus dispersed soap thickener an aliphatic carboxylic acid of relatively higher molecular weight and of lower water solubility than the acid in the disoap in relatively small amount to increase free aliphatic carboxylic acid content of the soap, filtering and washing the soap thus increased in free acid content and recovering a soap that has a mole ratio of total free aliphatic carboxylic acid to excess hydroxide of 0.05 to 1.0.
- 55 2. The method as described in claim 1 wherein the soap thickener is aluminum di-2-ethyl hexoate, the liquid medium is water, and the added higher molecule weight aliphatic acid is a coconut oil acid having more than 8 carbon atoms per molecule.
- 60 3. The method of improving the solvation properties of a hydrocarbon oil soap thickener which comprises adding a water-soluble aluminum salt to an alkali metal salt of an aliphatic carboxylic acid having 8 to 10 carbon atoms per molecule whereby an aluminum soap of said C₈ to C₁₀ aliphatic carboxylic acid is precipitated, adding to said aluminum soap a sufficient amount of higher aliphatic carboxylic acid having more than 8 carbon atoms per molecule and a lower water solubility than said C₈ to C₁₀ aliphatic carboxylic acid to obtain a mole ratio of total free aliphatic carboxylic acid to excess hydroxide of 0.05

to 1.0 in said aluminum soap, filtering and washing said aluminum soap with a substantial quantity of water and drying said aluminum soap prior to mixing it with said hydrocarbon oil.

4. The method as described in claim 3 wherein the C_8 to C_{10} aliphatic carboxylic acid used to prepare the aluminum soap contains 8 carbon atoms per molecule. 5

5. The method as described in claim 3 wherein the C_8 to C_{10} aliphatic carboxylic acid used to prepare the aluminum soap is 2-ethyl hexoic acid. 10

6. The method of improving the solvation properties of a hydrocarbon oil soap thickener which comprises adding a water-soluble aluminum salt to an alkali metal salt of a C_8 aliphatic carboxylic acid whereby an aluminum soap of said C_8 aliphatic carboxylic acid is precipitated, adding about 0.5 to 1 weight percent of coconut aliphatic carboxylic acid to said aluminum soap filtering and washing said aluminum soap with a substantial quantity of water and drying said aluminum soap prior to mixing it with said hydrocarbon oil. 15
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