

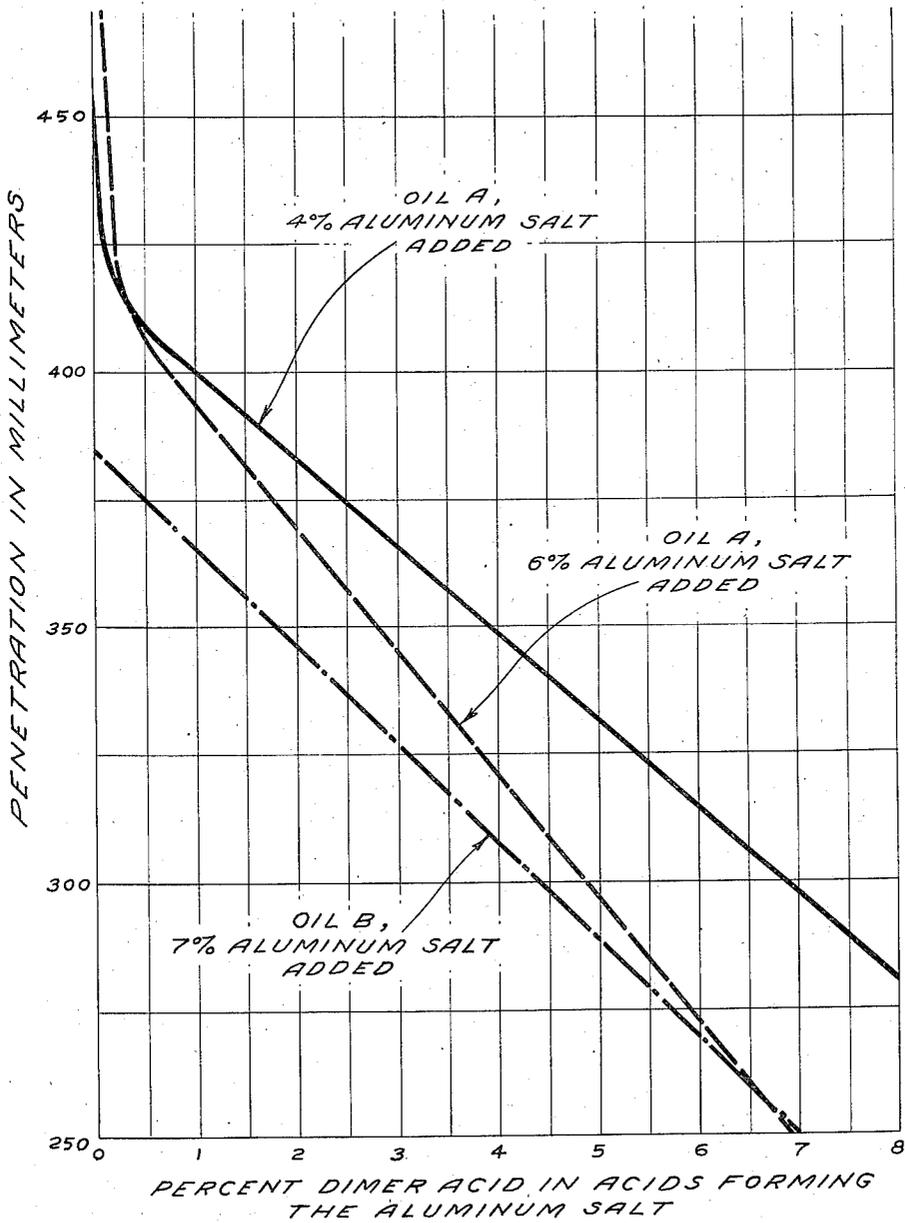
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ALUMINUM SOAP COMPOSITIONS AND GREASES CONTAINING THEM

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ALUMINUM SOAP COMPOSITIONS AND GREASES CONTAINING THEM

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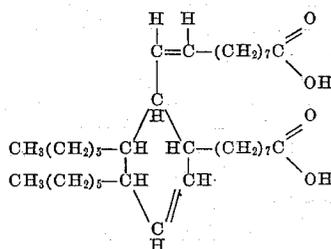
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7 Claims. (Cl. 252-35)

1

This invention relates to aluminum soap compositions of value in grease making, and to greases containing them. More particularly, the invention relates to the aluminum salts of dimerized polyunsaturated fatty acids of approximately 18 carbon atoms, to aluminum salts of mixtures of these dimer acids with fatty acids of 12-22 carbon atoms, and to grease compositions containing the mixed aluminum salts with or without the addition of small quantities of glycerine.

The heat-polymerization or dimerization of drying and semi-drying oil fatty acids of the type of linseed fatty acids, soybean fatty acids, cottonseed fatty acids and the like is well known. The polymerization products were studied and their structural formulas were described by T. F. Bradley in *Industrial and Engineering Chemistry* 32, 802-809 (1940). The dimers which result from the heat treatment of the fatty acids of drying and semi-drying oils at temperatures above 300° C. are dicarboxylic acids of approximately 36 carbon atoms; the product obtained by the heat polymerization of octadecadienoic acids is typical and corresponds to the following structural formula:



The present invention is based on the results which we have obtained by an investigation of the aluminum salts of this class of dicarboxylic acids, and particularly the aluminum salts of mixtures of from 0.5-1% to about 20% of the dimer acids with from 80% to 99.5% of monomeric aliphatic acids of 12-22 carbon atoms. Briefly, we have discovered that while the aluminum salts of the pure dimer acids do not increase substantially the viscosity of hydrocarbon solvents or dispersants such as lubricating oils, the corresponding aluminum salts of mixtures of these dimer acids with monomeric saturated higher fatty acids possess excellent gel-forming powers. This discovery has enabled us to prepare lubricating greases of improved gel strength or, if desired, greases of conventional gel strength containing smaller quantities of aluminum soaps.

Any of the commercially obtainable mixtures of higher fatty acids which contain polyunsaturated acids of approximately 18 carbon atoms may be used in preparing the dimer acids employed in practicing our invention. Typical sources of supply are cottonseed fatty acids having an

2

iodine-bromine value of 104-7, sesame oil fatty acids with an iodine value of 103-9, soybean acids having an iodine value of about 135-140, dehydrated castor oil fatty acids and the like. Other sources, the utility of which will be explained later, are commercial oleic acid, tall oil fatty acids, cottonseed foots acids and the like. Any of these fatty acid mixtures may be dimerized by the method described by Bradley; i. e., by heating their methyl esters at temperatures of 300-325° C. for 5-24 hours or longer, removing the monomer acids by distilling at 1 mm. of mercury pressure with the introduction of carbon dioxide at temperatures of about 200° C., and liberating the dimer acids from their methyl esters. A more convenient method, however, consists in heating the fatty acid mixtures in a closed vessel and in the presence of about 2-4% of steam at about 330 to 360° C. and 85-400 lbs. per square inch pressure for about 5 to 8 hours, followed by removal of the unpolymerized acids by vacuum distillation.

In preparing the aluminum soaps of high gel-forming power a mixture of dimer acid and monomeric higher fatty acids is used. Accordingly, for some purposes it is unnecessary to distill off the unpolymerized acids after heat treatment. Where a soap of an acid mixture having an iodine value about 90-100 is acceptable the product from the heat polymerization may be converted directly into its aluminum soap, or the material may be mixed with additional quantities of saturated or unsaturated higher fatty acids of 12-22 carbon atoms to obtain a product containing from about 1% to about 20% of dimer acids. Where the presence of unsaturated higher fatty acids is undesirable, as may be the case in grease making, the product from the heat polymerization may be hydrogenated at temperatures of 180-200° C. in the presence of an active nickel or copper hydrogenation catalyst.

When the purified dimer acids of approximately 36 carbon atoms are converted into aluminum salts the product is a white, amorphous solid which is insoluble in water but slightly soluble in and miscible with aliphatic and aromatic hydrocarbons at ordinary temperatures. Dispersions of from 1% to 10% of this new aluminum salt in hydrocarbon lubricating oils have been prepared, but these do not have the high viscosity normally associated with greases. On the other hand, the aluminum salts of mixtures of these dimer acids with monomeric saturated fatty acids, in the ratio of about 0.5-1% to 20% of the dimer acid and 85-99.5% of the monomer acid, possess excellent gel-forming properties. The aluminum salts of these mixtures are also white, amorphous and water-insoluble compounds.

The aluminum salts of mixed dimer acids and higher fatty acids of 12-22 carbon atoms, which

3

are claimed as new compositions of matter, are preferably prepared from the alkali metal salts or soaps of these acids. These alkali metal soaps are preferably formed by introducing the mixed acids slowly into an aqueous solution of sodium or potassium hydroxide or carbonate with vigorous agitation. The corresponding aluminum salts are precipitated from the resulting soap solutions by mixing them with an aqueous solution of aluminum sulfate, aluminum chloride or other inorganic, water-soluble aluminum salt. The formation of the aluminum salts or soaps of the organic acids is preferably carried out at elevated temperatures on the order of 40–75° C. and with vigorous agitation in order to obtain a product that can be more readily filtered and washed. After the aluminum salt formation is complete the precipitate is filtered and washed with hot water until it is substantially free from water-soluble salts, after which it is dried at temperatures up to 100–110° C.

The new aluminum salts of our invention may be used in grease making by any of the commercially acceptable methods. Thus, for example, quantities of from 1% to 20% of the aluminum soaps may be mixed with from 99% to 80% by weight of a hydrocarbon lubricating oil having a Saybolt viscosity of 100–120 sec. at 210° F. The mixture of oil and aluminum soap is preferably heated to temperatures of 120–140° C. and maintained within this range for a few minutes to permit the transformation of the gel to a jelly, after which the grease is cooled to its gel temperature and then more slowly to room temperature.

We have also found, as another important feature of our invention, that greases having reduced thixotropy can be obtained by adding glycerine or other aliphatic polyhydric alcohol along with our new aluminum soaps. This is most conveniently done by mixing the glycerine with the soap before it is added to the lubricating oil. In the preferred aluminum soaps, which are prepared from mixtures of 96% to 92% of fatty acids of 12–22 carbon atoms and 4% to 8% of dimer acids, we find that the addition of about 1% to 8% of glycerine is sufficient. However, when the soaps contain relatively large quantities of dimer acids such, for example, as 12–20% or more of the total organic acids, the proportion of glycerine can advantageously be increased to as much as 50%. This is because the gel-forming power of the dimer acid-fatty acid soaps in lubricating oils appears to go through a maximum at about 10% dimer acid when this property is measured in greases which have been worked for 60 strokes or more just prior to testing whereas this maximum is not noted in testing the same greases prior to working. Addition of the indicated quantity of glycerine overcomes to a great extent this difference between worked and unworked greases.

The greases of our invention are therefore composed of a major proportion of hydrocarbon lubricating oil of suitable viscosity having dispersed therein a minor quantity, usually within the range of 1% to 20% and preferably 4% to 8% by weight, of our new aluminum soaps and from 1–50% and preferably 1–8% of glycerine based on the weight of the soap. Other known or approved ingredients may also be present; thus, for example, the sodium, potassium and ammonium soaps of higher fatty acids of 12–22 carbon atoms are frequently used in grease making and may be added if desired. Antioxidants such

4

as tetramethyldiaminodiphenylmethane may also be added in amounts of 0.01% to 1% or more.

The invention will be further illustrated by the following specific examples. It should be understood, however, that although these examples may describe in detail certain of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

Example 1

A heat-polymerized polyunsaturated fatty acid was obtained by heating cottonseed fatty acids having a water content of about 3–4% for 6 to 8 hours at 330–360° C. in a closed vessel, followed by removing the unpolymerized acids by distillation under reduced pressure. The product had an iodine value of 80–95, an acid number of 186 and contained less than 3% of unsaponifiables.

A solution of 94.5 grams of sodium hydroxide in 4.75 liters of water was prepared at 70° C. and 300 grams of the dimer acid was added slowly with stirring. When the soap formation was complete it was mixed with a solution of 240 grams of an aluminum sulfate having an Al₂O₃ content of 17% in 580 cc. of water. The aluminum soap was precipitated at 70° C., and was washed with hot water until substantially free from sodium sulfate and dried to a moisture content of about 0.3%.

The product was an amorphous white powder which was stable on heating to 230° C. Between 230° and 240° C. it turned slightly brown and at 280° C. it decomposed without melting. Analysis showed it to contain 12.0% of Al₂O₃, which corresponds to a mixture of about 58% of a salt containing one aluminum atom for each mol of dimer acid and 42% of a salt containing 2 atoms of aluminum for each dimer acid molecule. This salt does not greatly increase the viscosity of hydrocarbon lubricating oils of 100–120 seconds viscosity when added thereto in amounts of 5% to 15%. This is the direct opposite of the results that are obtained when these amounts of the corresponding aluminum soaps of monomeric saturated higher fatty acids are added to the same oils.

Example 2

An alum solution was prepared by dissolving 410 lbs. of aluminum sulfate (17% Al₂O₃) in 1700 lbs. of water at 65° C.

A soap solution was made by adding with agitation a mixture of 732 lbs. of hydrogenated fish oil fatty acids and 34 lbs. of the dimerized cottonseed fatty acids described in Example 1 to a hot (65° C.) solution containing 314 lbs. of 50% NaOH in 12,000 lbs. of water. The hydrogenated fish oil acids had the following approximate analysis:

C ₂₁ H ₄₃ COOH	-----per cent---	20
C ₁₉ H ₃₉ COOH	-----do----	20
C ₁₇ H ₃₅ COOH	-----do----	23
C ₁₅ H ₃₁ COOH	-----do----	30
C ₁₃ H ₂₇ COOH	-----do----	7
Average molecular weight	-----	288

A charge of 11,000 lbs. of water at 65° C. was placed in a mixer having an impeller agitator and the soap solution and alum solution were added together in thin streams with vigorous agitation. The resulting aluminum soap was filtered, washed with hot water, pressed into pellets and dried at 100–110° C. The product was a

5

white, amorphous water-insoluble powder that melted between 145° C. and 160° C. Analysis showed it to contain 8.4% of Al₂O₃ and 0.3% moisture; the acid value was 13.1. The product had the following solubilities expressed as grams per 100 grams of solvent:

Solvent	25° C.	50° C.
CH ₃ OH.....	0.288	0.945.
Toluol.....	2.271	Gelled.
Alpha-Pinene.....	0.805	100% Soluble.
Stoddard.....	0.323	0.611.

Example 3

The procedure of Example 2 was repeated, but a mixture of 60 grams of the dimer acid and 940 grams of the hydrogenated fish oil acids was added to 408 grams of 48% NaOH in 1575 grams of water followed by reaction with 2200 grams of a 25% alum solution.

Example 4

A mixture of 950 grams of fatty acids from hydrogenated tallow and 50 grams of the dimer acid was used. The aluminum soap was prepared as in Example 2.

Example 5

Using the procedure of Example 2 an aluminum soap was prepared from a mixture of 80 grams of the dimer acid and 920 grams of hydrogenated tallow acids.

Example 6

An aluminum soap containing 10% of dimer acid soap, based on the weight of the carboxylic acids, was prepared from a mixture of 100 grams of the polymer acids and 900 grams of hydrogenated tallow acids.

Example 7

Many of the commercial grades of oleic acid contain a small proportion of octadecadienoic acids. An oleic acid of this type was heated in an autoclave for 3 hours at 340–350° C. in the presence of steam. Analysis of a sample of the product showed it to contain about 15% of dimer acid and about 85% of oleic acid.

To a 2000 gram portion of this material there was added 120 grams of finely divided Raney nickel catalyst and the mixture was introduced into an autoclave provided with heating coils and an agitator, heated with agitation to 180–200° C., and hydrogenated under 1500 lbs. per square inch pressure of hydrogen until the iodine value was reduced to 75.

One kilogram of this product was added slowly to a solution of 195 grams of sodium hydroxide in 2 liters of water at 70° C. followed by precipitation of the aluminum soap by mixing with a hot aqueous solution of aluminum sulfate. The product was washed with hot water, pelleted and dried to a moisture content of 0.4 by heating at 90–100° C. The dry aluminum salt was a white, water-insoluble powder that dispersed easily in hydrocarbon lubricating oil and possessed good gel-forming properties.

Example 8

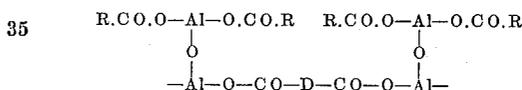
Greases were prepared by mixing varying quantities of the aluminum soaps described in Examples 2 to 6 with two hydrocarbon lubricating oils. One of these, designated as Oil A, was a mixed Pennsylvania and Mid-Continent stock

6

having a viscosity of 119 sec. at 210° F. Oil B was a Mid-Continent stock having a viscosity of 100–105 sec. at 210° F. The greases were made by thoroughly mixing the soaps with the lubricating oil, heating the mixture with agitation to 125° C., holding at this temperature for 4–5 minutes and cooling slowly to room temperature in an insulated oven.

The greases so prepared were tested for gel strength by the standard A. S. T. M. penetrometer method (Test D 217–48) as described in "1948 Supplement to A. S. T. M. Standards," Part III—A, pages 88 to 96. The results obtained with typical greases after working for 60 strokes are shown on the attached drawing. This drawing shows that the gel strength of the greases is increased substantially by the incorporation of as little as 0.5–1% of dimer acid in the organic carboxylic acids forming the aluminum salt and that proportionate increases are obtained up to a dimer acid content of 8%, based on the total amount of organic carboxylic acids. Additional tests have shown that still further improvements are obtainable when 10% to 20% of dimer acid is present in the organic acid mixture used to form the aluminum salts.

This improvement in gel strength is probably due to an interpolymerization of the molecules of aluminum stearate or other monomer acid by the dimer acid; i. e., the two carboxylic acid radicals of the dimer acid are attached to different aluminum stearate molecules and form there-with a polymer of the type:



in which R is the residue of a monomeric fatty acid of 12–22 carbon atoms and D is the residue of a dimerized polyunsaturated fatty acid of 18 carbon atoms. The existence of such a polymer would explain why a product of high gel strength is obtained when a mixture of monomer and dimer acids is used to form the aluminum salt, whereas the salt of the dimer acid itself has little or no gel-forming power; however, it should be understood that the practical value of this feature of the invention is based on the results obtained and not on the accuracy of any theory of explanation.

Example 9

Linseed fatty acids having an iodine value of 190 and a neutralization equivalent of 286 were polymerized by heating at 340° C. for 7 hours in a closed vessel containing a small amount of steam. A portion of the resulting mixture was distilled at reduced pressures of 1–2 mm. of mercury, whereby the monomeric acids were separated. The still residue was a dimerized fatty acid having an iodine value of 102.5 and a neutralization equivalent of 303. Three mixtures of this dimer acid with a hydrogenated fish oil acids described in Example 2 were prepared and converted into their aluminum salts. These mixtures contained 4%, 5% and 6% of dimer acid, the remainder being hydrogenated fish oil acids. Greases were made containing 4% of these aluminum salts and 96% of a Mid-Continent stock lubricating oil having a viscosity of 120 seconds at 210° F.

These greases were subjected to the penetrometer test in unworked condition and also after working for 60 strokes and 1000 strokes. The re-

7

sults are given in the following table, the penetration being expressed in millimeters:

Per Cent Dimer Acid	Penetration		
	Un-worked	60 Strokes	1,000 Strokes
4.....	216	342	345
5.....	189	332	349
6.....	207	322	340

Example 10

Greases were prepared as described in Example 8 using aluminum soaps made as described in Example 2 having small quantities of glycerine admixed therewith. This produced the result, which is desirable in some greases, of bringing the test values closer together for unworked and worked greases. In the following table the percent of dimer acid is based on the weight of the acids used in making the aluminum salt, the percent of aluminum salt is based on the weight of the grease and the percent of glycerine is based on the weight of aluminum salt.

Grease No.	Per Cent Al Salt	Per Cent Dimer Acid	Per Cent Glycerine	Penetration in mm.		
				Un-worked	60 Strokes	1,000 Strokes
1.....	5	5	0	143	268	298
2.....	6	5	3	344	371	378
3.....	6	5	5.6	346	380	385

Example 11

Another set of greases was made with the same hydrocarbon oil used in Example 10, but with 20% of dimer acid based on the total quantity of organic acid used in making the aluminum soap. By using relatively large quantities of both dimer acid and glycerine the thixotropic qualities of the grease can be still further reduced. This is evident from the following table in which the percent of aluminum salt is based on the weight of the grease and the percent of glycerine is based on the weight of aluminum salt.

Grease No.	Per Cent Al Salt	Per Cent Glycerine	Penetration in mm.		
			Un-worked	60 Strokes	1,000 Strokes
1.....	7	0	200	572	-----
2.....	5	33	346	373	369
3.....	6	28	326	352	361
4.....	6	83	345	393	429
5.....	7	14	313	342	342
6.....	7	24	318	346	335
7.....	7	48	340	347	362
8.....	8	42	334	326	318
9.....	9	37	315	298	310

These results show a considerable reduction in the breakdown of the gel with continued working as well as a closer correlation between the test values for unworked and worked greases.

What we claim is:

1. A soap composition consisting 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 saturated fatty acid of 12-22 carbon atoms

8

together with 1% to 50% of glycerine based on the weight of said aluminum salt.

2. A soap composition consisting of aluminum salt of a mixture of about 4% to 8% by weight of dimerized polyunsaturated fatty acids of 18 carbon atoms and about 96% to 92% of monomeric saturated fatty acid of 12-22 carbon atoms together with 1% to 8% of glycerine based on the weight of said aluminum salt.

3. A grease composition comprising a major proportion of a hydrocarbon lubricating oil and a minor quantity within the range of 1% to 20% by weight of the 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 saturated fatty acid of 12-22 carbon atoms.

4. A grease composition comprising a major proportion of a hydrocarbon lubricating oil and a minor quantity within the range of 1% to 20% by weight of the aluminum salt of a mixture of about 4% to 8% by weight of dimerized polyunsaturated fatty acids of 18 carbon atoms and about 96% to 92% of monomeric saturated fatty acid of 12-22 carbon atoms.

5. A grease composition comprising a major proportion of a hydrocarbon lubricating oil and a minor quantity within the range of 1% to 20% by weight of the 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 saturated fatty acid of 12-22 carbon atoms together with from 1% to 50% of glycerine based on the weight of said aluminum salt.

6. A grease composition comprising a major proportion of a hydrocarbon lubricating oil and a minor quantity within the range of 1% to 20% by weight of the aluminum salt of a mixture of about 4% to 8% by weight of dimerized polyunsaturated fatty acids of 18 carbon atoms and about 96% to 92% of monomeric saturated fatty acid of 12-22 carbon atoms together with from 1% to 8% of glycerine based on the weight of said aluminum salt.

7. A grease composition comprising a major proportion of a hydrocarbon lubricating oil and a minor quantity within the range of 1% to 20% by weight of the aluminum salt of a mixture of about 4% to 8% by weight of dimerized polyunsaturated fatty acids of 18 carbon atoms and about 96% to 92% of stearic acid together with from 1% to 8% of glycerine based on the weight of said aluminum salt.

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