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LUBRICATING OIL THICKENED TO A GREASE WITH AN ANHYDROUS CALCIUM SOAP OF AN ALKENYL SUBSTITUTED SUCCINIC ACID

John Walter Nelson, Lansing, and Joseph A. Verdol, Dolton, Ill., assignors to Sinclair Refining Company, New York, N. Y., a corporation of Maine

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This invention relates to lubricating greases and their manufacture. More particularly, the invention relates to greases containing as the essential thickening component an anhydrous calcium soap of an alkenyl substituted succinic acid.

Previous attempts have been made to prepare greases from the calcium soap of an alkenyl succinic acid in which the alkenyl group has from ten to twelve carbon atoms, and a mineral lubricating oil. These attempts produced a liquid, non-uniform product. We have now found, however, that calcium soap greases having a high dropping point and excellent shear and water stability can be produced from such alkenyl succinic acids provided the alkenyl group contains at least fourteen and up to about 40 carbon atoms.

Thus, the greases of our invention include a mineral lubricating base oil and sufficient to thicken the base oil to grease consistency of an anhydrous calcium soap of an alkenyl substituted succinic acid in which the alkenyl group contains at least 14 and up to about 40 carbon atoms. The amount of the soap component will usually be in the range of about 5 to 30 weight percent of the final grease composition, preferably about 10 to 25 weight percent.

The alkenyl substituted succinic acids used in forming the anhydrous calcium soap must have an alkenyl substituent containing at least 14 and up to about 40 carbon atoms. Preferably it has 18 to 35 carbon atoms. The alkenyl substituted acids are obtained by conventional procedures such as condensing maleic anhydride with an olefin having at least 14 carbon atoms. The condensation is carried out by heating the acid and olefin with stirring for several hours, preferably at reflux temperatures under slight pressure. The total condensation product can be employed in the grease making reaction or the total product can be fractionated or recrystallized to remove lighter material, for example, for recycle.

The olefin having at least 14 carbon atoms can be straight chain or branched but if branched, it should preferably be symmetrical. Preferably the olefin is obtained as the bottoms fraction from detergent propylene polymer production although it can be derived from various sources including propylene and butylene homo- and hetero-polymers. The olefin can be substituted or unsubstituted but if substituted, the substituent should be non-reactive. The olefin can have more than one olefinic linkage but preferably has only one. The olefinic linkage can be at the terminal position or towards or in the middle of the molecule such as in 17-pentatriacontene and 11-tricosene. For instance, when the olefin is 1-octadecene the reaction product has a normal side chain with the olefin being in the beta-position with respect to an alpha-carbon atom of the succinic anhydride or acid. In the case of the olefins 17-pentatriacontene and 11-tricosene, the double bond is in a similar position and the chains attached to the carbon atoms of the double bond contain 16 and 17 carbon atoms, respectively, in the case of 17-pentatriacontene and 10 and 11 carbon atoms, respectively, in the case of 11-tricosene. These carbon chains are normal in structure. When propylene polymer is used as the olefin, the double bond may be in the same position or terminal except that the carbon chains attached have multiple branched chains.

The lubricating base material can be a mineral lubricating oil fraction of the conventionally refined or solvent refined type. The mineral lubricating oil fraction can be derived from a paraffinic, naphthenic or Mid-Continent crude and is of lubricating viscosity, e. g. from about 50 SUS at 100° F. to 200 SUS at 210° F.

The greases of our invention are prepared by forming the soap in the presence of water and in the presence or absence of the lubricating base oil. Preferably, however, the acid is saponified in the presence of at least a portion of the lubricating base. Thus, for example, the lubricating base, water, the acid and lime are charged to a conventional grease kettle, the proportions being such that the anhydrous grease contains the desired soap concentration. The mixture is then gradually heated with stirring to an elevated temperature, for instance of the order of 350° F., until an essentially anhydrous grease is obtained. Instead of the alkenyl substituted succinic acid, the anhydride can be employed and instead of lime, calcium hydroxide or calcium carbonate can be used.

Premium grease compositions characteristically are substantially anhydrous, i. e., the finished greases have a water content below about 0.10 weight percent and preferably below about 0.05 weight percent. Grease compositions of the instant invention also are substantially anhydrous. Dehydration to result in this state can be accomplished in any manner but preferably by maintaining the temperature of the reaction mass, after completion of saponification, at a temperature above the boiling point of water for about 2 to 4 hours. While dehydration can be affected after finishing oil has been added, it is preferred to dehydrate prior to the addition of finishing oil in order that less material need be handled.

Materials normally incorporated in greases to impart special characteristics can be added to our compositions. These include oxidation inhibitors, corrosion inhibitors, extreme pressure agents and anti-wear agents. The amount of additives added to the grease compositions usually ranges from about 0.01 weight percent up to about 10 weight percent and, in general, can be employed in any amounts desired so long as the present invention is not deleteriously affected.

The following examples further illustrate the greases of our invention.

Example I

Equimolecular quantities of 1-octadecene and maleic anhydride were heated at 200 to 250° C. for 16 hours. The equipment used consisted of a round bottom laboratory flask equipped with a reflux condenser, a motor driven stirrer, a thermometer and a heating mantle. A portion of the crude reaction product was used to make anhydrous lime greases. Another portion was topped under a reduced pressure of 6–10 mm. Hg at 180°–200° C. to remove unreacted materials.

To a grease kettle were charged one pound of the crude octadecylene succinic anhydride produced above, 0.25 pound of lime, one pound of water and three pounds of a conventionally refined Coastal oil (300 SUS at 100° F.). The lime was slurried in the oil prior to charging the kettle to insure adequate dispersion. After stirring the mixture for about five minutes, steam was introduced into the jacket of the kettle. After about ten minutes a temperature of 170° F. was reached, a soap base had formed and free water was present. After heating and stirring for another twenty minutes, the temperature had risen to 230° F. and all free water had disappeared. During a ten minute period another one pound of oil was added to make the soap concentration 20%. The mass was then dehydrated over the next ninety minutes by heating to 330° F. It was then cooled and 0.05 pound of Age Rite Resin D was added as an oxidation inhibitor. (This inhibitor is a polymer of trimethyldihydroquinoline.) It is a reddish-brown, brittle resin in the form of small pellets having a specific gravity of 1.08 and a melting point of 100 to 120° C. It is insoluble in water, sparingly soluble in petroleum hydrocarbons and alcohols, but easily soluble in benzene. The grease was then milled in a Charlotte colloid mill at 0.005 inch clearance and 110° F. The electron micrograph of this grease showed long, flat, thin, sharply pointed fibers amongst amorphous material.

The test data on this grease is tabulated below in the first column. The table also contains data on other anhydrous lime greases made in a similar manner with other portions of the crude and topped anhydride.

Acid Purification	Topped	Crude	Crude
Soap, Percent	20	25	20
Penetrations:			
Unworked	320	348	226
After Working 60 Strokes	315	355	234
After Working 100 M Strokes	279	313	
Change from W. P	−36	−42	
After 100,000 Strokes Wet [1]	245	255	
Change from W. P	−70	−100	
Dropping Point, °F	500+	500+	500+
250° F. 6 Hr. Wheel Bearing Test	Pass		
Free Acid Percent as Oleic	0.455	0.437	0.356
Norma Hoffman Oxidation Test, Pressure Drop in 500 Hrs.:			
Regular ASTM, lbs	16	14	
Bronze Block, lbs	16	18	

[1] Containing 10 Percent water by weight.

It will be noted in the above table that the greases became harder after working 100,000 strokes in the ASTM mechanical worker, indicating excellent shear stability. Another desirable characteristic of the greases is their extremely high dropping point of 500+° F. The water stability of the greases is reflected in that they became harder after working 100,000 strokes while having 10% water incorporated into them. A small quantity of each grease was placed in a beaker of water and boiled for ten minutes without having the oil separated or the water become cloudy. This is another indication of their water stability.

Example II

In the same manner as in Example I, maleic adducts and anhydrous lime greases were prepared using two double straight chain alkenes and detergent propylene polymer bottoms. The double straight chain alkenes were 17-pentatriacontene and 11-tricosene. The test data

on the greases thus produced are presented in the table below.

Olefin Used	Pentatriacontene	Tricosene	Propylene Polymers [2]
Soap, Percent	20	25	20.
Penetrations:			
Unworked	262	360	213.
After Working 60 Strokes	304	364	247.
After Working 100 M Strokes	309	270	153.
Change from W. P	+5	−94	−94.
After 100 M Strokes Net [1]	352	355	192.
Change from W. P	+48	−9	−55.
Dropping Point, °F	335	466	500+.
250 °F. 6 Hr. Wheel Bearing Test			Pass G, 0.0 Leak.
Free Base	Basic	Basic	Basic.
Water, Percent	0.1	0.2	0.2.

[1] Containing 10% water by weight.

[2] This polymer is predominantly in the C_{14} to C_{18} carbon atom range. It has a boiling range of 235–305 °F. at 5 mm. (approximately 400–580 °F. at 760 mm.).

It will be noted in the above table that the greases became harder after working 100,000 strokes in the ASTM mechanical worker, indicating excellent shear stability. The greases also exhibited high dropping points. The water stability of the greases is again reflected in that they became harder after working 100,000 strokes while having 10% water incorporated into them. A small quantity of each grease was placed in a beaker of water and boiled for ten minutes without having the oil separated or the water become cloudy. This is another indication of their water stability.

We claim:

1. A lubricating grease including a mineral lubricating base oil and sufficient to thicken the base oil to grease consistency of an anhydrous calcium soap of an alkenyl substituted succinic acid in which the alkenyl substituent contains at least 14 carbon atoms.

2. The lubricating grease of claim 1 in which the soap is the calcium soap of octadecenyl succinic acid.

3. The lubricating grease of claim 1 in which the soap is the calcium soap of polypropenyl succinic acid.

4. A lubricating grease including a mineral lubricating base oil and about 10 to 25 percent by weight based on the grease of an anhydrous calcium soap of an alkenyl substituted succinic acid in which the alkenyl substituent contains at least 14 and up to about 40 carbon atoms.

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