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VISCOUS FLUID LUBRICANT

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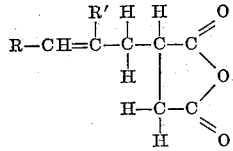
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3 Claims. (Cl. 252—40.5)

This invention relates to lubricants containing a minor amount of alkenyl succinic anhydride or acid. Particularly, the invention relates to lubricants comprising lubricating oil, metal salt as a thickener, and a small amount of an alkenyl succinic acid or alkenyl succinic anhydride, wherein the alkenyl group is preferably a high molecular weight group.

Alkenyl succinic acid, or its anhydride, has been found useful as an additive for imparting various properties to lubricants. In general, this alkenyl succinic acid can act as a plasticizer for grease, as a dispersant to obtain better dispersing of the thickener which can reduce clogging of small diameter feed lines operating under high pressure, etc. In the case of fluid and semi-fluid lubricants containing relative large amounts of low molecular weight fatty acid salt, e.g. calcium acetate, it has been found that the additive of the invention improves the spreadability and inhibits gelling of the lubricant at high temperatures.

Either alkenyl succinic anhydride or the corresponding acid can be used. However, the anhydrides are more readily obtainable since they can be simply prepared by reacting maleic anhydride with an organic compound having a double bond at its end to thereby give compounds of the general formula:



wherein R and R' can be hydrogen or hydrocarbon radicals, either substituted (e.g., chlorinated or sulfurized) or unsubstituted, and which can be aliphatic, acyclic, aromatic, etc., although at least one of said R and R' must be a hydrocarbon group. The total number of carbon atoms in R and R' will generally be 40 to 250, and preferably will be 50 to 120. Because of its ready availability and low cost, the alkenyl portion of the molecule is preferably obtained by reacting a polymer of a C_2 to C_5 monoolefin with maleic anhydride, said polymer generally having a molecular weight of about 700 to 3,000, e.g., about 800 to 1300. A preferred example of such an olefin polymer is polyisobutylene.

The preparation of alkenyl succinic anhydride is known in the art, for example, see U.S. 3,018,250, col. 3, lines 57 to 71, Example 1. The process simply involves heating about equal molar proportions of maleic anhydride and the olefinic material together.

The succinic acid or anhydride additive of the invention can be incorporated in amounts of 0.01 to 2.0 wt. percent, preferably 0.1 to 1.0 wt. percent, based upon the weight of the total composition, into fluid, semi-fluid, or normally solid lubricants, e.g. grease, containing a major amount of lubricating oil and about 1.0 to 40 wt. percent, preferably 2.0 to 30 wt. percent, of various materials such as: metal salts of C_2 to C_{30} carboxylic acids, polymeric thickeners (e.g., polymers of C_2 to C_4 monoolefins of 10,000 to 200,000 mol. wt. such as polyethylene), inorganic thickeners, (e.g., clay, carbon black, silica gel), etc.

The lubricating oil can be either a mineral oil or a synthetic lubricating oil. Examples of synthetic lubricating oils include diesters such as di-2-ethylhexyl sebacate, complex esters, polysilicones, Ucons, formals, polycarbonates, etc.

The carboxylic acid salt thickeners are generally formed by the neutralization of fatty acid with metal base. The fatty acid can be a high molecular weight fatty acid, an intermediate molecular weight fatty acid, or a low molecular weight fatty acid. The metal base will generelly be an alkali or alkaline earth metal base. Frequently, mixed metal salts of different molecular weight fatty acids are used. For example, a mixed-salt thickener can contain alkaline earth metal (frequently calcium) salts of 1 to 40, e.g. 5 to 20, molar proportions of a low molecular weight fatty acid (e.g. acetic acid) per molar proportion of higher fatty acid, e.g. oleic acid or capric acid. These mixed-salt thickeners are generally prepared by coneutralizing the various acids involved with metal base, e.g. lime, in situ in the lubricating oil. The lubricant can then be used as is, if a "cold sett" lubricant is desired, or it can be heated to temperatures of about 225° to 50° F. to dehydrate the lubricant. Either solid greases can be formed in the preceding manner, or fluids, or semi-fluids, can be prepared, depending upon the amount of lubricating oil used.

The high molecular weight fatty acids useful for forming metal salts include naturally-occurring and synthetic, substituted and unsubstituted, saturated and unsaturated, mixed and unmixed, fatty acids having about 13 to 30, e.g. 16 to 22, carbon atoms per molecule. Examples of such acids include stearic, 12-hydroxy stearic, di-hydroxy stearic, arachidic, oleic, ricinoleic, hydrogenated fish oil acids, tallow acids, etc.

Intermediate molecular weight fatty acids useful for preparing metal salts, include those fatty acids containing 7 to 12 carbon atoms per molecule, e.g., capric, lauric, caprylic, nonanoic, etc.

Suitable low molecular weight acids include C_2 to C_6 fatty acids. Acetic acid or its anhydride is preferred.

Various other additives may also be added to the lubricating composition (e.g. 0.1 to 10.0 weight percent each, based on the total weight of the composition). Specific examples of these additives include oxidation inhibitors such as phenylalpha-naphthylamine, tackiness agents such as polyisobutylene, stabilizers such as aluminum hydroxy stearate, rust preventives such as sodium nitrite, etc.

While generally useful as lubricants for a variety of purposes, lubricants can be made according to the invention which are particularly effective for lubrication of marine diesel engines. Although, marine diesel engines have become wide spread in their use, they have always had a serious wear problem with regard to the piston, the piston rings and the surface of the cylinder liner. In lubricating these diesel engines, a fluid or semi-fluid lubricant is generally sprayed or forced directly onto the cylinder and piston upon each stroke of the piston by means of a centralized force-feed lubrication system. The lubricant is to a large extent consumed during each stroke of the piston, thereby requiring continuous application of the lubricant. In order to be suitable for such marine diesel lubrication use, the lubricant should have a fluid or semi-fluid consistency. This is desired in order that the lubricant may be readily pumped through the aforementoned forced lubrication systems normally associated with marine diesel engines and will spread or wet the piston sufficiently during each stroke to achieve an overall coating on the piston surface. As indicated above, another requirement of such lubricants is that they have good antiwear properties. Because of the giant size of the pistons and cylinders used in such engines (e.g. piston and cylinder diameters of 36 inches are common), wear is a serious problem. Once the cylinder liner has worn more than about 0.6% of its diameter, it is necessary that it be replaced. Wear of the piston and rings is also an expensive problem. In a typical marine engine of 8 to 16 cylinders the replacement costs due to wear, may

run in the order of several thousand dollars per cylinder. Furthermore, the lubricant should be stable against sedimentation.

Lubricants for such marine diesel lubrication, which met the above requirements, have been made by thickening mineral lubricating oil with within the range of about 2 to 15 wt. percent of mixed calcium salts of acetic acid and intermediate molecular weight fatty acid, e.g. C_7 to C_{12} fatty acids. It has now been found that these marine diesel lubricants can be improved in several respects by adding a small amount of alkenyl succinic acid or anhydride. These improved lubricants have a reduced tendency to gel, particularly at high temperatures. Thus, in some engines operating at very high temperatures, gelling of the lubricant will interfere with pumping the lubricant through narrow diameter feed lines and will reduce the degree of spreading of the lubricant along the engine cylinder walls, thereby interfering with proper lubrication of the cylinder and piston. In addition, the alkenyl succinic anhydride results in a good dispersion of calcium acetate, improves the sight glass life, etc.

Polyisobutenyl succinic anhydride, used in the following Example I of the invention, was prepared as follows: 1200 pounds of polyisobutylene of about 1100 molecular weight (staudinger), and 150 pounds of maleic anhydride were heated together at a temperature of about 450–460° F. for about 24 hours. The reaction mixture was maintained in a N_2 atmosphere during the course of the reaction. The heated mixture was then cooled to about 212° F. and filtered. The recovered reaction product was a viscous material of amber color, having a saponification number of 83.3 mg. KOH/gm. of reaction product.

EXAMPLE I

Part A.—A lubricant concentrate was prepared as follows wherein all parts are by weight:

10.2 parts of hydrated lime was added to 69.6 parts of a mineral lubricating oil having a viscosity of 80 SUS at 210° F. in a steam jacketed grease kettle. The oil and lime were mixed together to form a slurry which was circulated from the kettle through a Charlotte mill and back to the kettle. To this circulating slurry was added 3.8 parts of Wecoline AAC acid, followed by the addition of 16 parts of glacial acetic acid. Upon the slow addition of the acetic acid, the temperature of the circulating stream rose to about 200° F. The batch at this point had a free alkalinity of 0.10 wt. percent calcium as NaOH. Heating was then initiated and the temperature of the mixture was raised to 300° F. to dehydrate the composition, followed by cooling by passing cold water through the kettle jacket. 0.4 part of phenyl α-naphthylamine as an oxidation inhibitor was added upon cooling to about 200° F. After the material in the kettle had cooled to just below 125° F., 10 parts of a mineral lubricating oil (80 SUS at 210° F.) solution containing 5 wt. percent of the polyisobutenyl succinic anhydride described above, was added for every 90 parts of material already in the kettle. The resulting lubricant concentrate was homogenized through a Charlotte mill and was a soft solid grease.

A finished marine diesel cylinder lubricant was next prepared by simply diluting the cooled lubricant concentrate with additional mineral lubricating oil of 80 SUS at 210° F. viscosity, using 3 parts of diluent per part of lubricant concentrate. This diluted product was mixed, Charlotte milled and deaerated to give the final product.

The Wecoline AAC acid used above is a commercial acid derived from coconut oil and consisting of about 46 wt. percent capric acid, about 28 wt. percent caprylic acid and about 26 wt. percent lauric acid.

It will be noted that the polyisobutenyl succinic anhydride was added to the lubricant at a relatively low temperature, i.e. below 125° F. and after the lubricant had been dehydrated, in order to prevent reaction of the acidic alkenyl succinic anhydride with the excess metal base present. Otherwise, if the anhydride was added while the lubricant was at a higher temperature, a portion of said anhydride would probably react with the excess base present to form the salt of polyisobutenyl succinic acid which is less desirable for the purposes of this invention than the polyisobutenyl succinic anhydride. Alternatively, the lubricant could be made exactly neutral, or even left slightly acidic. Under these latter conditions, addition of the polyisobutenyl succinic anhydride could not be expected to form salt of said anhydride, even if added to the hot lubricant, e.g. 350° F.

Part B.—A comparison marine diesel cylinder lubricant was prepared in a manner similar to that described in Part A, except that the oil solution of the polyisobutenyl succinic anhydride was not added.

The compositions of Part A and B, as well as the major physical properties are summarized in the following table:

	Example I	
	Part A	Part B
Final Formulation (Wt. Percent):		
Polyisobutenyl succinic anhydride (100%)	0.13	----------
Glacial Acetic Acid	3.63	4.00
Hydrated Lime	2.30	2.55
Wecoline AAC Acid	0.90	0.95
Phenyl α-naphthylamine	0.10	0.10
Mineral Lubricating Oil, 80 SUS at 210° F	92.94	92.40
Properties:		
SSU, Vis/100° F	1,501	1,600
SSU, Vis/210° F	94.1	124
Centrifuge Test, percent sediment	0.8	0.8
Manzell Lubricator Life, days	67+	5
Spreadability Test at 400° F	Spreads	Gels
Oven Gellation Test:		
300° F	No gel	No gel
374° F	No gel	Gels solid

The Manzell Lubricator test was carried out by passing the lubricant under test through a Manzell Lubricator at the rate of 2 quarts of lubricant a day. The Manzell Lubricator includes a sight-glass filled with an aqueous solution containing 20 wt. percent of calcium nitrate tetrahydrate as the sight-glass fluid. These lubricators are widely used in conjunction with marine diesel engines. The lubricator permits visual observation of the rate of flow of the lubricant which is forced into the bottom of the sight-glass and then floats up through the higher density sight-glass fluid to an upper line from where it is then forced to the cylinder being lubricated. The product of Part A went for 67+ days without displacing the aqueous fluid in the sight-glass. On the other hand, the comparison lubricant, Part B, went for only 5 days before the sight-glass fluid had become sufficiently displaced so as to require disassembling and cleaning. Since there is usually a sight-glass for each cylinder of a marine diesel engine, it is highly desirable from a labor standpoint to clean the sight-glasses as seldom as possible.

The Oven Gellation Test was carried out by filling an ASTM pour point jar ¾ full with the lubricant to be tested. The test lubricant is heated for four hours at 374° F. and is then allowed to cool for 45 minutes. The jar is then examined to see if the lubricant has gelled. It is seen that at the 374° F. heating level, the comparison lubricant of Part B had gelled solid, while the product of the invention represented by Part A had not gelled, but instead remained fluid. This gelling, or lack of gelling, is used as an indication of the spreading ability of the lubricant when it hits the hot cylinder it is being used to lubricate. For example, a cylinder at a temperature of 374° F., when hit by the comparison lubricant of Part B would cause the lubricant to gel so as to interfere with the spreadability of the lubricant along the cylinder walls. On the other hand, the product of Part A will not form a gel at this temperature and as a result will remain fluid so that it can rapidly spread along the cylinder to more evenly wet the cylinder with the lubricant and hence lubricate more effectively.

In the Spreadability Test, the lubricant is simply dropped onto the iron surface of a hot plate at 400° F. to see whether it spreads or gels. This test, is of course, another indication of how the lubricant will behave on a hot cylinder.

The other test results show that the additive acted somewhat as a plasticizer in making a softer, i.e. a less viscous lubricant.

While the preceding has been primarily directed towards lubricants useful as marine diesel lubricants, the additive of the invention can be used for other lubricants. For example, 1 wt. percent of the hereinbefore described polyisobutenyl succinic anhydride can be added to a lubricating grease consisting of mineral lubricating oil of 80 SUS viscosity at 210° F. which is thickened to a grease with 15 wt. percent of sodium stearate. The finished grease is more uniform and the soap dispersed in smaller crystals. This results in greater ease of dispensing with less tendency to plug centralized lubrication systems.

To further illustrate the invention, Example I, Part A can be exactly repeated but using a mineral oil solution containing 5 wt. percent of polyisobutenyl succinic acid wherein said polyisobutenyl group has a molecular weight of about 1100, in place of the solution of 5 wt. percent of polyisobutenyl succinic anhydride of Example I, Part A.

What is claimed is:

1. A viscous, fluid lubricant suitable for the lubrication of marine diesel engine cylinders consisting essentially of a major amount of mineral lubricating oil, about 2 to 15 wt. percent of calcium salts of acetic acid and C_7 to C_{12} fatty acid in a molar ratio of about 5 to 20 molar proportions of salt of acetic acid per molar proportion of salt of said C_7 to C_{12} fatty acid, and about 0.1 to 1.0 wt. percent of polyisobutenyl succinic anhydride wherein said

polyisobutenyl group has a molecular weight of about 700 to 3,000 molecular weight.

2. A viscous fluid lubricant suitable for the lubrication of marine diesel engine cylinders comprising a major amount of mineral lubricating oil, about 2 to 15 wt. percent of calcium salt of acetic acid and C_7 to C_{12} fatty acid in a relative molar ratio of about 5 to 20 molar proportions of salt of said acetic acid per molar proportion of salt of said C_7 to C_{12} fatty acid, and about 0.1 to 1.0 wt. percent of polyisobutenyl succinic anhydride wherein said polyisobutenyl group has a molecular weight of about 800 to 1,300 molecular weight.

3. A viscous fluid lubricant suitable for lubrication of marine diesel engines and having a reduced tendency to gel at high temperatures, comprising a major amount of mineral lubricating oil and about 2 to 15 wt. percent of calcium salt of acetic acid and C_7 to C_{30} fatty acid in a molar ratio of 5 to 20 molar proportions of acetic acid per molar proportion of said C_7 to C_{30} fatty acid, and a gel inhibiting amount, within the range of about 0.01 to 2.0 wt. percent of a material selected from the group consisting of alkenylsuccinic anhydride and alkenylsuccinic acid, wherein said alkenyl group is a polymer of a C_2 to C_5 monoolefin, said polymer having a molecular weight of about 700 to 3,000, and wherein said weight percents are based upon the total weight of said lubricant.

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