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FRICTION REDUCING ADDITIVES FOR LUBRICANTS

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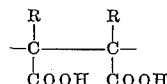
The present invention relates to friction reducing additives for lubricants and, particularly, to additive materials which may be incorporated in lubricating oils and greases to reduce the coefficient of friction between metallic bearings, especially bearings of the journal type.

The operation of various types of machinery, and particularly of heavy machinery, where starting torques are relatively high, frequently involves starting difficulties and high power consumption. In the past, various materials have been proposed for reducing the coefficient of friction such as fatty acids and soaps, e. g., of the C_8 to C_{22} fatty series. While the exact mechanism is not clearly understood, it appears that the appreciable reduction in the friction coefficient which is obtained by using such soaps and acids may result from a reaction between metal (or the metal oxide which may cover the metal surface) and the additive to produce a monolayer of metal soap on the surface of the bearing. Such monolayers have excellent low friction characteristics, for sliding friction particularly, but the monolayers also have the disadvantage, apparently, of being removed rapidly, resulting in excessive wear. It seems, in fact, that monolayers of soap tend to be removed and renewed so rapidly that there is a constant metal reaction taking place. On the other hand, when multi-layers of soap in lubricants are utilized to reduce friction, they tend apparently to be self-repairing under certain operational conditions. If they are incorporated in liquid vehicles they appear to repair themselves without excessive wear under conditions of boundary lubrication, e. g., when bearings of the journal type are operating under high load conditions at relatively low velocities.

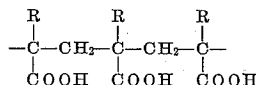
The ordinary soaps and fatty acids used in greases, gear oils, and the like, commonly react with the bearing metals to produce metallic compounds which are oil-soluble. In the presence of lubricating oil, they appear to be susceptible to washing away from the metal surface. Where air or oxygen is present, and particularly in the presence of moisture and heat, this process of metal salt or soap formation and solution progresses rapidly. As a result, the metallic bearing materials may be corroded or dissolved quite rapidly under conditions of high load, especially in the presence of moisture, heat and oxygen or air. Particularly in heavy machinery of the type used in paper mills operating under heavy loads in direct contact with steam and/or water, corrosion of bearings and journals progresses at a rapid rate. One important object of the present invention, therefore, is to overcome such wear and corrosion.

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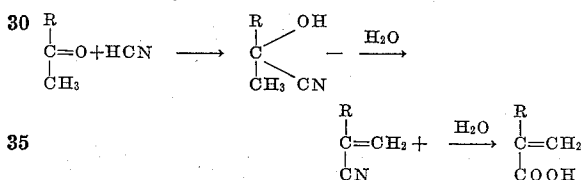
According to the present invention, polymeric materials comprising fatty acids of a type having at least moderate solubility in lubricating oils but forming with bearing metals, relatively oil-insoluble products, in the form of metallo-organic complexes containing polymeric materials, may be used to overcome the difficulties mentioned above. Acids of the general formula



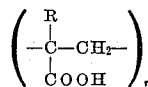
where R is a hydrocarbon chain of at least 8 carbon atoms appear to be satisfactory in theory although not readily obtainable on the market. Another type of polymer of higher molecular weight which is satisfactory for the present purposes has the general formula



where any of the radicals R is an aliphatic hydrocarbon chain of at least 8 carbon atoms and may be as high as about 22 carbon atoms. The latter material may be derived in a manner similar to that used for producing acrylic acid or polyacrylic acid, being synthesized as follows:



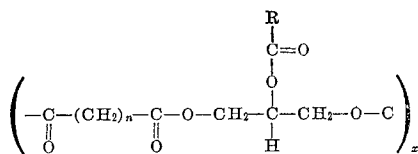
which polymerizes to



Since neither of the foregoing compounds is available commercially at the present time, it has been found according to the present invention that certain resinous or polymeric materials of the alkyd or so-called "glyptal" type derived from glycerine and phthalic anhydride, which contain acidic constituents and which may readily be prepared or are readily available on the market, may be used in lieu of those represented in the above formulas. It is preferred that these materials be soluble in oil, at least in the proportions employed, and preferably in proportions up to 5% by weight or a little higher. Also, the reaction products of polybasic acids, or their anhydrides, with polyhydric alcohols may be used, the product being modified by treatment with

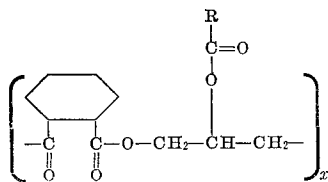
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fatty acid, produces resinous additive materials having the characteristics desired. Reaction products such as those of the general formula



where n is a small integer preferably between 1 and 8, and x is an integer of such value as to make an oil-soluble resin product may be prepared by known methods. As previously indicated, the metal-containing reaction or chemisorption product of this additive, formed by contact with the bearing metal, tends to be quite oil-insoluble.

Where the polybasic acid constituent of the resin or other polymer is of aromatic type, such as phthalic acid, the above product may be represented, so far as its acidic component is concerned, by the general formula



x having a value, as indicated above, such that the resin itself is oil-soluble but its reaction or chemisorption product, salt or the like, formed with the bearing metal, is relatively oil-insoluble. The anhydrides of the dibasic acids are preferred over the acids themselves because they react more readily though either can be used.

Specifically, compounds of the type described in the last two formulas above have been prepared by condensing glycerol and stearic or behenic acids with phthalic, succinic or maleic anhydrides. The modified alkyd resins are preferred, although the related acrylic resins, similarly modified, may be used, as suggested above. Alternatively, the glycerol monostearate or the corresponding behenic acid partial ester of glycerol may be condensed with any of the above anhydrides. These resinous or polymeric derivatives may be added to lubricating oils and greases in proportions of 0.01 to 1 or 2% by weight, based on the total composition. Proportions of 0.1 to about 1.0%, especially about 0.2 to 0.5%, are specifically preferred.

In carrying out the invention, condensates prepared according to the preceding paragraph were added to mineral base lubricating oil in various concentrations. The starting friction and the running friction in relatively heavy bearing journals were measured at very low sliding velocities, e. g., about 12 inches per minute. With very small concentrations of additive the friction coefficient dropped off rapidly as the concentration of the acid-containing resin in the oil was increased up to about 0.5% by weight, based on the total lubricant. Above 0.5% concentration, the friction coefficient levelled out.

The acid-containing additives preferably have a moderately low acid number when that number represents available acid. However, these resinous materials may contain a substantial proportion of acid which is tied up in the polymer. Modified acrylic resins may be used. Free fatty acids, in any substantial quantities, are corrosive and are to be avoided, but acids having free

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carboxyl groups, which otherwise are tied up in the polymer, are very satisfactory.

EXAMPLE I

A resin was prepared by condensing 74 grams of phthalic anhydride with 46 grams of glycerol and 142 grams of technical stearic acid. The finished condensation product had an acid number of 7.4 and was a dark brown resinous material solid at room temperature.

EXAMPLE II

A product was prepared in much the same manner as Example I, using 74 grams of phthalic anhydride, 50 grams of glycerol and 142 grams of stearic acid, technical grade. This product had an acid number of 9.0 and was also a dark brown solid resinous material at room temperature.

In lieu of the anhydride it is possible, of course, to use the corresponding acid.

EXAMPLE III

A composition was prepared by condensing 23.2 grams of maleic acid with 71.6 grams of glycerol monostearate. This produce which had an acid number of 18.0 was a yellowish solid at room temperature. It was partially soluble in mineral lubricating oil of 300 S. S. U. viscosity at 100° F. The mineral oil had a viscosity index of 54. When the oil was heated to 125° C. there was no insoluble residue even when the resin was used in 5% concentration by weight.

EXAMPLE IV

Another composition was prepared of 10.0 grams succinic anhydride, 9.2 grams glycerol and 34.5 grams behenic acid. This product had an acid number of 100.0 and was also a solid resinous material with moderate solubility in mineral lubricating oil.

All four of the resins produced according to the foregoing examples were dissolved in a mineral base lubricating oil of about 300 S. S. U. viscosity at 100° F. (54 viscosity index), by heating the oil and resin mixture to a temperature of 130° C. Thereafter, the lubricants were cooled to room temperature and were centrifuged in order to separate any oil-insoluble portions. In the case of Example III, appreciable quantities of the 5% solution were separated but the quantities separated were negligible in the other examples.

In order to be certain that the reduction of friction which was found was not due entirely to an increase in viscosity of the resin-oil solution, viscometric measurements were taken on several samples of various concentrations with results as indicated in Table I:

Table I

VISCOSITY OF OILS AND ADDITIVES (100° F.)

Alkyd	Solution by Weight	Viscosity of Solution (S. S. U.)
Example I.....	5% in 300 viscosity S. S. U. 54 V. I. oil.	333
Do.....	10% in 300 viscosity S. S. U. 54 V. I. oil.	375
Example II.....	5% in 300 viscosity S. S. U. 54 V. I. oil.	334
Do.....	10% in 300 viscosity S. S. U. 54 V. I. oil.	382
Example III.....	5% in 300 viscosity S. S. U. 54 V. I. oil.	307
Base Oil Only.....	300 viscosity S. S. U. 54 V. I. oil.	295
Mineral Oil Only.....	900 viscosity S. S. U. 40 V. I. oil.	900

It will be noted in Table I that a mineral lubricating oil of 900 S. S. U. viscosity and viscosity

index of 40 was compared with the base oil and also with the base oil containing various proportions of the additives. Friction measurements also were compared with the oil of 900 S. S. U. viscosity and with the base oil of 300 S. S. U. viscosity (at 100° F.), using steel journals against bearings of Babbitt, steel and Phosphor bronze, respectively. Plastic bearings of "Teflon" and of "polythene" were used with the steel journals. For comparative purposes, the same oil of 300 S. S. U. viscosity and 54 viscosity index was used throughout as the vehicle for the resinous acid-containing additive and for the other additives listed. Results of the friction coefficient tests are summarized in Table II.

Table II

COEFFICIENT OF SLIDING FRICTION FOR VARIOUS LUBRICATING SYSTEMS

Additive	Description	Babbitt, C. F. ¹	Steel, C. F. ¹	Phosphor Bronze, C. F. ¹
None	900 visc. 40 V. I. Lubricating mineral oil	0.423	0.447	0.433
Do	300 Visc. 54 V. I. Lubricating mineral oil	0.501	0.521	0.417
Example I	5% solution in 300 visc. 54 V. I. oil	0.329	0.339	0.342
Example II	do	0.314	0.349	0.329
Example III ²	10% solution + 0.6% Ca(OH) ₂ in 300 Visc. 54 V. I. oil	0.236	0.299	0.305
Stearic Acid	1% in 300 visc. 54 V. I. oil "A"	0.295	0.339	0.309
Do	5% in 300 visc. 54 V. I. oil "A"	0.531	0.610	0.447
Do	10% in 300 visc. 54 V. I. oil "A"	0.551	0.595	0.422
Graphite	Rubbed against Babbitt	0.270		
Do	As above, in presence of oil	0.221		
Do	2% dispersion in oil, blended by means of Waring Blendor	0.393	0.393	0.388
Do	5% in 300 visc. 54 V. I. oil "B"	0.467	0.427	0.403
None	Oil "C" 200 S. S. U. viscosity	0.496	0.575	0.393
Example III	5% Maleic-glycerol monostearate in Oil "C"	0.221	0.280	0.289
Calcium Stearate	1% dissolved by heat in 300 visc. 54 V. I. oil "C"	0.265	0.383	0.339
Do	1% dispersion in Waring Blendor + oil	0.305		
Example III	5% Maleic-glycerol monostearate	0.275	0.295	0.299
Do	0.2% Maleic-glycerol monostearate	0.290	0.319	0.339
Do	0.02% Maleic-glycerol monostearate	0.359	0.373	0.373
Example IV	Behenic-glycerol-succinic anhydride 2%	0.184	0.314	0.319
Behenic Acid 2%	Not very soluble in oil at room temperature	0.334	0.314	0.275
Steel-"Teflon" Bearing	No oil, C. F. ¹ =0.113			
"Polythene" Bearing	No oil, C. F. ¹ =0.417			
Do	+ oil, C. F. ¹ =0.369			

¹ Coefficient of friction.² Ca(OH)₂ used here to completely neutralize any acid.

It should be noted that the coefficients of friction set forth in the foregoing table are relative and not absolute. The so-called coefficient here is actually a measure of two variables, viz., of interference between rugosities, which depends on the finish of the bearings, and of the tendency of two contacting metal surfaces to adhere or weld together.

Copper corrosion tests were conducted by placing mechanically polished copper strips in various solutions of the respective examples as follows:

- 2% of stearic acid in a medium grade lubricating oil.
- 2% of maleic acid-glycerol monostearate resin (Example III) of acid number 18 in the same oil.
- Oil without additive.
- 0.18% stearic acid in mineral oil (equivalent to acid number of 6). These were heated at 100° C. for 20 hours in an air oven.

Copper tests showed that the stearic acid had a distinct green discoloration after 4 hours at 100° C. and this color increased in intensity with time. The product of Example III showed no noticeable copper corrosion. The solution (d) containing 0.18% of stearic acid was tested to determine whether copper corrosion is directly proportional to acid number. It was found that the stearic acid was substantially more corrosive to copper, even in the low concentration of 0.18%, than the resin of Example III. As noted above,

Example III resin had a much higher acid number than Examples I and II though not so high as Example IV.

In general, the invention contemplates the use of proportions from 0.1 to as much as 5% of the oil-soluble modified or acid-containing resins which form oil-insoluble complexes with the base metals as contained in bearings, previously discussed. Conventional anti-oxidants, oiliness agents, extreme pressure additives and viscosity index improvers may be added without departing from the spirit of the invention. The additives are particularly suited for use in mineral base lubricating oils but they may also be incorporated in synthetic oils such as the dibasic acid esters,

and oils of the polyglycol or glycol ether type, used alone or in mixtures with each other, and/or mineral base lubricants. The friction reducing agents of the present invention may also be used in lubricating greases with beneficial results of the same order.

It will be noted in reference to Table II that the average bearing metals lubricated with straight mineral lubricating oil have sliding friction coefficients in the neighborhood of 0.500. With the additives of the present invention, these coefficients drop to the order of 0.300, being as low as 0.184 in one case. This very substantial reduction in sliding friction is of considerable value in the lubrication of large journal bearings as in paper mills and in heavy machinery of other types where starting torques frequently impose extremely heavy loads on electric driving motors. Reduction in overload starting is particularly useful. Saving in power consumption moreover is very considerable.

Another aspect of the present invention involves the use of the resinous modifiers, and related materials, to inhibit oxidation of the lubricant. Resins prepared by condensing glycerol partial esters of long chain fatty acids (C₁₆ to C₂₂) with phthalic, succinic, itaconic, maleic and other closely homologous and analogous polybasic acids and anhydrides have been found to be effective agents for preventing discoloration of lubricating oils and greases.

When hydrocarbon oils and greases are heated in the presence of air, they tend to absorb oxygen.

Their viscosities increase and they harden and produce sludge in varying degrees, depending upon their chemical stability. The rate of darkening may, in many cases, be taken as a measure of the rate of oxidation. Certain of the condensation products of polybasic acids and long chain substituted polyhydric alcohols are found to reduce the rate of darkening very appreciably. The resinous condensation products must be oil-soluble and their action appears to be rather specific. The following data show changes in light transmission and viscosity after 40 cc. samples of the materials indicated were heated in open beakers for 24 hours at 300° F. All additives were used in 1% concentration. The base oil was a refined lubricating oil of about 300 S. S. U. viscosity at 100° F. and a viscosity index of 95.

Table III

Composition	Percent Light Transmission		Viscosity, S. S. U. at 100° F.	
	As Prepared	After Heating	As Prepared	After Heating
Base Oil.....	100	30	293	311
Base Oil+Maleic acid-glycerol monostearate resin.....	87	87	305	308
Base Oil+commercial anti-oxidant A.....	77	1	293	307
Base Oil+commercial anti-oxidant B.....	96	0	297	312

The resin was prepared by condensing equimolar proportions of maleic acid and glycerol monostearate. This resin had an acid number of 18.

From the foregoing, it appears that these modified alkyl type resins have several advantageous properties. They may be used in lubricants—

- (1) To waterproof the silica in silica base greases.
- (2) Act as friction reducing ingredients in oils and greases generally.
- (3) Inhibit oxidation in lubricants and greases generally.

For purposes of preventing oxidation, the modified resins may be used in proportions of 0.1 to 2% or more, based on the total weight of the composition. Proportions of 0.5 to 1% are specifically preferred.

What is claimed is:

1. A lubricating composition for heavy journal metallic bearings operating at elevated temperatures in the presence of moisture, comprising a mineral oil base lubricant containing 0.1 to about 1% by weight, based on the total composition, of a fatty acid modified resin selected from the

group consisting of the condensation products of glycerol with a dicarboxylic acid material selected from the group consisting of phthalic, succinic and maleic acids and their anhydrides modified by treatment with long chain fatty acids having about 12–22 carbon atoms, and the condensation products of C₁₂–C₂₂ long chain fatty acid esters of glycerol with said dicarboxylic acid materials, said resin having free acidity to the extent of an acid number of about 7–100 and having sufficiently active carboxylic groups to form substantially oil-insoluble chemisorption products with the metal of said bearings at the operating temperature, said resin being substantially devoid of free fatty acid which would form oil-soluble soap with said metal.

2. A lubricating composition comprising a major proportion of mineral base lubricating oil and 0.1 to 1%, based on the weight of the total composition, of an oil-soluble resinous condensation product of glycerol and phthalic anhydride modified by treatment with a fatty acid of the C₁₂ to C₂₂ range to bring the acid number between about 7.4 and 9.0, said resin being of such molecular weight that the metal soaps thereof are substantially oil-insoluble.

3. Composition according to claim 2 containing about 0.2 to 0.5% of said modified resin.

4. A lubricating composition comprising a major proportion of mineral base lubricating oil and a minor but oxidation inhibiting proportion of about 0.1–1% by weight of the resinous condensation product of C₁₂–C₂₂ long chain fatty acid partial esters of glycerol with a dibasic acidic material selected from the group which consists of phthalic, succinic, and maleic acid and their anhydrides, said condensation product having an acid number of about 7–10 anhydrides.

5. A composition comprising a major proportion of mineral base lubricating oil and 0.1 to 1% by weight of the resinous condensation product of glycerol monostearate and maleic acid.

6. Composition according to claim 5 containing 0.5 to 1% of said condensation product.

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