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LUBRICATING COMPOSITIONS

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This invention relates to improved lubricating compositions and to the process of preparing them and, more particularly, to the class of lubricants existing as plastic solids or jellies.

Grease-like compositions having good lubricating properties can be prepared by dispersing compounds of bentonite with organic bases in a lubricating oil. Not all of the lubricating compositions thus prepared, however, are resistant to leaching by water

The preparation of bentonite-organic base compounds is described in U S. Patent No. 2,033,856, issued March 10, 1936. These compounds are prepared by bringing together the bentonite and the organic base in the presence of aqueous mineral acid to effect base exchange. The organic bases should preferably be titratable with mineral acids. Among the reactive bases are many alkaloids, and cyclic, aliphatic, and heterocyclic amines. Some of the preferred bentonite-organic base compounds are prepared by bringing together a bentonite clay and such organic bases as aliphatic amines, their salts, and quaternary ammonium salts. Examples of such amines and salts are: decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, hexadecyl ammonium acetate, octadecyl ammonium acetate, dimethyldioctyl ammonium acetate, dimethyldidodecyl ammonium acetate, dimethyldodecylhexadecyl ammonium acetate, dimethyldicetyl ammonium acetate, dimethylhexadecyloctadecyl ammonium acetate, dimethyldioctadecyl ammonium acetate and the corresponding chlorides and quaternary ammonium chlorides. The organic bases employed should be such as to impart substantial organophilic properties to the resulting compounds. The amines and salts listed above produce bentonite-organic base compounds suitable for use in producing grease-like compositions, but the bentonite-organic base compounds produced from the lower molecular weight bases, i. e., bases containing 10 to 20 carbon atoms are preferred in that they are less expensive than the compounds prepared from the higher molecular weight bases. The lubricants prepared from an oil and a bentonite-organic base compound containing 10 to 20 carbon atoms have excellent lubricating properties but they have the disadvantage of being easily leached by water. Thus, until now, lubricants prepared from an oil and a bentonite-organic base compound containing 10 to 20 carbon atoms could not without excessive loss of the lubricants be used where the lubricants might come in contact with water.

We have discovered that lubricants consisting essentially of a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in an oil can be improved particularly with respect to their water-leaching characteristic without affecting other desirable lubricating properties by dissolving in the oil a polymer selected from the group consisting of polymerized ethylene, polymerized esters of acrylic acid and polymerized esters of alpha-methacrylic acid. Thus, we have found that a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymer selected from the group consisting of polymerized ethylene, polymerized esters of acrylic acid, and polymerized esters of alpha-methacrylic acid results in lubricants having improved water-leaching characteristics.

In compounding the compositions of the present invention, various compounding and blending procedures may be used. In accordance with a preferred embodiment of the invention, the polymer is first dissolved in the oil. Solution of the polymer in the oil can be accomplished either by dissolving the preformed polymer in the oil or by adding the ester to the oil and then polymerizing the ester in situ. Then the bentonite-organic base compound is dispersed in the polymer-containing oil by gradually adding the bentonite compound with stirring at a temperature of about 140° F. Dispersion of the bentonite compound in the polymer-containing oil can be facilitated by the use of one or more solvating agents. Suitable solvating agents are polar organic compounds such as organic acids, esters, alcohols, ethers, ketones, and aldehydes, especially low molecular weight compounds of these classes. Examples of suitable solvating agents are ethyl acetate, acetic acid, acetone, methyl alcohol, ethyl alcohol, benzoyl chloride, butyl stearate, cocoanut oil, cyclohexanone, ethylene dichloride, ethyl ether, furfural, isoamyl acetate, methyl ethyl ketone, and nitrobenzene. Ordinarily, only a small amount of such agents is required; however, as much as about 50 per cent by weight based on the amount of the bentonite compound can be used.

The mineral oil ingredient in the compositions provided by this invention may be any of the hydrocarbon oils of lubricating grade, such as customarily used in compounding greases. The oil may be a refined or semi-refined paraffinic-, naphthenic-, or asphaltic-base oil having a viscosity of about 50 to 4,000 SUS at 100° F. If desired, a blend of oils of suitable viscosity may be employed instead of a single oil, by means of which any desired viscosity within the range of 50 to 4,000 SUS at 100° F. may be secured. The viscosity of the oil has little effect on the dropping point of the compositions, but more viscous oils produce compositions having greater stickiness and adhesive properties than do the lighter oils. The oil content of the compositions prepared according to this invention may comprise about 75 to about 95 per cent or more by weight of the total composition. The particular oil as well as the exact amount of oil employed depends upon the characteristics desired in the final composition.

The polymerized ethylene is a polymerization product of ethylene having a molecular weight of about 1,000 to 30,000 or more. Polyethylenes having a molecular weight within this range are characterized by the following approximate characteristics:

Softening point, °C.	110
Viscosity at 130° C., poises	1×10^6
Tensile strength, p. s. i.	1,800
Elongation, percent	550
Yield, p. s. i.	1,475

These polymerized ethylene compounds are obtained by the thermal or catalytic polymerization of ethylene at high pressure. The method of forming the polymers is not a part of the present invention.

The polymerized esters of acrylic acid and alpha-methacrylic acid employed in accordance with the invention are preferably prepared as described in U. S. Patent No. 2,091,627, issued August 31, 1937, by heating the monomeric esters at 70° to 100° C. in the presence of a small amount of a polymerization catalyst such as peroxides or ozonides. The esters can be polymerized and then added to the oil or the esters can be added to the oil and then polymerized. Esters suitable for the purpose of this invention are prepared by the esterification of acrylic acid or alpha-methacrylic acid with a monohydric alcohol containing at least 5 carbon atoms, i. e., the amyl, hexyl, heptyl, octyl, nonyl, decyl, lauryl, myristic, cetyl and octadecyl esters of acrylic acid and alpha-methacrylic acid. The esters are preferably those derived from the straight chain monohydric primary saturated alcohols containing from 8 to 18 carbon atoms. When an ester is mentioned it is understood, of course, that a mixture of esters is also intended since many of the commercial alcohols, particularly the long-chain aliphatic alcohols, contain a mixture of alcohols. Likewise, the polymerization products used in accordance with the invention may be a mixture of two or more polymers. For example, we may use a mixture of polymerized n-lauryl-alpha-methacrylate, n-myristic-alpha-methacrylate and n-cetyl-alpha-methacrylate. Instead of a

simple mixture of polymers, we can use co-polymers which result when a mixture of two or more of the monomeric esters is polymerized. The method of forming the esters and the method of forming the polymers are not a part of the present invention.

The polymers of ethylene, alkyl acrylates, and alkyl alpha-methacrylates are employed in an amount sufficient to increase the water-resistant characteristic of the lubricant and insufficient to substantially change other desirable characteristics. This amount usually corresponds to about 0.4 to 5.0 per cent by weight based on the weight of the total composition.

The polymerized methacrylic acid esters can be used in their undiluted normally viscous state; however, from the standpoint of the ease in handling these materials, both during their preparation and during subsequent use, it is preferred to employ an inert solvent to render the polymers less viscous. Thus, polymer concentrates having any desired viscosity can be prepared by dissolving the polymer in various inert solvents such as toluene, lubricating oil, hydrocarbons boiling in the gasoline boiling-point range, and the like. The amount of solvent employed will depend, of course, upon the particular polymer and the particular solvent as well as upon the viscosity of the concentrate desired. Polymer concentrates suitable for the purpose of this invention can comprise about 25 to about 55 per cent active ingredient, that is, about 75 to about 45 per cent neutral solvent, without deleteriously affecting the beneficial properties of the lubricating compositions. The polymerized methacrylic acid esters can be employed in amounts between about 0.4 and 5.0 per cent by weight based on the weight of the lubricating composition. It will be understood, of course, that when polymer concentrates are used the amount of concentrate used will be an amount sufficient to incorporate between about 0.4 and 5.0 per cent by weight of the polymer in the composition. In other words, if a concentrate containing 40 per cent active ingredient is used, the amount of said concentrate would be between about 1.0 and 12.5 per cent by weight based on the weight of the lubricating composition.

Suitable polymerized esters for the purpose of this invention are commercially available under the trade name "Acryloid." Materials marketed under this trade name are understood to be a mixture of polymerized esters of methacrylic acid and have a molecular weight range of about 10,000 to about 25,000. Because of the difficulty encountered in determining the true molecular weight of a polymer of this type, inspection standards are frequently established with reference to the viscosity of a standard quantity of polymer in a solvent such as toluene. Thus, the molecular weights of polymers of the same chemical type can be compared by means of viscosity determinations of standard solutions. Viscosities generally can be determined much easier than molecular weights and at least for laboratory control purposes are indicative of the relative molecular weights of various polymers. For example, the relative molecular weights of the various polymers can be expressed in terms of centistoke viscosity at 100° F. of a 30 per cent solution of polymer in toluene. On this basis, we can use polymers whose relative molecular weight is between about 140 and about 375 centistokes.

The bentonite compounds employed in preparing the bentonite-organic base compounds for use in accordance with the invention are compounds composed of a montmorillonite mineral in which at least a part of the cation content of the mineral has been replaced by an organic base. Clays that swell at least to some extent on being contacted with water and contain as a primary constituent a mineral of the group known as montmorillonites are generally referred to as bentonites. Such clays, which contain exchangeable alkali metal atoms either naturally or after treatment, constitute the raw materials employed in making bentonite-organic base compounds used in the compositions of this invention. So far as known, all naturally occurring montmorillonites contain some magnesium and certain of them, as exemplified by Hector clay, contain such a high percentage of magnesium that they largely have magnesium in the place of the aluminum content characteristic of the more typical montmorillonites.

The amount of the bentonite-organic base compound used may vary over wide limits depending upon the particular oil with which it is to be blended and upon the properties desired in the final lubricating composition. While we prefer to use amounts in the order of about 3 to 20 per cent by weight, it should be understood that depending upon the consistency of the composition desired, less than 3 per cent or more than 20 per cent of the bentonite compound can be employed. When a bentonite compound is mentioned, it is understood, of course, that one or more of such compounds is intended.

When it is desired to produce compositions having improved oxygen stability, we advantageously employ a small amount of a diaryl amine. As examples of some of the diaryl amines which may be used in the compositions of this invention may be mentioned diphenylamine, phenyl alpha-naphthylamine, phenyl beta-naphthylamine, alpha alpha-, alpha beta-, beta beta-dinaphthylamines, and the like. Other diaryl amines as well as their derivatives wherein one or more hydrogen atoms on one or both of the aromatic nuclei are replaced by a substituent group may be used. The substituting group may, for example, be one selected from the class of aryl, alkyl, amino, aryloxy and alkyloxy radicals, so long as the presence of the substituent does not render the diaryl amine insoluble in oil, or soluble in water or otherwise adversely affect the effectiveness of the diaryl amine. The amount of the diaryl amine employed will depend to a large extent upon the severity of the conditions to which the composition is subjected, as well as the particular diaryl amine used. For instance, when the composition is subjected to prolonged use under oxidizing conditions, such as under extreme temperature and pressure, the diaryl amine requirement will be much greater than when relatively mild operating conditions are encountered. Generally, however, the amount of the diaryl amine employed is between about 0.1 and 1.5 per cent by weight based upon the weight of the total composition. In any case, an amount sufficient to substantially inhibit oxidational deterioration is employed.

In order to illustrate the improved water-resistant properties of the compositions of the present invention, a number of lubricating compositions were prepared. In preparing these lubricating compositions, a lubricating oil base having a viscosity of approximately 650 SUS at 100° F. was prepared by mixing 95 parts by weight of acid-treated Texas oil having a viscosity of 500 SUS at 100° F. with 5 parts by weight of naphthenic type residual oil having a viscosity of 175,000 SUS at 100° F. Various amounts of polymerized ethylene were then added with stirring to separate portions of the lubricating oil base. The polymerized ethylene was a solid having a molecular weight of about 20,000. A commercially available polymerized methacrylic acid ester was added to additional portions of the oil base.

The polymerized methacrylic acid ester employed in preparing a composition of the invention for test purposes was a commercially available concentrate containing approximately 40 per cent by weight of active ingredient. The active ingredient is believed to be polymerized lauryl-alpha-methacrylate. The active ingredient in a 30 per cent toluene solution has a relative molecular weight when expressed in terms of viscosity at 100° F. of 160 centistokes. Typical properties of the 40 per cent commercially available concentrate are as follows:

Gravity, °API	27
Specific gravity	0.89
Flash point, °F.[1]	400
ASTM pour point, °F	+20
Viscosity:	
cs. at 100° F	5,750
SUS at 100° F	27,500
cs. at 210° F	671
SUS at 210° F	3,100
Color, ASTM	2
Neutralization No.	0.10

[1] When diluted with three parts mineral oil having a flash point of 400° F.

When solution of the polymer in each of the samples was complete, 6.5 parts by weight of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms, namely, octadecyl amine bentonite, were dispersed in the polymer-containing oil mixture. Two parts by weight of methanol were used in the blending procedure to aid in dispersing the octadecyl amine bentonite.

The resistance to leaching by water of the compositions

prepared as described above when compared with a similar composition containing no polymer is shown in the following table:

Composition, percent by Wt.	A	B	C	D	E	F
Lubricating oil base	91.5	90.5	88.5	86.5	90.5	86.5
Octadecyl amine bentonite	6.5	6.5	6.5	6.5	6.5	6.5
Methanol	2.0	2.0	2.0	2.0	2.0	2.0
Polymerized lauryl-alpha-methacrylate concentrate (40 percent active ingredient)		1.0	3.0	5.0		
Polymerized ethylene					1.0	5.0
Water resistance (Rotating rack; water sprayed at rate of 500 cc./min. for 15 min.):						
Percent lubricant retention @ 80° F	2.3	64.0	70.4	83.5	87.2	61.0
Percent lubricant retention @ 90° F	2.3	11.1	27.9	40.6	21.1	62.1
Percent lubricant retention @ 100° F	0.0	2.6	7.2	15.5	19.7	43.4
Percent lubricant retention @ 120° F		2.5	2.4	6.2	6.6	11.0

It can be seen from the data in the above table that the compositions B to F containing from 1 to 5 per cent of either polymerized ethylene or polymerized lauryl-alpha-methacrylate concentrate gave remarkably improved results with respect to water-leaching characteristics.

This application is a continuation-in-part of our copending application, Serial No. 132,212, filed on December 9, 1949, now abandoned.

While the invention has been described with reference to specific details and examples of the production and properties of the compositions of our invention, it is to be understood that the invention is not intended to be limited to such details and examples, except as recited hereinafter in the appended claims.

We claim:

1. A lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymer selected from the group consisting of polymerized ethylene, polymerized esters of acrylic acid, and polymerized esters of alpha-methacrylic acid, wherein the amount of said bentonite compound is sufficient to produce a composition having the consistency of a grease and wherein the amount of said polymer is sufficient to improve the water-leaching characteristic of said lubricant.

2. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymer selected from the group consisting of polymerized ethylene, polymerized esters of acrylic acid, and polymerized esters of alpha-methacrylic acid wherein said bentonite compound is present in said lubricant in an amount corresponding to about 3 to about 20 per cent by weight of the lubricant and wherein the amount of said polymer is sufficient to improve the water-leaching characteristic of said lubricant.

3. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymer selected from the group consisting of polymerized ethylene, polymerized esters of acrylic acid, and polymerized esters of alpha-methacrylic acid wherein said bentonite compound is present in said lubricant in an amount corresponding to about 3 to about 20 per cent by weight of the lubricant and wherein said polymer is present in said lubricant in an amount corresponding to about 0.4 to about 5.0 per cent by weight of said lubricant.

4. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and polymerized ethylene having a molecular weight between about 1,000 and about 30,000.

5. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymerized ester of acrylic acid and a monohydric alcohol containing at least 5 carbon atoms.

6. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymerized ester of alpha-methacrylic acid and a monohydric alcohol containing at least 5 carbon atoms, wherein said polymerized ester is present in said lubricant in an amount sufficient to improve the water-leaching characteristic of said lubricant.

7. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymerized ester of acrylic acid and a straight chain monohydric primary saturated alcohol containing between 8 and 18 carbon atoms.

8. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymerized ester of alpha-methacrylic acid and a straight chain monohydric primary saturated alcohol containing between 8 and 18 carbon atoms, wherein said polymerized ester is present in said lubricant in an amount sufficient to improve the water-leaching characteristic of said lubricant.

9. An improved lubricant comprising a dispersion of a compound of a bentonite and an organic base containing 10 to 20 carbon atoms in a solution of an oil and a polymerized ester of alpha-methacrylic acid and a straight chain monohydric primary saturated alcohol containing between 8 and 18 carbon atoms wherein said bentonite compound is present in said lubricant in an amount corresponding to about 3 to about 20 per cent by weight of the lubricant and wherein said polymerized ester is present in said lubricant in an amount corresponding to about 0.4 to about 5.0 per cent by weight of said lubricant.

10. An improved lubricant consisting essentially of a uniform mixture of about 75 to about 95 per cent by weight of a lubricating oil, about 3 to about 20 per cent by weight of octadecyl amine bentonite, and about 1 to about 5 per cent by weight of polymerized ethylene having a molecular weight of about 20,000.

11. An improved lubricant consisting essentially of a uniform mixture of about 75 to about 95 per cent by weight of a lubricating oil, about 3 to about 20 per cent by weight of octadecyl amine bentonite, and about 1 to about 5 per cent by weight of polymerized lauryl-alpha-methacrylate in the form of a 40 per cent by weight mineral oil concentrate having a viscosity of about 27,500 SUS at 100° F.

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