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LUBRICATING OIL COMPOSITIONS HAVING EXTREME PRESSURE CHARACTERISTICS

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My invention relates to a superior lubricating oil composition. More particularly the invention is directed to a novel lubricating oil composition having improved extreme pressure and anti-friction properties.

With the advent of high compression internal combustion engines, much difficulty has been experienced in formulating a suitable lubricating oil composition capable of operating under severe conditions to protect effectively metal surfaces which come in contact with the oil. It is well known that the high pressure occurring in certain types of gears and bearings may cause a film of lubricant to rupture with subsequent damage to the machinery. It has been shown that base lubricants such as mineral oil and/or synthetic oil can be improved with regard to their protective effect on surfaces by the addition of certain substances so that excessive wear, scuffing and seizure which normally follow a break in the film of lubricant can be prevented even under the most unfavorable pressure and speed conditions. Lubricants possessing this highly desirable property are called extreme pressure lubricants.

Certain classes of compounds can be used to improve specific properties of base lubricants. Thus, compounds containing sulfur, chlorine, phosphorus or lead or combinations of these elements may improve the extreme pressure properties of a lubricant. However, the simple presence of these elements does not guarantee extreme pressure properties and various compounds that do have these properties can vary considerably in their effectiveness. It is generally believed that the effectiveness of an extreme pressure additive is related to its ability to react with and form a protective coating on a bearing surface to be lubricated. To be most effective, however, the additive must be present in sufficient concentration at the surfaces to form an adequate film. One method of realizing this surface concentration is the use of polar or other type molecules which have an affinity or attraction for surfaces. Thus, as opposed to the use of a non-polar molecule which will be present in more or less equal concentration throughout the bulk of the lubricant, a polar type molecule will tend to give a greater concentration of additive at the metal surface where it is needed.

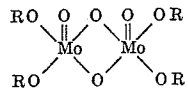
The use of molybdenum as a lubricant particularly in the form of molybdenum disulfide has increased as those skilled in the art have found this material to have outstanding lubricating characteristics. Compounds such as boron nitride, cadmium iodide and graphite have a suitable crystal structure but fail in other respects to meet necessary extreme pressure requirements. Further boron nitride does not have any affinity to metal surfaces; cadmium iodide is effected by moisture; and graphite has a low affinity to metal surfaces; thus it depends on absorbed gases or liquids for its lubricating characteristics. Over the years the chemical industry has been faced with the difficulties of adding a suitable solid such as molybdenum disulfide to a fluid lubricant which normally results in settling, plugging of narrow orifices, cleavance of lines, valve sticking, ring clogging and the like. My composition overcomes these difficulties while obtaining lubricating advantages from a molybdenum material.

My invention is directed to a lubricating oil composition consisting essentially of a major amount of lubricating base oil, a minor amount of molybdate ester and a sulfurized fatty oil or a sulfurized olefin.

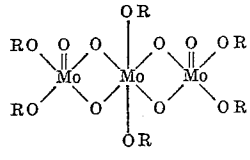
The esters of my composition are the base-oil compatible, i.e. soluble, dispersible or miscible, aliphatic monohydric alcohol esters of molybdic acid. The aliphatic ester radicals in general contain at least four carbon atoms and preferably are saturated with from one to all of the ester groups containing 8 to 20 carbon atoms. The amount of ester added to the base oil may vary depending upon particular characteristics required although sufficient ester must be present to give the desired effect. In general from about .1% to about 10% of ester by weight of final composition is used with about 1 to 5% being preferred. The alkyl esters of molybdic acid which are employed in the lubricating oil compositions according to this invention are conveniently prepared by the usual reactions. The mixtures of reactants are ordinarily heated to accelerate esterification. For present purposes, the alkyl esters of molybdic acid or alkyl molybdates, as they are commonly called, are preferably prepared by the reaction of an aliphatic alcohol and molybdenum compounds such as molybdic anhydride or molybdenum trioxide, ammonium molybdate, ammonium paramolybdate and molybdanyl chloride. As an example, the reaction product can contain about 2 moles of alcohol radical for every mole of molybdenum trioxide.

The alcohols which are generally reacted with the molybdenum compounds referred to above are aliphatic alcohols containing up to 20 carbon atoms. The aliphatic radicals may be straight chain or branched chain or cycloaliphatic in nature. Either primary, secondary or tertiary radicals are suitable, but primary and secondary radicals are preferred for desirable physical properties in the base oil and apparent effectiveness. Examples of these alcohols include n-butyl alcohol, tertiary butyl alcohol, n-hexyl alcohol, cyclohexyl alcohol, n-octyl alcohol, 2-ethylhexanol, isooctyl alcohol, decyl alcohol, dodecyl alcohol, tridecyl alcohol, octadecyl alcohol, etc. or their mixtures. Higher aliphatic alcohols are preferred, the term here being used in its commonly accepted sense as covering alcohols of eight carbon atoms or more. Such alcohols impart desirable physical characteristics to the alkyl molybdates prepared from them. Branched chain alcohols, for example, those derived by the well known Oxo process are particularly suitable. Decyl and tridecyl alcohols of this latter type have been found to be

effective. My molybdate esters may have structures such as:



and



where RO is the alcohol radical.

My composition can contain a base-oil compatible sulfurized fatty oil such as sulfurized sperm oil, sulfurized rape seed oil, sulfurized cotton seed oil, etc. These oils in general are esters and glycerides of acids of 12 to 24 carbon atoms. A particularly effective material employed is sulfurized sperm oil which contains about 5 to 15 weight percent of combined sulfur. In general from about 0.5 percent of sulfurized fatty oil to about 15% of the final composition is employed with a preferred amount being from about 1 to 8 percent by weight of the final composition.

Another sulfur-containing material useful in the present invention is a base oil-compatible sulfurized olefin hydrocarbon. This sulfurized olefin is usually prepared by the reaction of an aliphatic olefin, preferably branched chain, of 8–32 carbon atoms with sulfur and comprises about 25–75% sulfur by weight. Although sulfurized hydrocarbons having as little as 10% sulfur by weight are sometimes used, the more highly sulfurized materials, in an amount from about 0.1 to 5%, preferably about 0.5 to 2%, by weight of the lubricant composition are most often employed to give a fully satisfactory multipurpose material. As an example the sulfurized hydrocarbon may be a material in which the hydrocarbon has a structure similar to di- or poly-isobutylene and contains about 46% S.

The natural and synthetic oils of lubricating viscosity are suitable base oils for the compositions of the invention. They include hydrocarbon or mineral lubricating oils of naphthenic, paraffinic, and mixed naphthenic and paraffinic types. They may be refined by any of the conventional methods such as solvent refining and acid refining. Synthetic hydrocarbon oils of the alkylene polymer type or those derived from coal and shale may also be employed. Alkylene oxide polymers and their derivatives such as the propylene oxide polymers and their ethers and esters in which the terminal hydroxyl groups have been modified are also suitable. Synthetic oils of the dicarboxylic acid diester type including dibutyl adipate, di-2-ethylhexyl sebacate, di-n-hexyl fumaric polymer, di-lauryl azelate, and the like may be used alone or in blends containing complex or polyesters or other thickening agents. These esters are frequently made from dibasic acids, alcohols and glycols of 6 to 12 carbon atoms. Alkyl benzene types of synthetic oils such as tetradecyl benzene, etc. are also included.

The extreme pressure compositions of this invention are effective in the form of compounded lubricating oils containing conventional additives such as oxidation inhibitors, detergents, VI improvers, antifoaming agents, rust inhibitors, oiliness or film strengthening agents, wear inhibitors, dyes and the like. Base-oil compatible chlorinated hydrocarbons can be included in my compositions without causing the high wear that frequently accompanies their use. A typical chlorinated hydrocarbon is a product usually containing about 25 to 75% chlorine by weight and made by the reaction of gaseous chlorine with high-boiling saturated or unsaturated aliphatic hydrocarbons, including cycloaliphatics, of say 8 to 32 carbon atoms. The materials are used in amounts similar to my sulfurized olefin.

The ester of the present invention may be prepared by various conventional means such as shown in Example I.

EXAMPLE I

1800 grams of tridecanol (OH value=279) and 750 ml. of toluene as solvent were placed in a 5-liter reaction flask. 200 grams of MoO_3 were dissolved in 4 liters of H_2O and 350 ml. of NH_4OH. A nitrogen atmosphere was supplied to the reaction flask. After heating the alcohol solution to about 110° C., the molybdate solution was added slowly over a period of 5 hours with constant stirring in a 105–110° C. temperature range. Water was constantly removed, and reaction was continued for 48 hours, gradually increasing the reaction temperature to 250° C. The product was then filtered, recovering the solids, and the solvent and excess alcohol removed by vacuum distillation to 150° C. 850 grams of product were recovered which analyzed to be 14.8% of molybdenum by weight.

The data of following Table I demonstate the increased extreme pressure and anti-wear properties of my composition.

Table I

Weight Percent Composition:								
SAE 90 Mineral Gear Oil, 82.5 SUS at 210° F	100	98	99.5	99.5	98	96	97.5	95.5
Sulfurized Sperm Oil (12% S)		2				2		2
Sulfurized Hydrocarbon [1] (46% S)			0.5				0.5	
Chlorinated Hydrocarbon [2] (50% Cl)				0.5				0.5
Tridecanol Molybdate Ester [3]					2	2	2	2
Laboratory Tests:								
Viscosity, SUS—								
at 100° F	933	963	920	933	915	934	928	959
at 210° F	82.5	84.7	81.8	82.4	82.2	84.2	82.4	83.7
Viscosity Index	90	92	89	89	91	93	90	90
Pour, °F	0	5	0	5	5	0	0	5
Percent Sulfur		0.24	0.23			0.24	0.23	0.24
Percent Chlorine				0.25				0.25
Percent Molybdenum					0.18	0.18	0.18	0.18
Performance Evaluation:								
Timken Safe Load, lbs	7	20	30	10	7	15	30	27
Falex Breakdown, lbs	1,250	3,500	4,500	1,000	3,250	4,500	4,500	4,500
SAE at 300 r.p.m., lbs	166	348	374	397	141	347	381	412
Shell 4-Ball Wear Test, mm. scar (7 Kg., 2 Hrs., 110° C., 640 r.p.m.)	0.55	0.33	0.38	0.64	0.37	0.39	0.36	0.47
Shell 4-Ball EP Test—								
Weld, Kg	141	178	178	158	141	200	224	224
Mean Hertz Load	13.8	34.7	37.5	27.5	25.4	49.7	46.7	43.3

[1] Sulfurized polyisobutylene of 8 to 12 carbon atoms.
[2] Chlorinated branched chain paraffin of about 12 carbon atoms.
[3] Molybdate ester of tridecanol, see Example I.

Table II indicates more detailed data on the Falex breakdown load or low carrying capacity tests as shown in Table I.

Table II

Weight Percent Composition:								
SAE 90 Gear Oil	100	98	99.5	99.5	98	96	97.5	95.5
Sulfurized Sperm Oil (12% S)		2				2		2.0
Sulfurized Hydrocarbon [1] (46% S)			0.5				0.5	
Chlorinated Hydrocarbon [2] (50% Cl)				0.5				0.5
Tridecanol Molybdate Ester [3]					2	2	2.0	2.0
Falex Breakdown Load, lbs	1,250	3,500	4,500	1,000	3,250	4,500	4,500	4,500
Torque at:								
500 lbs. load	11	10	11	11	12	11	7	10
1,500 lbs. load		23	50		23	14	12	14
2,500 lbs. load		34	57		70	30	27	33
3,500 lbs. load		73	74			34	26	38
4,500 lbs. load			78			35	30	38
Temperature at:								
500 lbs. load	162	160	165	179	167	178	148	168
1,500 lbs. load		214	304		215	208	173	198
2,500 lbs. load		257	386		341	280	237	267
3,500 lbs. load		420	468			309	272	325
4,500 lbs. load			507			328	294	340
Seizure	Weld	Weld	None	Weld	None	None	None	None
Wear			Heavy		V. Heavy	Light	Med.	Med.
Ridging			Heavy		Coarse	Fine	Med.	Fine

[1], [2], [3] See Table I.

The following data indicate the advantages of using my compositions wherein the base oil is a synthetic lubricant.

Table III

Weight Percent Composition:				
Base Oil [1]	100	96	98	98
Molybdate Ester [2]		2	2	0
Sulfurized Sperm Oil (12% S)		2	0	2
Tests:				
Viscosity at—				
100° F., cs	13.04	14.25	13.27	13.78
210° F	3.444	3.625	3.488	3.609
Viscosity Index	162	160	163	168
ASTM Slope	0.690			
SAE at 300 r.p.m., lbs	318	335	110	227
Shell 4-Ball Wear Test (7 Kg., 2 Hrs., 110° C., 640 r.p.m.)	0.51	0.50	0.42	0.47
Shell 4-Ball EP Test—				
Weld, Kg	141	200	141	178
Mean Hertz Load	21.0	44.5	38.6	28.5

[1] Di-2-ethylhexyl sebacate with 0.1% free sebacic acid (Plexol-201J).
[2] Molybdate ester of tridecanol of Example I.

Tables I, II and III clearly demonstrate the improved lubricating properties of my new composition where a sulfurized fatty oil or sulfurized olefin is used in conjunction with molybdate esters in mineral or synthetic lubricating oils to produce superior extreme pressure and antiwear properties.

I claim:

1. A lubricating composition consisting essentially of a major amount of a base oil of lubricating viscosity, about .1% to 10% by weight of a base oil-compatible aliphatic monohydric alcohol ester of molybdic acid, said alcohol containing 4 to 20 carbon atoms and about 0.5 to 15% by weight of a base oil-compatible member selected from the group consisting of sulfurized fatty oils and sulfurized olefins of 8 to 32 carbon atoms.

2. The lubricating composition of claim 1 in which the ester of molybdic acid is present in an amount of about 1 to 5% and the member selected from the group consisting of sulfurized fatty oils and sulfurized olefins which is present is about 1 to 8% when a sulfurized fatty oil and about .1 to 5% when a sulfurized olefin.

3. The lubricating composition of claim 2 which contains sulfurized sperm oil.

4. The lubricating composition of claim 2 which contains sulfurized polyisobutylene.

5. The lubricating composition of claim 2 in which the base oil is a mineral oil.

6. The lubricating composition of claim 2 in which the alcohol group of the ester contains about 8 to 20 carbon atoms.

7. The lubricating composition of claim 2 which contains about 0.1% to 5% of a base oil-compatible chlorinated hydrocarbon of 8 to 32 carbon atoms.

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