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EXTREME PRESSURE LUBRICATING COMPOSITIONS

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This invention relates to extreme pressure lubricating compositions and particularly to extreme pressure lubricating oils containing phosphorus and sulfur as extreme pressure agents.

It has long been known that lubricating oils of mineral oil base, while being highly satisfactory lubricants for many types of bearings, lack requisite film strength for protecting machine elements which are subject to high unit pressure. It is also known that various chemical compositions may be added to mineral lubricating oils to increase the film strength or to provide a protective coating on the metal when the normal lubricating film fails so as to prevent actual metal to metal contact under momentary conditions of extreme pressure.

A familiar example of a mechanism which requires an extreme pressure lubricant is the hypoid gearing commonly used in automotive vehicles where unit pressures are frequently in excess of 100,000 pounds per square inch and may reach instantaneous values as high as 400,000 or more. In the prior art it has been suggested that various compositions which include such elements as sulfur or phosphorus or chlorine, or two or more of these in combination, may be used to impart extreme pressure properties to the lubricant. In particular, in the prior art, use has been made frequently of sulfurized oils, that is, oils wherein sulfur has been incorporated and usually heated or "cooked" to form some sort of reaction product capable of releasing free sulfur upon a rise in temperature so that the sulfur thus released can react with the metal to form a metal sulfide film on the part being lubricated. This film, which is of microscopic thickness, is sufficient to afford the required momentary protection, but sulfur compounds of this character are frequently unduly corrosive under low load conditions, or they lack the high extreme pressure properties required for some purposes, or they tend to precipitate or sludge out of the oil, or they are otherwise deficient or objectionable.

It has also been suggested in the prior art that phosphorus, or phosphorus compounds such as sulfides of phosphorus, may be reacted chemically with oils and other ingredients to impart extreme pressure properties to lubricants.

It has now been found that by control of temperature and other conditions certain phosphorus compounds, such as P_4S_3, can be physically dissolved in sulfurized fatty materials without reacting chemically, or at least without reacting to an objectionable degree. It is therefore one object of the present invention to introduce phosphorus compounds of this character into lubricating oils without causing substantial chemical reaction to take place. It is a further object of the present invention to control the conditions of preparation as well as the ingredients so as to

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provide a highly effective extreme pressure agent which is not objectionably corrosive or subject to other deficiencies common to phosphorus and sulfur compounds of the prior art.

It has also been suggested in the prior art that a sulfide of phosphorus might be dispersed in mineral lubricating oil to impart extreme pressure properties thereto (Patent No. 2,235,161) and also that a mineral base lubricating oil might have its extreme pressure properties improved by adding thereto a sulfurized and phosphorized sperm oil (Patent No. 2,274,025). In the first instance the dispersion has not proved entirely satisfactory for some purposes since it tends to precipitate out of the lubricant, particularly during long periods of storage, and in the second place a chemical reaction takes place between the ingredients which results in a product having less satisfactory characteristics than that which results when the chemical reaction is inhibited, as will appear from data incorporated below in this specification.

EXAMPLE 1

As an example of a composition prepared according to our invention, a mild extreme pressure base is first prepared by heating 88% by weight of a natural winter sperm oil and 12% flowers of sulfur to 385° F., holding the mixture at this temperature for 60 to 90 minutes, and thereafter cooling and quenching with one part of mineral lubricating oil, obtained from Mid-Continent crude having a viscosity at 210° F. of about 175 S. S. U., to four parts of the sulfurized product. The cooling can, of course, be carried out by any convenient means. This base material so prepared contains no sulfur in active form, as measured by either of two standard copper strip tests. For example, a 10% solution of the additive in mineral oil (SAE 90 grade) does not blacken copper in one hour at 250° F., or in three hours at 210° F.

98% by weight of the mild extreme pressure base prepared as just described is next combined with 2% by weight of P_4S_3. The above ingredients are preferably stirred and heated to 200° F. in about 10 minutes. Thereafter they are held at 200° F. for 15 minutes and then cooled. The resulting product contains approximately 9.0% sulfur and 1.1% phosphorus, and is an extreme pressure agent which can be added in appropriate proportions, for example 10% by weight, to conventional mineral base lubricants of appropriate viscosity. Such lubricants may, of course, contain other materials such as corrosion and oxidation inhibitors, pour point depressors, viscosity index improvers, and the like. The percentage of extreme pressure agent, prepared as above, may be varied within rather wide limits, for example from 1 to 20% of the final composition or

more, as will be obvious to those skilled in the art.

EXAMPLE 2

3,920 grams of a sulfurized mild extreme pressure base, prepared as described above in Example 1, is heated to 170° F. and then 80 grams of P_4S_3 are added with stirring. Thereafter the temperature is raised further to 200° F. and held at that temperature for 15 minutes. The temperature is next reduced to 170° F. and 40 grams of "Deactivator C," described below, are added. Thereafter the composition is cooled and is found to be a satisfactory extreme pressure additive as indicated by data which will be set forth below.

EXAMPLE 3

A mild extreme pressure base is prepared substantially as indicated above in Example 1 except that the quantity of sulfur employed is about half that used in the first and second examples. 1,880 grams of natural winter strained sperm oil 45 are heated to a temperature of 285° F. and 120 grams of sulfur, 6% of the final product by weight, are added. The mixture is then stirred and heated further to 385° F. and held at that temperature for about 90 minutes. Thereafter the mixture is permitted to cool naturally to room temperature. 10 grams of P_4S_3 are next added to the cool mixture and the temperature raised gently to 210° F. with stirring. The mixture is held at this temperature for about one hour and the product then again cooled naturally. Even after this relatively long treatment at 210° F., the product is found to contain a substantial quantity of unreacted phosphorus sulfide, although a partial reaction had taken place in this case. As in the former examples, the resulting product is found to have good extreme pressure properties.

We have discovered further that compositions prepared according to Examples 1 and 2, while quite satisfactory for extreme pressure purposes per se, are somewhat corrosive and that the undesirable corrosive properties can be improved by adding a small quantity of any of several commercial metal deactivators. In Example 2 a metal deactivator was added as a part of the preparation.

As indicated in the data below the lubricants which lack the metal deactivator fail to pass the copper corrosion test whereas those which include it, generally speaking, are satisfactory in this respect. Among the deactivators which are contemplated for use in this connection are the following:

Salicylaldehyde-ethylenediamine condensation product, "Deactivator A"

Salicylaldehyde-propylene diamine condensation product, "Deactivator C"

Iso-octyl phenol methyl amine polymer, "Deactivator B"

Benzoyl acetone-ethylene diamine condensation product

Benzoyl acetone-propylene diamine condensation product

"Deactivators A and C" consist of Schiff bases prepared by condensing two mols of salicylaldehyde with one mol of ethylene diamine or propyline diamine, respectively, by methods well known in the art. "Deactivator A" is a substantially pure product, while "Deactivator C" contains about 20% of toluene added to liquefy the product.

"Deactivator B" may be prepared by heating one mol of isooctyl phenol in mineral oil with 1.5–2.5 mols of paraformaldehyde and 1.5–2.5 mols of ammonia until the water of reaction has been removed, and then raising the temperature to approximately 300° F. for one to three hours. This product contains about 50% of active ingredient and 50% mineral oil.

The relative effects of the extreme pressure compositions described in the various examples above with and without metal deactivators and inhibitors added are shown in the following table. The S. A. E. 90 mineral base test oil actually used in these tests is a 50–50 blend of propane extracted Mid-Continent lubricating oil and a phenol extracted Mid-Continent oil. The first mentioned oil has A. P. I. gravity of 21.9, flash point 585° F., viscosity 204 S. S. U. at 210° F., viscosity index 85, Conradson carbon test of 2.86, sulfur content 0.92%. The second has a gravity of 29.8, A. P. I., flash point 445° F., viscosity 58 S. S. U. at 210° F., viscosity index of 105, Conradson carbon 0.07, and sulfur content of 0.34%.

The P_4S_3 reaction product shown in the above table is prepared as follows:

980 grams of the mild extreme pressure base described in Example 1 (prepared from sperm oil, sulfur and mineral oil) are heated with 20 grams of P_4S_3, with stirring, as follows:

Temperature:	Time, hours
210–230° F	2
235–240° F	1
255± 5° F	1

Test data on extreme pressure additive blends

[Additives blended in SAE 90 mineral base oil.]

Test No.	Additives		Tests on Mineral Oil Blends			
	E. P. Agent	Metal Deactivator	Timken Machine Load [1]	SAE Machine [2]	Almen Machine [3]	Copper Strip Test [4]
1	None	None	10	20	2	Pass.
2	10% Sulfurized Sperm Oil.[5]	do	33	20	7	Do.
3	10% Example 1	do	68	220	15	Fail.
4	9.6% Example 1[6]	0.1% "Deactivator C"	51			Pass.
5	10% Example 3	None	59			Fail.
6	9.5% Example 1	0.5% "Deactivator B"	51	200		Pass.
7	10% Example 2	(contains "Deactivator C").	51	192		Do.
8	9.5% Example 1	0.5% "Deactivator C"	59	192		Do.
9	10% P_4S_3 Reaction Product.	None	33	125		Do.

[1] Pounds load on lever arm.
[2] Scale pounds carried at 1000 R. P. M.
[3] Number of 2-pound weights carried-shock loading.
[4] CRC–L–16–445 Procedure (U. S. Army Specification).
[5] Mild E. P. base prepared as in Example 1.
[6] Also contains 0.3% degras.

This product is found to contain 9.05% sulfur and 1.07% phosphorus in a substantially combined form. It will be noted that, while the contents of sulfur and phosphorus are essentially the same as in Example 1, the load carrying ability, as measured by both the Timken and SAE machines is substantially reduced by the long heating at relatively high temperatures required to obtain a chemical combination.

It has previously been believed that this long heating at high temperatures was essential in order to prevent excessive corrosion of the copper and bronze parts present in many mechanisms. It has been shown above, however, that a product of superior extreme pressure properties can be produced by avoiding prolonged heating or high temperatures, and that corrosion may be inhibited by the use of metal deactivators. The composition of the present invention, therefore, represents a distinct advance in the art because it provides at one and the same time (1) improved load carrying properties, (2) protection of copper and bronze parts from corrosion when required, and (3) a manufacturing process much shorter and easier than those previously known.

The composition effects of various inhibitors and deactivators may be shown by the following data which are obtained by using a standard active sulfur lubricant containing the deactivators of various types and the various quantities as indicated.

Effect of metal deactivators

Active Sulfur Lubricant Containing Deactivator as Shown	Copper Strip Test (1 Hr. at 250° F.)
No deactivator	Black.
0.15% "Deactivator A"	Peacock.
0.50% "Deactivator B"	Light Peacock.
0.10% "Deactivator C"	Do.

In general, the preferred composition is prepared by using about 90% of mineral oil of the appropriate lubricating grade and viscosity combined with about 10% of the additive although the proportions may be varied from 1 to 20% or more of the latter as indicated above. The additive itself preferably consists of a sulfurized fatty oil in which is dissolved under conditions of relatively low temperature, that is not materially in excess of 200° F., a small amount of a phosphorus sulfide, particularly phosphorus sesqui-sulfide (P_4S_3) in sulfurized sperm oil. The percentage of phosphorus sulfide used may be varied from as little as 0.1% to about 5% although the range preferred is 1 to 2% as indicated. Other sulfurized fatty oils such as lard oil, corn oil, partially hydrogenated fish oils, etc., may be used in lieu of sulfurized sperm oil. The percentage of metal deactivator is usually smaller than that of the phosphorus sulfide. This ingredient may comprise 0.1 to 2% by weight of the extreme pressure composition (additive), about 1% being preferred. Based on the finished lubricant, which preferably contains about 10% of the composition, the over-all content of phosphorus sulfide is preferably about 0.1 to 0.2%, though it may vary from 0.01 to 0.5%. The metal deactivator, similarly, is used to the extent of about 0.01 to 0.2%, preferably about 0.1%, based on the weight of the finished lubricant. The metal deactivator may be omitted entirely for some purposes, although it is very desirable where copper or bronze bearings, etc., are used, since extreme discoloration or corrosion of these parts may otherwise result.

It will be understood from the foregoing that

the essence of the present invention is the use of a phosphorus sulfide, particularly P_4S_3, dissolved in, but not substantially reacted with, sulfurized fatty oil. It will be understood, of course, that the final composition may contain other materials, such as anti-oxidants, thickeners, soaps, detergents, pour point depressors, oiliness agents, and viscosity index improvers. While the product of the invention is particularly suitable for the lubrication of hypoid gears as mentioned above, the composition may also be used in various types of lubricants, greases, cutting oils, and for other analogous purposes, as will be apparent to those skilled in the art.

What is claimed is:

1. The method of preparing an extreme pressure lubricating composition which comprises heating a major proportion of a fatty oil with a minor proportion, by weight, of sulfur to a temperature of 300° to 450° F., quenching with a minor proportion of mineral oil, cooling to a temperature not exceeding about 200° F. and thereafter, adding 0.1 to 5% of a phosphorus sulfide, holding the temperature while dispersing the phosphorus sulfide into said oil for a period of about 15 minutes to about one hour and further cooling to about 170° F. and then adding 0.1 to 2% of a metal deactivator.

2. The method according to claim 1 in which the phosphorus sulfide is P_4S_3.

3. A composition consisting essentially of a sulfurized fatty oil treated with about 0.5 to 2%, based on the weight of said sulfurized oil, of a phosphorus sulfide at a temperature ranging between 170° to 210° F. for a period of about 15 minutes to one hour during which the phosphorus sulfide is substantially dispersed in said sulfurized fatty oil but substantially unreacted therewith.

4. A composition according to claim 3 where the phosphorus sulfide is P_4S_3.

5. A composition according to claim 3 wherein said sulfurized fatty oil is sulfurized sperm oil.

6. A composition consisting essentially of a mineral base lubricating oil containing about 1 to 20% by weight, based on the total composition, of an extreme pressure additive, said additive consisting essentially of a sulfurized fatty oil treated with about 0.5 to 2%, based on the weight of said sulfurized oil, of a phosphorus sulfide at a temperature ranging between 170° to 210° F. for a period of about 15 minutes to one hour during which the phosphorus sulfide is substantially dispersed in said sulfurized fatty oil but substantially unreacted therewith, said composition including also about 0.1 to 2% of a metal deactivator.

7. A composition according to claim 6 wherein said phosphorus sulfide is P_4S_3.

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