Patented Feb. 17, 1953

2,628,940

UNITED STATES PATENT OFFICE

2,628,940

EXTREME PRESSURE LUBRICANT

Elmer B. Cyphers, Cranford, and Walter E. Waddey, Elizabeth, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application February 3, 1949, Serial No. 74,483

2 Claims. (Cl. 252—46.7)

1

This invention pertains to extreme pressure lubricants and compositions for imparting extreme pressure or load-carrying properties to lubricating oils. The invention also pertains to a method for preparing extreme pressure agents, incorporating elements such as sulfur, phosphorus, and the like, in such a manner that they will be available for suitable chemical activity under heavy load conditions.

As is well understood in the art, ordinary mineral base lubricating oils and greases which are used to lubricate opposed metal surfaces are likely to fail under extreme heavy load conditions. For example, certain machine elements such as the hypoid gears commonly used in automotive vehicles may be subjected at times to extremely heavy pressures of the order of hundreds of thousands of pounds per square inch. If the film of lubricating oil separating the opposed elements fails, as it is likely to do under such pressure, the surfaces will contact each other directly, generating high temperatures due to friction, with resultant seizure or excessive wear and early failure. Extreme pressure additives containing active sulfur, phosphorus, or chlorine, or two or more of these, are effective for reacting immediately with the metal surfaces at their higher temperatures to form a protective metal sulfide, phosphide, or chloride film which serves temporarily as a lubricating medium until the normal oil film between the parts can be reestablished. Extreme pressure additives are, therefore, reactive with the metals they lubricate to form extremely thin protective films thereon when the temperature rises due to normal oil film failure. It is known in the art that good extreme pressure lubricants may be produced by adding to mineral base lubricating oils and greases sulfur-chlorine additives of the type described in U. S. Pat. No. 2,124,598.

Lubricants containing this type of additive are excellent for the lubrication of hypoid gears subjected to low-torque, high-speed conditions, such as the hypoid gears used on passenger carrying automotive vehicles but are not well suited for use under high-torque, low-speed conditions, such as are found in heavy truck operations. It is also known that sulfurized and phosphorized esters of rosin acids of the type described in copending application Serial No.

2

712,050 filed November 25, 1946, now Patent No. 2,488,618, issued Nov. 22, 1949, in the names of E. B. Cyphers and G. M. McNulty, yield lubricants especially suitable for use in high-torque, low-speed operations, but only moderately effective under low-torque, high speed conditions. It is an object of our invention to provide, in a single additive, the excellent high speed properties of the sulfur-chlorine type additive and the excellent high-torque properties of the sulfur-phosphorus-ester type additive.

While this may be accomplished by mixing, in suitable proportions, the two types of additives, such a blend is not well suited for use in most mineral oil base stocks, because such a mixture has a severe depressing effect on the viscosity index of the oil to which it has been added. Often, this depression of viscosity index is so severe that the resulting composition has little or no utility in lubricating practice unless mineral oils of very high viscosity index are readily available.

According to the present invention, it has been discovered that compositions having excellent extreme pressure properties, under both high speed and high-torque conditions, and avoiding viscosity index depression, may be obtained by blending with the base stock an additional or third component comprising sulfurized, or sulfurized and phosphorized fatty bodies, sulfurized fatty bodies containing no phosphorus being preferred. The fatty body containing sulfur alone is preferred for the reason that a blend containing said fatty body exhibits superior load-carrying capacity compared with a blend containing a sulfurized and phosphorized fatty body.

It is also possible to prepare lubricants of considerable merit from phosphorized esters of rosin containing little or no sulfur mixed with sulfurized fatty bodies containing no phosphorus, and with the sulfur-chlorine products previously described. The phosphorized rosin esters in such a mixture may be prepared by treating the esters with P_4S_3, P_4S_7, P_2S_5, PCL_3, P_2O_5, and the like at temperatures between about 150° F. and 300° F.

The agents that are added to oil base stocks within the comprehension of this invention are:

a. Organic compounds containing both sulfur

and a halogen, prepared by reacting a halogenated compound having an aliphatic chain with an inorganic sulfur salt so as to replace only a portion of the halogen with sulfur; an example is a sulfur and chlorine-containing compound prepared by the reaction of chlorinated aliphatic acids, esters, or hydrocarbons with an alkali or alkaline earth metal sulfide or polysulfide;

b. Rosin acids, esters, alcohols, abietic acids and esters, hydrogenated derivatives of rosins and abietic acids and esters and alkyl substituents of hydrogenated and unhydrogenated rosins and abietic acids and esters, containing phosphorus or phosphorus and sulfur.

Specific examples of rosin derivatives which may be employed are: methyl abietate, methyl ester of rosin acids, abietic acid esters of ethylene glycol, glycerol, octanol, and isopropanol, esters of dihydroabietyl alcohol, dextropimeric acid and the like.

c. Sulfurized and phosphorized fatty oils, acids, esters, and other fatty bodies. Or more particularly, sulfurized fatty oils, acids, esters, and other fatty bodies. Specific examples of fatty bodies which may be employed include: sperm oil, lard oil, methyl oleate, degras, isopropyl oleate, cottonseed oil, corn oil, peanut oil and the like.

In producing the lubricating oil blend of the present invention, the additive materials, which individually per se do not form a part of the invention, are prepared by any of the methods described in the art cited above.

Thus, in one example, the sulfur and chlorine-containing material was prepared by bubbling chlorine gas through a mixture containing about 40% paraffin wax and 60% kerosene to produce a chlorinated mixture containing about 37% chlorine. This was then condensed with sodium polysulfide by refluxing in an alcoholic solution until all of the alkaline polysulfide had reacted. The alcohol was then removed by distillation under vacuum and the product filtered and washed with an aqueous caustic solution to reduce its corrosiveness toward copper, the final product containing 6.0% sulfur and 30.3% chlorine.

The sulfur and phosphorus-containing rosin derivatives may be prepared from a commercial grade of methylated rosin produced by esterification of rosin with methyl alcohol and commercially known as "Abalyn." Suitable conditions for sulfurizing are by heating with sulfur at a temperature in the range from about 250° F. to about 500° F. The sulfurized product, or in some cases the unsulfurized rosin ester, is phosphorized by heating with a bi-elemental phosphorus compound, for example, P_4S_3, P_2S_5, P_4S_7, P_2O_5, etc., to a temperature between 150° and 300° F., preferably between 200° and 250° F., for a suitable time such as 2–20 hours until a product, which does not blacken copper when tested in a 10% concentration in mineral oil for one hour at 250° F., is obtained.

The fatty body is prepared by reacting it with from 3 to 12%, preferably 6% by weight of sulfur at a temperature of 250°–500° F. until a non-corrosive product, as defined above, is obtained. If phosphorizing also is desired, the sulfurized product is treated with a bi-elemental phosphorus compound such as P_4S_3, P_4S_7, P_2S_5, P_2O_5, PCL_3, etc. Preferably phosphorus sesquisulfide is used at a temperature between 150° and 300° F.

The three additive materials are blended in varying proportions, depending on the use to which the blend is to be put.

The proportion of the sulfur and chlorine-containing aliphatic compound (*a*) required to provide a proper balance of high-torque, low speed, and low-torque, high-speed properties generally varies between 15 and 50% by weight of the total additive, and preferably between 30 and 40%, the remainder being a mixture of *b* and *c*, *b* being a phosphorized or phosphorized and sulfurized rosin derivative and *c* being a sulfurized or phosphorized and sulfurized fatty body in various proportions.

It is generally preferred to adjust the proportions of the phosphorized or phosphorized and sulfurized rosin derivative *b* and the sulfurized or sulfurized and phosphorized fatty body *c* to yield a mixture which has little or no viscosity index depressing effect, the preferred ratio being about 60:40. However, when some viscosity index improvement is required ratios as high as 75:25 may be employed, and where a mild viscosity index depressing effect can be tolerated, ratios as low as 40:60 may be used. A preferred blend contains from 30 to 50% phosphorized and sulfurized rosin or rosin acid derivative, 20% to 35% sulfurized (or sulfurized-phosphorized) fatty body and 20% to 50% sulfurized and halogenated aliphatic compound. This blend may be added to lubricating oils or greases in proportions ranging from 1.0 to 20 weight percent based on total composition.

Our invention will be more fully understood by reference to the following examples:

EXAMPLE I

An extreme pressure additive was prepared by blending by weight:

	Percent
P_4S_3-treated sulfurized Abalyn	42
Sulfurized sperm oil	28
Sulfur-chlorine containing wax-kerosene mixture	30

Ten percent by weight of this additive was blended with an SAE 90 grade mineral oil having the following characteristics:

Vis./100	SUS	939.3
Vis./210	SUS	85.1
Vis. index		95

The blended lubricant was tested on the SAE and Timken machines according to the test procedures L–17 and L–18, respectively described in the Handbook of the Coordinating Research Council, Inc., 1946 edition.

EXAMPLE II

For comparison with Example I, an additive was blended from 42 weight percent P_4S_3-treated sulfurized Abalyn, 28% P_4S_3-treated sulfurized sperm oil and 30% of a caustic-washed sulfur and chlorine-containing paraffin wax-kerosene mixture. A 10% blend of this additive in a SAE 90 mineral oil base stock was prepared and tested, with the results shown in the table.

EXAMPLE III

An additive containing slightly different proportions of ingredients was prepared from

	Percent
P_4S_3-treated sulfurized Abalyn	39
P_4S_3-treated sulfurized sperm oil	26
Sulfur-chlorine containing wax-kerosene mixture	35

A 10% mineral oil blend was tested as before, the data being shown in the table.

EXAMPLE IV

An additive containing still different proportions of ingredients was prepared by blending

	Per cent
P_4S_3-treated sulfurized Abalyn	30
P_4S_3-treated sulfurized sperm oil	20
Sulfur-chlorine containing wax-kerosene mixture	50

This additive was also blended with mineral oil in 10% concentration and tested as before, with the results shown in the table.

In addition to the data on the foregoing examples, the table includes comparable data on the performance of the ingredients of the additive mixtures. It will be noted that, in every example, the lubricants of our invention carry higher loads on the SAE machine than comparable quantities of any of the individual ingredients, and much higher than would be expected from an examination of the individual values weighted in proportion to the percentage of each in the mixture.

With regard to the Timken test data, it will be observed that the loads carried by the lubricants of Examples II, III and IV are approximately in the range which would be expected from a weighted average of the values obtained from the individual ingredients. However, in Example I, the lubricant carried a Timken load not only well in excess of the weighted average for the individual ingredients, but even greater than the best single ingredient (P_4S_3-treated sulfurized Abalyn) in the full 10% concentration.

We have thus discovered a number of combinations of additives exemplified by Examples II, III, and IV, which are superior in performance to any of the individual constituents as measured by the SAE machine. Since performance on this machine is widely accepted as an indication of performance in automotive gears under conditions of low-torque and high-speed (passenger car operation), these materials are shown to be unexpectedly useful for this type of service.

We have also discovered certain other combinations, exemplified by Example I, which not only perform with unexpected merit on the SAE machine but also carry unexpectedly high loads on the Timken machine. Since the Timken performance is believed to be indicative of performance in hypoid gears under conditions of high-torque and low-speed (truck operations), the latter type of additive is unexpectedly effective as an all-purpose lubricant for both passenger cars and trucks.

Table

Composition	SAE Machine Scale pounds at 1,000 R. P. M.	Timken machine load p. s. i.
SAE 90 mineral oil	60	9,500
3.5% sulfur-chlorine containing wax-kerosene mixture	131	
10% P_4S_3 treated sulfurized Abalyn	80	33,400
10% P_4S_3 treated sulfurized sperm oil	100	31,200
Example I	178	35,200
Example II	170	25,600
Example III	190	28,200
Example IV	190	33,600

It is to be understood, of course, that conventional antioxidants, viscosity index improvers, and the like may be added to the lubricants of our invention, as will be obvious to those skilled in the art. It is also to be understood that our invention is not limited by any theory of operation or by the particular examples cited, but only by the appended claims.

What is claimed is:

1. A lubricating oil additive material having the characteristic of imparting desirable extreme pressure properties to a lubricating oil with which it is blended consisting of about 50% by weight of a reaction product of a chlorinated wax-kerosene mixture with sodium polysulfide, about 30% by weight of a P_4S_3-treated sulfurized methylated rosin, and about 20% by weight of a P_4S_3-treated sulfurized sperm oil.

2. A mineral lubricating oil composition consisting essentially of a mineral oil base stock containing combined therein about 10% by weight, based on the weight of the total composition, of a mixture comprising about 50% of a reaction product of a chlorinated wax-kerosene mixture with sodium polysulfide, about 30% by weight of a P_4S_3 treated sulfurized methylated rosin, and about 20% by weight of a P_4S_3 treated sulfurized sperm oil.

ELMER B. CYPHERS.
WALTER E. WADDEY.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,124,598	Turner	July 26, 1938
2,392,468	Engelke	Jan. 8, 1946
2,415,837	Musselman et al.	Feb. 18, 1947
2,424,204	Zimmer et al.	July 15, 1947
2,442,134	Lieber et al.	May 25, 1948
2,488,618	Cyphers et al.	Nov. 22, 1949