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EXTREME PRESSURE LUBRICANTS

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3 Claims. (Cl. 252—42.7)

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This invention relates to improved lubricants and more particularly to oil and grease lubricating compositions intended for lubricating moving metal parts which contact each other under high pressures, such as high film strength oils for bearings and engines, extreme pressure lubricants for gears, and cutting oils as used for machining various metals, etc.

In the lubrication of hypoid or other gears, various chlorinated or halogenated materials are used alone or in combination with sulfur compounds, and sometimes phosphorus compounds are very effective in carrying the high loads demanded of extreme pressure lubricants, but they have one disadvantage, namely, the tendency to rust the gear surfaces which are being lubricated. They also cause corrosion and staining of ferrous and copper-bearing alloys used in bearings, bushings, pistons, etc. Also sulfur alone or in the presence of chlorine as present in cutting fluids, usually causes a black stain such as copper sulfide on copper alloys.

The primary object of the present invention is to prevent such undesirable corrosion of metals; and another object of the invention is to prevent that corrosion without at the same time interfering with the high load carrying capacity of the extreme pressure lubricant.

Broadly the invention comprises incorporating into an extreme pressure lubricant containing active halogen, and if desired active sulfur, a small amount of an oil-soluble corrosion-preventing compound having the general formula $(RY)_mM$, in which R represents an organic group, Y is an element in the right-hand side of group VI of the Mendeleeff Periodic Table, M is a metal selected from groups I to IV of the periodic table, and m represents the valence of the metal M.

The lubricating oil base stock to be used according to this invention may be prepared from various crudes, such as paraffinic, naphthenic, or mixed base crude oils, and may consist of fractions or residuals obtained by distillation into cuts having any desired wide or narrow boiling range, and the lubricating oil base stock may have been subjected to any of the various known refining treatments, such as solvent extraction, acid treating, clay treating, soda washing, or contacting with various chemical treating agents, such as aluminum chloride, boron fluoride, etc.

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For use as an extreme pressure lubricant, it is generally desired to use a lubricating oil base stock having characteristics within the following approximate limits:

Property	Minimum	Maximum
Viscosity at 210° F. (sec. Saybolt Univ.)	35	350
Viscosity Index	−25	150
Flash Point, ° F.	275	600

In order to improve the load carrying capacity of the mineral lubricating oil base stock such as those referred to, compounds of materials containing halogen in an active form are added. The invention is particularly applicable to extreme pressure lubricants containing corrosive chlorine compounds, for instance, chlorinated aliphatic or aromatic hydrocarbons such as chlorinated fatty acids, esters, etc., paraffin wax, kerosene, gas oils, petroleum or coal tar solvents, and derivatives thereof, in which a portion of the chlorine has been replaced by sulfur or phosphorus and sulfur. The amount of chlorine, especially the active chlorine, to be used will, of course, depend upon the severity of the conditions under which the lubricant is to be used but will generally vary between the approximate limits of 0.5% to 60% in the chlorinated organic compounds or between the approximate limits of .05% and 10% based on the total weight of lubricant (exclusive of any water which may be used as in the preparation of water-soluble type cutting oil).

In preparing extreme pressure lubricants of the halogen type, it is frequently desirable to incorporate sulfur compounds especially to increase the stability of the lubricant at high temperature and for this purpose sulfurized fatty or mineral oils or sulfur compounds such as organic sulfides, mercaptans, di- or poly-sulfides, xanthates, xanthogen sulfides, thio carbamates, thiocyanates, etc., may be used in which generally from about 0.2% to 30% of sulfur is incorporated in the active or combined state. Based on the total weight of lubricant, the proportion of sulfur should normally be between the limits of about 0.2% and 10%.

Instead of using separate chlorine compounds and sulfur compounds, it is possible to use single

aterials in which both sulfur and halogen have een incorporated by treatment of hydrocarbons, itty oils or other oxygenated hydrocarbons with sulfur halide or by reacting the halogen compound with an inorganic sulfide, poly-sulfide, thio arbamate, thiocyanate, or xanthate.

Also phosphorus-bearing materials may be incorporated as extreme pressure agents in the lubricants. These phosphorus-bearing materials may be incorporated with sulfur, or sulfur and chlorine separately or combined in one molecule.

The phosphorus, chlorine and sulfur bearing compounds may be prepared by reacting phosphorus sesquisulfide with a chlorinated hydrocarbon such as chlorinated wax, kerosene, fatty acids, esters, gas oil, petroleum or coal tar derivatives, in which a portion of the chlorine has been replaced by phosphorus and sulfur.

Also a phosphorus-chlorine compound may be prepared by reacting phosphorus tri-chloride with a fatty acid or ester. By another method phosphorus sulfo chloride may be reacted with fatty acids or esters and the product incorporated in mineral oil to form an extreme pressure lubricant.

The corrosion-preventing addition agent having the general formula $(RY)_mM$ to be incorporated according to the present invention will now be discussed more in detail. The organic group R should preferably be a hydrocarbon group, or a hydrocarbon group containing one or more non-hydrocarbon substituted groups such as hydroxyl-keto, amino, carboxyl, thioether, etc., which are either inert in respect to the anti-corrosive properties of this addition agent, or which actually increase this anti-corrosive property. The hydrocarbon groups may be alkali, aryl, aralkyl, alkaryl, etc. As alkyl groups, those having more than 8 carbon atoms are especially satisfactory such as octyl, lauryl, cetyl, octadecyl, ceryl, etc., as well as mixed alkyl groups such as those obtained from paraffin wax. Examples of suitable aryl groups are phenyl, naphthyl, di-phenyl, anthracyl, phenanthryl.

The benzyl group is representative of aralkyl groups which may be used; and alkaryl groups to be used may be those corresponding to toluene, isopropyl benzene, secondary amyl benzene, tertiary amyl benzene, octyl benzene, benzene containing alkyl groups derived from paraffin wax, as well as corresponding alkylated derivatives of polynuclear aromatic compounds such as naphthalene, phenanthrene, etc.

In compounds having the formula $(RY)_mM$, the element Y is preferably either oxygen or sulfur, and of these two the former is preferred, primarily from the point of view of the ease of manufacture and availability of raw materials, although in some instances sulfur may be advantageously used.

The metal M is preferably selected from either group I, examples being lithium, sodium, potassium and copper; group II, examples being magnesium, calcium, zinc and barium; or group IV, examples being tin and lead. In some cases aluminum may be used to advantage, especially in instances where the corresponding divalent metal salts are not quite sufficiently soluble in mineral oil, and where the aluminum salts are soluble by reason of the fact that the aluminum is trivalent and combines with three organic radicals. Corresponding thio alcoholates can be used, or in other words, metal mercaptan derivatives, e. g., calcium lauryl mercaptide, barium octadecyl mercaptide.

Some specific examples of classes and compounds falling within the above described classification will now be mentioned.

Metal alcoholates having the general formula $(RO)_mM$, where R is an alkyl group and m and M have the same definitions as given above, e. g.:

Calcium octadecylate
Calcium laurylate
Magnesium cetylate
Barium alcoholate salts of the alcohols obtained by mild oxidation of paraffin wax or by hydrogenation of acid produced by the oxidation of paraffin wax.

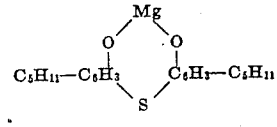
Metal phenolates having the general formula $(RArO—)_mM$, where Ar represents an aromatic nucleus and R represents one or more alkyl groups, e. g.:

Calcium iso-octyl-phenolate
Magnesium tertiary butyl phenolate
The lead salt of phenol alkylated with wax alkyl groups
The barium salt of beta naphthol alkylated with wax alkyl groups
The tin salt of alkylated phenols contained in cashew nut oil
The sodium salts of salicylic acid derivatives with the metal replacing the hydrogen of the hydroxyl group.

Metal phenolate sulfides containing groups having the general formula $MO(R)ArS_n—$, where M is a metal, preferably a polyvalent metal, R represents one or more alkyl groups, Ar is an aromatic group, n is 1 to 5, and the O atom is attached directly to the aromatic nucleus Ar, e. g.:

Magnesium tertiary amyl phenolate sulfide
Calcium tertiary amyl phenolate sulfide
Barium tertiary amyl phenolate sulfide
Lead iso-octyl phenolate sulfide
Magnesium phenolate sulfide containing two tertiary butyl groups attached directly to the benzene nucleus.

Ar may represent polynuclear aromatic groups such as those derived from naphthalene, diphenyl, etc. Such compounds are preferably made by reacting an alkylated phenol with a sulfur mono- or poly-halide, e. g., S_2Cl_2 or SCl_2. Although the structure of the resulting reaction product is not known with certainty, and, a mixture of products may perhaps be formed, one probable structure, for magnesium tertiary amyl phenolate sulfide is:



This may also be called the magnesium salt of tertiary amyl phenol thioether. Other metal phenolate sulfides, which may also be called metal salts of alkylated oxyaromatic sulfides, may be used, such as those disclosed in Mikeska application Serial No. 246,073, filed December 16, 1938.

In preparing the metal salts such as those described above, all of the valences of the metal need not be combined to identically the same type of organic radicals. In other words, mixed compounds can be used such as barium laurylate cetylate which is the barium alcoholate salt of lauryl alcohol and cetyl alcohol. Similarly mixed metal phenolate salts may be used such as the magnesium salt in which one valence of the magnesium is connected to the oxygen of a tertiary butyl phenolate radical and the other valence of

the metal is connected to the oxygen of an iso-octyl phenolate radical.

The amount of the oil-soluble anti-corrosive metal compound to be used according to this invention may vary over a fairly large range, depending upon the type and amount of active halogen compound used and upon the type of the metal compound used, as well as upon the severity of the operating conditions under which the lubricant is to be actually used in service. Ordinarily, however, the amount of the metal compound should be about 0.1 to 10.0% by weight on the basis of the total extreme pressure lubricant, and usually it should be between the approximate limits of 0.3% and about 2.0%.

If desired, other known addition agents or lubricants may be incorporated in the lubricant prepared according to the present invention; for instance, fatty oils, esters, thickeners such as polyisobutylene having a molecular weight above 1000, pour depressants, antioxidants, oil-soluble fatty acids, dyes, sludge dispersers, etc., may be added.

The objects and advantages of the invention will be more clearly understood from a consideration of the following examples.

Example 1

An extreme pressure lubricant was prepared by incorporating 10% of sulfurized sperm oil (containing 9.6% of sulfur), and 7% of chlorinated paraffin wax (containing 40% of chlorine) into a mineral lubricating oil base stock derived from a paraffinic crude having the following characteristics:

Saybolt vis./210° F	seconds	92
V. I		95
Pour	°F	0

This lubricant was subjected to the Almen corrosion and wear test and was found to show a wear of 2.4 mg. loss on the Almen pin and bushings after 15 minutes of testing with 4,000 lbs. load, and in the corrosion test (A, described below), the test pieces were found to be rusted after 24 hours of exposure to moist air.

(A) A sample of the oil was tested on the Almen test machine for 15 minutes with a load of four weights, then the test oil and test pieces were placed in a bottle and moist air passed through for 24 hours; the steel became corroded. The wear is determined by weighing the pin and bushings before and after the test for determining the loss and weight in milligrams.

In another type of test, 25 ccs. of the oil being tested and 5 ccs. of water were put in a 50 cc. beaker in which there was a polished steel rod; this steel rod showed rusting in 16 hours at a temperature of 180° F.

The Almen corrosion and wear test was repeated except that 1% by weight of the barium salt of di-isobutyl (iso-octyl) phenol sulfide was incorporated into the extreme pressure lubricant, and the resulting compounded lubricant was found in the wear test to show a loss of 3.9 mg. and in the corrosion test to show no evidence of rust or stain, thus indicating that this barium salt very satisfactorily prevented the rusting without substantially increasing the amount of wear.

Example 2

The second part of Example 1 was repeated except that the metal salt used as anti-corrosion agent was 1% of the magnesium salt of tertiary amyl phenol sulfide. The resulting lubricant showed a wear of 7.5 mg. which is still relatively low and there was no rust or stain in the corrosion test.

Example 3

The second part of Example 1 was repeated except that 1% of the lead salt of tertiary amyl phenol was used as the anti-corrosion agent. The resulting lubricant showed 2.6 mg. loss in the wear test and showed no rust or stain in the corrosion test.

Example 4

The second part of Example 1 was repeated exactly except that the anti-corrosion agent used was 1% by weight of the barium salt of di-isobutyl (isooctyl) phenol. The resulting lubricant showed a 2.4 mg. loss in the wear test and no rust or stain in the corrosion test, thereby indicating that the barium salt not only prevented rusting and staining in the corrosion test, but did so without any increase in the amount of wear.

Example 5

An extreme pressure lubricant was prepared by incorporating 10% of a sulfur-chlorine base made by reacting a chlorinated kerosene with sodium polysulfide, in a mineral oil. This lubricant was subjected to the Almen corrosion and wear test and was found to show a wear of 2.3 mg. loss on the Almen pin and bushings after 20 minutes with 8000 lbs. load, and in the corrosion test, after 24 hours of exposure to moist air, the test pieces were found to be rusted.

The same test was repeated except that 1% by weight of the calcium derivative of octadecyl alcohol was added to the extreme pressure lubricant. On the wear test a loss of 3.1 mg. was noted, and in the corrosion test there was no evidence of rust.

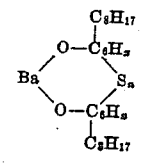
Example 6

Another sample of the sulfur chlorine lubricant described in Example 5 was compounded with 0.40% of the barium salt of the naturally occurring long chain aliphatic substituted phenol obtained from cashew nut hulls. Upon running the wear and corrosion test it was found that the addition of the barium salt to the extreme pressure lubricant did not substantially increase the wear, and there was no evidence of rust.

It is not intended that this invention be limited to any of the particular examples which have been given for illustration only, nor by any of the theories as to the operation of the invention but only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. An extreme pressure lubricating agent containing chlorine in active form, sulfur, and a corrosion preventing amount of a compound having the general formula



where n is 1 to 2, and x is a number satisfying valence requirements.

2. An extreme pressure lubricant comprising a major proportion of a mineral lubricating oil base stock, about 7% by weight of chlorinated paraffin wax containing from 40–60% of chlorine, at least a substantial proportion of which is in active

form, and about 1% by weight of barium di-isobutyl phenolate sulfide having the general formula shown in claim 1 and which is suitable as a corrosion preventing agent.

3. Lubricant according to claim 2 also containing a substantial amount of sulfurized sperm oil.

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