

UNITED STATES PATENT OFFICE

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EXTREME PRESSURE LUBRICATING
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This invention relates to extreme pressure lubricating compositions and particularly to extreme pressure lubricants of the general type which are used as driving axle and transmission lubricants for automotive vehicles and the like.

As is well understood in the art, certain machine elements which are subjected at times to frictional contact under very high unit pressures require special lubricants which are capable of providing an effective lubricating film under conditions where the ordinary oily lubricating film breaks down.

In the past it has been the practice to incorporate in lubricating compositions of the character referred to above, certain chemicals which while essentially unreactive at ordinary temperatures become highly reactive with the metal surfaces they are designed to lubricate when the temperature rises above normal, due to some unusual condition, such as a momentary application of very high unit pressures.

It has been suggested in the prior art that lubricating compositions containing active phosphorus and active sulfur may be suitable for the purposes mentioned above. The use of halogenated hydrocarbons, especially chlorinated hydrocarbons, for a similar purpose also is known. According to the present invention however, by a new combination of certain types of phosphorus and sulfur-containing materials with certain lubricating materials, and also with halogenated hydrocarbons, improved lubricating compositions may be prepared. At the same time, we avoid excessive corrosion to metals which has sometimes resulted in the past from the use of phosphorus and sulfur-containing materials in lubricants, as for example, in the so-called active sulfur type of extreme pressure lubricant.

Specifically, we have found that a lubricating composition consisting essentially of 70 to 95 parts by weight of mineral lubricating oil, 1 to 15 parts of a halogenated hydrocarbon, and 1 to 20 parts of the reaction product of a fatty body, sulfur, and a phosphorus sulfide will provide a particularly effective lubricant for driving axles of automotive vehicles, particularly where hypoid gears are involved. In general the halogenated hydrocarbon will be combined with from one-half to four times its weight of the reaction product, this extreme pressure composition then being added to 3 to 10 times its weight of mineral lubricating oil to make the finished lubricant. The extreme pressure additive may be separately prepared and marketed, for use in ordinary lubricating oils, or the finished lubricant may be prepared, as desired.

The reaction product referred to above may be obtained by mixing a fatty material, elemental sulfur, and a phosphorus sulfide, and heating the

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mixture to a suitable temperature for a period long enough to effect a substantially complete reaction between the ingredients. Thus, we may use a fatty oil, such as sperm oil, sulfur, and a phosphorus sulfide, such as phosphorus pentasulfide, the mixture being subjected to a temperature of 250° to 450° F., preferably about 350° to 400° F. The time of heating will vary with the temperature and with the particular ingredients employed. The time will commonly run from one-half to twelve hours.

As a specific example of our invention, we heated about 100 parts of sperm oil and about 12 parts, by weight, of sulfur to a temperature of 365° F. for 1¾ hours. Thereafter, about one part of phosphorus pentasulfide was added and the temperature raised to 390° F. and kept at that temperature until the mixture no longer showed corrosion by the standard 3 hour copper strip test at 210° F. The test was conducted by using 10% of the reaction product in a conventional lubricating grade of mineral oil. The time for the second heating just mentioned is ordinarily about 45 minutes.

The reaction product produced as indicated above was incorporated in a lubricant by blending 10 parts of it with 85 parts of mineral oil and 5 parts of chlorinated wax (containing 40% chlorine).

The complete formula of the foregoing composition is as follows:

EXAMPLE I

	Per cent
Mineral lubricating oil (100 S. S. U. at 210° F.)	84.5
Chlorinated wax (40% chlorine content)	5.0
Pour point depressant	0.5
Sperm oil	8.8
Sulfur	1.12
Phosphorus pentasulfide	0.08

A lubricant prepared as indicated above was subjected to standard inspections and tests where the following data were obtained:

Table I

Gravity, ° A. P. I.	23.1
Flash °F.	415
V./100 (Saybolt Seconds Universal)	1098
V./210 (Saybolt Seconds Universal)	89.3
V. I.	89
Pour Point, °F.	-10
Copper corrosion:	
210° F. (3 hour)	very light red
300° F. (1 hour)	black
Steel corrosion (in presence of water):	
(a) (G. M.) mgms. loss	3
(b) U. S. Army Spec. 2-	
105B	one small spot

S. A. E. machine test (1000 R. P. M. on the main shaft; 14.6/1 slip ratio; 79 lbs./second loading rate) ----- 275 scale lbs.

Heat stability: ¹

S. A. E. machine test (500 R. P. M.) ----- 500

High temperature oxidation: ²

Per cent evaporation ----- 2.1

Per cent increase in viscosity ----- 7.0

Almen machine wear test (mgms. loss after 20 minutes with 4 weights on lever arm) ----- 3.0

Foaming test (Mixmaster test) -- nil

¹ After heating 48 hours at 200° F.

² 100 hours at 300° F. in open beaker in oven.

For use as an extreme pressure additive, 1 to 4 parts of the reaction product may be combined with 1 to 2 parts of the halogenated hydrocarbon. The resulting composition may be used directly as a lubricant, but will normally be used in proportions of 5% to 30% in lubricating oil of mineral oil base. Various fatty oils and/or acids may be added as desired.

The reaction product of fatty oil, sulfur, and phosphorus sulfide may be used by itself as an extreme pressure additive. However, its use in combination with a chlorinated or other halogenated hydrocarbon is preferable.

As suggested above lubricating compositions, particularly mineral oils, containing sulfur and phosphorus have been employed in the past for extreme pressure purposes. In some cases, however, these have not been satisfactory since the active sulfur and phosphorus have caused the lubricants to corrode the metal parts being lubricated. When such compounds are combined with compositions including chlorine or other halogens, they are particularly likely to cause corrosion of copper, steel, and other metals. In general, compositions including halogens with or without sulfur and phosphorus, tend to be corrosive and compositions containing all these materials normally would be expected to have high corrosive tendencies.

By combining the phosphorus and sulfur with fatty material, such as sperm oil, in the manner described above, the objectionable corrosive tendencies of the ingredients are largely, if not entirely, overcome. Preferably, as described in the specific example mentioned above, the oil is first sulfurized by heating it with elemental sulfur for a suitable length of time and the phosphorus sulfide is added later. It is possible, however, to mix together the fatty oil, sulfur, and the phosphorus sulfide, preferably phosphorus pentasulfide, at the outset, the whole being heated to a suitable temperature, at least 250° F. and preferably above 300° F. until the desired reaction has taken place. The time required for reaction varies with the temperatures employed.

While the exact nature of the reaction product produced by combining sperm oil, sulfur, and phosphorus pentasulfide is not known with accuracy, apparently the phosphorus and sulfur are so fully combined with the fatty oil, when the reaction is complete, as to produce a very stable composition. This stability protects the metal surfaces to be lubricated against corrosion at ordinary temperatures, but when the metal surfaces become heated to a substantial degree, as they do when the normal protective oil film breaks down, there is an immediate release of mildly active sulfur, chlorine, or phosphorus, or two or more of these materials, to react with

the metal and to establish on the surface of the metal a protective film of metal chloride, sulfide or phosphide, of submicroscopic thickness on the metallic surface. This film provides momentary lubrication on failure of the oil film until the latter can be re-established.

It will be understood that other fatty materials than sperm oil, such as lard oil, rapeseed oil, and other vegetable and animal fats, and fatty acids derived therefrom, may be used. Also other sulfides of phosphorus, for example, phosphorus sesquisulfide, may be employed in lieu of phosphorus pentasulfide.

While chlorinated wax is mentioned specifically above and is a preferred halogenated hydrocarbon material, other chlorinated, brominated, or otherwise halogenated hydrocarbons, such as chlorinated or brominated kerosene, may be employed. Various related halogen-containing compounds may be substituted for the chlorinated or brominated kerosene, wax and the like, as will be apparent to those skilled in the art.

The type of mineral lubricating oil employed will depend upon the particular type of lubricant desired. A desirable formula utilizes a mixture of mineral oils having respectively rather low and rather high viscosity indexes. Thus, the mineral oil may consist of about one part of an oil having a viscosity of 100 S. S. U. at 100° F. with a viscosity index of 30, combined with 6 parts of a mineral oil with a viscosity of 100 S. S. U. at 210° F. and a viscosity index of 80. Such a mixture of oils was used in the specific formula mentioned above. It is desirable, though not always necessary, to add a suitable pour point depressant, usually an organic polymer, in proportions of 0.1 to 2% by weight. Other conventional modifier materials, such as detergents, oxidation inhibitors, viscosity index improvers, and the like, may be incorporated, as is well understood in the art.

It should be emphasized that high-torque rear axles, such as those used on trucks and busses, present particularly difficult lubricating problems. The standard testing machines used for ordinary lubricants, such as the S. A. E. machine and the Timken machine, have proved to be inadequate for testing high-torque axle lubricants. Service tests in actual operation produce results which are somewhat incompatible with those obtained by standard laboratory techniques. While many relatively simple types of extreme pressure lubricants may lubricate a rear axle or other driving axle satisfactorily under normal conditions of operation, a specific combination of active chemical elements appears to be required for heavy duty service.

As a further example the following data were obtained regarding a typical prior art lubricant. This lubricant was found to be unsatisfactory for truck axle lubrication in mountain service tests conducted by the Chrysler Corporation.

EXAMPLE II

A composition was prepared having the following ingredients in the weight proportions indicated:

	Per cent
Sperm oil -----	13.19
Sulfur -----	1.7
P ₂ S ₅ -----	0.11
Mineral lubricating oil, 100 S. S. U. @ 100° F., viscosity index 31 -----	12.8
Mineral lubricating oil, 106 S. S. U. @ 210° F., viscosity index 80 -----	72.2

This composition showed an A. P. I. gravity of 24.5, flash point 430° F., viscosity of 1072 S. S. U. @ 100° F. and 90.7 @ 210° F., viscosity index 93, and pour point 0° F. In the standard copper corrosion test it showed a very light red corrosion at 210° F. and a black corrosion at 300° F. No steel corrosion occurred. The S. A. E. testing machine showed a rating of 155 at 1000 R. P. M. The G. M. stability test, 48 hours at 200° F. showed 360 at 500 R. P. M. on the S. A. E. machine. In the G. M. oxidation test, 100 hours @ 300° F., evaporation was only 2% and the increase in viscosity 5.9%. The Almen wear test showed a loss in bearing weight of 3.3 milligrams and the G. M. foaming test was negative. The details of these tests were generally the same as in Table I.

Judging from the above, the lubricant of Example II might be considered quite satisfactory but, as previously indicated, it failed to pass the Chrysler mountain service tests in actual truck operation.

The following table gives comparative data of a number of standard lubricants, with a comparison between various types and the compositions of Example I and II.

Table II

	A	B	C	D	E	F	G
Composition: Base Material.....	Fatty oil.....	Fatty oil+sulfur compound.	Fatty oil+tri- cresyl phos- phate.	Wax+sulfur compound.	Fatty oil.....	Fatty oil+ wax.	Fatty oil.
Active Chemical Ele- ments.	S, P.....	S, P.....	S, P.....	S, Cl.....	S, Cl, Pb.....	S, P, Cl.....	S, P.
Laboratory Tests: Timken O. K. Load, lbs.	59.....	51.....	51.....	45.....	68.....	25.....	
S. A. E. @ 1000 R. P. M. lbs.	90.....	315.....	90.....	330.....	80.....	275.....	155.
Chrysler Mountain Service test.	Fail.....	Fail.....	Fail.....	Fail.....	Pass.....	Pass.....	Fail.

The overall quantities of extreme pressure additives were roughly equal, sulfur content being of the order of 1 to 2%, phosphorus 0.05 to 0.15%, and chlorine about 2%. Compositions A, B, C, D, and E were commercial products of various producers. Composition F corresponded to Example I and composition G to Example II, given above. It should be noted that whereas composition A gave a very high Timken test and compositions B and D gave good tests on the S. A. E. machine, all three failed on the mountain test.

From the results shown in Table II it appears that, in general, extreme pressure compositions containing only two active chemical elements do not provide adequate lubrication under heavy duty service conditions as, for example, commercial trucking over mountains. When three different active chemical elements are suitably combined in a lubricant—as in compositions E and F—its load-carrying ability may be considerably increased. It appears that the addition of a third active chemical element provides a different type of lubricating film and/or enhances the film-forming tendencies of the other two elements present, thus increasing the extreme pressure properties of the lubricant. The data obtained in connection with the present invention indicate that the combination of a halogen, in the form preferably of a chlorinated wax or chlorinated kerosene, with sulfur and phosphorus, preferably reacted with a fatty material is most satisfactory. While sperm oil is a preferred fatty oil, other fatty oils and acids may be used such as rapeseed oil, hydrogenated fish oil acids, and the like.

We claim:

1. A lubricating composition consisting essentially of 70 to 95 parts by weight of mineral oil, 1 to 15 parts of a halogenated hydrocarbon wax, and 1 to 20 parts of the reaction product of 60 to 100 parts by weight of sperm oil, 10 to 30 parts of sulfur, and $\frac{1}{2}$ to 2 parts of a phosphorus sulfide subjected to a temperature of 250° to 450° F. for a period of $\frac{1}{2}$ to 12 hours.
2. A lubricating composition consisting essentially of 70 to 95 parts by weight of mineral oil, 1 to 15 parts of a halogenated hydrocarbon wax, and a quantity sufficient to substantially inhibit corrosiveness toward metals of the reaction product of 60 to 120 parts by weight of sperm oil, 10 to 30 parts of sulfur, and $\frac{1}{2}$ to 2 parts of a sulfide of phosphorus heated to a reaction temperature of 250° to 450° F. for a period sufficient to effect substantial completion of reaction.
3. A lubricating composition consisting essentially of 70 to 95 parts by weight of mineral base lubricating oil, 1 to 15 parts of a halogenated hydrocarbon wax, and 1 to 20 parts of the reaction product of 60 to 120 parts by weight of sperm oil, 10 to 30 parts sulfur, and $\frac{1}{2}$ to 2 parts of a sul-

fide of phosphorus, heated to substantial completion of reaction at a temperature between 250° and 450° F.

4. A lubricating composition consisting essentially of 84.5% mineral base lubricating oil, 5% chlorinated wax, 0.5% pour point depressant, and 10% of the reaction product of 60 to 120 parts by weight of sperm oil, 10 to 30 parts of sulfur and $\frac{1}{2}$ to 2 parts of phosphorus pentasulfide heated to a temperature of 250° to 450° F. for a sufficient time to effect a substantial reaction.

5. A non-corrosive extreme pressure additive for lubricating oils consisting essentially of 1 to 2 parts of a halogenated hydrocarbon wax and 1 to 4 parts of the reaction product of 88 parts by weight of sperm oil, 11.2 parts of sulfur and 0.8 part of phosphorus pentasulfide, reacted by mixing the components of said reaction product together and heating to a temperature of 250° to 450° F. for $\frac{1}{2}$ to 12 hours.

6. A non-corrosive extreme pressure additive for lubricating oils consisting essentially of 1 to 2 parts by weight of a halogenated hydrocarbon wax and 1 to 4 parts of the reaction product of 70 to 95 parts by weight of sperm oil, 5 to 25 parts of sulfur and 0.5 to 5 parts of a sulfide of phosphorus, said components of said reaction product being mixed together and reacted at a temperature of 250° to 450° F. for a period of time sufficient to effect a substantial completion of reaction.

7. A process for preparing a non-corrosive extreme pressure additive for use in driving axle lubricants which comprises mixing 70 to 95 parts

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by weight of sperm oil with 5 to 25 parts of sulfur and 0.5 to 5 parts of a sulfide of phosphorus, heating said mixture to a reaction temperature range between 250° and 450° F. for a period of time from ½ to 12 hours to effect a substantial reaction between said components and adding ½ to 2 parts of chlorinated wax to the part of said reaction product.

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