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EXTREME PRESSURE LUBRICANT CONTAINING MANGANESE NAPTHENATE AS AN ANTIRUST AGENT

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The present invention relates to extreme pressure lubricants and particularly to an improvement in the type of extreme pressure lubricant described in U. S. Patent No. 2,468,520, issued to the present applicants on April 26, 1949. It relates especially to an improvement by which the tendency of such extreme pressure lubricants to cause rust or corrosion of steel and other ferrous metals is greatly reduced.

As pointed out in detail in said Patent No. 2,468,520, the combination of halogenated hydrocarbons with phosphorus-and sulfur-containing fatty materials in lubricating oil, especially mineral base lubricating oil, greatly increases the load bearing capacity of said oil. The patent points out the advantages of using a composition consisting approximately of about 70 to 95 parts by weight of lubricating oil, 1 to 15 parts of a halogenated hydrocarbon and 1 to 20 parts of a fatty material treated first with sulfur and later with phosphorus sulfide. The lubricant so described has been found to have excellent load bearing properties in that it successfully passes drastic requirements for operation at low speed and high torque, while at the same time being suitable for use under high speed-low torque conditions. It has been found, however, that under some conditions the lubricant described in said patent has a marked tendency to cause rusting of steel and other ferrous metal parts after a prolonged period of time. It is a specific object of the present invention to overcome the tendency of such an extreme pressure lubricant, containing active sulfur, phosphorus and halogen in sufficient quantities to impart substantial load bearing properties to the lubricant, to cause ferrous metal corrosion.

In order that a lubricant of the character referred to above may be acceptable for general use over prolonged periods, it is quite important that it should not cause appreciable rusting of steel, iron or other ferrous metal in the presence of moisture. At the same time, the lubricant should be one which does not permit rapid wear of the parts being lubricated, notwithstanding their operation under heavy load conditions.

In an effort to eliminate the rusting which is promoted to some extent by the extreme pressure composition described in the aforesaid patent, various conventional rust inhibitors, including certain amines, sulfonates, phenols and partial esters of certain polyhydric alcohols, were all tried but were found to be relatively ineffective in the presence of chlorine or other halogen combined with both active sulfur and active phosphorus. Thereafter, a series of metallic salts, especially metal naphthenates, were investigated and some of these showed some promise as rust inhibitors. Some of the salts investigated, for example, calcium and magnesium naphthenates, were too insoluble in the lubricant to be effective rust inhibitors. On the other hand, certain other naphthenates, specifically those of aluminum and lithium, were found to be unsuitable since

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they formed gels and did not disperse properly for rust inhibiting action.

Certain other metal naphthenates and other salts were deficient because, although they tended to inhibit rust formation, they tended to promote sludging, particularly at elevated temperatures. A test was devised whereby each lubricant was subjected to a 100-hour laboratory heat test at a sustained temperature of 300° F. At the end of the heat test period, the various samples were examined for sludging, it being considered that more than about 1 to 2% of a material insoluble in naphtha would be unsatisfactory. It appears that the 100-hour heat test at the temperature of 300° F. is a reasonably sound indicator of stability in service under the conditions commonly encountered in the rear axles of automotive vehicles, especially those of heavy trucks and buses operating in mountainous terrain.

Of all the metal salts tested, manganese naphthenate showed the best all-around service when all factors are considered. Other manganese salts of non-aromatic acids and of comparable molecular weight and oil-solubility appear to be suitable. Useful quantities are about 1 to 10% of the soap, or a quantity of about 0.1 to 1% of manganese metal content. Preferred quantities are about 2.5 to 5% of the soap, based on the weight of the total composition, or 0.25 to 0.5% manganese metal on the same basis. Some of the other materials showed slightly less rust while being deficient in stability or in the amount of wear permitted in the standard Almen test. The naphthenates and other salts of those metals which showed satisfactory wear characteristics, or satisfactory stability or solubility characteristics, were markedly deficient in inhibiting rusting of steel.

The lubricants tested were all evaluated by running the standard Almen pin in a split bushing for 25 minutes under a load of at least 4 weights. To obtain wear data, the pin and bushing were weighed before and after each test. A loss in total weight of more than 5 milligrams is considered excessive.

The rusting test to which the various compositions were subjected was carried out under load conditions (usually 4 weights) sufficient to develop a temperature in the oil of at least 200° F. The temperature varied somewhat with various compositions, depending upon the friction developed. After running until the oil was heated to the temperature indicated, the pins and bushing were allowed to drain at a temperature of 180° F. Thereafter, they were placed in a bell jar humidifier containing a beaker of water. After 24 hours, the steel parts were rated visually for the degree of rusting using a reading of severe, medium, trace and nil. Lubricants permitting not more than a trace of rusting appear to be satisfactory.

As indicated above, various salts and especially the naphthenates of various metals were tested, including those of lead, tin, iron, chromium, cobalt, barium and manganese, in addition to those of magnesium, calcium, aluminum and lithium which could not be used at all because they were insoluble or formed gels. The manganese naphthenates were found to have exceptionally good properties in very small concentrations. In general, they may be used in quantities of from 0.1 to about 1% by weight, based on the metal content of the salt, or more may be used if desired, in extreme pressure compositions containing the active halogen, sulfur and phosphorus as referred to above.

In general, the lead naphthenates gave very high wear, as indicated by considerable losses in weight in the Almen test. The same appears to be true of other lead salts and soaps. The tin naphthenates were highly effective against rusting but they permitted excessive wear and also formed considerable quantities of sludge in the heat test. Iron naphthenate gave too high a wear test and showed excessive sludging in the heat test. Chromium naphthenate did not show excessive wear but failed to reduce rusting sufficiently. Cobalt naphthenate showed similar results.

In the case of barium naphthenate, the lubricant permited too high a rate of wear and did not sufficiently correct the rusting. By contrast, manganese naphthenate gave a satisfactory wear test, showing a loss of only 5 milligrams. The manganese compound permitted only a trace of rust which is acceptable and showed acceptably low sludge formation in the heat test.

On the whole, the experiments showed that the salts of manganese, such as the naphthenate and comparable non-aromatic salts, are efficient inhibitors to prevent the corrosion of ferrous metals when extreme pressure lubricants of the halogen-sulfur-phosphorus type are employed as in automotive vehicle rear axle lubrication.

The foregoing data are summarized below in the table. The composition used as a base lubricant was prepared by combining chlorinated wax of 40% chlorine content with sperm oil treated first with sulfur and thereafter with phosphorus pentasulfide under the conditions set forth in Patent No. 2,468,520. The procedure described in said patent in connection with the first example thereof was followed in preparing the basic lubricant. Briefly, 100 parts by weight of sperm oil were treated with about 12 parts by weight of sulfur to a temperature of 365° F. for 1¾ hours. Thereafter, about 0.8 part by weight of phosphorus pentasulfide were added and the temperature raised to 390° F. for ½–1 hour. The mixture was kept at the elevated temperature until a 10% solution of the base in neutral oil no longer showed corrosion by the standard 3-hour copper strip test at 210° F.

The lubricating composition tested as a basis for comparison contained approximately 85% mineral oil, 5% chlorinated wax and 10% of the sulfur and phosphorus sulfide treated fatty material. Various quantities of the various metal salts (naphthenates) were added, as indicated in the table.

It will, of course, be understood that the invention is not necessarily limited to compositions of the specific type just described. In general, the manganese oil-soluble salts which do not gel in oil are satisfactory. From the data obtained, manganese naphthenate appears especially to be an effective rust inhibitor in any extreme pressure lubricant which contains active halogen, sulfur and phosphorus in proportions sufficient to increase substantially the load bearing properties. The invention is not limited to the naphthenates, however, but includes the other oil-soluble manganese soaps. Such are particularly appplicable to lubricants of the type mentioned above containing about 1 to 15% by weight, based on the total composition, of a halogenated hydrocarbon, the hydrocarbon preferably being one having a molecular weight at least as high as the average molecular weight of kerosene. Chlorinated kerosene, chlorinated wax or chlorinated gas oil fractions, or mixtures of any of these and other conventional chlorinated hydrocarbons obviously may be used. Chlorinated wax and chlorinated kerosene are specifically preferred in that order.

The fatty material may be a sperm oil or lard oil or other fatty oils such as fish oils, vegetable oils, and the like, may be used. In general, these are first cooked with sulfur at a temperature of between about 225° and 450° F. for a short time, for example ½ hour to 3 or 4 hours, and thereafter they are heated, preferably for about ½ hour to several hours, with a phosphorus sulfide within the same temperature range, preferably at a slightly higher temperature. The total heating time may be as little as ¼ hour or as much as 12 hours, or more. Any of the phosphorus sulfides may be used, phosphorus pentasulfide and phosphorus sesquisulfide being preferred because of their availability.

The complete test results are as follows:

TABLE

Effect of metal naphthenates on rust prevention

	Composition	Wts.	Almen Test		Humidity, Amount of Rust	Heat Sludge, Per Cent Insol. in Naphtha
			Temp., °F.	Loss, mg.		
1	Base Lubricant[1] (per cent metal)[2]	4	175	3	Severe	Trace
2	Base+0.5 Pb	4	215	1,000	Trace	0.5
3	Base+0.25 Pb	4	230	25	Medium	----------
4	Base+0.5 Sn	4	240	10	Nil	4.5
5	Base+0.25 Sn	5	210	2.5	Medium	----------
6	Base+0.5 Fe	4	225	500	Nil	4.4
7	Base+0.25 Fe	4	190	10	Medium	----------
8	Base+0.5 Cr	4	210	5	do	Nil
9	Base+0.5 Co	4	220	3	do	3.8
10	Base+0.5 Ba	4	225	10	do	Nil
11	Base+0.5 Mn	4	210	5	Trace	2.1
12	Base+0.25 Mn	4	210	5	do	0.8

[1] Basic composition had the following composition, by weight: 8.8% sperm oil, 1.12% sulfur, 0.08% P_2S_5; 5.0% chlorinated wax; 15.0% mineral oil of 115 S. S. U. at 100° F., vis. index of 30; 70.0% mineral oil of 100 S. S. U. at 100° F., vis. index of 80.

[2] Quantity of rust inhibitor expressed as metallic element in the naphthenate. A composition containing 0.25% of manganese in the form of the naphthenate contains about 2.8% of the naphthenate itself.

What is claimed is:

1. An extreme pressure lubricating composition consisting essentially of about 80 to 82.5% by weight of mineral base lubricating oil, about 10% of sulfurized and phosphorus sulfide treated fatty oil, about 5% chlorinated hydrocarbon of about 40% chlorine content, said hydrocarbon being of at least as high an average molecular weight as kerosene, and 2.5 to 5% of manganese naphthenate.

2. Composition according to claim 1 wherein said fatty oil is sperm oil.

3. Composition according to claim 1 wherein said chlorinated hydrocarbon is chlorinated paraffin wax.

4. Composition according to claim 1 wherein said chlorinated hydrocarbon is chlorinated wax.

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REFERENCES CITED

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

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Number	Name	Date
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