

1

3,175,972

LUBRICANT COMPOSITION AND METHOD

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This invention relates to improved high pressure fluid lubricants. In one aspect, this invention relates to lubricant compositions comprising a paraffinic base oil, extreme pressure lubricant additives, and a solid hydrocarbon polymer. In another aspect, this invention relates to a process for preparing improved fluid lubricants which comprises the steps of heating a paraffinic base oil, dispersing therein a solid hydrocarbon polymer and subsequently adding an extreme pressure lubricant additive.

It is known that extreme pressure additives can be added to petroleum base stocks to produce gear oils. For example, organic compounds containing sulfur, chlorine, lead or phosphorus have proved to be useful, the decomposition products of these compounds leading to the formation of high melting inorganic lubricant films on the metal surface. Among the types of compounds previously disclosed are compounds containing sulfur or compounds of oxygen and sulfur, organic chlorine compounds (chlorinated wax), organic sulfur compounds (sulfurized fats, sulfurized olefins) and organic compounds containing lead. Compositions consisting of one or more such additives have proved to be useful, for example, a mixture of metal naphthenates, sulfurized hydrocarbons and chlorinated hydrocarbons, such mixtures commonly referred to as SCL-type additives.

When extreme pressure lubricant additives are employed with paraffinic oils, the resulting compositions sometimes are unstable. For example, upon storage of oils containing these additives, sediments develop, forming at times an undesirably high amount of such sediment. Such an oil is unsatisfactory for obvious reasons; for example, storage stability is poor, valuable additive components precipitate out, and lubricating gears with such an oil could cause excessive wear or other damage due to settling of the precipitates during idle periods.

It is an object of this invention to provide an improved high pressure fluid lubricant composition which is stable in storage and use, and has improved lubricity. It is another object of this invention to provide a process for producing such an improved lubricant composition.

Other aspects, objects, and the several advantages of the invention are apparent from a study of this disclosure, and the appended claims.

According to our invention, improved extreme pressure lubricant composition is formed from a paraffinic base oil, an extreme pressure lubricant additive, and a normally oil insoluble hydrocarbon polymer. Further according to our invention, improved lubricant may be formed comprising 50 to 99.4 weight percent of a paraffinic base oil, 0.5 to 45 weight percent of extreme pressure lubricant additive, and 0.1 to 5 weight percent of a hydrocarbon polymer. Further, according to our invention, the hydrocarbon polymer may be selected from solid polymers of ethylene and copolymers of ethylene with minor amounts of copolymerizable olefins. Polymers having a density between 0.900 and 1.000 gram per cc. at 25° C. and more

2

especially those polymers having a density between 0.940 and 1.000 gram per cc. at 25° C. are used. The 0.5 to 45 weight percent of extreme pressure lubricant additive may comprise one or a blend of two or more of the following: metal naphthenates, phosphorized oils, sulfurized oils, phosphorized-sulfurized oils, and chlorinated hydrocarbons.

Further, according to our invention, there is provided an improved process for producing extreme pressure fluid lubricants comprising heating a paraffinic base oil, dispersing therein a normally oil soluble hydrocarbon polymer, cooling and adding thereto an extreme pressure additive. Also according to my invention, the paraffinic base oil is heated to a temperature of at least 250° F. and preferably within the range between 325 and 450° F., the composition is cooled to a temperature below the cloud point to obtain uniform dispersion, and the extreme pressure lubricant additive is added at a temperature below about 200° F.

Thus, according to our invention, fluid lubricants which are particularly suitable as gear oils are formulated so as to contain 50 to 99.4 weight percent of a highly paraffinic base oil, .5 to 45 weight percent of one or a blend of two or more extreme pressure additives selected from polyvalent metal naphthenates, sulfurized hydrocarbons and chlorinated hydrocarbons, and 0.1 to 5 weight percent of normally oil-insoluble, highly dispersed hydrocarbon polymers, said polymers preferably being the homopolymers and copolymers of ethylene having a density within the range of 0.900 to 1.000. The incorporation of the polymer permits utilization of paraffinic oils without attendant formation of sludge during storage and use.

In the preparation of lubricants, the use of paraffinic hydrocarbons is desirable since, under oxidizing conditions, such hydrocarbons yield practically no sludge or oil-insoluble products. However, many extreme pressure additives such as the SCL-type additives are not normally compatible with paraffinic oils. We have discovered that this compatibility is greatly enhanced by incorporating in the lubricant composition a normally oil-insoluble polymer. The preferred polymers are the polymers of ethylene and copolymers of ethylene and copolymerizable olefins. Extreme pressure additives which are stabilized by incorporation of the polymer in the composition comprise polyvalent metal naphthenates, sulfurized hydrocarbons and chlorinated hydrocarbons as more fully described below.

In accordance with this invention lubricant compositions are prepared with paraffinic base oils, polymer, and an extreme pressure additive within the following ranges.

Component:	Weight percent
Paraffinic base oil	50-99.4
Polymer	0.1-5
Extreme pressure additive	0.5-45

In a preferred embodiment, the extreme pressure additive in the above table comprises from 0 to 10 weight percent metal naphthenates, from 0 to 25 weight percent sulfurized oils and from 0 to 10 weight percent chlorinated hydrocarbons, all of the percentages being based on total lubricant composition, each being present in an amount sufficient that the total of the three falls within the 0.5-45 weight percent range specified above. In another embodiment, the extreme pressure additive in the

above table comprises a phosphorized-sulfurized hydrocarbon containing from 0.1 to 0.5 weight percent phosphorus and from 10 to 15 weight percent sulfur. The amount of additive employed will be within the range given above for the components of the gear oil.

The paraffinic hydrocarbon oils employed as the base stocks are unrefined or refined products. Generally refined products are employed which are deasphalted and dewaxed, and which are solvent extracted to reduce the amount of aromatic hydrocarbons to a value below 10 percent by volume, preferably below 5 percent by volume. Dewaxing may be carried out by any conventional method, i.e., by solvent dewaxing using propane or solvent mixtures, such as methyl ethyl ketone or methyl isobutyl ketone with benzene.

Selective solvents which remove the aromatic hydrocarbons from petroleum fractions are well known. Such solvents can be employed, when desired, to achieve base stocks of the desired high paraffinic content. Suitable selective solvents for aromatic hydrocarbons include, among others, the various phenols, sulfur dioxide, furfural, and β,β -dichlorodiethyl ether. The raffinate oils are commonly treated to remove residual traces of solvent and can be further refined, e.g., clay treated and fractionated, to obtain base stocks of desired viscosity grade. Some suitable processes have been reviewed by Nelson, "Petroleum Refining Engineering," McGraw-Hill Book Company, New York (1958).

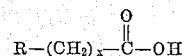
The hydrocarbon polymers which stabilize the extreme pressure components in the base oil are preferably the solid polymers of ethylene and copolymers of ethylene with minor amounts of copolymerizable olefins. Comonomers which can be employed are preferably 1-olefins having from 3 to 8 carbon atoms and are illustrated by the following: propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, isobutylene, 2-methyl-1-butene and 4-methyl-1-pentene. The preferred polymers are those having a density between 0.940 and 1.000 g./cc. at 25° C. However, polymers having a lower density, e.g., 0.900 to 0.940 g./cc. give useful results. The higher density products contribute not only to lubricant stability but also greatly enhance the lubricity of the composition. Suitable methods for preparing these preferred polymers are described in U.S. 2,825,721. Other methods for preparing suitable polymers include the so-called organometallic processes, including such catalyst systems as a trialkylaluminum in conjunction with a transition metal compound such as TiCl_4 .

The preferred polymers, it should be noted, are not normally soluble in the paraffinic base oils. By this it is meant that the polymers can only be dissolved in such oils by heating the polymer and oil mixture to elevated temperatures, generally above 250° F. At lower temperatures, these solid polymers are substantially insoluble. In the practice of this invention, the polymers are first dispersed or dissolved in the oil by heating, e.g., to a temperature of at least 250° F. and preferably within the range between 325 and 450° F. The solution is then cooled, with or without agitation, to a temperature below the cloud point to obtain a uniform dispersion. The extreme pressure additive can be blended with the oil prior to, during or subsequent to mixing with the polymer. Preferably, however, additives other than the polymer are mixed after the polymer solution has been cooled to a temperature below about 200° F. so as to avoid decomposition or volatilization of the additives.

By polyvalent, heavy metal salt of naphthenic acids is meant the compounds formed by neutralization of naphthenic acids with polyvalent metal atoms having an atomic number of 28 or greater. Examples of metals forming suitable salts include zinc, cadmium, barium, tin, lead, nickel and antimony. Of these, the lead salts are commonly preferred. By the term "naphthenic acids," it is meant the acid products derived from kerosene and gas oil, other petroleum lubricating oil fractions and sim-

ilar products. These acids can be naturally occurring or synthesized, for example, by oxidation of hydrocarbons occurring in such petroleum fractions.

Naphthenic acids can be extracted from petroleum fractions by caustic scrubbing, followed by acidification of the resulting extract so as to liberate the acids. Sodium hydroxide is commonly employed as the caustic, and sulfuric acid is preferred as the acid for reasons of economy. The liberated acids can be decanted and purified. Acids having 6 to 25 carbon atoms are most preferred, although products comprising acids of lower and/or higher molecular weight can be advantageously employed. Acids of the desired molecular weight range can be obtained by distillation of the crude, liberated acids. It is understood that the products comprise one or more acids. As is well known, the acids are oily liquids, volatile with steam, and boiling without appreciable decomposition in the range of about 200 to 300° C. The most common acids are derivatives of cyclopentane, such as $\text{C}_5\text{H}_9\text{COOH}$, of cyclohexane, such as $\text{C}_6\text{H}_{11}\text{COOH}$, and of cycloheptane, such as $\text{C}_7\text{H}_{13}\text{COOH}$. Numerous other acids may be used. By way of illustration, other suitable derivatives of cycloalkanes include compounds having the structure



where R is cyclopentyl, cyclohexyl and cycloheptyl, and x has a value of 1 to 20.

These naphthenic acids can also be prepared by oxidation of hydrocarbons. Hydrocarbons of the naphthenic type are oxidized by air at temperatures of 100 to 250° C., especially in the presence of catalysts, such as manganese salts and the organic acids then separated from the oil.

Processes for converting the acids to metal salts are similar to the well-known processes for making soaps of the fatty acids. The acids are mixed with a compound of a metal, preferably the carbonate, bicarbonate, the hydrous oxide or hydroxide, or the salt of a readily volatile acid, such as the salts of hydrochloric acid or acetic acid and the mixture heated to effect neutralization of the naphthenic acids and to remove volatile acids and water.

The sulfurized oils employed in the lubricant composition include sulfurized fatty oils, sulfurized hydrocarbon oils and phosphorized-sulfurized oils. Many such products are commercially available. These products commonly contain from 2 to about 15 weight percent of sulfur. Illustrative methods for preparing suitable products are described in U.S. 2,822,332 and U.S. 2,356,843.

The chlorinated hydrocarbons employed in the formulation of these improved lubricants are the products obtained by chlorination of hydrocarbon waxes, and of olefin polymers. The preferred products contain from about 10 to about 60 weight percent chlorine. For example, there can be employed chlorinated polymers of ethylene, said polymers ranging in molecular weight from about 1,000 to about 100,000, having a chlorine content within the range of about 10 to about 60 weight percent. Chlorinated paraffin waxes are frequently preferred since they are readily available, commercial products.

Example I

For these examples, a paraffinic base stock was prepared by mixing a commercial 10-stock and a commercial 250-stock oil. These oils had been prepared by distillation of a Mid-Continent crude oil to obtain a topped crude which was vacuum distilled to yield raw stocks of the desired viscosity grade. The raw stocks were solvent extracted with phenol, and the paraffinic raffinate was separated and propane dewaxed. The properties for the 10-

5

stock and 250-stock oils prepared by this process were as follows:

	10-stock	250-stock
Viscosity, SUS at 100° F.....	101.9	4130
Viscosity, SUS at 210° F.....	39.61	209.7
Viscosity index, Minimum.....	100	97
Gravity, ° APL.....	33.4	24.9
Pour point, ° F.....	+15	+15
Flash point, COC, ° F.....	395	615
Carbon residue, Conradson, Wt. percent.....	0.0	0.9

The base stock was a blend comprising 58.5% by weight of 10-stock and 41.5% by weight of 250-stock. Using this base stock, two gear oils were prepared having the following composition:

	Weight Percent in—	
	Control Gear Oil A	Gear Oil B
Base stock.....	75	73
Additive blend.....	25	25
Polyethylene.....	0	2

The additive blend is a commercial extreme pressure additive consisting essentially of a mixture of sulfurized fish oil, chlorinated hydrocarbon and lead naphthenate. The additive is marketed under the name of Elco SCL by the Elco Lubricant Corporation of Cleveland, Ohio. This product has the following approximate analysis:

	Weight percent
Lead naphthenate	20
Chlorinated hydrocarbon	20-25
Sulfurized fish oil	55-60

The solid polyethylene has a density of 0.960 g./cc. at 25° C. and a melt index of 5 and was prepared by solution polymerization of ethylene over a chromium oxide containing catalyst as in U.S. 2,825,721.

Gear oil A was prepared by mixing the SCL additive blend with the oil which was heated to a temperature of 100° F. The components were mixed for 15-20 minutes with vigorous agitation with a high speed mixer.

Gear oil B was similarly prepared except that the polymer was first dissolved in the base stock. The oil was heated to about 350° F. and the polymer added. Heating of the mixture was continued over about a 30 minute period, during which time the temperature increased to about 400° F. The solution was cooled to about 100° F., and the SCL additive blend incorporated as stated above for gear oil A.

Portions (about 400 ml.) of each of the above gear oils were stored in pint size bottles for a period of 3½ months. Periodic observations showed that gear oil B remained substantially unchanged and no precipitation was apparent.

With gear oil A, sediments developed which formed a compact mass on the bottom of the container. After the 3½ month storage period, the supernatant liquor was decanted and the weight of the settled portion was found to be 11.3 weight percent of the gear oil. This represents an undesirably high amount of sediment.

Example II

In a series of runs, a gear oil containing SCL additive and polyethylene was compared with a commercial SCL gear oil. In these runs, SCL concentrate is identical to the SCL additive described in Example 1. In these runs, a modified dynamic corrosion test cell using a Timken A-2037 cone and a Timken A-2126 cup was employed as the test bearing cell. The modification which was used was to support the base on a large ball thrust bearing. A dial indicator calibrated as a spring scale was used to measure the force at the end of the torque arm extending from the test cell housing.

6

In each of the runs, the test bearing was submerged in the gear oil to be tested. A 150-pound thrust load was applied and the speed was set at 850 r.p.m. The test temperature was then controlled to the desired value. The results are expressed below in the form of a table.

Temp., ° F.	Relative Friction for Gear Oil X	Relative Friction for Gear Oil Y
30.....	123.5	99.0
80.....	39.5	38.1
100.....	136.0	136.0
150.....	136.0	136.0
200.....	136.0	136.0
250.....	136.0	136.0

1 Threshold for force indicator.

In the above table, gear oil X was an SAE 90 commercial gear oil sold under the trade name of Elco 28 gear oil. This gear oil contained 25 percent of SCL concentrate and 75 percent of a naphthenic-containing base stock. Gear oil Y in the above table was prepared in the manner of gear oil B of Example I and contained 28.5 percent of SCL concentrate and 2 percent of polyethylene, having a density of 0.960 gram per cc. and melt index of 5 and prepared by solution polymerization of ethylene over a chromium oxide containing catalyst as in U.S. 2,825,721, the remainder being paraffinic base stock. The values for relative friction are on an arbitrary scale but are on the same scale for both gear oils, the lower values being desirable.

Example III

Two gear oils were formulated and tested in the following manner. In one gear oil formulation, a control formulation, 100 parts by weight of a mixture containing 96 parts of an SAE-20 stock and 4 parts by weight of an SAE-250 stock were mixed with 4.5 parts by weight of Lubrizol Anglamol 81, a commercial extreme pressure phosphorized-sulfurized additive having a specific gravity at 60° F. of 0.985 and an SUS viscosity at 210° F. of 140. The additive contains 12.6 weight percent sulfur and 0.33 weight percent phosphorus. 0.2 part by weight per 100 parts base stock of a commercial pour point depressant sold under the trade name of Santopour C was added to the gear oil formulation. Santopour C is a commercial pour point depressant having a specific gravity of 0.91 at 60° C., a viscosity of 460 SUS at 210° F., and a flash point of 300° F., sold by Monsanto Chemical Co.

The other gear oil, representing gear oils of this invention, was identical to the above blend except that 3 parts by weight per 100 parts base stock of a solid polyethylene was added to the formulation. The polyethylene used was identical to that employed in Example I and was added to the base stock by the method employed in Example I.

The two gear oils were then tested by Timken wear test. The conditions used for the test were one hour at a load of 30 pounds. Details of the Timken E.P. tester and its operation are set forth in "Proposed Method of Testing for Measurement of Extreme Pressure Properties of Lubricants," A.S.T.M. Bulletin No. 228, pages 28-32, February 1958. For these tests, the so-called OK load procedure was followed, and the width of the scar on the steel test specimen was measured after a 10-minute test period by means of an optical micrometer.

The test block in the run using the gear oil containing no polyethylene had a scar width of 0.052 inch. Under the same conditions, the test block from the test using the gear oil containing polyethylene according to the method of this invention had a scar width of 0.030 inch. It can be seen that considerably less wear result when the gear oils of this invention were employed.

In addition to the data given in the above example, tests were made in a Ford Falcon to determine the steering torque with commercial gear oil and the gear oil of this invention. In a first test, the sector box was filled with SCL gear oil, a blend containing 28.5 percent SCL con-

concentrate as described in Example I, 3 percent of SCL concentrate commercial lubricating additive sold under the trade name of Elco No. 3, the remainder being base lubricant. The chassis of the Falcon in this test was greased with factory filled grease. In a test at ambient temperature (75–80° F.), the torque in inch pounds was 30.2, while at 0° F., the torque was 42.5 inch pounds. This represents an increase in steering torque of 40.7 percent in dropping the temperature from 75–80° to 0° F. In a second test, the SCL gear oil was the same, and 2 percent of the polyethylene of the preceding example was added to the gear oil. In this run, the chassis was lubricated with a grease containing Phillips polyethylene, as disclosed in our copending application Serial Number 37,332, now Patent No. 3,112,270, filed June 20, 1960, by Bill Mitacek and John P. Graham. The torque at ambient temperature (75–80° F.) was 28.4 inch pounds, and 33.7 inch pounds at 0° F. This represents an increase in steering torque of only 18.6 percent. Thus, a significant decrease in torque can be obtained by using the polyethylene-containing lubricants.

Throughout this specification, in determining the polymer densities referred to, the specimens are prepared by compression molding the polymer at 340° F. until completely molten followed by cooling to 200° F. at a rate of about 10° F. per minute. Water is then circulated through the mold jacket to continue the cooling to 150° F. at a rate not exceeding 20° F. per minute. The polymer is then removed from the mold and cooled to room temperature.

Density is determined by placing a smooth, void-free, pea-sized specimen cut from a compression molded slab of the polymer in a 50 ml. glass-stoppered graduate. Carbon tetrachloride and methylcyclohexane are added to the graduate from burrettes in proportion such that the specimen is suspended in the solution. During the addition of the liquids the graduate is shaken to secure thorough mixing. When the mixture just suspends the specimen, a portion of the liquid is transferred to a small test tube and placed on the platform of a Westphal balance and the glass bob lowered therein. With the temperature shown by the thermometer in the bob in the range 73–78° F., the balance is adjusted until the pointer is at zero. The value shown in the scale is taken as the specific gravity. With the balance standardized to read 1.000 with a sample of distilled water at 4° C. the specific gravity will be numerically equal to density in grams per cc. Melt index is determined by the method of A.S.T.M. D1238–57T except that five samples are taken and an average of these is determined.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims thereto, the essence of which is an improved lubricant comprising a paraffinic base oil and an extreme pressure lubricant additive, stabilized by the addition of a hydrocarbon polymer and a process for producing an improved lubricant comprising heating a paraffinic base oil, dispersing therein a normally oil-

insoluble hydrocarbon polymer, reducing the temperature to obtain a uniform dispersion, and adding an extreme pressure lubricant additive below a temperature which will cause decomposition or volatilization of the additive.

We claim:

1. An improved fluid lubricant comprising 50 to 99.4 weight percent of a paraffinic base oil, 0.5 to 45 weight percent of an extreme pressure additive selected from the group consisting of polyvalent metal naphthenates, sulfurized hydrocarbons, chlorinated hydrocarbons and mixtures thereof, and 0.1 to 5 weight percent of a normally oil-insoluble finely dispersed solid copolymer of ethylene and a copolymerizable olefin having 3–8 carbon atoms per molecule.

2. An improved fluid lubricant comprising 50 to 99.4 weight percent of a paraffinic base oil, 0.5 to 45 weight percent of an extreme pressure additive selected from the group consisting of polyvalent metal naphthenates, sulfurized hydrocarbons, chlorinated hydrocarbons and mixtures thereof, and 0.1 to 5 weight percent of a normally oil-insoluble finely dispersed solid polymer of ethylene.

3. An improved fluid lubricant comprising 50 to 99.4 weight percent of a paraffinic base oil, 0.5 to 45 weight percent of an extreme pressure additive selected from the group consisting of polyvalent metal naphthenates, sulfurized hydrocarbons, chlorinated hydrocarbons and mixtures thereof, and 0.1 to 5 weight percent of a polymer of ethylene having a density between 0.940 and 1.00 gram per cc. at 25° C.

4. An improved fluid lubricant comprising 50 to 99.4 weight percent of a paraffinic base oil, 0.5 to 45 weight percent of an extreme pressure additive selected from the group consisting of polyvalent metal naphthenates, sulfurized hydrocarbons, chlorinated hydrocarbons and mixtures thereof, and 0.1 to 5 weight percent of a normally oil-insoluble finely dispersed solid copolymer of ethylene and a 1-olefin having 3 to 8 carbon atoms, said copolymer having a density between 0.940 and 1.000 gram per cc. at 25° C.

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