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LUBRICANT COMPOSITION CONTAINING MOLYBDENUM NAPHTHENATE

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U.S. Cl. 252—24 **6 Claims**

ABSTRACT OF THE DISCLOSURE

An improved lubricant composition comprising an oily substance containing a controlled proportion of molybdenum naphthenate dissolved therein and which may further include a sulfur-containing compound in controlled amounts.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional application of copending application Ser. No. 751,740 now Pat. No. 3,598,847, filed Aug. 12, 1968, for "Method for Making Molybdenum Naphthenate," which is assigned to the same assignee as the present invention.

BACKGROUND OF THE INVENTION

Organic metallic compounds, and particularly organic molybdenum compounds, are achieving increased acceptance as catalysts in chemical reactions as performed in petro-chemical industries. Molybdenum naphthenate compounds have also been heretofore listed for use as a gasoline additive for the purpose of controlling surface ignition in internal combustion engines by combination with lead deposits.

Molybdenum naphthenate compounds of the types heretofore suggested for use as catalysts in chemical reactions have been synthesized in the laboratory employing materials and conditions which are not adaptable to large capacity commercial processing equipment and have produced the molybdenum naphthenate compounds in relatively low yields, detracting from a more widespread use of this material due to economic considerations.

In accordance with the discovery comprising the present invention, molybdenum naphthenate compounds can now be satisfactorily synthesized employing techniques which are amenable to commercial processing equipment and which produce the compounds in high yields, enabling the supply of the compound in commercial quantities and at reasonable cost. A further aspect of the present invention is the discovery of a new use of the molybdenum naphthenate compound, as well as the compound itself produced in accordance with the process.

SUMMARY OF THE INVENTION

The benefits and advantages of the method comprising the present invention are achieved by employing an organic molybdenum intermediate, specifically molybdenyl bis-acetylacetonate, as the source of the molybdenyl cation, which is reacted with naphthenic acid, or a mixture of commercially available naphthenic acids, in a heated and agitated reaction media for a period of time sufficient to effect the formation of molybdenum naphthenate. The product is isolated and recovered from the reaction mixture and is usually obtained in yields in excess of 90%. As a further feature of the present invention, it has been been found that the addition of from about 0.5% to about 5.0% by weight of molybdenum naphthenate in lubricating oils, preferably in further combination with elemental sulfur or a sulfur containing compound, improves the antifriction and extreme-pressure lubricating characteristics of the lubricating oil.

Further advantages and benefits of the present invention will become apparent upon a reading of a description of the preferred embodiments of the invention and the typical examples provided.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The molybdenum naphthenate compound is a dark purple viscous liquid having a molybdenum content of about 5% to about 6% and has been found to have general hydrocarbon solubility and to form stable solutions in lubricating oils which may also contain other compatible additives. The slight variation in the molybdenum content of the molybdenum naphthenate compound will vary depending upon the particular source of the naphthenic acid used for reaction with the organic molybdenum intermediate, as well as the particular reaction conditions employed.

In accordance with the discovery comprising the present invention, the molybdenum naphthenate compound is synthesized by heating a reaction mixture consisting essentially of molybdenyl bis-acetylacetonate

$$(MoO_2(C_5H_7O_2)_2$$

and naphthenic acid (RCOOH) for a period of time sufficient to effect a coreaction between the constituents and effect a replacement of at least one acetylacetonate group with a naphthenate group. The expression RCOOH used for designating naphthenic acid is intended to encompass a mixture of monobasic acids of cycloparaffins which are conventionally known as naphthenic acids. The commercial source of such naphthenic acids which are suitable for use in the practice of the method of the present invention are from petroleum refining operations and are conventionally separated by extraction with alkali followed by subsequent acidification of the resultant solution of the alkali salts. The crude naphthenic acid mixture consists chiefly of a mixture of cycloparaffin carboxylic acids, which are principally derived from either cyclopentane or cyclohexane and cycloheptane and a great variety of homologs and higher molecular weight analogs are also present. Conventionally, the acids of commercial mixtures of naphthenic acids have molecular weights in the range of from about 180 to about 350.

The other reaction constituent, molybdenyl bis-acetylacetonate, is a yellow crystalline solid having a melting point of about 183–185° C., and is readily synthesized by a variety of techniques such as coreacting in an aqueous reaction media ammonium paramolybdate and acetylacetone, which is slowly acidified by the addition of dilute nitric acid thereto, effecting the formation of a yellow precipitate. The precipitate is readily removed by filtration and thereafter dried, yielding the molybdenyl bis-acetylacetonate in substantially high yields. Alternative satisfactory techniques which are known in the art can be employed for preparing the molybdenyl bis-acetylacetonate for use in the subsequent synthesis of the molybdenum naphthenate compound.

In order to synthesize the molybdenum naphthenate compound, a reaction mixture is prepared by admixing molybdenyl bis-acetylacetonate and naphthenic acid which, in accordance with the stoichiometry of the reaction for forming a molybdenum mono-naphthenate compound, theoretically requires the use of one mol of naphthenic acid for each mol of molybdenyl bis-acetylacetonate present. Preferably, the mol ratio of naphthenic acid to the molybdenyl bis-acetylacetonate is controlled from about 5:1 up to about 10:1, providing an excess of naphthenic acid over that required and further enhancing the formation of the molybdenum naphthenate compound. Lower ratios of naphthenic acid to the molybdenyl bis-acetylacetonate can be employed. Such lower ratios, however, which may range from as low as about one mol up to about 5 mols of naphthenic acid per mol of molybdenyl bis-acetylacetonate are generally undesirable due to the incomplete reactivity of the reaction constituents and the difficulty in handling the viscous reaction mixture. It is ordinarily necessary when employing such lower ratios to effect a thinning of the viscous reaction mixture with an organic solvent, such as mineral spirits, to facilitate its manipulation. At the higher ratios, the naphthenic acid itself constitutes the reaction solvent and when employed in such excess amounts, enables the formation of a substantially homogeneous reaction mixture.

In accordance with the preferred practice of the present invention, the reaction medium is formed utilizing the undiluted reaction ingredients. It is also contemplated, however, that suitable solvents can be employed to form the liquid reaction mixture. Solvents suitable for this purpose include a variety of organic inert liquids which have a sufficiently high boiling point to minimize a substantial evaporation thereof when heated to the temperature at which the reaction takes place. A material typical of one suitable for this purpose is a high boiling mineral oil.

The formation of the molybdenum naphthenate compound is achieved by vigorously agitating the reaction constituents and progressively heating the reaction mixture employing a pressure-temperature relationship so as to effect a vaporization and continuous removal of the acetylacetone formed as the conversion proceeds. The acetylacetone, as well as decomposition products thereof, can be recovered by condensation and the acetylacetone itself can be utilized for synthesizing additional molybdenyl bis-acetylacetonate for subsequent coreaction with the naphthenic acid.

In accordance with a preferred technique of the method comprising the present invention, the reaction constituents are degassed prior to heating, effecting a removal of any entrapped or dissolved air to avoid the formation of peroxides in the reaction mixture, which have a tendency to promote autoxidation of the molybdenum-naphthenate product formed. Degassification of the reaction mixture can be conveniently achieved by repetitive evacuations of the reaction vessel during vigorous agitation of the reaction constituents with intervening destructions of the vacuum employing an inert gas, such as nitrogen for example. In order to avoid introduction of oxygen during the reaction, the reaction is preferebaly carried out in a protective atmosphere employing a suitable inert gas, such as nitrogen.

The temperature to which the reaction mixture is heated is in part determined by the pressure within the reaction vessel. This temperature-pressure relationship is correlated so as to effect a vaporization and removal of the acetylacetone formed during the reaction. Comparatively high yields of the molybdenum naphthenate product have been obtained employing inert gas atmospheres at or about atmospheric pressure and in which the reaction medium is slowly heated from room temperature to a temperature of about 190° C., and thereafter held at a temperature of from about 190° C. to about 210° C. for a period of time sufficient to effect a removal of the acetylacetone, followed thereafter by a cooling of the reaction mixture. It has been found, as evidenced by one of the following examples, that a heating of the reaction mass for prolonged periods of time in excess of about 190° C. results in a yield of the molybdenum naphthenate product of less than about 90%, which is postulated as resulting from a thermal decomposition of the molybdenyl bis-acetylacetonate and/or molybdenum naphthenate product formed. On the other hand, it has been found that temperatures in the order of from about 160° C. to about 200° C. and preferably from about 190° C. to about 200° C. promote the conversion of the molybdenyl bis-acetylacetonate to the molybdenum naphthenate product, and it is for this reason that the reaction is preferably carried out at or about atmospheric pressure or at only slight partial vacuums to facilitate a removal of the acetylacetone decomposition product.

It has been observed that during the reaction, some of the distillate recovered is acetic acid, which presumably is derived from the acetyl fragment of acetylacetone liberated during the reaction and which is believed consumed between about 130° C. and 190° C. as a reductant, effecting a partial conversion of the initially-formed hexavalent molybdenum naphthenate product to the pentavalent state in which oxygen abstraction from the molybdenyl group occurs. This side reaction in which a pentavalent molybdenum naphthenate product is formed is of importance particularly where the product is to be used as a catalyst in hydrocarbon solution and in which instance improved solution stability has been experienced. Since the reduction reaction occurs at an elevated temperature of from about 130° C. to about 190° C., it is desirable to correlate the temperature-pressure relationship and the rate of heating through this range to promote the formation of at least some pentavalent molybdenum naphthenate compounds. Rapid heating through the foregoing temperature range has, in some instances, resulted in yields which are less than optimum. Similarly, the rapid removal of the acetylacetone formed from the reaction mixture also inhibits the conversion of some of the hexavalent molybdenum naphthenate product to the pentavalent molybdenum state.

In view of the foregoing considerations, and further in view of the fact that acetylacetone has a vapor pressure of approximately 600 millimeters (mm.) at 130° C., partial vacuums in the order of from about 600 mm. up to about atmospheric pressure (760 mm.), or slightly above (800 mm.), can be satisfactorily employed in accordance with the practice of the present invention. It has further been observed, based on analyses of the acetylacetone and acetic acid recovered, that in most of the molybdenum naphthenate compound produced, only one acetylacetonate was displaced leaving one acetylacetonate ligand in the final product. The presence of these unique mono-naphthenate compounds is also believed to contribute toward the stability of the resultant molybdenum naphthenate product.

It will be apparent from the foregoing that due to the complexity of the reaction and side reactions and the variations in the specific molecular structure of the mixture of commercial naphthenic acids used, the molybdenum naphthenate product, as herein described, and as set forth in the subjoined claims, is intended to encompass a mixture of molybdenum naphthenate compounds such as molybdenum mono and dinaphthenate compounds in which the molybdenum is in the hexavalent state, as well as molybdenum naphthenate compounds in which the molybdenum is in a pentavalent or lower state as a result of the reduction of the molybdenyl group by acetylacetone, as well as wherein only one acetylacetonate has been displaced by a naphthenate on the molybdenyl or residuary molybdenum group. The relative proportions of the various feasible molybdenum naphthenate compounds in the resultant product will vary in accordance with the specific chemistry and purity of the starting materials, as well as the particular conditions within the ranges as hereinabove set forth in which the reaction is performed. Analyses conducted have not clearly chemically identified the molybdenum naphthenate product although the stoichiometry implies that the predominant portion is of the mono-naphthenate form.

It will be apparent from the foregoing that the method for synthesizing the molybdenum naphthenate compound in accordance with the present invention consists in the preparation of molybdenyl bis-acetylacetonate which is reacted with naphthenic acid and wherein the recoverable portion of the acetylacetone formed is removed for recycling and further manufacture of molybdenyl bis-acetylacetonate. By a careful control of the proportions and the temperature and duration of the reaction, yields are obtained of the molybdenum naphthenate product which usually exceed 90% based on the molybdenum content of the starting reactants. The resultant molybdenum naphthenate compound, in addition to its capacity as a catalyst for chemical and petro-chemical processing, such as an oxidation catalyst for olefin epoxidation reactions, has also been discovered in accordance with a second aspect of the present invention to enhance the extreme-pressure lubricating characteristics of organic lubricants, such as gear oils, for example, either alone or preferably in the presence of sulfur or a sulfur-containing material.

In order to further illustrate the method comprising the present invention, the following examples are provided. It will be understood that the examples as hereinafter set forth are provided for illustrative purposes and are not intended to be limiting of the scope of the invention as set forth in the subjoined claims.

EXAMPLE I

Into a 250 ml. Erlenmeyer flask equipped with a Teflon-molded magnet bar and connected to a distilling receiver and a condenser is added 4.08 grams (0.0125 mol) of molybdenyl bis-acetylacetonate (melting point 183–185° C.) and 20.3 grams (0.0795 mol) of naphthenic acids. The naphthenic acids used are obtained from Enjay Chemical Company and have an average molecular weight of 255–256 and an acid value of 220. The molybdenyl bis-acetylacetonate is obtained by preparing a solution containing 6.1 parts by weight of ammonium paramolybdate dissolved in 30 parts of water or, alternatively, 5 parts by weight of molybdic oxide in 30 parts by volume of water in combination with 2.5 parts by volume of concentrated ammonium hydroxide (29% NH_3). The foregoing aqueous solution is added to a second solution containing 70 parts by volume of water and 18 parts by volume of acetylacetone. The two solutions are agitated and are slowly acidified with a 7% nitric acid solution until a yellow precipitate forms. Approximately 25 parts by volume of the nitric acid solution is required. After stirring for a period of about an hour, the resultant aqueous reaction solution is filtered and the yellow precipitate recovered is washed and thereafter vacuum dried.

The reaction mixture containing the naphthenic acid and molybdenyl bis-acetylacetonate is degassed by employing a vacuum-type oil pump and imposing a high vacuum on the mixture, while subjecting it to vigorous agitation followed by repetitive destructions of the vacuum using nitrogen.

At the completion of the degassing operation, the reaction mixture is heated in an oil bath while under a slight positive nitrogen pressure. The temperature of the reaction mixture is raised from 26° C. to 190° C. over a 72 minute heating period and thereafter to 198° C. over a 51 minute period. At this point, 0.2 ml. of condensate is obtained. The oil bath temperature is then gradually raised to a maximum of 207° C. over a 54 minute period and a total of 0.85 ml. of condensate is collected. Thereafter, the bath temperature is lowered over a 35 minute period to 201 C. and is held within a temperature of from about 201 to about 202 C. for a period of 43 minutes. At the completion of this period, the rate of condensate collection is extremely slow and a total of 1.2 ml. is collected.

An analysis of the condensate reveals that it contains 75.5% by volume of acetylacetone which compares to a total acetylacetone of 1.28 ml. theoretically present on a molecular equivalent basis of the molybdenyl bis-acetylacetonate charged to the flask. Gas liquid chromatography analyses of the condensate reveals that acetic acid is also a major component and that water and acetone are minor components of the condensate.

The weight of the crude reaction product recovered is 23.28 grams and this product is extracted with 100 ml. of hexane and filtered to isolate 0.62 gram of a black solid, flammable in a burner flame. This solid contains 0.0966 gram of molybdenum accounting for 8.13% by weight of the molybdenum in the starting material. The hexane filtrate is evacuated by vacuum at a temperature of 60° C. by which 21.4 grams of a dark purple liquid is obtained which, on ignition analysis, reveals it to contain 4.96% molybdenum corresponding to an 88% yield based on the starting molybdenyl bis-acetylacetonate. An infrared absorption analysis of this product reveals a medium intensity peak at 1538 $cm.^{-1}$, which is absent in naphthenic acids.

A solution of the molybdenum naphthenate product is prepared in Havoline motor oil, which is found to be stable for a period of over four months.

EXAMPLE II

A second synthesis of the molybdenum naphthenate compound is prepared employing the same general procedure as previously described in connection with Example I. A quantity of 14.7 grams (0.0451 mol) of molybdenyl bis-acetylacetonate and 55 grams (0.216 mol) of naphthenic acids are placed in a flask and degassed. The bath temperature thereafter is gradually raised from 26° C. to 191° C. over a period of about 85 minutes and thereafter is raised from 191° C. to 196° C. over a 171 minute period. The temperature of the bath is thereafter maintained in the range of 195° C. to 196° C. for an additional 53 minutes to complete the heating cycle. During the period that the bath temperature is above 191° C., 4.7 ml. (3.92 grams) of condensate is collected, which, in accordance with gas-liquid chromatography analyses, shows the condensate to contain 66% by volume of acetylacetone (0.0303 mol) and 25.5 volume percent acetic acid (0.021 mol). The crude reaction product weighs 65.3 grams and is extracted with 500 mls. of hexane and filtered to separate the insoluble solids.

The resultant hexane filtrate is evaporated by vacuum at 85° C. to a constant weight of 54.6 grams. The product contains 7.05% molybdenum, representing a yield of 89% based on the initial molybdenyl bis-acetylacetonate employed.

EXAMPLE III

A molybdenyl bis-acetylacetonate is employed but prior to addition to the reaction flask is dried overnight under vacuum in a desiccator containing a desiccant. A total of 10 grams (0.0307 mol) of molybdenyl bis-acetylacetone and 40 grams of naphthenic acid are charged to the reaction flask and are degassified at room temperature in a manner as previously described in connection with Example I. The reaction mixture is magnetically stirred and while under a slight positive nitrogen atmosphere, the oil bath temperature is gradually raised from 25° C. to 180° C. over a period of 4 hours and 17 minutes. During the heating of the reaction mass, the following color changes are observed at the corresponding bath temperatures: at 39° C., a green color; at 138° C., a blue color and at 175° C., a brown color.

The bath temperature is thereafter gradually raised from 180° C. to a maximum of 200° C. over a period of 2 hours and 46 minutes during which time 2.9 ml. of condensate is collected. Gas-liquid chromatographic analysis of the condensate reveals it to contain 54% by volume acetylacetone, 22.1% by volume acetic acid, and 15.6% by volume acetone. The weight of the crude product obtained is 47.5 grams and is extracted with 50 mls. of hexane and filtered to provide a purple solution. The dark brown insoluble solid recovered on the filter weighs 1.2 grams. The resultant purple hexane filtrate is vacuum evaporated to a constant weight of 44.3 grams which, on ignition analysis, demonstrates the product as containing 6.3% by weight molybdenum. This corresponds to a 95% conversion of the molybdenum originally introduced as molybdenyl bis-acetylacetonate.

The molybdenum naphthenate compounds prepared in accordance with the foregoing examples were used in accordance with a second feature of the present invention as an additive to lubricants to evaluate their anti-wear and extreme-pressure lubricating characteristics. The specific molybdenum naphthenate compound employed was in the form of a purple liquid and had an average molybdenum content of 6.31% by weight. The following test oils were employed for evaluating the molybdenum naphthenate lubricant additive:

TEST OILS

Sample	Oil	Description	Source
A	Flowrex 200	Naphthenic base oil	Mobil Oil Corporation.
B	Rubrex 150	Paraffinic base oil	Do.
C	Havoline SAE 20	Formulated motor oil	Texaco.
D	Dentax 90	Base gear oil	Shell Oil Company.
E	Elco 28	Extreme-pressure gear oil	Elco Corporation.
F	Mineral oil	Heavy viscosity (200–210 SUS)	E. H. Sargent Company.

Oil solubility tests were conducted utilizing the molybdenum naphthenate compound at a molybdenum level of 0.25% by weight corresponding to a total additive content of 4% molybdenum naphthenate. The solubility tests were conducted by adding the molybdenum naphthenate to the oil and thereafter employing a mechanical shaker for agitating the lubricant blend for a period of 90 minutes. Each resultant blend was thereafter diluted with petroleum ether and filtered, and the percentage of solid remaining was measured as indicative of the degree of oil solubility. These solubility tests indicate that molybdenum naphthenate possesses good oil solubility characteristics and based on storage stability tests on the blends, reveals that in unformulated oils a stable solution is achieved over a period in excess of 90 days, while in completed formulated oils, such as Samples C and E, the additive is substantially indefinitely stable.

Lubricant performance evaluations were thereafter conducted employing the six oil samples at various additive levels alone or in combination with an elemental or sulfur-containing additive. Lubrication performance tests were conducted employing a Falex test apparatus for measuring the effect of the load-carrying capacity of the sample oils with and without the additive. In addition, similar tests were conducted employing the 4-ball E.P. test machine for the purpose of measuring the extreme-pressure properties or load-carrying capacity of the lubricating oils with varying concentrations of the molybdenum naphthenate additive. This latter test procedure is identified as Federtl Test Method Standard No. 791—Lubricants, Liquid Fuels and Related Products; Methods of Testing—Method No. 6503 (Dec. 12, 1955). In essence, this test consists of four metal balls stacked in a pyramid in which the bottom three balls are held stationary and the fourth ball is positioned on top of the three balls and rotated to leave a wearing scar on each of the three lower balls at their points of contact. The average diameter of the so-called wear scar on each of the stationary balls is measured at the completion of the test to indicate how effective the lubricant is in preventing wear. This same test was also employed to determine the maximum load to which the rotating ball can be subjected before it becomes welded to the lower three balls; that is: how effective the lubricant is in preventing welding.

Based on an examination of the data of the Falex test machine on the six sample oils employing a molybdenum metal content of 0.025% corresponding to a 0.4% by weight molybdenum naphthenate additive content revealed no appreciable improvement of the oils at this level. An increase of the additive from the 0.4% to a 4% by weight level corresponding to a metallic molybdenum content increased from 0.025% to 0.25% by weight revealed a substantially improved load capacity for the low formulated oil Samples A, B, D and F, while the two fully formulated oils, namely: Samples C and E, were not appreciably improved in their load-carrying capacity by the addition of the molybdenum naphthenate additive at this level.

A further test on the Falex machine was conducted on Sample D oil, which revealed in successive tests to have a load capacity of 700, 600 and 900 pounds, respectively. Duplicate tests on this Sample D oil containing 0.5% sulfur revealed load capacities of 700 and 900 pounds. Sample D oil containing 0.5% by weight sulfur and 0.5% of equivalent molybdenum (8% by weight of the molybdenum naphthenate additive) revealed an increase in duplicate tests of its load capacity to 2300 pounds.

The addition of 4% by weight of naphthenic acid to each of sample oils A–E revealed it has no lubricating ability by itself.

Samples oils A–E containing 4% by weight of the molybdenum naphthenate additive (0.25% by weight of metallic molybdenum) were subjected to tests on the 4-ball machine. Small improvements were observed in the wear scar at loads of 70 kilograms for the additive containing oil as compared to the oil samples without the additive, while relatively significant improvements were generally obtained in the weld load for the same oil samples incorporating the additives.

A synergistic effect in the anti-weld performance of the lubricant was observed by combining the molybdenum naphthenate additive with elemental sulfur. In order to evaluate the effect of the combination of sulfur additions in the presence of molybdenum naphthenate additive, Sample B oil was prepared containing 0.1%, 0.3% and 0.5% by weight sulfur employing two different sulfur sources; namely: (1) using elemental flours of sulfur and (2) using sulfurized sperm oil. Tests were conducted on the 4-ball test machine with each form of sulfur additive, both with and without the molybdenum naphthenate additive. These test results are set forth in the following table;

Lubricant	Weld scar (mm). at indicated load of—		Weld load (kg.)
	70 kg.	110 kg.	
No sulfur addition			
Sample D (base)	0.40	2.72	200
Base plus 0.25% molybdenum	0.44	3.12	200
Base plus 0.50% molybdenum	0.44	3.28	200
Sulfur added as elemental sulfur			
Base plus 0.10% sulfur	0.40	1.60	240
Base plus 0.30% sulfur	0.40	0.86	340
Base plus 0.50% sulfur	0.40	1.13	360
Base plus 0.50% molybdenum plus 0.10% sulfur.	0.40	1.88	360
Base plus 0.50% molybdenum plus 0.30% sulfur.	0.40	0.87	450
Base plus 0.50% molybdenum plus 0.50% sulfur.	0.40	0.49	450
Sulfur added in the form of sulfurized sperm oil			
Base plus 0.10% sulfur	0.40	2.49	190
Base plus 0.30% sulfur	0.40	2.05	200
Base plus 0.50% sulfur	0.41	2.09	220
Base plus 0.50% molybdenum plus 0.10 % sulfur	0.41	3.24	220
Base plus 0.50% molybdenum plus 0.30 % sulfur.	0.40	0.48	240
Base plus 0.50% molybdenum plus 0.50% sulfur.	0.41	2.27	240

It is apparent from the foregoing tests that in oils containing sulfur in addition to the molybdenum naphthenate additive, total lubricating performance is improved with better results being obtained with elemental sulfur than with sulfurized sperm oil. Generally, the addition of the molybdenum naphthenate additive to a sulfur-containing oil gives consistently greater weld load as measured on the 4-ball machine andin the load capacity as evaluated on the Falex tester. The anti-weld performance as evaluated by the 4-ball machine is better with the combination of elemental sulfur and the molybdenum naphthenate than that to be predicted from the sum of the separate effects of these two substances, indicating a synergistic effect on the use of the combination of these two additives in a lubricant. It will be understood that the term "lubricant," as herein employed, is intended to encompass pastes and greases, as well as motor and gear oils previously described.

Based on the foregoing and other test data and in consideration of the specific type of lubricant and the amount and nature of the additives contained therein, if any, the use of the molybdenum naphthenate additive provides for an improvement in the performance of the lubricant when employed in amounts generally ranging from about 0.2% up to about 10% by weight based on the weight of the lubricant. Amounts in excess of about 10% by weight have been observed not to provide any appreciable improvement over that obtained with 10% and therefore the use of amounts in excess of about 10% is ordinarily not economically justified. The elemental sulfur or sulfur-bearing compound is preferably employed in combination with the molybedenum naphthenate additive and may be present in an amount, based on available sulfur, from about 0.05% up to about 1.0% by weight based on the lubricating oil. Ordinarily, the sulfur is controlled in proportion to the molybdenum naphthenate additive so as to be present in a molybdenum to sulfur atomic ratio of about 1:2 to allow the in situ formation of molybdenum disulfide. In addition to the elemental sulfur and sulfurized sperm oil, alternative satisfactory sources of sulfur include, for example, sulfurized terpene, dibenzyl disulfide, mercaptobenzothiazole, and the like.

While it will be apparent that the described of the preferred embodiments as herein described are well calculated to achieve the benefits of the present invention, it

will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

What is claimed is:

1. A lubricating composition comprising a major amount of a hydrocarbon lubricating oil containing an amount sufficient to impart extreme pressure properties of molybdenyl naphthenate acetylacetonate dissolved therein.

2. The lubricating composition as defined in claim **1**, wherein said molybdenyl naphthenate acetylacetonate is present in an amount of from about 0.2% to about 10% by weight.

3. The lubricating composition as defined in claim **1**, further containing an effective amount of sulfur.

4. The lubricating composition as defined in claim **2**, further containing elemental sulfur in an amount of from about 0.05% to about 1% by weight.

5. The lubricating composition as defined in claim **2**, further containing a sulfur-containing compound selected from the group consisting of sulfurized sperm oil, sulfurized hydrocarbons, mercaptobenzothiazole, and mixtures thereof dissolved therein and present in an amount of from about 0.05% to about 1% by weight based on the available sulfur in said sulfur-containing compound.

6. The lubricating composition as defined in claim **2**, further containing sulfur present in an amount so as to provide an atomic ratio of sulfur to molybdenum of about 2:1.

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