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CRANKCASE LUBRICANT FOR SPARK IGNITION ENGINES

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The present invention relates to improved crankcase lubricants and pertains more particularly to a novel compounded lubricating oil composition having properties making it especially adapted for use in gasoline engine crankcase lubrication. The invention concerns an improved crankcase oil having several important properties which heretofore were not simultaneously obtained in one composition.

For the past several years much effort has been expended in the automobile and oil industries to improve the performance of motor cars. This has been effected by improvements in engine design and in increased octane ratings for gasolines. Also, higher level compounding has been employed in crankcase lubricants to promote engine cleanliness and low wear when the more severe conditions encountered in start-stop city driving particularly in engines with close-fitting parts which are critical to these conditions, and reduced clearances between working parts encountered in modern motor cars. These compounding agents are employed in greater amounts to combat the deleterious effects of engine deposits such as piston lacquer and crankcase sludges, which are more critical problems in the gasoline engines of recent design, as found particularly in those of higher compression ratios and smaller clearances. For instance, hydraulic valve lifters commonly are partially or completely stuck by deposits and therefore particular attention must be given to the crankcase lubricant in order to avoid deposition of material in the valve lifters and the damage resulting from such deposits. Widely employed as compounding agents for imparting detergency and reduced wear characteristics to a crankcase lubricating oil and hence for promoting engine cleanliness are oil-soluble polyvalent metal phenates such as calcium alkyl phenates and oil-soluble metal sulfonates such as calcium mahogany sulfonates formed from sulfonic acids derived from petroleum. Commonly, the phenates and sulfonates are employed in combination to reduce wear and deposits.

A primary function of a crankcase lubricant is to reduce friction and thereby to increase the efficiency of the engine operation. With reduced friction less energy in the form of consumed gasoline is expended in merely bringing the engine operation up to the point of zero power output. For minimizing friction and, likewise, for ease of starting in cold weather, low viscosity oils have been employed. Crankcase oils of such nature have been designated as SAE grades 10W, 20W, etc.—the suffix indicating that the oil is a winter-grade oil having certain low viscosities at low temperature for startability in cold weather. Such low viscosity oils, however, suffer from the disadvantage of being consumed at a higher rate than the higher viscosity motor oils. The excessive consumption may result in an oil mileage as low as 50–60 miles per quart of oil for certain types of operations. Even some so-called multi-graded oils commercially available have oil mileages of one-half or less than that of SAE 30 grade crankcase oil. Because of such poor consumption characteristics the oil supply in automotive

equipment is required to be replenished frequently in order to prevent damage to the engine for lack of sufficient lubrication. As a consequence, many motor car manufacturers in recent years have recommended the use of SAE grade 30 oil for maximum oil economy. Thus, the desirable properties of good gasoline mileage and ease of cold weather starting have not been obtained with a crankcase lubricant giving low oil consumption characteristics.

Heretofore various materials, usually polymeric materials, have been proposed as addends to improve the viscosity index of lubricating oil stocks other than 100% paraffinic oils which have the lowest viscosity-temperature coefficient of uncompounded mineral oils. It has been said that the effect of these so-called "viscosity index improvers" is to give false viscosities and hence the resultant oils are not expected to give the oil consumption characteristics indicated by their viscosities as conventionally measured. In other words, the oil would be expected to be consumed at the rate indicated by the viscosity of the oil alone rather than by the viscosity of the oil compounded with a viscosity index improver. As stated by another expert, it is generally recognized that viscosity index improvers have one fundamental limitation: because they increase the viscosity of the fluid base, they cannot be used to make a high viscosity index liquid with a low viscosity unless a liquid base of very high volatility can be tolerated. Heretofore it has been believed that the front end volatility characteristics of the base oil controlled oil consumption.

Another problem confronting modern motor car operations resides in the tendency of the engine in the course of use to require a gradually increasingly higher minimum octane rating for the gasoline to avoid incipient knocking. This phenomenon of octane rating increase becomes critical with the several very high compression engines now on the market; for example, with some such engines the octane rating increases to the point that the highest octane gasoline commercially available is insufficient to avoid incipient knocking particularly when the engine is being forced, such as when climbing a hill.

While heretofore some of these various desirable properties have been attained to some extent in certain lubricants and others of these properties have been attained in other lubricants, one crankcase lubricant has not had all of these properties simultaneously. Indeed, it was believed that some of the properties, such as low friction, could only be attained at the expense of other properties, such as low oil consumption. Now, in spite of the long expressed desire, the proper combination of materials has been discovered, which results in a crankcase lubricant having all of the desired properties to a sufficient extent.

Accordingly, an object of this invention is to provide a crankcase lubricant which simultaneously imparts the following characteristics to engine operation: low friction and hence resulting high gas mileage, low minimum cranking temperatures and hence good startability in cold weather, low oil consumption, low engine wear, good engine cleanliness and relative freedom from engine deposits, and reduced build-up of gasoline octane rating requirements.

It was found that the compounding agents commonly used in crankcase lubricants to promote engine cleanliness and low wear could not be employed without adversely affecting other desired properties of the lubricant. Likewise, it has now been found, as set forth more fully hereinbelow, that the other ingredients and the base oil must have certain characteristics.

The foregoing objects and advantages are obtained by a crankcase lubricant having as its essential components a selected low viscosity, narrow boiling range hydrocarbon oil, which comprises at least 85% of the composition, an oil-soluble methacrylate ester polymer of a certain molecular weight range and in a specified concentration, and a small amount, sufficient to impart detergency and antiwear characteristics to the composition, of an alkaline earth metal glycoxide-alkaline earth metal sulfonate material stably dispersed in filterable form in said oil.

As illustrated more fully hereinbelow, this new lubricant composition has the characteristics with respect to friction of that of SAE 10W grade oil. As compared to a conventional SAE 30 grade oil, the new lubricant gives increased gasoline mileage amounting in short trip operation typical of stop-and-go city driving to an improvement of up to about 15% in gasoline mileage in actual motor car city driving tests. Surprisingly, the oil mileage is not as low as is normal for SAE 10W grade oil but has been found to be at least equivalent to a conventional SAE 30 grade oil. Thus the new lubricant uses less gasoline per mile without any increase in oil consumption as compared with the best compounded SAE grade motor oil on the market. In other words, the new lubricant is responsible for direct saving in gasoline, and unexpectedly does so without consuming additional lubricant.

Not only is the finding of concomitance of increased gasoline mileage and low oil consumption unexpected, but also it is surprising to find that in a majority of engine tests with our preferred composition a lower oil consumption is obtained than would be predicted from the usual viscocity measurement of our final composition. In fact, our composition meeting the SAE 30 grade classification shows in some tests a lower oil consumption than a conventional SAE 30 grade oil of high quality and in certain engines even lower consumption than an SAE 40 grade oil; this result of the comparative tests is contrary to the expected lower oil consumption for the higher SAE grade oil.

Further, our versatile new lubricant with its good detergency and wear characteristics is not obtainable with the commonly employed additives mentioned hereinabove. Such common additives adversely affect one or more of the desirable properties of the lubricant. For example, the use of polyvalent metal phenates such as sulfurized calcium cetyl phenate causes a greater increase in viscosity as the temperature is lowered than is found with the oil of the present invention; hence, such phenate oils give greater friction at low temperatures and consequently result in lower gasoline mileage. Stated another way, the use of phenates as the detergent in place of our special additive in the new lubricant composition results in a lubricant which is unsatisfactory for efficient low temperature operation and good cold weather starting. Also, our new lubricant is superior to such phenate compounded crankcase oils in that it gives increased gas mileage. Thus, the choice of compounding agent for good detergency and low wear characteristics is critical, because the aforementioned phenates adversely affect the desired properties and the glycoxide-sulfonate material is surprisingly free of such adverse effects. Further, the glycoxide-sulfonate material has been found in many instances to bring about an increase in the viscosity index of the composition, which effect is not obtained with the conventional improving agents.

Further, the combination of components results in a lubricant composition having a pour point which is lower than predictable from the nature and amounts of the components. For example, a lubricant prepared from a base oil having a pour point of +15° F., in accordance with this invention, had a pour point of —45° F., whereas other lubricants containing similar amounts of polymer and base oil have pour points 10–20° F. higher.

More particularly, the alkaline earth metal glycoxide-alkaline earth metal sulfonate material is a dispersion of the product of reaction between an alkaline earth metal base and an alkylene glycol, said dispersion in oil being stabilized with an oil-soluble alkaline earth metal sulfonate to form a filterable composition. The apparent reaction product can also be described as a glycolated metal base or a glycoxide, which may be modified by other reactants as described hereinbelow. The metal sulfonate is believed to form micelles in oil solution and as such effects the dispersion or solubilization of the glycoxide or modified glycoxide.

The glycoxide-sulfonate material can be produced by forming a mixture of lubricating oil, ethylene glycol, an oil-soluble, alkaline earth metal sulfonate and an inorganic alkaline earth metal base (i. e., oxides or hydroxides). Sufficient heat is supplied to effect the reaction between the metal base and ethylene glycol before or after the addition of the oil and sulfonate and also after the addition of the oil and sulfonate to remove a substantial portion of the ethylene glycol, i. e., such as remains uncombined. Solids, such as unreacted metal base, are removed by filtration. In the initial mixture at least 2, but not usually more than 50, mols of ethylene glycol are employed for each mol of inorganic metal base. The sulfonate dispersant and inorganic metal base are usually incorporated in a sulfonate/metal base mol ratio of about 0.1–2:1, an excess of 10% of the metal base often being added above this amount. The oil is preferably of the same character as the base oil component of the final composition as described hereinbelow and is employed in sufficient amount to disperse the glycoxide material and sulfonate. Ordinarily it is not convenient to form concentrates containing less than about 50% by weight of oil. When a calcium petroleum mahogany sulfonate (ca 1000 mol. wt.) and lime are employed, the sulfonate dispersant is normally present in an amount of at least one part for each 0.6 part (dry weight basis) of the metal base, expressed as CaO. While ethylene glycol is preferred because of its efficiency on a weight basis, the higher dihydric alcohols, particularly the vicinal alkane diols of less than 5 carbon atoms can be employed on occasion. The alkaline earth metals referred to above include calcium and barium, of which the former is normally preferred. When calcium glycoxide is employed, particularly the larger amounts relative to the sulfonate dispersant, it is preferred that prior to the removal of ethylene glycol and the filtration, a carboxylic acid or its metal salt (or mixtures) be added in an amount so as to yield 0.3 to 1.5 mols of metal salt per mol of calcium glycoxide in order to inhibit gel formation which hinders filtration and which tends to increase the viscosity of the glycoxide oil concentrate as well as the final lubricant composition. Suitable carboxylic acids are those having 1 to 3 carbon atoms starting with formic acid and preferably are hydroxy carboxylic acids including carbonic, glycolic and latic acids. Particularly efficacious is the combination of an alpha hydroxy carboxylic acid, such as glycolic acid, and a non-hydroxy carboxylic acid, such as formic acid, in about equimolar amounts. These metal carboxylates, added as salts or formed in situ from the acids, are believed to become part of the dispersed material and hence modify the dispersed glycoxide. Thus, the term "glycoxide material" does not exclude the presence of these metal carboxylates, and the term "dispersed metal base" contemplates a dispersion of metal carboxylate as well as metal glycoxide; for convenience, the term "glycoxide material" in its generic sense will ordinarily be used.

Normally, the glycoxide-sulfonate material will be prepared as a concentrated oil solution which is 20 to 40 times more concentrated than the final lubricant composition. The viscosity of this oil concentrate should be kept as low as possible; for an oil concentrate containing about 1000 mM/kg. of total metal the viscosity is preferably below about 250 SSU at 210° F., although the viscosity may in some cases be as high as 450 SSU, or as low as 220 SSU or less. It is especially advantageous for minimizing the viscosity increase due to the addition of agents other than the methacrylate polymer to incorporate the hereinbelow-described thiophosphate and sulfide inhibitors into said concentrate and to subject the resulting mixture to heat treatment, preferably at a relatively low temperature such as 130–150° F. for a period of about 2 to 6 hours, prior to combining with the oil component of the final composition. Such pretreatment of the concentrate has been found to yield a final composition having a lower viscosity than otherwise possible.

In the final lubricant composition, the amount of total metal, both dispersed metal base (glycoxide and carboxylate) and metal sulfonate dispersant, is from about 20 to 120 millimols per kilogram (i. e., "mM/kg.") of the composition. For optimum detergency and wear characteristics consistent with the other desired properties such as minimum formation of pre-ignition promoting deposits for gasoline engine service, said total metal preferably is above 30 mM/kg. but usually less than 60 mM/kg. The mol ratio of dispersed metal as glycoxide and carboxylates to sulfonate metal in the final composition will generally range from .50, preferably at least 1.0, to about 10.0. More particularly, for each mol of metal sulfonate dispersant, there is 1.0–10.0, preferably 2–6, mols of metal glycoxide, and 0–4.0, preferably 0.3–1.5, mols of metal carboxylates. In the preferred range of metal glycoxide the mol ratio of glycoxide to carboxylate will be from 1.0 to 3.0:1, and preferably about 2:1.

In terms of millimols of metal per kilogram of final composition, and within the above foregoing limits as to ranges and ratios, the amount of dispersed metal base as glycoxide and carboxylates can range from about 7 to 110 mM/kg. but is preferably 15–55 mM/kg., and the metal in the form of sulfonate dispersant can be 2–80 mM/kg., but is preferably 3–30 mM/kg.

The oil-soluble methacrylate ester polymer preferably has a molecular weight ranging from about 250,000 to 500,000, as determined by light scattering measurements. These particular polymers not only improve the viscosity index and lower the pour point of the final composition, but also undergo a peculiar phenomenon during use in the engine. These polymers apparently are capable of suffering reversible molecular weight degradation in the areas of the engine where they are subjected to high shear stresses. The apparent lowering of the molecular weight of the polymers and consequent decrease in the viscosity of the lubricant composition is temporary, and when the lubricant composition flows away from the zones of high shear stresses to areas of low shear the apparent viscosity of the lubricant is reestablished at a relatively high value. The apparent molecular weight degradation seems to be at least partially induced by shearing action which may cause an actual breakdown of the molecule or micelle or may result in a stretching of a compressed molecule or a straightening out of a curled up molecule or particle. This effect is especially pronounced with the polymers in the preferred molecular weight range and is found to a lesser extent with the methacrylate ester polymers having molecular weights as low as 10,000 and as high as 5,000,000. The phenomenon of reversibility of the apparent molecular weight degradation has been found to be possessed to a high degree, evidently uniquely so, by the methacrylate ester polymers employed in combination with the alkaline earth metal glycoxide-alkaline earth metal sulfonate material. Also, the effect may be promoted by the presence of thiophosphate and sulfide inhibitors. Whatever the mechanism may be, the phenomenon gives startling results in attaining in one lubricant, inter alia, first, the advantage of low friction at high shear rates with resulting high gasoline efficiency and, second, the concomitant advantage of low oil consumption. In a preferred embodiment of our new lubricant invention there is obtained both the characteristics of a normal SAE 10W grade oil with respect to engine startability at low temperatures and high gasoline mileage and the low oil consumption qualities of a conventional SAE 30 grade oil. One theory, not intended to be binding, which may be offered as an explanation of the outstanding results is that in the areas between the piston and cylinder walls and in the films within and surrounding the journals and bearings within the crankcase, the viscosity of the lubricant is sufficiently low at the high shear rates to result in a low frictional drag on the rapidly moving parts. At the same time the viscosity of the lubricant is relatively high at the piston ring-groove interfacecs where the shear rates are relatively low, whereby the high viscosity minimizes the leakage of lubricant through the piston ring grooves on into the combustion chamber and thus effects a reduction in oil consumption.

The methacrylate polymers can be designated as poly(alkyl methacrylates) in which the alkyl group preferably has 8–16 carbon atoms, although alkyl radicals having as little as 6 or as great as 20 carbon atoms are not excluded. In general, the alkyl chain length should be sufficient to give the desired oil solubility at the concentration desired but not so high as to decrease substantially the viscosity index improvement or the reversibility of the apparent molecular weight degradation. Suitable polymers are obtained from methacrylic acid esterified with various alcohols including hexyl, octyl, nonyl, lauryl, cetyl, and octadecyl alcohols or mixtures thereof. Mixtures of alcohols can be derived from various sources, for example, by dehydrogenation of naturally-occurring oils like cocoanut oil. Such mixtures are sold under the names "Lorol," "Lorol B" and "Lorol R" and are mixtures of straight-chain primary alcohols ranging from 10 to 18 carbon atoms; one such mixture is predominantly (about 85%) lauryl alcohol along with a small amount of C_{14} alcohol and lesser amounts of C_{10} and C_{16} alcohols. Illustrative linear polymers are poly(lauryl methacrylate), poly(octyl methacrylate), etc. of various average molecular weights. Such polymers are sold by Rohm & Hass Company under the name "Acryloid" with various identification numbers. "Acryloid 710" is understood to be a polymer of methacrylic acid esters of alcohol mixtures predominating in lauryl alcohol. Other "Acryloids" are polymers of lauryl methacrylate having different average molecular weights or of alkyl methacrylates wherein the alkyl group averages from 10 to 16 carbon atoms and is derived from mixtures of alcohols. "Acryloid 710" has an apparent molecular weight based on viscosity increase measurements of 10,000–30,000, while light scattering determinations indicate a weight of 150,000–200,000. A 30% (on an oil-free basis) solution of "Acryloid 710" in toluene has a viscosity at 100° F. of 160 centistokes; "Acryloid 710" at 1.5 weight percent (on an oil-free basis) increases the viscosity of a California base oil from 65 SSU to 85 SSU at 210° F. Other illustrative "Acryloids" at 30% concentrations in toluene give the following viscosity measurements: No. 763—350 cs.; No. 794—600 cs.; and No. 747—90 cs. The various "Acryloids" are normally available as 40% (dry basis) of polymer dissolved in oil.

The methacrylate polymer is employed in amounts ranging from about 1.5, especially above 2.5%, to 5% by volume of the final lubricant composition, and in a preferred embodiment of the present invention sufficient polymer is added to increase the viscosity of the final composition to 60–70 SSU at 210° F. as measured by ASTM Test Procedure D–88–44. For example, with an oil base having a viscosity of about 40 SSU at 210° F. and a viscosity index of about 90, sufficient polymer of a proper molecular weight is added to bring the viscosity up to about 65 SSU, thereby producing in conjunction with the glycoxide-sulfonate material a crankcase lubricant having the hereinabove-described ideal characteristics to a high degree.

The hydrocarbon oil component of the present invention must have certain properties which are critical for the complete fulfillment of the objects of this invention.

We have found that neither the viscosity at any specific temperature nor the viscosity index alone is determinative in selecting the proper base oil. Both of these factors must be in certain ranges and, further, to attain all the desired characteristics of the preferred embodiment the oil must have a minimum boiling point spread. Thus, the base oil has a viscosity ranging from about 5000 to 8000 SSU at 0° F. (determined as noted below), a viscosity index of 85–120 and a boiling range of not more than about 50° F. difference between the 10% and 90% points as determined by the ASTM D–1160 procedure at a pressure of 1 mm. of mercury. The viscosity at 0° F. is found in accordance with SAE recommended practice as described in Federal Specification VV–L–791c, "Lubricants and Liquid Fuels"; General Specifications (Methods for Sampling and Testing) which is available from the Superintendent of Documents, Washington, D. C. Preferably the base oil also has a flash point above 400° F. and a pour point of less than +15° F. Suitable oils meeting these specifications can be derived such as by solvent refining, acid treating, etc., from various crudes, such as paraffinic, naphthenic or mixed base crude oils, or can be obtained by synthesis such as the Fischer-Tropsch process.

In our preferred embodiment which consists of a final lubricant composition having to an especially high degree the desired properties of high gasoline mileage, good cold weather engine starting characteristics, and low oil consumption, care is taken in the selection of the base oil along with the nature and amount of the polymer and the glycoxide-sulfonate material, which has been found necessary to obtain the desired high quality final lubricant composition, because of the interdependence of the properties of the individual components. Thus, the amount and molecular weight of the polymer together with the viscosity of the base oil, as well as the glycoxide-sulfonate material, are chosen so that the viscosity at 0° F. for the final composition is less than 12,000 SSU. Also, the final viscosity index which is dependent primarily on the base oil and the polymer is selected to give a viscosity for the final composition of at least 60 SSU but usually less than 70 SSU at 210° F. as measured by ASTM Test Procedure D–88–44. Ordinarily the higher the viscosity of the base oil within the above stated range, the lower the amount of the polymer and the higher its molecular weight will be used to get the optimum viscosities at 0° F. and 210° F. Stated another way, the amount of polymer added along with the glycoxide-sulfonate material to the base oil is not more than that which raises the 0° F. viscosity above 12,000 SSU but, while adhering to this limitation, is the maximum for raising the 210° F. viscosity to 60–70 SSU. The higher molecular weight polymers within the range specified above give on an equal weight basis the greater viscosity increase at 210° F. From a viscosity index standpoint, the oils having the lowest viscosity index within the above range require the use of base oils having the lower 0° F. viscosity and the greater amount of polymer. The foregoing directions are given by way of example to enable one skilled in the art to readily select the proper proportions and properties within the specified ranges for the individual components in order to obtain a final crankcase lubricant composition which meets the SAE classifications for both 10W and 30 grade oils.

The thiophosphates which are preferably incorporated in the new crankcase lubricant of the present invention are generally polyvalent metal salts of esters of thiophosphoric acids wherein the ester radicals can be hydrocarbon radicals such as alkaryl or alkyl groups which may be the same or different. Particularly efficacious are mixed alkyl esters having less than 4 carbon atoms in one alkyl group and 6 to 18 carbon atoms in the other group. Although various metals such as calcium, barium, etc., may be employed, the zinc salts are especially desirable. Illustrative thiophosphates are the zinc salts of butyl hexyl dithiophosphoric acid, methyl hexyl dithiophosphoric acid, butyl methylisobutylcarbinol dithiophosphoric acid, dioctyl dithiophosphoric acid, dihexadecyl dithiophosphoric acid, dibutylphenyl dithiophosphoric acid, dicetylphenyl dithiophosphoric acid, etc. The thiophosphates may be used in amounts as low as .05% and up to about 5% by weight although amounts ranging from 0.1 to 2% are preferred. In terms of millimols per kilogram of metal the thiophosphates are most desirably present in the final composition in concentrations of from 3 mM/kg. to about 10 mM/kg.

Suitable sulfur inhibitors are the various oil-soluble sulfur antioxidants such as aliphatic polysulfides, e. g., dihexadecyl tetrasulfide; multi-bridged thioalkyl compounds, such as are formed by reaction of polychlorinated wax and sodium polysulfide and as exemplified further in U. S. Patent 2,514,625; sulfurized olefins such as sulfurized terpenes, reaction products of terpenes and phosphorus sulfides such as P_2S_5; etc. Preferably, the sulfide inhibitor is a non-aromatic compound. Generally, the sulfide inhibitor will be used in amounts from 0.05% up to 3 or 4%, preferably from about 0.1% to 1.5% by weight of the final lubricant composition.

To illustrate further the present invention, there are presented hereinbelow examples of preparations of variout formulations and the results of numerous tests thereon:

Example 1.—A series of formulations were prepared with a base oil derived by solvent refining of a California waxy crude and having the following properties: ASTM viscosities of 140 SSU at 100° F. and 42 SSU at 210° F., a viscosity index of about 85, a flash point of 400° F., a pour point of +15° F., and the following ASTM D–1160 distillation at 1 mm. of mercury pressure:

Percent distilled:	Temp. (° F.)
Initial	290
5	327
10	337
20	352
30	357
40	361
50	364
60	367
70	370
80	373
90	381
95	385
97.5	424

To this base oil was added in each formulation 6.4% (40% solution in oil) of "Acryloid 710" plus 0.25% of a sulfurized diparaffin wax sulfide, 6 mM/kg. of a zinc cetylphenyl dithiophosphate and the various amounts as indicated below of a glycoxide-sulfonate material. This last was prepared as an oil concentrate as follows: 75 grams of ethylene glycol and 22 grams of lime were admixed and then to the admixture was added 10.8 grams of glycolic acid, 7.4 grams of formic acid, 100 grams of calcium mahogany sulfonate along with 200 grams mineral oil. The resulting mixture was heated to effect the reaction and also to remove unreacted glycol as well as water of reaction. After filtration, the oil concentrate contained 4.5% by weight of calcium (calculated as calcium metal) and a viscosity of 250 SSU at 210° F. Sufficient of this oil concentrate was added to portions of the above-described compounded base oil to give 28 mM/kg., 39 mM/kg., and 65 mM/kg., as total metal, of the glycoxide-sulfonate material for compositions A, B and C, respectively. These compositions had the properties shown in Table I.

Table I

Composition	Viscosity (SSU) at—			Vis. index	ASTM pour pt. ° F.	ASTM color
	100° F.	210° F.	0° F.			
A	290.5	60.4	9,300	139	−40	3½
B	297.4	61	9,700	139	−40	4
C	312.6	62.2	10,500	138	−40	4

The data in Table I illustrate that compositions A, B and C with different amounts of the glycoxide-sulfonate material satisfy the requirements for both SAE grade 10W and SAE grade 30 oils. The data also show the excellent viscosity indices and low pour points obtainable for compositions of the present invention.

Example 2.—To illustrate the present invention further, preparations were made of compositions similar to composition B in Example 1 except that in the case of composition D, 6.8% (40 oil solution) of "Acryloid 710" was employed and in the case of composition E, a zinc mixed dialkyl dithiophosphate was substituted. The properties of these compositions are tabulated as follows:

Table II

Composition	Viscosity (SSU) at—			Vis. index	ASTM pour pt. ° F.	ASTM color
	100° F.	210° F.	0° F.			
D	301.3	62.0	9,500	140	−50	4
E	281.4	60.2	8,500	141	−50	3½

Likewise, as indicated by the foregoing data, compositions D and E have highly satisfactory properties.

Example 3.—For comparison, formulations were prepared similar to composition A of Example 1, except that in place of the glycoxide-sulfonate material, there was substituted: for composition F, 10 mM/kg. of a calcium petroleum mahogany sulfonate plus 20 mM/kg. of a sulfurized calcium cetyl phenate; for composition G, 15 mM/kg. of said sulfonate and 35 mM/kg. of said phenate; and for composition H, 10 mM/kg. of said sulfonate and 40 mM/kg. of said phenate. The properties of these compositions are as follows:

Table III

Composition	Viscosity (SSU) at—			Vis. index	ASTM pour pt. 0° F.	ASTM color
	100° F.	210° F.	0° F.			
F	330.2	62.1	13,000	133	−40	6
G	371.3	64.9	16,000	131	−15	8
H	383.5	65.8	18,000	130	−10	8

These data illustrate that the substitution of the phenate-sulfonate combination for the glycoxide-sulfonate material adversely affects the viscosity index and raises the viscosity at 100° F. and at 0° F. so that the oils do not satisfy the requirements for an SAE 10W grade oil.

Example 4.—A crankcase lubricant meeting the requirements for SAE 10W, 20W and 30 grade oils was prepared with the following composition by weight: 87.5% of the selected base oil described below, 6.8% (40% oil solution) of "Acryloid 710," and 5.7% of an oil concentrate which had been previously heat-treated as described hereinabove and which contained sufficient of each agent to give the following amounts in the final composition: 40mM/kg. of the glycoxide-sulfonate material described in Example 1, 6 mM/kg. of zinc dicetylphenyl dithiophosphate and 0.25% of sulfurized diparaffin wax sulfide. The base oil was the same as that described in Example 1. The resulting lubricant had the following physical properties: viscosities of 301 SSU at 100° F., 62.6 SSU at

210° F., and 9000 SSU at 0° F.; a flash point of 425° F., a viscosity index of 141, and an ASTM pour point of −45° F. This lubricant will give in an engine operating at 32° F. a cranking speed 54% greater than the speed obtained in the same engine at the same temperature with a conventional SAE 30 grade lubricant.

Example 5.—The gasoline and oil mileage characteristics of the crankcase lubricant composition of Example 4 were compared to those of a reference oil in several hundred thousand miles of road test in a fleet of taxis and two fleets of passenger cars. In these tests all the vehicles were operated alternately with the test oil for one drain period and then the reference oil for a drain period, the cycle being repeated as many times as possible during the test. The reference oil was a conventional heavy duty compounded SAE 30 grade motor oil. The taxi fleet averaged 3500 miles of driving per month per vehicle in predominantly city traffic driving with an occasional highway trip; cold starts were limited to one or two per operating day and average engine temperatures were 150° F. and 160° F. for crankcase oil and jacket coolant, respectively. Passenger car fleet A averaged more than 1000 miles per month driving in relatively open country at relatively high speeds and ambient temperatures. The cars of fleet B were operated predominantly in city traffic on short trips and experienced a relatively large number of cold starts per month, the vehicles averaging 490 miles of driving per month. The following table summarizes the results of the fleet taxis:

Table IV

Fleet	Ave. total test, miles	Ave. oil mileage, miles/quart		Ave. gas mileage, miles/gallon		Percent Improvement	
		Ref. oil	Test oil	Ref. oil	Test oil	Oil mileage	Gas mileage
Taxi	132,700	589	656	11.9	12.4	11	4
A	49,000	758	789	15.5	16.2	4	5
B	14,000	761	911	11.0	12.9	20	17

Example 6.—Another series of tests were carried out with heavy duty trucks powered by General Motors engines which were used in long distance gasoline hauling in the lower San Joaquin Valley accumulating mileage of approximately 10,000 miles per month under high-speed, high-load conditions. The crankcase lubricant composition of Example 4 was used as the test oil in comparison with conventional compounded diesel engine crankcase lubricating oils of SAE 30 and SAE 40 grades.

The average oil mileage for these tank trucks when operated with the test oil of the present invention was 42% greater than that observed with the SAE 30 reference oil, and 21% greater than that observed with the SAE 40 grade reference oil.

Example 7.—The improvement in power output by the use of the present lubricants was measured in a chassis dynamometer with a 1953 Cadillac, a 1953 Chevrolet power glide and a 1952 Plymouth. The test oil was the crankcase lubricant composition of Example 4, and the reference oil was a conventional heavy duty compounded SAE 30 grade motor oil. Under full throttle maximum power operation an improvement of 7% was observed in the Cadillac, 4% in the Chevrolet, and 3% in the Plymouth.

The increase in power observed in the chassis dynamometer test was also demonstrated on the road in the Cadillac and Chevrolet by a 5% reduction in time required to accelerate from 0 to 60 miles per hour when the test oil of the present invention was used in place of the reference SAE 30 grade oil.

Example 8.—Two California Highway Patrol cars used for highway patrol and pursuit were tested on a chassis dynamometer for high speed performance both with a test oil of the present invention and a reference oil. The test oil was the lubricant composition of Example 4 and the reference oil was a heavy duty commercial compounded motor oil of SAE 30 grade.

To determine the relative performance of the two oils under usual operating conditions, the cars—a 1952 Oldsmobile Model 88 and a 1953 Oldsmobile Model 88—were brought to the chassis dynamometer directly from service and no tune-up or mechanical work was done on the cars immediately prior to or after the tests. The oil in the cars as received was drained and replaced with reference oil. The maximum speed was determined. Comparative tests were then run by draining the engine crankcase and filter and refilling with the test oil. The test was repeated.

The maximum relative speed of the 1953 Oldsmobile showed an increase of 4.5 miles per hour and the 1952 Oldsmobile an increase of 5.5 miles per hour. The horsepower curves showed an increase in power over the entire range tested for both cars when using the test oil. This improvement in horsepower would result in faster acceleration to top speed as well as an increase in the top speed.

Example 9.—Another series of tests were conducted under city traffic driving conditions wherein the car was driven four trips daily for a distance of 3½ miles over a specified route. One trip was made in late afternoon and the car parked overnight. The next trip was made in the early morning and the car parked until noon, at which time a round trip was made with one-half hour of parking at the terminus. This cycle was repeated for three days on the test oil and then for three days on the reference oil. The test oil was a lubricant composition of Example 4 and the reference oil was a conventional heavy duty compounded SAE 30 grade oil. The improvements, due to the use of the test oil, in gasoline mileage for the several tests and with different drivers ranged from 8% to 17%.

Example 10.—The lubricant composition of Example 4 was tested for its performance from the standpoint of maintaining engine cleanliness in a standard 40-hour, FL–2 Chevrolet engine test using a low grade gasoline especially prone to cause engine deposits, the conditions being those defined in the FL–2 Test Procedure described in the June 21, 1948, report of the Coordinating Research Council on Engine Test C. R. C. FL–2, entitled "Research Techique for Determining the Effect of Fuels and/or Lubricants on Formation of Engine Deposits During Moderate Temperature Operation." This procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2500 R. P. M. and 45-brake horsepower for 40 hours, and therefore closely, and reproducibly, simulates the relatively "cold" engine conditions which are normally experienced in city driving. At the end of the test the engine was dismantled and the amount of engine deposits on the piston determined as follows: Average piston rating was obtained by individually rating (on a scale of 0–10 representing the absence of any deposit) the amount of deposit on each piston skirt and averaging the individual ratings so obtained for the various pistons. In a like manner, varnish ratings were obtained for each of the rocker arm cover, the push rod cover, the cylinder wall, and the oil pan. Similarly, sludge ratings (on the same scale) were obtained for the rocker arm assembly, the rocker arm cover plate, the push rod cover plate, the oil screen, and the oil pan. These ten different ratings were added to give a total engine rating. Under the conditions of this test an over-all engine rating of above 75 is indicative of satisfactory performance, a conventional heavy duty compounded SAE 30 grade motor oil giving an engine rating of about 80. The total engine rating obtained for the test oil of the present invention was 81.8, indicating that the present lubricants have satisfactory engine cleanliness characteristics.

Example 11.—The effectiveness of the lubricant composition of Example 4 in controlling hydraulic valve lifter deposits was measured in a Chevrolet power glide engine operated in accordance with the EX–2 Test Procedure of the Coordinating Research Council as reported in the September 1952 report, entitled "Lubricating Engine Test Designed to Simulate Deposits in Stop and Go Field Service." This test is a 96-hour cycling test employed to evaluate low temperature deposits and to measure the effectiveness of oils in controlling lifter deposits. For this latter purpose the degree of discoloration of the plunger of the hydraulic valve lifter is used as the basis for comparison. An oil compounded with diesel engine lubricating oil type commercial additive to a level equivalent to Series I lubricants (i. e., Army Specification 2–104B, Supplement I) was used as a high standard of comparison; this reference oil permitted the formation of a light gray discoloration while dark gray discolorations are observed with conventional heavy duty compounded motor oils. The new and improved crankcase lubricant composition of Example 4 was equivalent in degree of discoloration of lifter plungers to the highly compounded Supplement I lubricant.

Example 12.—The Standard L–4 Chevrolet engine test described in a Coordinating Research Council circular, entitled "Test Procedure for Determining Oxidation Characteristics of Heavy Duty Crankcase Oils," was employed with a test oil of the composition set forth in Example 4 above. This test measures the control of high temperature deposit formation and oxidation stability of the oil. The test procedure is to run a Chevrolet engine for 36 hours at a jacket temperature of 200° F., and a sump temperature of 280° F. Bearings are weighed before and after the test and the average bearing weight loss is recorded as the corrosion. Ratings of the varnish and sludge are made for the various parts, and a total engine rating determined therefrom, as in the FL–2 Chevrolet engine test described in Example 9.

The test results were a total engine rating of 98.4 and a copper-lead bearing weight loss of 55 mg. per bearing.

Example 13.—A lubricant composition prepared in accordance with Example 4 was evaluated in a Plymouth engine operated for 100 hours at 165° F. oil temperature and 175° F. jacket temperature at 2500 R. P. M. and 25-brake horsepower. This procedure closely simulates taxicab service conditions. The cylinder wear was determined by micrometer measurements before and after the test at the top, bottom and several intermediate points, and micrometer measurements were also used to determine the top ring side clearance increase. The results of the test were as follows:

Cylinder	Cylinder wear, inches	Top ring side clearance increase, inches
1	−0.0001	0.0000
2	0.00005	0.0003
3	0.0000	0.0005
4	0.0000	0.0002
5	−0.0001	0.0000
6	0.00015	−0.0007
Average	0.0000	0.00005

These data indicate excellent low wear properties for the new lubricant.

Example 14.—The high temperature wear characteristics of an oil composition prepared as in Example 4 were evaluated in an L–4 Chevrolet test as described in Example 11, except that the engine was run for 100 hours instead of 36 hours. The wear was determined by the difference in micrometer measurements made before and after the test for each part, and the average change for all such parts recorded. The results of the test were as follows:

Average cylinder wear	inches	0.00031
Average wrist pin wear	do	0.00045
Average wrist pin bushing wear	do	0
Average cam shaft journal wear	do	0.00015
Average cam shaft bushing wear	do	0.00045
Average main bearing journal wear	do	0.0001
Average con rod bearing journal wear	do	0.000095
Average top ring weight loss	mg	38
Average push rod weight loss	mg	5.9

Example 15.—A Plymouth road test car equipped with a radioactive top piston ring was employed in two series of comparative tests. The amount of ring wear is determined by the amount of radioactive iron dispersed into the circulating lubricant. In comparative tests, a lubricant composition prepared in accordance with Example 4 gave in 1260 test miles an average ring wear rate of 0.0048 mg. of iron per mile as compared to a wear rate of 0.0054 mg. over 1144 test miles for a conventional heavy duty compounded SAE grade 30 motor oil.

Example 16.—A series of determinations were made of the effect on octane requirement of a 1952 Plymouth by the use of the lubricant composition of Example 4 as the test oil and for comparison a conventional heavy duty compounded motor oil as a reference. These were carried out using a standard road octane requirement test conducted in accordance with the procedure outlined in Coordinating Research Council Designation E–1–748, entitled "Research Technique for Determination of Octane Number Requirements of Vehicles on the Road." This test is conducted on a series of reference fuels and ascertains the octane number of the fuel required for incipient knocking of the engine over a standard road course within the normal speed range of the vehicle. For the purpose of the test, the fuel line of the engine is disconnected at the suction side of the fuel pump and a special 5/16 inch line run into the cab of the car where the primary reference fuels are carried.

The test was started with the car showing an odometer reading of 11,700 miles. After filling the crankcase with the test oil, the car was run for 800 miles with a standard premium gasoline which was used throughout the subsequent tests. The octane requirement measured as described above was 75 at the end of the 800-mile period. Thereafter, the car was driven for 1122 miles with the reference oil at the end of which period the octane requirement was found to be 80. Following this, the car was then driven 850 miles with the test oil and the octane requirement dropped to 75.

Example 17.—In another series of tests, eight Plymouths in a taxicab fleet were operated for approximately 14,000 miles, all on the same gasoline. The test oil and reference oil of Example 16 were used in four cars each. At the end of the period, the octane requirement of all the cars was determined in accordance with the method referred to in Example 16. It was found that the average octane requirement of the cars using the test oil was four numbers lower than the average requirement of the cars using the reference oil.

Example 18.—Another formulation was prepared with a base oil derived by solvent refining from an East Texas crude and having the following properties: ASTM viscosities of 139 SSU at 100° F. and 42.4 SSU at 210° F., a viscosity index of about 99, a flash point of 440° F. and an A. P. I. gravity of 32.2°, and ASTM D–1160 distillation points at 1 mm. of mercury of 370° F. at 10% and 458° F. at 90%. A lubricant composition composed of 87.8% of this base oil, 6.5% of the methacrylic polymer solution used in Example 4 and 5.7% of the oil concentrate employed in Example 4 had the following properties: ASTM viscosities of 62.1 SSU at 210° F., 291 SSU at 100° F. and 7500 SSU at 0° F., a viscosity index of 143 and a pour point of —45° F. This indicates that with the higher 10% distillation points, i. e., above about 350° F., the spread between the 10% and 90% points can be greater such as up to 90°, provided that the viscosities of the polymer-containing lubricant are in the specified ranges.

This lubricant composition gave a total engine rating of 98.4 and a bearing weight loss of 65 mg. per bearing in the standard L–4 Chevrolet engine test referred to in Example 11. Also, this oil gives improved oil and gas mileage when compared to a conventional compounded heavy duty SAE 30 grade motor oil.

Example 19.—A variation of the lubricant composition of Example 18 was prepared by using as the base oil a solvent refined oil from mixed mid-continent and coastal crudes. Such base oil has ASTM viscosities of 139.5 SSU at 100° F. and 42.5 SSU at 210° F., a viscosity index of about 100, flash point of 415° F., a pour point of 0° F., A. P. I. gravity of 32.1°, and ASTM–D–1160 distillation points at 1 mm. of mercury pressure of 372° F. at 10% and 455° F. at 90%. A lubricant composition of this base oil with the remaining components the same as in Example 18 had the following properties: ASTM viscosities of 62.2 SSU at 210° F., 288.4 SSU at 100° F., and 8000 SSU at 0° F., a viscosity index of 144, a flash point of 435° F. and a pour point of —45° F.

This lubricant composition gave a total engine rating of 99.4 and a bearing weight loss of 61 mg. per bearing in the standard L–4 Chevrolet engine test referred to in Example 11. Also, the lubricant gave oil and gas mileages superior to conventional compounded SAE 30 grade motor oil.

While the lubricant composition of the present invention essentially contains the selected hydrocarbon base oil component, the glycoxide-sulfonate material and the methacrylate polymer and preferably in addition contains the thiophosphate and sulfide agents described hereinabove, the resulting composition with its outstanding performance characteristics will not ordinarily need further agents. However, it is within the contemplation of the present invention, in some instances and/or for special purposes, to incorporate in the composition other agents such as extreme pressure agents, blooming agents, oiliness agents, foam inhibitors, dyes, other agents which affect the viscosity index or pour point, corrosition inhibitors, etc.

We claim:

1. An improved gasoline engine crankcase lubricant which meets the viscosity requirements of an SAE 10W oil at 0° F. and the viscosity requirements of an SAE 30 oil at 212° F. consisting essentially of the combination of (*a*) a hydrocarbon lubricating oil having a viscosity ranging from 5,000 to 8,000 SSU at 0° F., a viscosity index of 85 to 120 and a boiling range of not more than a 50° F. difference between the 10% and 90% boiling points as determined by the ASTM D–1160 procedure at a pressure of 1 mm. of mercury, said oil comprising at least 85% of the final composition of the lubricant, (*b*) 2.5 to 5% by volume of an oil-soluble, alkyl methacrylate polymer having alkyl groups of from 6 to 20 carbon atoms and a molecular weight between 100,000 and 500,000, as determined by light scattering measurements, the viscosity and viscosity index for said hydrocarbon oil and the amount and molecular weight of said polymer being such that the final composition has viscosities of less than 12,000 SSU at 0° F. and 60 to 70 SSU at 210° F., (*c*) 30 to 60 millimols per kilogram of an inorganic metal base substance consisting of a dispersion of the product of reaction between an alkylene glycol of less than 5 carbon atoms and an alkaline earth metal base selected from the group consisting of oxides and hydroxides, said dispersion being stabilized in oil with an oil-soluble alkaline earth metal sulfonate, the ratio of metal as dispersed metal base substance to metal as sulfonate dispersant ranging from 1.0:1 to about 10:1, said reaction product being obtained by forming a mixture containing said metal

base and said glycol in a ratio ranging from 2 to 50 mols of glycol for each mol of said metal base and heating said mixture for a sufficient time to effect the reaction between glycol and metal base, (*d*) 0.1 to 2% by weight of an oil-soluble polyvalent metal salt of an ester of thiophosphoric acid, and (*e*) 0.1 to 1.5% by weight of an oil-soluble aliphatic polysulfide antioxidant.

2. The lubricant of claim 1 wherein said alkaline earth metal in the inorganic metal base substance and in the sulfonate dispersant is calcium.

3. The lubricant of claim 1 wherein said polyvalent metal salt of an ester of thiophosphoric acid is a zinc salt.

4. An improved gasoline engine crankcase lubricant which meets the viscosity requirements of an SAE 10W oil at 0° F. and the viscosity requirements of an SAE 30 oil at 212° F. consisting essentially of the combination of (*a*) a hydrocarbon lubricating oil having a viscosity ranging from 5,000 to 8,000 SSU at 0° F., a viscosity index of 85 to 120 and a boiling range of not more than a 50° F. difference between the 10% and 90% boiling points as determined by the ASTM D–1160 proceded at a pressure of 1 mm. of mercury, said oil comprising at least 85% of the final composition of the lubricant, (*b*) 2.5 to 5% by volume of an oil-soluble, alkyl methacrylate polymer having alkyl groups of from 6 to 20 carbon atoms and a molecular weight between 100,000 and 500,000, as determined by light scattering measurements, the viscosity and viscosity index for said hydrocarbon oil and the amount and molecular weight of said polymer being such that the final composition has viscosities of less than 12,000 SSU at 0° F. and 60 to 70 SSU at 210° F., (*c*) 30 to 65 millimols per kilogram of metal base material stabilized in oil with an oil-soluble alkaline earth metal sulfonate, the ratio of metal as dispersed metal base material to metal as sulfonate dispersant ranging from 1.0:1 to about 10:1, said metal base material consisting of (1) the product of reaction between ethylene glycol and an alkaline earth metal base selected from the group consisting of oxides and hydroxides, and (2) an alkaline earth metal salt of an organic carboxylic acid having 1 to 3 carbon atoms, and there being present in the lubricant composition for each mol of sulfonate dispersant 1 to 10 mols of said reaction product and 0 to 4 mols of said carboxylic acid salt, said reaction product being obtained by forming a mixture containing said metal base and said glycol in a ratio ranging from 2 to 50 mols of glycol for each mol of said metal base and heating said mixture for a sufficient time to effect the reaction between glycol and metal base, (*d*) 0.1 to 2% by weight of an oil soluble polyvalent metal salt of an ester of thiophosphoric acid, and (*e*) 0.1 to 1.5% by weight of an oil-soluble aliphatic polysulfide antioxidant.

5. The composition of claim 4 wherein is present for each mol of sulfonate dispersant 2 to 6 mols of said ethylene glycol reaction product and 0.3 to 1.5 mols of carboxylic acid.

6. The lubricant of claim 4 wherein said alkaline earth metal in the inorganic metal base substance and in the dispersant is calcium.

7. The lubricant of claim 4 wherein said polyvalent metal salt of an ester of thiophosphoric acid is a zinc salt.

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