

1

3,385,791

LUBRICANT OIL COMPOSITION

Charles C. Colyer, Crown Point, Walter W. Frank and John V. Peterson, Portage, and William L. Sieker, Crown Point, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana
 No Drawing. Continuation-in-part of application Ser. No. 441,841, Mar. 22, 1965. This application Sept. 15, 1967, Ser. No. 668,165

3 Claims. (Cl. 252—32.7)

ABSTRACT OF THE DISCLOSURE

High severity service function over extended oil drain range, e.g., 2,500 to 6,000 mile, recommended by manufacturers of automobile engines having positive crankcase ventilating devices is provided by crankcase lubricating oil formulations having an essential combination of three additive components dissolved in hydrocarbon oils of lubricant oil class. The essential combination is (a) oil-soluble nitrogen- and boron-containing dispersant-detergent having a weight ratio of nitrogen to boron in the range of 0.1 to 0.5 weight percent nitrogen per weight percent boron that are boric acid borated disuccinimides of a bis(polyaminoethyl)symmetrical urea, (b) oil soluble calcium or magnesium sulfonate of high alkalinity such as those having a total base number of at least 300, and (c) oil-soluble zinc dialkyldithiophosphates whose two alkyl groups are of different carbon contents with one alkyl group having three or four carbons and the other alkyl group being primary alkyl with from five to ten carbons. The three additives are present in the concentrations to provide on the basis of 100 gallons of oil from 3 to 20 pounds of (a), an amount of (b) equivalent to 1.05 to 3.2 pounds of calcium and an amount of (c) to provide 0.25 to 1.2 pounds of zinc. Dispersant-detergent (a) is, for example, derived by boric acid boration of the disuccinimide product of the reaction between two moles of 400 to 2,900 molecular weight polybutenyl substituted succinic anhydride with one mole bis(polyaminoethyl) urea under conditions for splitting out and removing water of reaction. The bis(polyaminoethyl)urea is the product of reacting two moles of polyethylene polyamine (e.g., tetraethylene pentamine) with one mole of urea with the splitting out and removal of two moles of ammonia.

Related application

This application is a continuation in part of our earlier-filed application Ser. No. 441,841, filed Mar. 22, 1965 and is now abandoned.

Background of the invention

This invention relates to lubricant oils. More particularly, it concerns the provision of a lubricant oil composition containing an essential combination of additives whose function is not only to protect the lubricated parts of an internal combustion engine but also protects positive crankcase ventilator valves from malfunction.

During the past half century, increasingly severe requirements have been imposed on lubricant oils for internal combustion engines. As engine performance was increased, so also were the various specifications on motor oil performance.

2

Beginning about 1946, engine performance levels were elevated so drastically that entirely new lubricant performance tests had to be devised. An oil that was entirely satisfactory for all automobile models in one year would, because of higher cylinder compression ratios, higher engine temperatures, higher frictional loads on bearings and other surfaces, and other factors, fail to meet the standards of the next year's models.

Until 1961 the formulators of motor oils had little difficulty keeping pace with increasing requirements of higher performance engines. True, some oils performed better than others, and a few were even ahead of the market requirements.

But in 1961 and 1962 the picture changed drastically. American automobile manufacturers announced that henceforth they were recommending crankcase oil changes considerably in excess of the 1,000 or 2,000 mile changes advised by the manufacturers. With this recommendation facing them, producers of motor oils were faced with the realization that no existing motor oil could be expected to meet the greatly extended oil-drain specification recommended. Additives previously used to improve various aspects of motor oil performance would provide but a starting point for the development of oils capable of functioning for the newly suggested mileage extension between oil changes, up to 6,000 mile requirement between crankcase lubricant oil changes.

The problem of providing an extended service motor oil formulation is a serious one. In essence, an oil must be capable of providing satisfactory lubrication for a period of from three to six times as long as had been required in the past. At the same time it must maintain the crankcase as well as other parts of the engine free of harmful sludge deposits, and must afford protection against rust and corrosion as well as wear protection for engine parts such as valve lifters which are in extreme contact pressure. Moreover, long service motor oils must retain the characteristics of suitability for diesel engines as well as spark-ignition engines such as oxidation stability, viscosity maintenance, cold starting characteristics, certain combustion chamber control features, and oil mileage and fuel economy which consumers have come to expect from all premium grade oils. While additives are known which are capable of increasing one or perhaps two of these characteristics, there are many sources of specific interactions with other lubricant additives that only careful and extensive experimentation leads to truly useful motor oil formulations suitable for the more severe extended service.

At about the same time of the announced intent to recommend substantially increased mileage use of crankcase lubricating oil compositions, there were also announced regulatory measures to be imposed on the operation of internal combustion engines in an attempt to reduce air pollution by engine combustion by-products which were alleged to be the source of irritants to eyes and the respiratory system and to contribute in large urban areas to the atmospheric condition known as "smog." It has been known for some time that combustion chamber by-products are forced past piston rings which function to seal the combustion chamber of the cylinders from the crankcase. The crankcase of an internal combustion engine normally vented at atmospheric pressure was at a much lower pressure than either the pressure of

the compressed mixture of air and fuel, 120 p.s.i.g. and higher, in the combustion chamber before ignition of the fuel therein or of the hot expanding gases therein during combustion providing the power stroke driving force. The substantial pressure differential permitted the blow-by of combustion mixture and combustion by-products from the combustion chamber to the crankcase.

One of the aforementioned regulatory measures was directed against the direct venting of the crankcase to the atmosphere and required reintroduction of the blow-by vapors and/or gases into the combustion chambers for more complete burning thereof to less obnoxious products. Another regulatory measure was directed to the treatment of the exhaust, combustion chamber combustion products discharged to the exhaust manifold and thence to the atmosphere. The ultimate solution was to achieve a higher degree of engine waste product conversion to at least less harmful products. Crankcases could be ventilated to the air intake system before or after carbureting the air with the hydrocarbon fuel. Crankcase ventilation into the intake air filter or between the filter and carburetor causes the deposition of solids, e.g. carbon particles, entrained in the gases and/or vapors from the crankcase in the air filter or on parts of the carburetor having close operating tolerances thereby causing plugging of the air filter and/or the carburetor. Furthermore, such venting methods were not always positive and complete.

The crankcase could be positively vented by connecting the crankcase vapor space to the fuel-air intake manifold which is at subatmospheric pressure during engine operation because of the suction caused by the intake stroke of the pistons. The pressure in the fuel-air intake manifold decreases as the engine speed increases and a reduced pressure can be obtained which would cause a large portion of the liquid crankcase lubricant composition to be drawn out and charged with the fuel-air mixture into the combustion chambers. Drastic lubrication failures would thereby result. To prevent this removal of crankcase lubricant at the lower intake fuel-air manifold pressures a valve is placed in the ventilating line between the crankcase and the intake manifold to control the pressure between the crankcase and said intake manifold but still permitting the positive ventilation of the crankcase. Such a valve is referred to as a "positive crankcase ventilator" valve and is hereinafter designated PCV valve. The PCV valve is designed to operate completely open when the engine is not operating or at idle and then gradually restrict flow to throttle the pressure differential as the engine speed increases. The PCV valve never completely closes.

The gases and/or vapors from the crankcase contain sludge and varnish formers, water vapor, corrosive vapors and solids entrained in the gases and/or vapors. Thus the PCV valve can become fouled and rendered inoperative from sludge and/or varnish deposits, corrosion and rust. Sludge and/or varnish deposits in the intake manifold or on the intake valves and valve seat surfaces and corrosion or rusting of the valve seats adversely impair the operation of the internal combustion engine. Also, the same sludge and/or varnish formers as well as suspended fine solids enhance the formation of deposits on the upper surfaces of the combustion chamber and piston thereby requiring an increase in anti-knock requirement of the fuel for satisfactory smooth engine operation. Thus a still more severe requirement is placed on the crankcase lubricating oil composition by the PCV valve over and above those already imposed by increased heat and oxidation stability, wear, rust, depositing of sludge and varnish and corrosion in the engine because of longer oil use at higher maximum temperatures, increased stop and go driving as well as intermittent engine operation during which the engine barely reaches operating temperature and then is shut off. The crankcase lubricant oil must not only function for a greatly increased mileage between drains but also must prevent malfunction of the PCV valve by pre-

venting materials which would corrode and/or deposit in or on the valve from reaching the PCV valve.

There has now been discovered a motor oil which satisfies the requirements of oils for extended drain periods now being recommended by engine builders and prevents the malfunction of the PCV valves. In addition to retaining the features possessed by conventional premium grade motor oils, the motor oil of the invention provides durability, resistance to oxidation, corrosion, rust, wear, sludge and varnish deposition and protection of the PCV valves against malfunction to a degree unapproached by closely related motor oil formulations.

Summary of the invention

According to the invention, the novel motor oil comprises a mineral lubricating oil base having as essential additives a particular combination of (a) a nitrogen-boron containing reaction product detergent-dispersant, (b) a calcium or magnesium salt of an oil-soluble organic sulfonic acid having a total base number of at least 300 mg. KOH per gram and (c) a heat stable zinc salt of a dialkyl diester of dithiophosphoric acid. The oil also advantageously contains one or more viscosity index improvers and an anti-foam additive.

As indicated, the oil of the invention comprises a mineral base with a combination of three essential additive components in a particular combination. This combination provides for each 100 gallons of formulated oil (a) in the range of from 3 to about 20 pounds of the nitrogen-boron containing reaction product detergent-dispersant, advantageously a boron containing derivative obtained from an alkyl substituted succinic acid or anhydride and a polyamino urea, (b) an amount of Ca or Mg 300 total base sulfonate to provide the chemical equivalent of 1.05 to 3.2 pounds Ca, and (c) a zinc salt of a dialkyl (one C₃ to C₅ alkyl and one C₅ to C₁₀ alkyl) dithiophosphoric acid in an amount to provide 0.25 to 1.2 pounds of zinc. Such zinc salt preferably has primarily primary alkyl groups of optimum heat stability. Typically the alkyl groups of the zinc salt are mixtures of isopropyl with primary amyl, octyl and decyl and isobutyl with primary amyl, octyl and decyl with at least 55 mole percent primary alkyl. Additionally the composition advantageously contains a polyisobutylene viscosity index improver and/or a polymethacrylate viscosity index improver, and a silicone anti-foam agent. Concentrates of the combination of additives dilutable with lubricant base oil stock to the aforementioned concentrations are also contemplated.

In the ensuing portions of this specification the several components of the motor oil formulation of this invention will be discussed independently and illustrative detailed specific compositions will be presented. Then, the results of testing this specific formulation will be presented and discussed.

The tests to which the present lubricant oil are subjected are exceptionally severe. In respect to the properties of engine performance, oxidation stability, oil mileage, cold starting ability, fuel economy, and combustion chamber control, the lubricant oil composition of this invention is required, of course, to at least equal the performance of a formulated motor oil that has been approved and accepted on the basis of its performance for engine lubrication. With respect to the properties of long crankcase life, rust protection and wear protection, engine cleanliness, PCV valve protection as well as conformity to SAE 10W-30 requirements, the inventive motor oil is required to surpass commercially available premium grade oils by a substantial margin.

Lubricant base oil

The base oil in which the aforementioned combination of essential additive ingredients is dissolved is a petroleum-derived lubricant vehicle, preferably one which has been solvent extracted with phenol, furfural, and the like and/or propane dewaxed to improve its temperature-viscosity

performance. The oils generally are in the lubricating oil viscosity range; e.g., from about 50 SSU at 100° F. to about 300 SSU at 210° F., but normally are required to conform to more exacting specifications for motor oils of a particular service, as for example to the various Society of Automotive Engineers tests.

The base oil will usually constitute from about 75 to about 85 volume percent of the formulated lubricant, but this percentage may be either lower or higher, e.g., 50-90 volume percent, depending upon the amounts of the respective additives.

In addition to petroleum hydrocarbon sources, synthetic lubricants or natural hydrocarbons other than those petroleum derived can also be used to provide the base oil. Hydrogenated coal derived hydrocarbons suitably converted, by methods known to the art, to hydrocarbon oils of desirable viscosity index characteristics, shale oil, polybutenes, etc., can also be used for this purpose.

Nitrogen and boron-containing reaction products derived from alkenyl substituted succinic acid or anhydride

An essential compound of the combination of additives for the lubricant oil formulations of this invention is the nitrogen-boron containing alkenyl substituted succinic acid or anhydride derived reaction product dispersant detergent. These N-B-containing dispersant detergents are desirably present in a concentration in the range of from about 3 to 20 pounds per 100 gallons of the formulated lubricant and are preferably present in concentrations in the range of 9 to 17 pounds per hundred gallons of the formulated lubricant oil.

A wide variety of N-B-containing dispersant-detergent additives can be used but the preferred additives of this class are derived from alkenyl substituted succinic acid or anhydride having 30 or more carbon atoms in the alkenyl hydrocarbon substituent. These N-B-containing dispersant-detergents are prepared by reacting a polyamino urea with the alkenyl substituted succinic acid or anhydride (an alkenyl succinic acid producing compound) at a temperature in the range of about 170 to 485° F. to form a di(alkenyl succinimide) of the polyamino urea as a first reaction product. Then the first reaction product is reacted at a temperature in about the same temperature range (i.e., 170° to 485° F., preferably 250° to 350° F.) with a boron compound such boron oxide, boron halide, boron acids and esters of boron acids, preferably boric acid.

The polyamino urea reactants are not a new composition of matter. Their preparation is described in U.S. Patent No. 2,644,759 where the polyamino ureas are characterized as pigment wetting agents useful in the preparation of printing inks. Polyamino ureas preferred as reactants for the above N-B-containing dispersant-detergent are the polyamino ureas prepared by reacting an alkylene amine with urea in the ratio of two moles alkyl amine per mole urea. Reaction between the alkylene amine and urea liberate two moles of ammonia per mole of urea and is suitably carried out at a temperature above 200° F. and preferably in the range of 250° to 350° F. The reaction product is a symmetrically substituted urea and can be described as having two alkylene amine moieties joined by one carbonyl group:

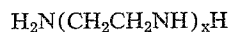


Each of the valences of the carbonyl carbon are attached to one nitrogen of one mole moiety of the alkylene amine.

The foregoing N-B-containing disuccinimides of polyamino ureas are dispersant-detergent additives having suitable oil solubility even for preparing concentrates when obtained from alkenyl substituted succinic acids or anhydrides having in the alkenyl hydrocarbon substituent group at least 30 carbon atoms and desirably from 30 to 200 carbon atoms. The alkenyl hydrocarbon substituent group is preferably that resulting from the reaction of

liquid viscous polybutene of the aforementioned carbon content with maleic anhydride.

The alkylene amine reactant for the preparation of the polyamino urea used to obtain the N-B-containing dispersant-detergent additives is preferably an "ethylene amine" of the class represented by the formula



wherein x is from 1 to 10. These ethylene amines include ethylene diamine, and such polyethylene polyamines are obtained by reacting 3 to 10 moles of ammonia with 2 to 9 moles of 1,2-dichloroethane. Polyethylene polyamines having 3 to 6 nitrogens (x is 3 to 6 in the formula) are preferred of the ethylene amines and these are exemplified by diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentethylene hexamine. Such polyethylene polyamines might also be named amino-polyazethyl amines. Thus the preferred polyamino ureas might also be named 1,3-bis(α -amino-ethyl- β -polyazethyl)ureas to indicate that they have at least one terminal ---NH_2 group on each ethylene amine moiety attached to the carbonyl carbon of the urea.

The N-B-containing dispersant-detergent additives are suitably prepared by reacting about two moles (1.8 to 2.2 moles are desirable and 2.0 moles are preferred) of alkenyl substituted succinic anhydride per mole of polyamino urea and from 0.4 to 1.5 gram atoms of boron compound per gram atoms of nitrogen of the ethylene amine reactant. The preferred N-B-containing dispersant-detergent has a boron content expressed as the ratio of weight percent boron (B) to weight percent nitrogen (N), thus B/N weight ratio, in the range of 0.2 to 0.3. Suitably the B/N ratio can be 0.1 to 0.5.

Generally, the alkenyl substituted succinic acids and anhydrides can be reacted with the polyamino urea reactant in the presence of a reaction diluent. A volatile solvent such as toluene or xylene can be used as the diluent. The volatile solvent is removed at the end of the reaction to aid in the removal of by-product water. Less volatile solvents such as the liquid viscous polyolefins, liquid viscous polypropylenes and polybutenes, and/or low viscosity lubricant base light oil blending stocks such as an SAE-5 solvent extracted mineral oil can be advantageously used as reaction solvents because they need not be removed from the product resulting from the reaction of the substituted succinic acid and/or anhydride and polyamino urea. The reaction of the boron compound with the product resulting from the reaction of the substituted succinic acid and/or anhydride with polyamino urea can be conducted in the presence of the less volatile solvents. It is advantageous when the substituted succinic acid and/or anhydride reaction product with polyamino urea is prepared in a volatile solvent, to carry out the boration step (reaction with the boron compound) and then remove the solvent. But when using the preferred boron compound, boric acid, it is preferred to prepare the N-B-containing dispersant-detergent additives by reacting the substituted succinic acid or anhydride, polyamino urea and boric acid in the two reaction steps in the presence of the less volatile solvents retainable in the final product and remove only by-product water. Thus the N-B-containing dispersant-detergent additives are obtained as solutions thereof in liquid viscous polybutenes and/or light mineral oil blending stocks in a concentration in the range of 25 to 70, preferably 40 to 60, weight percent of the dissolved N-B-containing dispersant-detergent additive.

The following preparation is illustrative of the aforementioned solutions of the N-B-containing dispersant-detergent additives useful according to this invention.

Dispersant-detergent solution

To a 3,000 gallon kettle vented through a stack to the atmosphere there is charged 1,254 gallons (9,600 pounds) of a solution of polybutenyl substituted succinic anhydride

having a molecular weight of about 960. This solution contains 54 weight percent of the substituted succinic anhydride dissolved in a mixture of 860 molecular weight polybutene and solvent extracted SAE 5W oil. Thus, 5.4 moles of the polybutenyl succinic anhydride are charged. Also charged to the kettle are 339 gallons of additional solvent extracted SAE 5W oil. The resulting mixture is heated to 250–260° F. while blanketed with an inert gas such as nitrogen. Thereafter 122 gallons (1,095 pounds or 2.7 pound moles) of a polyamino urea (obtained by reacting in the ratio two moles tetraethylene pentamine with one of urea under conditions splitting out and removing two moles of ammonia per mole of urea) is pumped in over 60 minutes. This di(pentamino)urea, 1,3-bis(tetraethyl tetraamino)urea, has a nitrogen content of about 30.5%, a total base number (MgKOH/gram) of about 815, a SSU viscosity at 210° F. of about 72, a gravity of about 9.0 and a 365° F. flash point. The reaction mixture is heated to 300° F. and held at this temperature for about 2 hours while sparging nitrogen through the reaction mixture to aid in the removal of by-product water, about 97 pounds.

There is combined with the resulting solution of disuccinimide of di(pentamino)urea 600 pounds of boric acid slurried in 150 gallons of solvent extracted SAE 5W oil. The slurry of boric acid in oil is added as rapidly as possible without causing excessive foaming by liberation of water vapor. Thirty minutes is a suitable boric acid slurry addition time. The slurry preparation vessel and charge line are washed with an additional 100 gallons of SAE 5W oil and this 100 gallon wash goes into the reaction vessel. The resulting mixture is held at 300° F. for one hour. Nitrogen is then sparged into and through the reaction mixture for 2 hours at 300° F. to dry the reaction mixture. Thereafter the product (solution of N-B-containing dispersant-detergent) is filtered with a filter aid and cooled to ambient temperature. The product contains about 40 weight percent of the borated disuccinimide of di(pentamino)urea, has a nitrogen content of 2.07 weight percent, a boron content of 0.58 weight percent, a B/N weight ratio of 0.28 to 1.0, a gravity of 7.68 pounds per gallon, a SSU viscosity at 210° F. of 900 and a flash point of 380° F.

In a like manner N-B-containing dispersant-detergents having a B/N ratio of 0.1:1 to 0.5:1 can be prepared by suitable adjustment of the amount of boric acid used. Also the N-B-containing dispersant-detergent can be prepared in like manner from polyamino ureas derived from reaction of diethylene triamine, triethylene tetramine, pentaethylene hexamine and mixtures of polyethylene polyamines (those four polyethylene polyamines plus tetraethylene pentamine) having the nitrogen content in weight percent equal to the weight percent nitrogen in pure tetraethylene pentamine. Such a mixture is commercially available under various trade names and is believed to be the partially distilled product from the reaction of 1,2-dichloroethane and ammonia using an excess of dichloroethane. Moreover, in like manner solutions of N-B-containing dispersant-detergent can be obtained from polybutenyl succinic anhydride of molecular weight in the range of about 495 to about 2,900 in place of the 960 molecular weight polybutenyl substituted succinic anhydride of the illustrated process.

Highly basic calcium or magnesium oil-soluble sulfonates

The calcium and magnesium oil-soluble sulfonates used to prepare the compositions of this invention have a total base number of at least 300. Such an alkalinity is in excess of the normal or just neutralized sulfonic acids. Consequently, the calcium and magnesium sulfonates of such high alkalinity are prepared in a solvent, generally a light mineral oil blending stock such as SAE-5W. Concentrates of such highly alkaline calcium and magnesium sulfonates containing 30 to 40 weight percent of the calcium and magnesium sulfonate "soaps" are usually prepared. The

high alkalinity is provided by adding to a solution of an oil-soluble organic sulfonate such as mahogany acids, sour oils, sulfonic acids derived from the sulfonation of alkylated benzenes and especially alkylated benzenes boiling higher than alkylated benzenes having propylene tetramer or butylene trimer alkyl substituent groups. Preferably the sulfonates are derived from sulfonic acids having 30 to 200 alkyl carbon atoms. The solutions of such organic sulfonic acids are admixed with dispersions of calcium hydroxide containing an excess of calcium hydroxide over that stoichiometric amount to neutralize the sulfonic acids. Through various techniques, for example, by adding carbon dioxide or ammonium carbonate, the excessive quantities of calcium hydroxide are converted to very finely dispersed calcium carbonate. A typical highly alkaline calcium sulfonate is as follows:

Calcium sulfonate soap - 30 weight percent.
Total calcium ----- 11.5%.
Total base number ----- 300 milligrams KOH per gram.
Specific gravity ----- 9.4 pounds per gallon.

The highly alkaline magnesium sulfonates are prepared in a similar manner substituting for calcium hydroxide, of course, magnesium oxide or hydroxide in amounts necessary to provide solutions containing the mixture of magnesium soap and dispersed magnesium carbonate in an amount to provide a total base number of at least 300 milligrams KOH per gram of solution. The use of highly alkaline magnesium sulfonates having a total base number of at least 300 are preferred for use in formulating lubricant oil compositions to be used as crankcase lubricants for spark ignited automobile engines.

Zinc dialkyldithiophosphate additive

As hereinbefore stated, the zinc dialkyldithiophosphate component of the novel combination of lubricant oil additives are those zinc dialkyldithiophosphates obtained from dialkyldithiophosphoric acids having in their alkyl groups a mixture of isopropyl groups and primary alkyl groups of from C₅ to C₁₀ or a mixture of sec. butyl and C₅ to C₁₀ primary alkyl groups. In general, the primary alkyl groups are those obtained from the C₅ to C₁₀ oxo alcohols.

These zinc dialkyldithiophosphates are generally prepared in the presence of lubricant mineral oil blending stock.

Exceptionally useful zinc dialkyldithiophosphates for the purposes of this invention are those having alkyl groups in the ratio of 65 mole percent isopropyl and 35% oxo-decyl, 44 mole percent isobutyl and 56 mole percent primary amyl, 65 mole percent isobutyl, 25 mole percent primary amyl and 10 mole percent oxo-octyl and 60 mole percent isobutyl, 35 mole percent primary amyl and 5 mole percent oxodecyl.

Typical of the foregoing zinc dialkyldithiophosphates are those having the following compositions and specific gravities.

A

Weight percent Zn ----- 6.41
Weight percent P ----- 5.56
Weight percent S ----- 11.12
Pounds per gallon ----- 8.57

B

Weight percent Zn ----- 8.07
Weight percent P ----- 7.00
Weight percent S ----- 14.00
Pounds per gallon ----- 9.01

C

Weight percent Zn ----- 9.22
Weight percent P ----- 7.00
Weight percent S ----- 14.00
Pounds per gallon ----- 16

The foregoing three solutions of zinc dialkyldithiophos-

phate contain about 58 weight percent, 73 weight percent, and 83 weight percent zinc salt.

Preferred embodiments

To illustrate lubricant compositions of this invention the following lubricant oil formulations are given.

EXAMPLE 1

An SAE grade 10W-30 oil is formulated from the following ingredients:

| | Volume percent |
|--|----------------|
| SAE-5W base oil | 43.2 |
| SAE-10 base oil | 40.0 |
| N-B dispersant-detergent | 5.0 |
| High alkalinity magnesium sulfonate | 2.0 |
| Zinc dialkyldithiophosphate (type B) | 0.8 |
| Viscosity index improver (polybutene type) | 7.0 |

The N-B dispersant-detergent used in the foregoing formulation is obtained from the reaction of polybutenyl succinic anhydride (molecular weight of about 860) with polyamino urea from tetraethylene pentamine and with boric acid as reactants. The dispersant-detergent has a B/N ratio of 0.247:1.0.

This formulated lubricating oil composition has the following typical inspections.

| | Typical inspections |
|-------------------------------------|---------------------|
| Gravity, ° API | 29.1 |
| Flash, ° F. | 400 |
| ASTM pour, ° F. | -35 |
| Extrapolated viscosity, 0° F., SUS | 10,000 |
| Viscosity, 100° F., SUS | 320 |
| Viscosity, 210° F., SUS | 63.5 |
| Cold crank at 0° F. | 11,000 |
| Zinc, percent wt. | 0.093 |
| Phosphorus, percent wt. | 0.082 |
| Sulfur, percent wt. | 0.38 |
| Magnesium, percent wt. | 0.18 |
| Nitrogen, percent wt. | 0.093 |
| Boron, percent wt. | 0.023 |
| ASTM D-664 Method total base number | 7.5 |
| Sulfated ash content, percent wt. | 1.0 |

EXAMPLE 2

An SAE grade 5W-20 lubricating oil formulation is prepared from the following ingredients:

| | Volume percent |
|--|----------------|
| SAE-5 base oil | 86.2 |
| N-B containing dispersant-detergent | 5.0 |
| High alkalinity magnesium sulfonate | 2.0 |
| Zinc dialkyldithiophosphate (type B) | 0.8 |
| Viscosity Index Improver (polyacrylate type) | 6.0 |

In the foregoing formulation the same solution of the N-B dispersant-detergent described in Example 1 is used. Typical inspection values for this lubricating oil composition are:

| Typical inspections | |
|---------------------------|-------|
| Gravity, ° API | 29.7 |
| Flash, ° F. | 385 |
| ASTM pour, ° F. | -35 |
| Viscosity, SUS: | |
| Extrapolated, 0° F. | 3800 |
| Cold crank, 0° F.: | |
| 100 | 196 |
| 210 | 55.3 |
| Zinc, percent wt. | 0.093 |
| Phosphorus, percent wt. | 0.082 |
| Nitrogen, percent wt. | 0.093 |
| Boron, percent wt. | 0.023 |
| Magnesium, percent wt. | 0.18 |
| Sulfur, percent wt. | 0.38 |
| D-664 TBN mg. KOH/gm. | 7.5 |
| Sulfated ash, percent wt. | 1.0 |

EXAMPLE 3

An SAE 20W-40 oil is formulated from the following ingredients:

| | Volume percent |
|--|----------------|
| SAE-10 base oil | 15.0 |
| SAE-20 base oil | 73.2 |
| N-B detergent-dispersant Solution (N/B=0.247/1.0) | 5.0 |
| High alkalinity magnesium sulfonate | 2.0 |
| Zinc dialkyldithiophosphate (type B) | 0.8 |
| Viscosity Index Improver (polyacrylate type) | 4.0 |

Typical inspection values for this lubricating oil composition are:

| | Typical inspections |
|---------------------------|---------------------|
| Gravity, ° API | 27.2 |
| Flash, ° F. | 455 |
| ASTM pour, ° F. | -20 |
| Viscosity, SUS: | |
| Extrapolated, 0° F. | 32,000 |
| Cold crank, 0° F.: | |
| 100 | 534 |
| 210 | 75.1 |
| Zinc, percent wt. | 0.093 |
| Phosphorus, percent wt. | 0.082 |
| Nitrogen, percent wt. | 0.093 |
| Boron, percent wt. | 0.023 |
| Magnesium, percent wt. | 0.18 |
| Sulfur, percent wt. | 0.42 |
| D-664 TBN mg. KOH/gm. | 7.5 |
| Sulfated ash, percent wt. | 1.0 |

Such formulations (Examples 1, 2 and 3) used in the Lincoln Sequence V engine test, hereinafter described, give total sludge ratings values of 45 to 48 and total varnish ratings in the range of 38 to 42. When used in the PCV valve test in fleet operated vehicles, PCV valve plugging is not encountered even at 10,000 miles of operation without change.

Rust prevention tests

To evaluate the ability of formulated lubricant oil of Example 1 to inhibit engine rusting, the Oldsmobile MS Sequence II (for low temperature rust and corrosion) and III (for high temperature oxidation) tests, in modified form, were selected. These MS tests were developed by Detroit automobile manufacturers "to define the minimum performance requirements of oils classified for service MS for use with automotive gasoline-powdered engines." Test conditions for the two Oldsmobile sequences are shown below. In each test a standardized fuel is used.

Test conditions are shown below.

MS test conditions

[Engine—1964 V-8 Oldsmobile Engine with Two-barrel Carburetor]

| Test Sequence | II | III |
|--|----------|------------|
| Operating Conditions: | | |
| Speed, r.p.m. | 1,500±20 | 3,400±20 |
| Load, blp. | 25±2 | 85±2 |
| Coolant Out, °F. | 95±2 | 200±2 |
| Coolant In, °F. | 90±2 | 190±2 |
| Oil Sump, °F. | 120±2 | 265±2 |
| Air-Fuel Ratio. | 12.0±0.5 | 16.5±0.5 |
| Intake Air Humidity, grains/lb. of dry air at 80±2° F. | 80±5 | 80±5 |
| Oil Consumption, Qts. | (1) 5 | |
| Blow by rate, c.f.m. at 100° F. and 29.7 inches Mercury. | 0.8±1 | 0.0 to 0.2 |
| Crankcase oil filter tube removed and plugged. | Yes | Yes |
| Test Schedule, Hours. | 20 | 40 |
| Oil Filter. | Yes | Yes |

¹ Maximum.

The results of these tests are as follows:

Oil used in Example 1:

| Varnish deposits ¹ — | |
|---------------------------------|-----|
| Baffle (Bottom) | 9.5 |
| Piston skirts, avg. | 9.7 |
| Rocker arm cover | 9.4 |

Oil used in Example 1:—Continued

Varnish deposits ¹—Continued

| | |
|------------------------|-------------|
| Top engine cover | 9.5 |
| Oil pan | 9.2 |
| Total | 47.3 |
| Average | 9.5 |

Sludge deposits ¹—

| | |
|-------------------------------|-------------|
| Rocker arm covers | 9.5 |
| Top engine cover | 9.6 |
| Oil pan | 9.5 |
| Rocker cover | 9.7 |
| Total (¾ of sum) | 48.0 |
| Average | 9.6 |

Total varnish and sludge

Rust ¹—

| | |
|--------------------------------|-----|
| Valve lifter bodies | 8.9 |
| Valve lifter plungers | 9.3 |
| Valve lifter ball checks | 9.4 |
| Pushrods | 9.1 |
| Relief valve plunger | 9.3 |
| Average | 9.3 |

Lifter plunger sticking

Scuffing cam noses and lifters

Avg. Cu Pb bearing Wt. loss, mg.

Wear, inches:

Avg. combined cam and lifter

Max. combined cam and lifter

Oil consumption, qts.

¹ Evaluations made visually and ratings assigned on a scale of 0 to 10 where 10 is no varnish, sludge or rust, i.e. part examined is clean.

Lincoln Sequence V Test

The Lincoln MS Test Sequence V developed by Ford Motor Company, tests the low temperature discrepancy characteristics of a lubricating oil. Briefly the test consists of using the oil to be tested as a lubricating oil in a V-8 Lincoln engine under prescribed test conditions. Accordingly, five quarts of oil are placed in the crankcase and the engine is started and run in accordance with the four hour cycle:

| | Phase 1 | Phase 2 | Phase 3 |
|--------------------------------------|---------|----------|----------|
| Duration..... | 1 45 | 2 2 | 1 75 |
| Speed, r.p.m..... | 500±25 | 2,500±25 | 2,500±25 |
| Load, Brake Horsepower..... | (1) | 105±2 | 105±2 |
| Temperature, ° F.: | | | |
| Water Out..... | 115±5 | 125±5 | 170±5 |
| Oil Sump..... | 80±5 | 80±5 | 80±5 |
| A/F..... | 9.5±0.5 | 15.5±0.5 | 15.5±0.5 |
| Blow by rate, cubic feet per hour... | (2) | (2) | 160±3 |

¹ Minutes.
² hours.
³ Not specified.
⁴ No load.

The four-hour cycle is repeated four times a day followed by an 8-hour shutdown. A total of 48 cycles, 192 hours total running time, are made and the engine is disassembled and inspected. Oil consumption should not exceed 8 quarts for 192 hours running time. The disassembled engine parts are inspected for deposits of varnish and sludge among other observable results as set out in the table below. Engine components are examined visually and rated on a scale of 1 to 10, 10 being a perfect reading indicating no sludge or varnish. A rating of 50 for total sludge and for total varnish is considered perfect; a rating of 10 for piston varnish is considered perfect; a rating of 60 percent or lower is considered passing for screen clogging; and a rating of 50 percent or lower is considered passing for a ring plugging.

In this test the formulated lubricant oil composition of Example 1 is used and compared with two other lubricant oil formulations. The first comparative lubricant oil formulation has a composition similar to lubricant oil

formulation of Example 1 except that the detergent-dispersant is a boric acid borated product of an 860 molecular weight polybutenyl succinic anhydride reacted with tetraethylene pentamine in a mole ratio of two moles of the substituted anhydride per mole of the polyamine and the borated product has 1.14 percent nitrogen and 0.68 percent boron by weight for a B/N ratio of 0.596 to 1.0. This lubricant oil formulation is called "Oil A." The second comparative lubricant oil formulation is an accepted SAE reference 10W-30 oil and is hereafter referred to as "SAE Reference Oil."

Lincoln test results

| | Pass | Example 1 | Oil A | SAE Reference Oil |
|-----------------------------------|------------------|-----------|-------|-------------------|
| Sludge: | | | | |
| Rocker Arm Assembly..... | | 8.4 | 6.1 | 4.7 |
| Rocker Arm Cover..... | | 7.7 | 5.8 | 4.5 |
| Top Engine Cover..... | | 6.5 | 6.1 | 3.3 |
| Oil Screen..... | | 10.0 | 9.7 | 2.0 |
| Oil Pan..... | | 9.4 | 7.0 | 6.1 |
| Push Rod Chamber..... | | 9.0 | 6.9 | 4.6 |
| Timing Gear Cover..... | | 8.9 | 7.7 | 4.8 |
| Valve Deck..... | | | 6.4 | 3.8 |
| ¾ Total (28.0 minimum)..... | | 42.8 | 34.6 | 21.1 |
| Varnish: | | | | |
| Piston, Avg. (7.0 min.)..... | | 9.0 | 8.0 | 5.5 |
| Rocker Arm Cover..... | | 7.2 | 6.4 | 8.1 |
| Top Engine Cover..... | | 8.6 | 7.6 | 8.2 |
| Oil Pan..... | | 9.4 | 6.6 | 7.6 |
| Cylinder Walls (BRT)..... | | 9.0 | 6.2 | 8.0 |
| Total..... | | 43.2 | 34.8 | 37.4 |
| Ring Sticking..... | (1) | (1) | (1) | (1) |
| Oil Ring Clogging, percent..... | ² 50 | 0 | 14 | 99 |
| Oil Screen Plugging, percent..... | ² 60 | 0 | 3 | 80 |
| Valve Lifter Sticking..... | (1) | (1) | (1) | (1) |
| Valve Lifter Varnish..... | (1) | (1) | (1) | 9.8 |
| Oil Consumption, Qts..... | ² 8.0 | 7.0 | 6.8 | 9.2 |

¹ None.
² Maximum.

Oxidation stability test

Oxidation stability, that is, the resistance of an oil to piston varnish deposit formation and bearing corrosion, is evaluated in the CLR L-38 engine test. This utilizes a single cylinder Labcco oil test engine operated at 3,150 r.p.m. with the oil temperature at 300° F. and the water temperature at 195° F. At the test conclusion, the copper-lead connecting rod bearings are weighed; bearing weight loss (BWL) should be less than 50 milligrams. The piston is visually evaluated according to a scale of 1 to 10; 10 represents a perfectly clean and varnish-free piston. Oil formulation of Example 1 is tested for 40 hours in a CLR L-38 engine. Total varnish or total sludge ratings of 50 indicates a clean engine.

The following results are observed:

L-38 oxidation stability test

| | |
|-------------------------------------|---------|
| | 40 hrs. |
| Total sludge | 50.0 |
| Piston varnish | 9.9 |
| Total varnish | 48.9 |
| Whole bearing weight loss, mg. | 19.6 |

Simulated PCV valve test

A 1963 Falcon 170 cubic inch displacement engine with oil filter, oil cooler, and an ice water cooled condenser in the crankcase vent line between the crankcase and intake manifold is operated with the lubricant oil formulation of this invention described in Example 1. The condenser in the crankcase vent line is operated under conditions which cause substantially all condensable materials to be returned to the crankcase thus providing conditions which are as severe as, if not more severe than, complete PCV valve plugging especially with respect to the severity of corrosive-wear in the valve train. The use of such a condenser under the type of engine operation hereinafter described simulating severe stop-and-go driving is an accelerated PCV valve test since the engine is always operating under conditions which occur at 100% PCV valve plugging rather than condi-

tions starting with a clean, fully operating PCV valve and progressing through 100% PCV valve plugging.

The engine is started and operated for 45 minutes at no load, 500 ± 25 r.p.m., $115 \pm 5^\circ$ F. coolant exit temperature and with oil sump temperature of 125° F. maximum. Then the engine is operated for two hours at a 30 horsepower load (about 50% load) at $2,500 \pm 25$ r.p.m. with $125 \pm 5^\circ$ F. coolant exit temperature and crankcase oil sump at $175 \pm 5^\circ$ F. temperature. These no load and 30 horsepower load operations are repeated alternately five times per day for a total of 13 hours and 45 minutes of run time. Then the engine is stopped for 10 hours and 15 minutes. The entire procedure is run for 4 days (total of 55 hours run time).

After the above-described four-day test the lifter, plungers, lifter barrels and push rods are examined for rust and the valve tips measured for wear. On the basis of a rating scale of 0 to 10 where the value of 10 indicates no rust, i.e., clean parts, the average rust rating of the aforementioned valve train parts was 9.4.

Lubricating oil formulation of Example 1 was tested in a 1964 Ford V-8 engine of 289 cubic inch displacement following a modified Lincoln Sequence V technique. The engine is equipped with a positive crankcase ventilation valve and is operated according to the following three-stage cycle.

| | 1st Stage | 2nd Stage | 3d Stage |
|---------------------------|------------------|-------------------|-------------------|
| Time, minutes..... | 45 | 120 | 75 |
| Speed, r.p.m..... | 500 ± 25 | $2,500 \pm 25$ | $2,500 \pm 25$ |
| Load, BMEP..... | (1) | $^2 95 \pm 2$ | $^2 95 \pm 2$ |
| Water exit, ° F..... | 115 ± 5 | 125 ± 5 | 170 ± 5 |
| Oil Temperature, ° F..... | 125 ± 5 | 175 ± 5 | 205 ± 5 |
| Air-Fuel..... | $^3 9.5 \pm 0.5$ | $^4 15.5 \pm 0.5$ | $^4 15.5 \pm 0.5$ |

¹ No load.

² 182 foot pounds or 86.6 O.B.H.P.

³ Rich.

⁴ Lean.

The positive crankcase ventilation (PCV) valve is checked initially and every 32 hours thereafter but is not cleaned during 192 hours of operation (a total of 48 cycles). Oil consumption should not exceed 7 quarts for the 192 hours. After 192 hours the engine is disassembled and its parts are examined and rated as in the Lincoln Sequence V Test. The main results of this test were as follows:

192 Hour—289 cubic inch Ford engine test

| | |
|--------------------------------|-----|
| Total sludge | 43 |
| Total varnish | 35 |
| Piston varnish | 8.3 |
| Oil rings plugged | 0 |
| Piston rings sticking | 0 |
| Lifters sticking | 0 |
| Oil screen plug, percent | 0 |
| Oil consumed, quarts | 5.4 |
| Blow by, average c.f.h | 128 |
| PCV valve plugging, percent: | |
| Vacuum 4 inches Hg: | |
| 96 hours | 0 |
| 192 hours | 1 |
| Vacuum 16 inches Hg: | |
| 96 hours | 3 |
| 192 hours | 6 |

It will be understood that this invention is not based on the discovery of any one of the disclosed oil-soluble nitrogen-boron-containing dispersant-detergent, the alkaline earth metal salts of hydrocarbon sulfonic acids or the heat stable zinc dialkyldithiophosphates as new compositions of matter or their individual usefulness as addition agents in lubricant oil compositions. Rather this invention is based on the discovery of a lubricant oil composition useful for the severe service function imposed by long drain life which composition comprises a major proportion of a hydrocarbon lubricating oil and an essential combination consisting of the disclosed (a) oil-soluble nitrogen-boron-containing dispersant-detergent, (b) the alkaline earth metal salt of hydrocarbon sulfonic

acid and (c) the zinc dialkyldithiophosphate in the amounts for each 100 gallons of lubricant oil composition. It will also be understood that other individual addition agents having functions other than the functions of the three essential addition agents can be added to the lubricant oil composition of this invention in amounts that do not effect the character and nature of the combination of the three essential addition agents. Such other addition agents include for example anti-foam agents, lubricating agents and viscosity index improvement agents.

Therefore, that claimed as invention is:

1. A lubricant oil composition comprising a major portion of a hydrocarbon lubricating oil and the combination of essential additives consisting of

(a) an oil-soluble nitrogen-boron-containing detergent-dispersant that is the boric acid borated derivative of a di(alkenylsuccinimide) of a symmetrical bis(amino-polyazethyl) substituted urea which disuccinimide is the product of an alkenyl hydrocarbon substituted succinic anhydride whose alkenyl substituent has from 30 to 200 carbon atoms reacted under conditions splitting out and removing water with the symmetrical bis substituted urea in the ratio of two moles of the substituted succinic anhydride per mole of the symmetrical bis substituted urea and the urea reactant is the product of a polyethylene polyamine having the formula



wherein x is a number from 2 to 6 inclusive, condensed with urea in the ratio of about two moles of the polyamine per mole of urea under conditions splitting out and removing two moles of ammonia per mole of urea, and the detergent-dispersant has an amount of boron related to the nitrogen in the ratio of 0.1 to 0.5 boron per 1.0 nitrogen on a weight basis;

(b) an oil-soluble alkaline earth metal salt of a hydrocarbon sulfonic acid whose hydrocarbon group contains an alkyl group of at least 30 carbon atoms and the salt has an alkalinity equivalent to a total base number of at least 300 milligrams KOH per gram; and

(c) a heat stable zinc dialkyldithiophosphate of whose two dialkyl groups one is an isopropyl or primary butyl group and the other is a primary alkyl group of 5 to 10 carbon atoms in size, in the amounts for each 100 gallons of lubricant oil composition of 3 to 20 pounds of the oil-soluble nitrogen-boron detergent-dispersant (a), the amount of alkaline earth metal salt (b) chemically equivalent to 1.05 to 3.2 pounds of calcium and an amount of zinc salt (c) to provide 0.25 to 1.2 pounds zinc.

2. The composition of claim 1 wherein magnesium salt of a hydrocarbon sulfonic acid is alkaline earth metal salt additive (b).

3. The composition of claim 2 wherein additive (a) the alkenyl substituted succinic anhydride reactant has a molecular weight of from 860 to 960 inclusive and the alkenyl substituent group is a polybutenyl group derived from a liquid viscous polybutene and tetraethylene pentamine is the polyethylene polyamine reactant for the symmetrically bis substituted urea reactant.

References Cited

UNITED STATES PATENTS

| | | | |
|-----------|--------|---------------------|-------------|
| 3,000,822 | 9/1961 | Higgins et al. | 252—32.7 |
| 3,076,841 | 2/1963 | Hutchings et al. .. | 252—33 XR |
| 3,087,936 | 4/1963 | Le Suer | 252—49.6 XR |
| 3,340,190 | 9/1967 | Deluga et al. | 252—33.4 |

DANIEL E. WYMAN, *Primary Examiner.*

P. P. GARVIN, *Assistant Examiner.*