United States Patent Office 3,523,082 Patented Aug. 4, 1970

3,523,082

LUBRICATING OIL COMPOSITION

Paul C. Vienna, Calumet City, Ill., and John J. Plemich, Whiting, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

No Drawing. Filed Jan. 26, 1968, Ser. No. 700,735
Int. Cl. C10m 1/40, 1/48, 1/50
U.S. Cl. 252—32.7 3 Claims

ABSTRACT OF THE DISCLOSURE

Lubricating oil compositions having improved water tolerance and rust inhibiting properties are obtained by incorporating in a petroleum lubricating oil a combination of (1) a calcium salt of a preferentially oil-soluble sulfonic acid, (2) a sodium salt of a preferentially oil-soluble sulfonic acid, and (3) butyl Cellosolve.

BACKGROUND OF THE INVENTION

Lubricating oil compositions, particularly adapted for use in internal combustion engines as crankcase oils, commonly have incorporated in a base petroleum lubricating oil well-known additives such as a zinc dialkyldithophosphate, a polymethacrylate viscosity index improver, a pour point depressor, such as a wax alkylated naphthalene and an anti-foam agent, such as a silicone polymer. Such compositions are often used as so-called "drive-away" oils.

One of the problems encountered with the conventional crankcase oil composition is the inability of such compositions to tolerate water which invariably enters the crankcase of internal combustion engines. That is, the lubricating oil composition does not have the property of holding water in suspension, and consequently when the engine is not being operated such water drops out of the oil composition causing rusting and/or corrosion.

SUMMARY

Internal combustion engine crankcase lubricating oils having a high water tolerance and inhibiting anti-rust properties are obtained, in accordance with the present invention, by incorporating in a petroleum lubricating oil from about 4.0% to about 6.0% of a calcium salt of a preferentially oil-soluble petroleum sulfonic acid, 0.5% of a sodium salt of a preferentially oil-soluble petroleum sulfonic acid and 0.5% butyl Cellosolve, the percentages being based on the total composition of the crankcase lubricating oil composition.

A typical crankcase lubricating oil formulation which meets the required performance specifications is set out below, in which the proportions are given in weight percentages:

Substantially neutral calcium salt of preferentially oil-soluble sulfonic acid—4.0–6.0%
Substantially neutral sodium salt of preferentially oil-soluble sulfonic acid—0.5%
Butyl Cellosolve (ethyleneglycol monobutyl ether)—0.5%
Zinc dialkyldithiophosphate—0–1.2%
Polymethacrylate V.I. improper—0.5%
Wax alkylated naphthalene pour point depressor—2.0%
Silicone polymer foam inhibitor—5 p.p.m.
Petroleum lubricating oil—Remainder

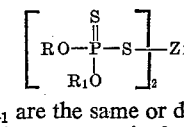
The zinc dialkyldithiophosphate is not a necessary component when the crankcase lubricating oil composition is to be used under relatively mild operating conditions, but is necessary when the crankcase oil is required to pass the L–38 Engine Test, also referred to as "CLR–38 Engine Test." This test is designed to evaluate high

temperature oxidation stability of a lubricating oil composition.

The preferentially oil-soluble calcium and sodium petroleum sulfonates employed are the substantially neutral salts of preferentially oil-soluble sulfonic acids having molecular weights from about 300 to about 500. The sulfonic acids are well known to those skilled in the art; especially usable are the preferentially oil-soluble sulfonic acids and preferably the preferentially oil-soluble petroleum sulfonic acids, referred to in the art as "mahogany acids." The sulfonic acids include such mahogany acids, unsaturated paraffin wax sulfonic acids, petrolatum sulfonic acids, monoparaffin wax-substituted naphthalene sulfonic acids, diparaffin wax-substituted phenol sulfonic acids, wax sulfonic acids, petroleum naphthalene sulfonic acids, fuel oil substituted-benzene sulfonic acids (synthetic alkyl aryl sulfonic acids) diphenyl ether sulfonic acids, diphenyl ether disulfonic acids, naphthalene disulfide sulfonic acids, naphthalene disulfide disulfonic acids, diphenyl amine disulfonic acids, diphenyl amine sulfonic acids, thiophene sulfonic acids, alpha-chloronaphthalene sulfonic acids, cetyl chlorobenzene sulfonic acids, cetyl-sulfonic acids, cetyl-phenol disulfide sulfonic acids, cetyl-phenol monosulfide sulfonic acids, cetoxy capryl-benzene sulfonic acids, dicetyl thianthrene sulfonic acids, dilauryl beta naphthol sulfonic acids, di-capryl nitro-naphthalene sulfonic acids; hydroxy substituted paraffin wax sulfonic acids, tetra-isobutylene sulfonic acids, tetra-amylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitroso paraffin wax sulfonic acids, cetyl-cyclopentyl sulfonic acids, lauryl-cyclo-hexyl sulfonic acids, mono- and poly-wax substituted cyclohexyl sulfonic acids, etc. Other usable preferentially oil-soluble sulfonic acids are well described in the art, for example, see U.S. 2,616,904; U.S. 2,626,207; and U.S. 2,767,209.

It is preferred to use preferentially oil-soluble sulfonic acids having molecular weights of from about 300 to about 500, derived from various petroleum fractions such as turbine oil, mineral lubricating oil, white oil distillates, heavy oil petroleum waxes (e.g., petrolatum paraffin wax and mixtures of various hydrocarbon wax fractions), etc. Such sulfonic acids are well known to the art. They can be obtained for example, by treating the petroleum fraction with concentrated or fuming sulfuric acid or sulfur trioxide; sulfonic acids derived in this manner are commonly called "mahogany acids." The calcium and sodium sulfonates are prepared from such sulfonic acids by conventional neutralization techniques, well known in the art, employing basic compounds such as calcium oxide, calcium hydroxide and sodium hydroxide to neutralize the sulfonic acids.

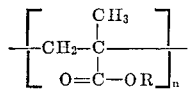
The zinc dialkyldithiophosphates when employed in the composition of the present invention, are well-known salts of the general formula:



in which R and R_1 are the same or different alkyl radicals. Such alkyl radicals may contain from 1 to about 15 carbon atoms; however, when one of the alkyl radicals contains less than 6 carbon atoms, the other alkyl radical should contain at least 6 and preferably at least 8 carbon atoms. The dialkyldithiophosphates are prepared by the reaction of P_2S_5 with alkanols having the desired number of carbon atoms; the alcohols being preferably primary alcohols or a mixture of primary and secondary alcohols. Examples of specific zinc dialkyldithiophosphates suitable for use in the composition herein-described are zinc dioctyl dithiophosphate, zinc isopropyl n-hexyl dithiophosphate, zinc n-butyl decyl dithiophosphate, zinc isopropyl nonyl

dithiophosphate, zinc n-butyl n-decyl dithiophosphate, zinc dilauryl dithiophosphate, zinc isopropyl n-heptyl dithiophosphate, zinc n-butyl isoamyl dithiophosphate and the like.

The polymethacrylate viscosity index improver is one having the general formula:



wherein R is an alkyl group or a mixture of alkyl groups containing from about 4 to about 20 carbon atoms, and n is a number providing a molecular weight of the polymer of about 10,000–30,000. Various polymethacrylates of this type are known which possess pour depressant and viscosity index improving properties. A very satisfactory material of this type is a polymer of the lower C_{4-14} alkyl methacrylate monomers. A commercial polymethacrylate, which is primarily a viscosity index improver, is sold under the trade name "Acryloid 710" wherein R comprises about 50 percent lauryl and 50 percent octyl groups and the molecular weight is about 10,000 to 20,000. Another commercially-available polymethacrylate is "Acryloid 615" wherein the alkyl groups are a mixture of groups derived from oxo-alcohols and the polymer has a molecular weight of about 10,000 to 30,000. Another suitable polymethacrylate is available under the trade name "Acryloid 150," in which the alkyl group is predominantly a mixture of 50% cetyl, 25% lauryl and 25% octyl groups and which has a molecular weight of about 10,000–15,000.

The pour point depressor used is a wax alkylated naphthalene which is well known as a pour point depressor for lubricating oils. These materials are in general prepared by chlorinating paraffin wax and condensing the chlorowax with naphthalene. A preferred product is that prepared by the process described in U.S. Pats. 1,963,917 and 1,963,918. Wax alkylated naphthalene products are marketed under trade names such as "Pourex" and "Paraflow." Other commercial pour point depressors such as those marketed under the trade name "Santapour" can also be used.

The silicone polymer foam inhibitor can be any of the well known liquid silicone polymers commercially available as anti-foam agents, such as dimethyl silicone polymer, diethyl silicone polymer, methyl alkyl silicone polymer, diphenyl silicone polymer, phenyl ethyl silicone polymer, methyl phenyl silicone polymer and other dihydrocarbon silicone polymers such as disclosed in U.S. Pat. No. 2,375,007.

The lubricating oil base is a petroleum oil in the lubricating oil viscosity range, i.e. from about 80 SSU at 100° F. to about 300 SSU at 210° F. and preferably having a viscosity of from about 150 to about 190 SSU at 100° F. The oil is preferably one which has been solvent extracted with solvents well known in the art, such as, for example, phenol, furfural, Chlorex liquid SO_2, nitrobenzene etc. Synthetic lubricating oils well known in the art may also be used.

Additives, in addition to those hereinabove mentioned, may be incorporated in the lubricating oil composition, such as for example E.P. agents, anti-wear agents, etc. Such additives are well known in the art.

PREFERRED EMBODIMENT

The following preferred formulation is illustrative of the present invention.

Component:

Substantially neutral calcium salt of preferentially oil-soluble petroleum sulfonic acid [1]—6.0%
Substantially neutral sodium salt of preferentially oil-soluble petroleum sulfonic acid [2]—0.5%
Butyl Cellosolve—0.5%
Zinc isopropyloctyl dithiophosphate—1.2%
Methacrylate alkyl ester polymer—"Acryloid 615" [3]—0.5%
Wax alkylated naphthalene—"Pourex"—2.0%
Silicone polymer foam inhibitor—5 p.p.m.
Solvent extracted S.A.E base petroleum oil—SSU at 100° F. of 170—89.3%

[1] Molecular weight of sulfonic acid—about 440.
[2] Molecular weight of sulfonic acid—about 480.
[3] Alkyl group derived from oxo-alcohols; molecular weight of polymer about 10,000.

One of the most rigid specifications for crankcase lubricating oils for use as drive-away engine oils is that required by International Harvester Specifications B21HR. The above preferred formulation was subjected to the various tests required by this specification with the following results:

Test	Formulation	B21HR specification
Gravity API	28.6	[1]
Flash, ° F	405	[1]
Pour, ° F	0/25	[2] 0
Viscosity at 100° F. SSU	191	[1]
Viscosity at 210° F. SSU	46.6	[3] 43.5
Viscosity at 0° F. SSU [4]	10,200	[2] 12,000
IHBT-9 [5] Rust Test 50 hrs	Pass	Pass
IHBT-7 Water Tolerance, 1% H_2O [5]	[7] 0.0	[2] 0.5

[1] Not specified in specifications.
[2] Maximum.
[3] Minimum.
[4] Extrapolated
[5] Refers to International Harvester Specifications.
[6] One percent water is shaken into a 100 cc. sample which then is allowed to stand quiescent for 7 days. Not more than 0.5 ml. dropout of water is permitted.
[7] Bright.

The importance of the named components, both in kind and concentration, to obtain the necessary results with respect to water tolerance and rust inhibition is illustrated by the data in the following table:

Component	Sample number 1	2	3	4	5	6
Substantially neutral calcium salt of preferentially oil-soluble petroleum sulfonic acid	6.0	6.0	4.0	4.0	4.0	4.0
Substantially neutral sodium salt of preferentially oil-soluble petroleum sulfonic acid	0.5	0.5	0.5	0.5	----	1.0
Butyl cellosolve	0.5	----	0.5	0.5	0.5	0.5
Zinc isopropyloctyl dithiophosphate	1.2	1.2	1.2	----	----	----
"Acryloid 615"	0.5	0.5	0.5	0.5	0.5	0.5
"Pourex"	2.0	2.0	2.0	2.0	2.0	2.0
Silicone polymer foam inhibitor (p.p.m.)	5	5	5	5	5	5
Extracted SAE 10 base petroleum oil	89.3	89.8	91.3	92.5	93.0	92.0
Test:						
Water tolerance test	Pass	Fail	Fail	Pass	Fail	Pass
Oil appearance	Bright	Cloudy	Bright	Bright	Cloudy	Bright
Dropout, percent	0.0	0.5	Separate	0.0	Separate	0.0
Rust test	Pass	----	Pass	Pass	----	Fail

NOTE.—The above compositions which contain the zinc dialkyldithiophosphate pass the L–38 engine test, while the compositions which do not, i.e. samples 4, 5, and 6, could not pass the L–38 Test.

The above data illustrate the importance of the proper ratio of the named components. Sample No. 1, the preferred formulation, passed each test. Formulations without the sodium sulfonate or butyl Cellosolve, as in Sample Nos. 2 and 5, failed to pass the water tolerance test. The presence of the zinc dialkylidthiophosphate in the formulation requires an increased level of calcium sulfonate as demonstrated by Sample Nos. 1, 3 and 4. Sample No. 1 with 6% of the calcium sulfonate passed all tests, including the L–38 Engine Test; reducing the amount of calcium sulfonate to 4.0% gave a product which failed the Water Tolerance Test but passed the L–38 Engine Test. On the other hand, Sample No. 4 containing 4% calcium sulfonate but no zinc dialkyldithiophosphate passed the Water Tolerance Test, but would fail the L–38 Engine Test. Increasing the amount of sodium sulfonate, as in Sample No. 6, gives a product having satisfactory water tolerance but fails in the rust test; the same is true if the butyl Cellosolve is increased excessively.

Percentages given herein and in the appended claims are weight percentages unless otherwise noted.

We claim:

1. The lubricating oil composition comprising essentially the following composition in which the proportions are given in weight percentage:

Substantially neutral calcium salt of a preferentially oil-soluble sulfonic acid—4.0–6.0%
Substantially neutral sodium salt of a preferentially oil-soluble sulfonic acid—0.5%
Ethylene glycol monobutyl ether—0.5%
Poly (C_4–C_{20} alkyl)methacrylate having a molecular weight of about 10,000 to about 30,000—0.5%
Wax alkylated naphthalene pour point depressor—2.0%
Silicone polymer foam inhibitor—5 p.p.m.
Lubricating oil—Remainder

2. The lubricating oil composition of claim **1** wherein

(a) the preferentially oil-soluble sulfonic acid is a petroleum sulfonic acid having a molecular weight of from about 300 to about 500, (b) the wax alkylated naphthalene is a paraffin wax alkylated naphthalene, and (c) the lubricating oil is a petroleum lubricating oil having a viscosity in the range of from about 80 SSU at 100° F. to about 300 SSU at 210° F.

3. The lubricating oil composition comprising essentially the following composition:

Substantially neutral calcium salt of a preferentially oil-soluble petroleum sulfonic acid—6.0%
Substantially neutral sodium salt of a preferentially oil-soluble petroleum sulfonic acid—0.5%
Ethylene glycol monobutyl ether—0.5%
Zinc isopropyloctyl dithiophosphate—1.2%
Alkyl methacrylate polymer having a molecular weight of about 10,000 to about 30,000—0.5%
Paraffin wax alkylated naphthalene pour point depressor—2.0%
Silicone polymer foam inhibitor—5 p.p.m.
Solvent extracted petroleum lubricating oil having a viscosity of about 170 SSU at 110° F.—89.3%

References Cited

UNITED STATES PATENTS

2,807,590	9/1957	McDonald et al.	252—33
2,943,052	6/1960	Caryle et al.	252—33
3,001,940	9/1961	Watson et al.	252—32.7

DANIEL E. WYMAN, Primary Examiner

I. VAUGHN, Assistant Examiner

U.S. Cl. X.R.

252—33, 33.4, 389