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OXIDATION INHIBITOR-DETERGENT MATERIAL

Guy M. Verley, Harvey, Ill., assignor to Sinclair Refining Company, New York, N.Y., a corporation of Maine

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This invention relates to the improvement of lubricating oil compositions and, more particularly, to the improvement of lubricating oil compositions by the inclusion of a new and effective oxidation inhibitor and detergent. Specifically, this invention relates to the improvement of lubricating oil compositions by affording therein an oil-soluble product obtained by reacting an oil-soluble metal diester dithiophosphate with an oil-soluble basic alkaline earth metal petroleum sulfonate.

In the development of lubricating oils, a great variety of additive agents have heretofore been suggested for use in the base oil for the protection of metallic surfaces which come in contact therewith, particularly internal combustion engines or the like, wherein oxidation of the base oil, corrosion and varnish and sludge formations are encountered. Generally, these deficiencies have been overcome by admixing with the base oil various detergents such as metal sulfonates and various oxidation inhibiting compounds such as the metal salts of the organic substituted dithiophosphoric acids and other inhibiting agents.

Previously, these antioxidants, detergents, etc. have been incorporated in the lubricating oil base by mixing minor amounts of the additives in the oil without heating or while heating only slightly to decrease the viscosity of the base oil and obtain faster distribution of components. This practice was followed since it was believed that excessive heating of the antioxidants would result in the decomposition and consequent weakening of its oxidation inhibiting properties and in the case of metal diester dithiophosphates, the formation of oil-insoluble degradation products.

In accordance with my invention, I have discovered a new additive which effectively inhibits or retards the tendency of mineral lubricating oils to undergo oxidation. The type of agent contemplated by my invention is characterized as a reaction product of an oil-soluble metal diester dithiophosphate and an oil-soluble basic alkaline earth metal petroleum sulfonate. The protection against oxidation is substantially greater than that resulting from the addition of the separate reactants to the base oil providing, however, that the metal of the diester is zinc, cadmium or barium.

The new additive agents and the improved lubricating oils of my invention can be prepared by adding to all or a portion of the mineral oil base of the final composition the oil-soluble metal salt of a diester dithiophosphoric acid and an oil-soluble basic barium petroleum sulfonate in such proportions that the molar equivalent ratios of the metal of the sulfonate to the phosphorus of the dithiophosphate is about 2 to 10:1, preferably about 2 to 5:1, and thereafter heating the mixture to the decomposition temperature of the metal diester dithiophosphate. It is believed that this thermal decomposition of the dithiophosphate produces mercaptans, olefins, hydrogen sulfide and acidic residue, the last-named being neutralized by the basic sulfonate to give the improved oxidation inhibiting reaction product.

I have described the additive as being prepared in-situ that is, by reacting the two constituents, the dithiophosphate and the sulfonate, directly in the mineral oil base. However, it is to be understood that this reaction product can also be prepared separately by reacting the dithiophosphate and the sulfonate under the stated conditions in an inert hydrocarbon solvent to form a reaction product concentrate and thereafter blending the concentrate in the desired proportion with the mineral oil base. Conveniently the solvent is the petroleum hydrocarbon employed to prepare the sulfonate as the sulfonate is available in solution in this hydrocarbon. Frequently, the sulfonate is less than 25% of its solution in the hydrocarbon and usually is in the range of about 10 to 20%. Such concentrates provide sufficient solvent for my reaction. Preferably, the solvent is not more than about 85 weight percent of the reaction mixture. The solvent usually boils above about 400° F. to avoid the use of superatmospheric pressures. No matter by which of the above methods the reaction product is prepared the final lubricating oil composition should contain a sufficient amount of this additive to impart the desired antioxidant and detergency properties to the oil. Generally, the final composition should contain about 2 to 10 percent, and preferably about 3 to 6 percent on a dry soap basis of the reaction product. Although the above product is referred to as a reaction product, I do not intend to be bound by this explanation since, in fact, it is entirely possible that no reaction takes place between the constituents.

I have found that the oxidation inhibiting properties of the reaction product are gradually improved by this heat treatment until a certain stage of decomposition has been attained and thereafter if the thermal decomposition is allowed to proceed further the antioxidant properties will decline. The most advantageous stage of decomposition is attained when between about 0.45 to 1.75, preferably about 1 to 1.2, alcohol groups per atom of phosphorus of the metal diester dithiophosphate have been removed as measured by recovering and analyzing the overhead. The length of time that the blend is to be heated in order to attain the optimum oxidation properties can depend upon the type of organic alcohol radical present in the diester dithiophosphate and the temperature to which the dithiophosphate mixture is heated. I have found that the desired antioxidation characteristics can be obtained by heating a secondary alcohol diester dithiophosphate to about 170° C. for five hours or to about 220° C. for five minutes while a primary alcohol diester dithiophosphate requires a slightly higher temperature to reach the same stage of decomposition, that is, a temperature of about 200° C. for five hours or a temperature of about 250° C. for five minutes. The important point for optimum efficiency, however, is that the conditions of time and temperature be chosen to obtain the splitting off of about 0.45 to 1.75, preferably about 1 to 1.2, alcohol radicals from the dithiophosphate while in the presence of the basic alkaline earth metal petroleum sulfonate. Generally, the temperature can range from about 170° C. up to about 300° C. or more, preferably about 180 to 225° C., with the time of heating being varied to yield the above-noted state of decomposition. Usually the period of heating will be from about five minutes to ten hours.

The oil soluble diester of the dithiophosphoric acids used in preparing the metal diester dithiophosphates of my invention can be of a large variety prepared by any of the conventional methods, for example, by reacting a sulfide of phosphorus, such as phosphorus pentasulfide, with an alcohol. The organic groups in the acid esters can be alkyl radicals containing from about 4 to 20 carbon atoms, preferably about 6 to 12 carbon atoms. Suitable alcohols which may be employed in preparing the acid esters include oxo-alcohols, primary and secondary alcohols such as heptanol, hexanol, 2-ethylhexanol, 4-methylpentanol-1, octadecanol-1, mixtures of alcohols such as those of high and low molecular weights, etc. which can be substituted as with chlorine or which contain an ether oxygen atom.

The salts of the above diester dithiophosphoric acids may also be prepared by any of the conventional methods such as by reacting a metal oxide or hydroxide with the above described thiophosphoric acid-esters to yield the desired organic substituted thiophosphate. In forming the salts of the above sulfur-containing, organic substituted, phosphoric acid-esters, I have found that the desired benefits will most advantageously be obtained if the metal is selected from the group consisting of zinc, cadmium and barium.

The sulfonates employed in my invention are the basic alkaline earth metal salts obtained from the oil-soluble sulfonic acids produced in the treatment of petroleum hydrocarbons, usually boiling primarily in the range from about 600 to 1000° F., with a sulfonating agent such as sulfuric acid, oleum or sulfur trioxide. It is preferred that these sulfonic acids have a molecular weight of about 400 to 600. The sulfonic acids show a titratable acidity and can be converted into the basic metal salts by neutralization with an excess of a basic inorganic metal compound to obtain a basic sulfonate of higher metal content than the normal salt. Generally, at least, about 1.5, and preferably at least about 2.0, equivalents of the metal compound are reacted; however, in the case of the calcium sulfonate as little as about 1.1 equivalents may be employed. Usually little is gained by using more than about 4 equivalents of the inorganic compound. When desired, the high base strength of the basic sulfonates can be decreased by further reacting with CO_2 without decreasing the neutralizing power for strong acids. The inorganic metal compounds to be used in neutralizing the sulfonic acids may be any of the alkaline earth metal oxides, hydroxides or carbonates such as calcium, strontium or barium. More specifically, a suitable basic barium sulfonate can be prepared by sulfonating a sweet West Texas gas-oil of 150 SUS at 100° F. viscosity and an average molecular weight of 450 with three 50 pounds per barrel oleum dumps. The oil solution is decanted from the insoluble slude and the clear oil solution of sulfonic acids is neutralized by adding about 2.5 equivalents of barium oxide dissolved in twice its weight of water. The water is topped off and the product filtered clear to obtain a basic barium sulfonate concentrate in gas-oil containing 3.6% of barium.

The base mineral oil used in the preparation of the lubricating composition will ordinarily be a mineral oil of lubricating viscosity, its characteristics depending upon the purpose for which the composition is intended and its service application. It is preferred, however, that the mineral oil have a viscosity of from about 50 SUS at 100° F. to 500 SUS at 100° F.

In order to illustrate the characteristics of the lubricating oil prepared in accordance with my invention, the following blends were compounded. Basic barium sulfonate prepared substantially as described above was blended with a mixture of dithiophasphates which consisted of about 70% zinc di-(4-methylpentyl) dithiophosphate and about 30% zinc diheptyl dithiophosphate (hereinafter referred to as heptanol special) diluted with about 50 percent of Mid-Continent neutral oil of about 200 SUS at 100° F., in amounts to give a molar equivalent ratio of barium of the sulfonate to the phosphorus of the dithiophosphates of 5 to 1. This mixture was divided into three samples. Sample (1) was blended with a Mid-Continent solvent treated neutral mineral oil having a viscosity of 160 SUS at 100° F. and a viscosity index of 98 in an amount to give a .9% barium and a .095% phosphorus content to the finished blend. This blend was not subjected to the heat treatment in accordance with my invention and was used as a reference blend. Sample (2) is the reference blend, subjected to the heat treatments as recorded in the following tables. Sample (3) is the mixture of concentrated additives in the proportions used to make the reference blend, subjected to preheat treatment as recorded in the following tables and subsequently blended with the same mineral oil and in the same proportions as that of the reference blend.

Table I shows the physical characteristics of the blends under the conditions stated.

Table I

Physical Properties	K. Vis/ 100 Cs.	K. Vis/ 210 Cs.	V.I.	OD Color	Pentane Insol., Percent
Sample 1	40.78	6.038	102	94	0.022
Sample 2 after heating 1 hr. at 200° C.	41.84	6.284	107	96	0.000
Sample 3 after heating at 200° C. for:					
0.25 hr.	45.91	6.831	113	97	0.016
1.00 hr.	42.74	6.417	109	90	0.016
3.00 hrs.	42.15	6.330	108	103	0.000

An inspection of Table I will reveal that the physical characteristics of the finished oil blend are not substantially changed due to the treatment in accordance with my invention.

In determining the extent of decomposition of the dithiophosphate the sulfur loss is evaluated by measuring the olefin and mercaptan recovery. The following table shows that the sulfur loss is small until about one alcohol group per phosphorus atom has been removed from the dithiophosphate. This requires prolonged heating at 200° C. for a secondary alcohol and prolonged heating at 250° C. for a primary alcohol dithiophosphate. The blends subjected to this treatment were prepared substantially as described for the reference blend of Table I.

Table II

Type of Dithiophosphate in Oil Blend	Heating Conditions		RO Loss per P Atom	Atoms of S lost per P Atom
	0° C.	Hrs.		
Zinc heptanol special	200	0.25	0.5	0.01
Do	200	1	1.4	0.08
Do	200	3	1.7	0.12
Zinc 2-ethyl hexyl dithiophosphate	200	0.5	0.2	0.00
Do	200	2	0.3	0.00
Do	200	5	0.5	0.00
Do	220	0.5	0.4	0.03
Do	220	2	0.7	0.06
Do	220	5	1.2	0.08
Do	250	0.1	1.0	0.03
Do	250	1.75	1.5	0.45
Do	250	5	1.7	0.83

As can be seen from this table when the dithiophosphate is decomposed within the preferred limits the amount of mercaptan formation will be small.

The extent of neutralization of the basic barium sulfonate by the thermal decomposition products of the dithiophosphate was measured by potentiometric titration of the residues. Table III shows the corresponding base number loss of these residues.

Table III

Type of Zinc Dithiophosphate Present in Oil Blends	Heating Conditions		pH of Blend	Base No. at pH 4	Loss of Base No. at pH 4	Moles of Acid Neutralized per P Atom
	Time by—	Temp., ° C.				
Heptanol special di thiophosphate		50	10.7	3.52	0.00	0.00
	0.25	200	8.2	2.20	1.32	0.77
	1	200	7.1	0.94	2.58	1.51
	3	200	6.4	0.52	3.00	1.76
2-ethylhexyl dithiophosphate		50	10.6	3.25	0.00	0.00
	0.5	200	10.4	2.9	.35	0.21
	2	200	9.8	2.68	.57	0.33
	5	200	9.2	2.41	.84	0.49
	0.5	220	9.7	2.76	.49	0.29
	2	220	8.7	2.03	1.22	0.71
	5	220	8.1	1.14	2.11	1.84
	0.1	250	8.3	1.57	1.68	0.98
	1.75	250	7.1	0.62	2.63	1.54
	5	250	7.0	0.54	2.71	1.59

The oxidation characteristics of the heated lubricating oil blends were compared with the oxidation characteristics of fresh or non-heated blends of the same lubricating oils by the following test.

[1] (Railroad oil oxidation test) A low temperature, long duration test consisting of passing 5 liters of oxygen per hour into 300 ml. of blend at 285° F. for 144 hours with 50 ml. makeup at 48 and 96 hours in the presence of 1" x 3" steel back copper-lead catalyst.

[2] (Oxygen absorption test) A high temperature, short duration test consisting of recirculating 3200 ml. of purified oxygen in a closed system through 75 g. of blend at 360° F. in the presence of the copper-lead catalyst until 2200 ml. of oxygen has been absorbed per 100 g. of blend or until 5 hours of exposure has been reached, whichever occurs first.

Table IV shows the results of the oxidation test using a zinc heptanol special dithiophosphate as the source of phosphorus and a basic barium sulfonate as the source of barium. The blends for this test were prepared in the same manner and in the same proportions and are correspondingly designated as those compounded for the physical characteristics test of Table I.

Table IV

Time of heating, hrs. at 200° C	0	1	0.25	1	3
Sample	1	2	3	3	3
Railroad oil oxidation test:					
Acid number at 144 hours	5.82	2.50	3.78	3.12	2.99
C_5 insolubles at 144 hrs.	3.056	0.018	0.027	0.025	0.023
Catalyst loss, mgs. at 144 Hrs.	−474.8	+0.8	0.0	+3.0	+6.9
Oxygen absorption test:					
Time, minutes	204	300	300	300	300
Average rate, ml. O_2/min./ 100 g. blend	10.7	5.1	5.4	1.84	2.1
Acid number 5 hrs. at 360° F	7.4	3.28	3.67	3.05	2.82
C_5 insol. 5 hrs. at 360° F	1.15	0.008	0.010	0.010	0.007
Catalyst loss 5 hrs. at 360° F	0.00	+0.6	+0.2	+0.8	+0.9
Flask	(1)	(2)	(2)	(2)	(2)

[1] Hv. tarnish.
[2] Clean.
The condition of the flask is considered to reflect the detergent characteristics of the oxidized blend.

Table V shows the results of the oxidation test using a zinc di-(2-ethylhexyl) dithiophosphate rather than a zinc heptanol special dithiophosphate as the source of phosphorus and a basic barium sulfonate as the source of barium. In all other respects, the blends were the same as those utilized in the previous test.

Table V

Preheat Temperature		200° C.			220° C.			250° C.		
Preheat Time, hrs.	0	0.5	2.0	5.0	0.5	2.0	5.0	0.1	1.75	5.0
Sample Number	1	2	2	2	2	2	2	2	2	2
Railroad oil oxidation test:										
Acid number at 144 hrs.	13.88	11.86	8.76	1.56	10.11	1.48	1.35	1.35	1.56	1.79
C_5 insolubles 144 hrs.	12.7	5.36	5.12	.01	6.2	0.49	0.04	0.03	0.03	0.008
Catalyst loss, mg. 144 hrs.	−927	−632	−515	−4	−466	+0.1	+18.6	+1.4	+3.9	+1.2
Silver corrosion EMD 325° F	−35	−30	−34.7	−26	−21.2	−30.7	−24.1	−37.8	−69.7	−39.3
Oxygen absorption test:										
Time, minutes	75	135	152	220	144	240	300	238	300	270
Average ml. O_2/min./100 g. blend	29.2	16.3	14.6	10.0	15.2	9.1	6.0	8.8	3.1	8.1
Acid number (5 hrs.)	12.2	12.0	10.3	6.8	12.6	6.5	3.50	6.20	3.48	4.95
C_5 insolubles (5 hrs.)	2.70	2.61	2.34	1.38	2.45	2.0	0.009	2.94	0.01	0.095
Catalyst loss (5 hrs.)	−19	−17.0	−16.3	−11	−5	−4.6	−0.6	−4.0	+.5	−5.2
Alcohol groups removed per P atom during preheat	0	0.21	0.33	0.49	0.4	.071	1.24	0.98	1.54	1.69

The tests referred to in Tables IV and V show a major improvement of the oxidation resistance of the heated blends, lower acid number, absence of insolubles and a lack of corrosiveness toward the copper-lead catalyst in comparison with the non-heated or reference blend. The condition of the flask in Table IV reflects the detergent characteristics of the oil blends. As can be seen the treatment in accordance with my invention had a substantial improvement on the cleanness of the flask. Inspection of Table V will further reveal that the temperature and time factors are not independent variables for obtaining the maximum oxidation resistance since the table shows that a short time at high temperature or a longer time at lower temperatures will give the same approximate results for the same dithiophosphate. This would indicate that the heat and time elements are not independent controlling factors in providing the improved oxidation resistance of the additive but rather that it is the extent of thermal decomposition of the dithiophosphate and possibly with its subsequent reaction with the basic sulfonate which produces the improved oxidation qualities. The time and temperature conditions may be adjusted to the thermal stability of the particular dithiophosphate utilized.

A 10 W–30 motor oil was blended and subjected to the same series of oxidation tests. The blend consisted of the following components: a major proportion of a Mid-Continent neutral solvent-treated mineral oil having a viscosity of 160 SUS at 100° F. and a viscosity index of 95, basic barium petroleum sulfonate to give a barium content to .95%, zinc heptanol special dithiophosphate to give a phosphorus content to .06%, nickel di-(2-ethylhexyl) dithiophosphate anti-wear agent to give a nickel content of .05%, 5.3% of polymethacrylate viscosity index improver and 0.0005% of a Dow-Corning polymethyl silicone antifoam agent.

Table VI shows the improved oxidation resistance characteristics of this blend heated in accordance with my invention in comparison to a similar non-heated blend. Little if any effect was noticed in the physical characteristics of the heated blend.

Table VI

	Railroad Oxidation				Oxygen Absorption				
	Acid Number	Vis./100 Increase, Percent	Catalyst Losses, mg.	Pentane Insol., Percent	Time	Avg. Rate, cc./min.	Catalyst Loss, mg.	Acid Number	Pentane Insol., Percent
No. 1: Not heated	7.38	22	17	4.381	278	7.90	0.8	5.9	5.05
No. 2: Heated 1 hr. at 200° C.	4.0	6	0	0.007	300	4.91	1.6	4.9	2.60

In order to illustrate more fully the advantage to be gained in the present invention by selecting the metal of the dithiophosphate from the group consisting of barium, zinc and cadmium several metal di-(2-ethylhexyl) dithiophosphates were prepared and blended with a lubricating base oil of the same type and in the same manner as described in conjunction with Table I. The metals selected for this series of tests were magnesium, calcium, iron, lead, copper, nickel, lithium, potassium and the three preferred metals barium, zinc and cadmium. These blends, prepared with the eleven different metals were subjected to the railroad oxidation and oxygen absorption tests both before heating and after heating at 250° C. The results of these tests are compared in Table VII below. Runs noted "A" are the non-heated reference blend and the runs noted "B" are the blends heated in accordance with the above conditions.

Table VII

Metal	Lithium		Potassium		Copper		Nickel	
Heat Treatment	A	B	A	B	A	B	A	B
Railroad Oxidation:								
Acid No. D974	15.85	18.38	14.28	15.60	5.28	13.50	5.93	3.80
Pentane insolubles, percent	4.69	8.65	9.42	8.23	7.86	3.70	0.25	0.025
Catalyst change, mg	−458.7	−482.5	−571	−382.5	−65	−13	−23	−39.2
Silver loss, mg. (EMD test at 325° F.)	31.1	17.2	30.4	24.1	4	8.5	12.0	10.6
Oxygen absorption:								
Time of absorption, mins	92	131	65	94	142	72	151	135
Avg. absorption rate per minute	23.8	16.8	33.8	23.4	15.5	30.2	14.5	16.2
(2) Acid D974 (5 hrs.)	14.3	11.0	16.5	14.7	11.1	18.1	10.8	12.4
(2) Pentane insolubles (5 hrs.)	0.09	.051	0.34	0.000	0.386	.075	0.754	0.070
(2) Catalyst change (5 hrs.)	−17.2	−9.4	−20.8	+5.1	−6.8	−1.3	−21.0	−43.5

Metal	Iron		Lead		Barium		Zinc	
Heat Treatment	A	B	A	B	A	B	A	B
Railroad oxidation:								
Acid No. D974	15.07	9.11	5.06	2.43	13.02	3.28	7.43	1.53
Pentane insolubles, percent	11.0	8.46	3.71	0.02	7.59	0.01	4.92	0.011
Catalyst change, mg	−467	−32	−73	−10.8	−279	−5.2	−688	+1.1
Silver loss, mg. (EMD test at 325° F.)	179.8	36.7	21.5	21.5	54	44.3	15.0	15.7
Oxygen absorption:								
Time of absorption, mins	80	75	175	192	94	213	127	264
Avg. absorption rate per minute	27.4	28.2	12.6	11.5	23.4	10.3	17.2	8.4
(2) Acid D974 (5 hrs.)	19.1	18.2	10.0	7.1	17.2	8.1	13.7	2.85
(2) Pentane insolubles (5 hrs.)	3.70	0.000	3.04	0.007	0.268	2.56	0.088	0.000
(2) Catalyst change (5 hrs.)	−3.7	−3.6	−29.4	−23	−31.5	−0.1	−32.6	−1.1

Metal	Cadmium		Magnesium		Calcium	
Heat Treatment	A	B	A	B	A	B
Railroad oxidation:						
Acid No. D974	7.94	1.34	17.13	22.85	16.23	6.5
Pentane insolubles, percent	4.39	0.02	6.04	14.03	8.681	5.51
Catalyst change, mg	−157.3	+1.2	−286	−981	−448	−207.3
Silver loss mg. (EMD test at 325° F.)	26.2	30.1	7.1	7.5	37.6	26.8
Oxygen Absorption:						
Time of absorption, mins	111	300	81	117	115	112
Avg. absorption rate per minute	19.8	4.7	27.1	19.8	19.0	18.0
(2) Acid D974 (5 hrs.)	16.8	4.29	14.0	8.6	13.2	11.6
(2) Pentane insolubles (5 hrs.)	5.6	0.018	.110	.059	0.065	0.03
(2) Catalyst change (5 hrs.)	−21.4	−9.6	−19.8	−5.8	−3.1	−3.2

As evidenced from an examination of this table much is to be gained by the proper selection of the metal for the dithiophosphate. For example, all of the blends using the preferred metals, e.g. barium, zinc and cadmium show a sharp reduction in acid number, substantially less oxygen absorption over the time period, a marked decrease in pentane insolubles, and a substantial reduction in catalyst change over those blends prepared with the other metals.

It is claimed:

1. An oil soluble material obtained by heating in a hydrocarbon solvent a basic alkaline earth metal petroleum sulfonate with a metal diester dithiophosphate, the organic groups in said diester being alkyl and containing from 4 to 20 carbon atoms in the molecule, said metal of said diester dithiophosphate being selected from the group consisting of zinc, cadmium and barium, said sulfonate and dithiophosphate being present in an amount to give a molar equivalent ratio of the metal from the said sulfonate to the phosphorus from the side dithiophosphate of about 2 to 10:1, said heating being carried out at a temperature of at least the decomposition temperature of the dithiophosphate and for a period of time sufficient to split off 0.45 to 1.75 alcohol groups per atom of phosphorus.

2. An oil soluble material prepared in accordance with claim 1 wherein the heating of the said material is carried out at a temperature of at least the decomposition temperature of the dithiophosphate and for a period of time sufficient to split off 1.0 to 1.2 alcohol groups per atom of phosphorus.

3. An oil soluble material prepared in accordance with claim 1 wherein the said heating is carried out at a temperature of about 180 to 225° C.

4. A lubricating oil composition consisting essentially of a major portion of a mineral oil base of lubricating viscosity and having added thereto a minor portion of the material of claim 1 effective to inhibit oxidation.

5. An oil soluble material prepared in accordance with claim 2 wherein the said heating is carried out at a temperature of about 180 to 225° C.

6. A lubricating oil composition consisting essentially of a major portion of a mineral oil base of lubricating viscosity and having added thereto a minor portion of the material of claim 2 effective to inhibit oxidation.

7. A lubricating oil composition consisting essentially

of a major portion of a mineral oil base of lubricating viscosity and having added thereto a minor portion of the material of claim 3 effective to inhibit oxidation.

8. A lubricating oil composition consisting essentially of a major portion of a mineral oil base of lubricating viscosity and having added thereto a minor portion of the material of claim 4 effective to inhibit oxidation.

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CERTIFICATE OF CORRECTION

Patent No. 2,916,448 December 8, 1959

Guy M. Verley

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 39, for "slude" read -- sludge --; line 56, for "dithiophasphates" read -- dithiophosphates --; columns 5 and 6, Table V, seventh column thereof, last item, for ".071" read -- 0.71 --; column 9, line 7, for the claim reference numeral "4" read -- 5 --.

Signed and sealed this 9th day of August 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents