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LUBRICATING OIL

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12 Claims. (Cl. 252—53)

This invention relates to a lubricating oil, and particularly to a motor oil adapted for lubrication of the bearings and cylinders of internal combustion engines, such as automotive engines, airplane engines, Diesel engines, and the like.

The modern development of internal combustion engines with extremely small clearance between piston and cylinder wall, together with the modern development of highly solvent-refined lubricating oils for use in the crank cases of such engines, has given rise to the problem of so-called varnish or lacquer formation. This varnish generally appears as a yellowish or reddish brown film which deposits upon the metal surfaces, including the piston rings and skirt, and cylinder wall during operation of the engine over extended periods of time. In the newest engines having extremely small clearances and high compression, the building up of this varnish film increases the frictional resistance to the reciprocation of the pistons, thereby raising fuel consumption and reducing power output; and this deposit may become so severe as to frequently result in seizure of the pistons when the motor is stopped and allowed to cool.

Further, the modern development of the highly refined motor oils together with the modern development of the new type bearings, including the connecting rod and main bearings of internal combustion engines, which has involved a departure from the old Babbitt bearings and has given rise to the new alloy bearings of the type of cadmium-silver, copper-lead, cadmium-nickel, and the like, has also presented the industry with the problem of bearing corrosion.

The majority of straight uncompounded refined lubricating oils on the market today are found to result in substantial varnish deposition and bearing corrosion when used as crankcase lubricants in these new type engines.

It is an object of the present invention to provide a lubricating oil which is effective to inhibit this varnish formation and bearing corrosion.

It is a further object of this invention to provide such a lubricating oil containing an additive which is of such character as not objectionably to effect, or even to improve, other desirable properties and tests of the motor oil, particularly stability in storage and service, resistance to oxidation and sludge formation, demulsibility, reduction in oil ring and compression groove deposits with prevention of ring sticking and reduction in piston and cylinder wear.

We have discovered that a mineral lubricating oil of the motor oil type, such as a modern highly solvent-refined lubricating oil, can be converted to one having exceptional ability to accomplish the objects set forth above by the addition thereto of a small proportion of an oil-soluble phosphite ester of an alkyl ether of an alkylene glycol having the general formula:



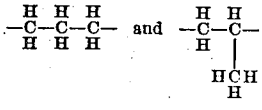
where X_1 is an alkyl-alkylene oxide radical of the type:

$$R_3(OR_4)_{n1}(OR_5)_{n2}$$

where R_3 is an alkyl radical having less than nine carbon atoms and including the alkyls from methyl to octyl, R_4 and R_5 are the same or different alkylene radicals (C_nH_{2n}) selected from the group consisting of ethylene and the propylenes, n_1 is 0 or 1, and n_2 is 1 or 2; and where X_2 and X_3 represent either hydrogen or the same or different alkyl-alkylene oxide radicals of the type of X_1 above. By the expression "alkylene radical" as used herein, it is to be understood that this includes the ethylene radical



and the two propylene radicals



in which the other two bonds are saturated by being attached to other atoms or radicals, and does not include the unsaturated olefins.

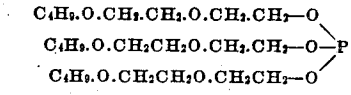
From the above, it will be understood that the phosphite esters of methyl to octyl ethers of glycols selected from the group consisting of mono- and poly-ethylene and propylene glycols are included. The two isomeric propylene glycols, including propylene glycol, $CH_3CHOHCH_2OH$, and the 1:3 glycol, tri-methylene glycol,

$$HOCH_2CH_2CH_2OH$$

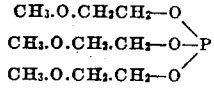
are included, as well as the corresponding polypropylene glycols. These polyglycols are formed by the condensation of one or more molecules of ethylene oxide or propylene oxide with ethylene or propylene glycol respectively. In general, we prefer those compounds which are phosphite esters of the mentioned alkyl ethers of glycols,

or polyglycols which contain not more than two added ethylene oxide or propylene oxide groups to an ethylene glycol or propylene glycol group respectively. The higher members of this series having more than three condensed groups generally have such high boiling points and are so difficult of separation as to render them of lesser value for purposes of the present invention.

The mono-alkyl ethers of mono-ethylene glycol have become familiarly known as "Cellosolves," whereas the mono-alkyl ethers of diethylene glycol have become familiarly known as "Carbitols." Thus, the phosphite esters of the methyl to octyl "Cellosolves" and "Carbitols" are included in this invention. The phosphite esters may be the tri-substituted normal esters, the di-substituted mono-hydrogen esters, or the mono-substituted di-hydrogen esters. As examples of compounds of this group which have been found highly effective for purposes of this invention, there are mentioned butyl "Carbitol" phosphite, which is the tri-substituted normal phosphite ester of the mono-butyl ether of diethylene glycol having the following formula:



and methyl "Cellosolve" phosphite which is the tri-substituted normal phosphite ester of the mono-methyl ether of ethylene glycol having the following formula:



These phosphite esters of alkyl ethers of alkylene glycols and their method of preparation are disclosed and claimed in the copending application, Serial No. 264,119, of Robert E. Conary and Harry V. Ashburn, filed March 25, 1939. For purposes of illustration, this invention is described in connection with the use as an additive of butyl "Carbitol" phosphite and methyl "Cellosolve" phosphite, although it is to be understood that the invention is not limited thereto. The butyl "Carbitol" phosphite was prepared by the addition of one mol of phosphorus trichloride to three mols of dry mono-butyl ether of di-ethylene glycol, in the presence of an excess equivalent to about 3.3 mols of dry pyridine and approximately an equal weight of dry benzene. The phosphorus trichloride was added dropwise to the mix of the butyl ether of di-ethylene glycol, pyridine and benzene, with adequate stirring while the temperature was held at about 23–50° F. After complete addition of the phosphorus trichloride, the mixture was allowed to warm up to room temperature, then heated to boiling and refluxed for about two hours. After cooling to room temperature, the mixture was washed with cold water until the wash water gave no acid test to litmus. The mixture was then dried over anhydrous sodium or calcium sulfate, the remaining pyridine, benzene and unreacted "Carbitol" removed by distillation under vacuum, and the desired product was obtained by vacuum distillation, passing over at approximately 455–465° F. under an absolute pressure of about 15–20 mm. mercury.

The methyl "Cellosolve" phosphite was obtained by a similar procedure, substituting the mono-methyl ether of ethylene glycol for the mono-butyl ether of di-ethylene glycol in the procedure outlined above, except that in this case the washing step with water and the drying step were omitted, and the mixture after refluxing and cooling was filtered to remove the precipitated pyridine hydrochloride. The methyl "Cellosolve" phosphite was obtained by vacuum distillation of the filtrate, passing over at approximately 290–305° F. under an absolute pressure of about 10–20 mm. mercury. Both phosphite materials are oily colorless liquids soluble in lubricating oil.

The additive is added to the mineral lubricating oil in a proportion of about 0.01–2.0% by weight, and preferably of the order of 0.1–0.5% by weight. The material dissolves readily in the lubricating oil at room temperature with agitation, but its solution may be facilitated by heating the oil mildly. It apparently forms a stable solution which is not subject to separation, precipitation or sedimentation in storage or under service conditions, and is not volatilized or lost in service conditions normally encountered in crankcase lubrication.

A rigorous test which is used to determine the effectiveness of additives to stabilize lubricating oils of this type against oxidation and inhibit varnish formation and bearing corrosion is the so-called Underwood Oxidation Test, which is described in a pamphlet dated August 1, 1938, of the Research Laboratories Division of the General Motors Corporation, entitled "Underwood Oxidation Testing Apparatus." This test briefly consists in abrading the inside or concave surface of half of a standard cadmium-silver automotive bearing by a motor-driven wheel covered with abrasive cloth until an evenly scratched surface is obtained. A copper strip 10 inches long by 2 inches wide is also abraded by sanding until an evenly scratched surface is obtained. The strip and bearing are cleaned by washing in solvent (a mixture of equal parts of denatured ethyl alcohol, toluol, and ethyl acetate), dried and weighed. The copper strip and bearing are then immersed in the oil to be tested in a box or trough equipped with pump recirculation for continuously circulating the oil over the bearing and strip, the apparatus having previously been carefully cleaned. The recirculating oil is heated to a temperature of about 325° F. and maintained at this temperature during the period of test of fifteen hours. This test as described is preferably modified by adding a small proportion of the order of 0.01% of iron oxide as iron naphthenate to the oil undergoing the test in order to catalyze the oxidation and bearing corrosion, and to more closely simulate the conditions encountered in crankcase lubrication where the oil is in contact with iron.

A sample of the oil undergoing test is withdrawn at 5-hour intervals, and likewise the bearing and copper strip are removed at 5-hour intervals, carefully cleaned, and weighed and again re-immersed in the oil bath. At the conclusion of the 15-hour run, the copper strip is removed, soaked for about ten minutes in precipitation naphtha to remove adhering oil, dried and weighed. The increase in weight is recorded as weight of varnish accumulation. The test bearing is likewise removed, carefully cleaned with solvent which is effective to remove both oil and the varnish film, dried and weighed, and the loss in weight is recorded as bearing corrosion in grams. The samples of oil from the two intermediate 5-hour periods and from the end of the run are tested for Saybolt Universal viscosity at

130° F., neutralization number, Conradson carbon residue, material insoluble in A. S. T. M. precipitation naphtha (expressed in mg. per ten grams of oil), and chloroform-soluble portion of the naphtha-insoluble residue (expressed in mg. per ten grams of oil). The above test was run first with the blank oil, then with the same blank oil containing the desired proportion of the additive.

The following are the results of a catalyzed Underwood Oxidation Test on a furfural-refined dewaxed Mid-Continent distillate lubricating oil of S. A. E. 10 grade, and the same oil containing 0.25% of the butyl "Carbitol" phosphite prepared as set forth above:

Test	Blank oil	Blank oil+0.25% butyl "Carbitol" phosphite
Percent iron oxide added as iron naphthenate	0.01	0.01
Neutralization number, 15 hours	19.9	3.6
Bearing corrosion, grams, 15 hours	2.172	0.031
S. U. viscosity @ 130° F., initial	94.5	94.5
S. U. viscosity @ 130° F., 15 hours	575	123.5
Percent increase in viscosity	508	30.7
Varnish deposit, mg	59	20

The above tests indicate very pronounced superiority of the compounded oil over the blank oil with respect to bearing corrosion as shown by the bearing corrosion test, with respect to oxidation stability as shown by the neutralization number and viscosity tests, and with respect to inhibiting varnish deposit as shown by the varnish deposit test.

The following are the results of a catalyzed Underwood Oxidation Test on a furfural-refined dewaxed Mid-Continent distillate oil of S. A. E. 10 grade, and the same oil containing 0.25% of methyl "Cellosolve" phosphite prepared as set forth above:

Test	Blank oil	Blank oil+0.25% methyl "Cellosolve" phosphite
Percent oxide added as iron naphthenate	0.01	0.01
Neutralization number, 15 hours	45.0	3.36
Bearing corrosion, grams, 15 hours	1.488	0.000
Percent naphtha insoluble, 15 hours	13.03	0.49
Percent chloroform soluble, 15 hours	12.05	0.44
Percent Conradson carbon, 15 hours	5.44	0.70
S. U. viscosity @ 130° F., initial	94.5	94.5
S. U. viscosity @ 130° F., 15 hours	1700	126.5
Percent increase in viscosity	1800	33.8
Varnish deposit, mg	42	15

The above tests indicate very pronounced superiority of the compounded oil over the blank oil with respect to bearing corrosion as shown by the bearing corrosion and copper loss tests, with respect to oxidation stability as shown by the neutralization number, naphtha insoluble, chloroform soluble, Conradson carbon and viscosity tests, and with respect to inhibiting varnish deposit as shown by the varnish deposit and chloroform-soluble tests.

Practical tests in an actual automotive engine confirmed the superiority of the compounded oil of the present invention in inhibiting varnish deposit. This test was run in a standard Chevrolet engine operated on a block for thirty hours at an equivalent of fifty miles per hour, or 1500 miles, with a crankcase temperature of about 290° F. for an S. A. E. 20 oil, and about 275° F. for S. A. E. 10 oil, with a jacket temperature of 212° F and crankcase ventilation of one cubic foot per minute. A series of tests was run on the same engine under these conditions, using for crankcase lubrication a furfural-refined dewaxed Mid-Continent distillate lubricating oil of S. A. E. 20 grade in comparison with the same oil containing a small proportion of an additive heretofore known to us as being very effective for varnish deposit inhibition, and termed herein for purposes of description a "compounded S. A. E. 20 oil"; and another series of tests was run on a furfural-refined dewaxed Mid-Continent distillate lubricating oil of S. A. E. 10 grade containing the same proportion of said last mentioned additive, and termed herein for purposes of description a "compounded S. A. E. 10 oil", in comparison with the same S. A. E. 10 oil (uncompounded) to which was added 0.25% of butyl "Carbitol" phosphite for one test, and 0.25% of methyl "Cellosolve" phosphite for another test.

At the completion of each run, the engine was taken down, the pistons removed, and the varnish deposit determined on the oil rings and the piston skirt. This was accomplished in each case by washing first with precipitation naphtha to remove retained oil, then washing with acetone to remove the acetone-soluble portion of the varnish which is found to represent the bulk of the varnish deposit, then evaporating this acetone solution to dryness, extracting the residue with precipitation naphtha to remove remaining traces of oil, again taking up in acetone solution and filtering to remove suspended carbon particles and impurities, and finally evaporating the acetone solution to dryness. The weight of the residue is expressed as mg. of varnish deposit and represents the combined deposit of the piston skirt and oil rings. The following results were obtained:

Crankcase oil tested	Varnish deposit in mg.
Blank S. A. E. 20 oil	827
Compounded S. A. E. 20 oil	315
Blank S. A. E. 20 oil	701
Compounded S. A. E. 20 oil	95
Blank S. A. E. 20 oil	567
Compounded S. A. E. 10 oil	614
S. A. E. 10 oil+0.25% butyl "Carbitol" phosphite	374
Compounded S. A. E. 10 oil	652
Compounded S. A. E. 10 oil	990
S. A. E. 10 oil+0.25% methyl "Cellosolve" phosphite	431
Compounded S. A. E. 10 oil	1,242

These tests show that the compounded oil is greatly superior to the uncompounded oil, and further show that the butyl "Carbitol" phosphite and the methyl "Cellosolve" phosphite of the present invention are markedly better than the previously known additive which was employed in the compounded oil tests for purposes of comparison. In explanation, it may be stated that a lighter lubricating oil of S. A. E. 10 grade for example, generally gives a greater deposition of varnish than a heavier lubricating oil of the same type and refining, and containing the same proportion of additive.

In addition to the advantages enumerated above, it is found that the phosphite esters of the alkyl ethers of the alkylene glycols of the present invention can be added to high grade typical motor oils without objectionably affecting the following desirable properties or tests of these oils, as illustrated in the annexed table setting forth tests on a furfural-refined dewaxed Mid-Continent lubricating oil of S. A. E. 30 grade in comparison with the same oil containing 0.25% butyl "Carbitol" phosphite, and in comparison with

the same oil containing 0.25% methyl "Cellosolve" phosphite.

Test	Reference oil S. A. E. 30 grade	Reference oil+0.25% butyl "Carbitol" phosphite	Reference oil+0.25% methyl "Cellosolve" phosphite
A. P. I. gravity	28.3	28.2	28.3
C. O. C. flash °F.	460	470	470
Fire °F.	525	525	510
S. U. viscosity at 100° F.	497	491	492
S. U. viscosity at 210° F.	62	62	61
Color—Lovibond 6"	240	270	255
Conradson carbon residue percent	0.09	0.08	0.08
Pour °F.	−5	0	−5
Cloud °F.	0	0	+2
Saponification No.	0.6	0.9	1.3
Ash percent	0.004	0.004	0.004

The compounded oils of the present invention also meet the Navy emulsion test, as determined by the United States Government test No. 320.12 as found on pages 76 et seq. of appendix 6, "Lubricants and Liquid Fuels," issued by the Navy Department August 1, 1928, with specifications set forth on page 7 of Naval Engineering Bulletin 31, "Lubricating Oil" published by the United States Government Printing Office in 1937. Briefly, these specifications require that an emulsion of lubricating oil having a Saybolt Universal viscosity at 210° F. in excess of 55 seconds with water at 180° F., or with a 1% NaCl solution at 180° F., shall break in less than sixty minutes. The following tests indicate the effectiveness of the above noted reference S. A. E. 30 oil compounded with 0.25% butyl "Carbitol" phosphite, and the same oil compounded with 0.25% methyl "Cellosolve" phosphite in meeting these specifications in comparison with the uncompounded reference oil:

Test	Reference S. A. E. 30 oil	Reference S. A. E. 30 oil+0.25% butyl "Carbitol" phosphite	Reference S. A. E. 30 oil+0.25% methyl "Cellosolve" phosphite
Water emulsion at 180° F., time of complete separation in minutes	<30	7	7
1% NaCl emulsion at 180° F., time of complete separation in minutes	<15	10	7

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating oil comprising a mineral lubricating oil containing 0.01–2.0% by weight of a phosphite ester of an alkyl ether of an alkylene glycol of the formula



where X_1 is an alkyl-alkylene oxide group of the type

$$R_3(OR_4)_{n1}(OR_5)_{n2}$$

where R_3 is an alkyl radical selected from the group consisting of methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl and octyl, where R_4 and R_5 are alkylene radicals (C_nH_{2n}) selected from the group consisting of ethylene and propylene, where n_1 is 0 or 1, and where n_2 is 1 or 2, and where X_2 and X_3 represent substances selected from the group consisting of hydrogen and alkyl-alkylene oxide radicals of the type of X_1 above.

2. A lubricating oil according to claim 1, in which the additive is a phosphite ester of an alkyl ether of a glycol selected from the group consisting of mono- and poly-ethylene glycols.

3. A lubricating oil according to claim 1, in which the additive is a phosphite ester of an alkyl ether of a glycol selected from the group consisting of mono- and poly-propylene glycols.

4. A lubricating oil according to claim 1, in which the additive is a phosphite ester of a butyl ether of di-ethylene glycol.

5. A motor oil for lubricating the bearings and cylinders of an internal combustion engine comprising a mineral lubricating oil within the motor oil viscosity range containing 0.01–2.0% of a tri-substituted normal phosphite ester of a mono-butyl ether of di-ethylene glycol.

6. A lubricating oil according to claim 1, in which the additive is a phosphite ester of the methyl ether of ethylene glycol.

7. A motor oil for lubricating the bearings and cylinders of an internal combustion engine comprising a mineral lubricating oil within the motor oil viscosity range containing 0.01–2.0% of a tri-substituted normal phosphite ester of the mono-methyl ether of ethylene glycol.

8. The method of lubricating bearing surfaces of an internal combustion engine, which comprises maintaining between the bearing surfaces, at least one of which contains a metal selected from the group consisting of cadmium, silver, copper, lead and nickel, a film of a mineral lubricating oil within the motor oil viscosity range which produces an effective lubricating action but which would normally tend to corrode the said bearing surfaces, and maintaining the effectiveness of said lubricating oil film while materially inhibiting the corrosiveness of the same to said bearing surfaces by incorporating in the said lubricating oil about 0.01–2.0% by weight of a phosphite ester of an alkyl ether of an alkylene glycol having the formula



where X_1 is an alkyl-alkylene oxide group of the type

$$R_3(OR_4)_{n1}(OR_5)_{n2}$$

where R_3 is an alkyl radical selected from the group consisting of methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl and octyl, where R_4 and R_5 are alkylene radicals (C_nH_{2n}) selected from the group consisting of ethylene and propylene, where n_1 is 0 or 1 and where n_2 is 1 or 2, and where X_2 and X_3 represent substances selected from the group consisting of hydrogen and alkyl-alkylene oxide radicals of the type of X_1 above.

9. The method according to claim 8, in which the mineral lubricating oil contains 0.01–2.0% by weight of a phosphite ester of a butyl ether of di-ethylene glycol.

10. The method according to claim 8, in which the mineral lubricating oil contains 0.1–0.5% by weight of the tri-substituted normal phosphite ester of the mono-butyl ether of di-ethylene glycol.

11. The method according to claim 8, in which the mineral lubricating oil contains about 0.01–2.0% by weight of a phosphite ester of the methyl ether or ethylene glycol.

12. The method according to claim 8, in which the mineral lubricating oil contains about 0.1–0.5% by weight of the tri-substituted normal phosphite ester of the mono-methyl ether of ethylene glycol.

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CERTIFICATE OF CORRECTION.

Patent No. 2,241,243. May 6. 1941.

ROBERT E. CONARY, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, first column, line 47, in the table, before "oxide" insert --iron--; page 5, first column, line 4, claim 11, for "or" read --of--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of June, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patent.

(Seal)

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