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LUBRICATING OIL

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This invention relates to an improved lubri-
cating oil, and particularly to an improved
lubricating oil adapted for use in internal com-
bustion engines, such as automotive engines, air-
craft engines, Diesel engines, and the like.

In the recent development of internal com-
bustion engines, and particularly with respect to
the Diesel engines, the increasing demand for
compactness, speed, power, and acceleration, has
brought about a marked change in the structural
design of the engines. The new designs provide
for a reduction in the clearances between the
lubricating surfaces, particularly between the
piston and cylinder walls, and operate at
much higher engine temperatures. Also, the
resulting higher bearing pressures, increased ro-
tative speeds, and the like, have necessitated a
departure from the use of the usual bearing
metals, such as babbitt, and require harder alloy
bearings of the type of cadmium-silver, copper-
lead, cadmium-nickel, and the like.

These changes in engine design have been con-
current with the development of solvent-refined
lubricating oils wherein the viscosity index and
other desirable features of the oils have been
greatly improved by refining the oils by certain
solvent-refining or solvent extraction processes.

It has been found, however, that when these
solvent-refined lubricating oils are used in the
crankcase of the improved engines they develop
a carbonaceous deposit upon the metal surfaces.
This deposit appears as a yellowish or reddish
brown film and is most prevalent upon the pis-
ton rings, piston skirt and cylinder walls. Over
extended periods of operation this deposit may
become so extensive as to clog the oil rings, fill
up the oil lines, and build up on the piston and
cylinder walls to such an extent as to eventually
result in seizure of the piston when the engine is
stopped and allowed to cool.

Upon close examination this carbonaceous de-
posit has been found to consist of two compo-
nents which may be differentiated by their solu-
bility in acetone. The portion of the deposit
soluble in acetone has been termed the "varnish"
component, while the insoluble portion is termed
the "lacquer" component.

Other undesirable features have become ap-
parent in the lubrication of the new alloy bear-
ings of the cadmium-silver, copper-lead, cad-
mium-nickel type with these solvent-refined
lubricating oils. These alloys are very suscep-
tible to chemical attack and their use at high
temperatures, high speeds, and high pressures,
is usually accompanied by an accelerated de-
terioration of the lubricant and a highly cor-
rosive reaction. It is quite possible that the
metals present in the bearings promote the de-
terioration of the oils by a catalytic reaction and

are, in turn, attacked by the deterioration prod-
ucts. Whatever the explanation of this deteri-
oration and corrosive reaction may be, the re-
sulting sludge formation within the oil and
etched or corroded bearings may seriously affect
the efficiency of the engine.

These problems, together with other problems
involving the stability of the oils in storage and
service oxidation changes, acid formation, vis-
cosity changes, sludging, and the like, have been
met by the incorporation of various "addition"
agents in the refined hydrocarbon oils. Under
these "addition" agents may be listed "anti-
oxidant" agents, "stabilizing" agents, "anti-cor-
rosion" agents, and the like. The utility of
these agents has been investigated in the labora-
tories and under service conditions, and, in many
cases, the agents have proven satisfactory for
their particular proposed use.

However, as pointed out above, the problems
involved in the lubrication of internal combus-
tion engines are not singular but rather in-
volve a plurality of problems, depending upon
the conditions and mode of operation of the
engines. It would seem to be a simple matter to
add to the oil a collection of the individual
agents, each selected for its specific purpose, but
the result of such an addition is not as simple
as it appears. The effect of the addition of two
or more agents is not always additive and fre-
quently one agent may lose its utility in the
presence of other agents. Furthermore, each
agent must be added in a definite amount to be
effective, and when two or more agents are added
together in their individual critical amounts, the
physical properties and the remaining desirable
features of the resulting oil usually are altered
and, in most cases, to an undesirable extent.

The particular problems of varnish and lacquer
formation, bearing corrosion, and deterioration
or sludge formation, are generally considered to
be the most serious in their effect upon the oper-
ation of internal combustion engines, especially
Diesel engines, and it is upon a solution to these
problems that the present invention is primarily
concerned. However, in considering these par-
ticular problems, such incidental problems as
color stability, stability in storage and service,
resistance to oxidation, and the like, must also
be kept in mind.

According to the present invention, it has been
discovered that a mineral lubricating oil of the
motor oil type, such as a highly solvent refined
lubricating oil, may be improved to such an ex-
tent as to minimize any varnish or lacquer
formation, bearing corrosion, or sludge forma-
tion, by the incorporation therein of a small
proportion of an oil-soluble neutral or basic
polyvalent metal salt of an organic ester of a

phosphorus acid. It is to be understood that the term "organic ester" is to include particularly the alkyl and naphthenyl esters and mixtures thereof, and the term "phosphorus acid" is meant to include the acid derivatives of the following phosphorus oxides:

P_2O —phosphorus monoxide
 P_2O_3 —phosphorus trioxide
 P_2O_4 —phosphorus tetroxide
 P_2O_5 —phosphorus pentoxide

The alkyl ester may be either straight or branched chain mono- or di-alkyl esters containing, in the case of a mono-ester, at least five and up to eighteen carbon atoms and, in the case of the di-alkyl esters, at least nine carbon atoms taken in combination as, for example, methyl-octyl or di-amyl esters. The naphthenyl esters embodied herein are derived from naphthenyl alcohols which are obtained by the carboxylic reduction of naphthenic acids and their esters and contain at least six and not more than eighteen carbon atoms.

Examples of the specific compounds within this group which have been found especially suited to the purposes of the invention are calcium isoamyl octyl ortho phosphate and calcium octyl pyro phosphate. Among the metal salts which have been found to be particularly effective are the calcium, magnesium, barium, tin, antimony, cobalt, aluminum, cadmium and zinc salts. Similarly, other organic esters falling within the class outlined above may be used, and include such mono-alkyls as the amyl hexyl, heptyl, octyl, etc., esters, together with their corresponding alkylated derivatives and isomers. Also such di-alkyls as the propyl-amyl, butyl-hexyl, propyl-octyl, amyl-hexyl, di-amyl, di-hexyl, etc., esters, together with their alkylated derivatives and isomers, may be used. The phosphorus acids are inclusive of the ortho, meta, and hypo phosphorous acids, and the ortho, meta, pyro, and hypo phosphoric acids.

This particular class of compounds may be prepared either by a direct neutralization of the phosphorus acid organic ester with a metal oxide or by a double decomposition reaction. In the particular case of calcium isoamyl octyl ortho phosphate, 50 grams of isoamyl octyl ortho phosphate are dissolved in 250 cc. of benzol and to the resulting solution a slurry of 10 grams of calcium oxide in 25 cc. of ethyl alcohol is added. The resulting mixture of calcium oxide and isoamyl octyl ortho phosphate is then refluxed for three hours and the reaction mass filtered through Filter-Cel. At this point it may be mentioned that any aromatic or paraffinic solvent, such as toluol, xylol or naphtha may be used in the place of benzol and the calcium oxide may be added directly without the use of alcohol. Upon removal of the solvent from the filtrate, 50 grams of a light-brownish-yellow, resinous mass was obtained which could be crushed to a powder. The product was found to be directly soluble in a lubricating oil and a concentrate prepared by dissolving the product in benzol, then mixing the required amount of lubricating oil, with subsequent removal of the solvent, was found to be very desirable in making blends. In the case of tin or antimony salts, the neutralized product is best obtained by double decomposition of the solid salt with a sodium salt solution.

These described compounds are incorporated in the lubricating oil in proportions ranging from 0.05–5.0% by weight, depending upon the type of lubricant used. The preferred range of propor-

tions in a lubricating motor oil is between 0.05 to 2.0%; in a Diesel lubricant from 0.05 to 5%; and in an aircraft lubricating oil from 0.05 to 3.0%.

It has been found that when lubricating oils containing a small proportion of the above-mentioned compounds are put to service tests, they not only minimize the lacquer and varnish formation, bearing corrosion, and sludge formation, but also possess unique detergent properties. The heretofore known addition agents have been used only as inhibitors of a particular undesirable feature of the lubricating oil, and it has not been attempted to remove the effects of the oil on the engine as in the case of varnish and lacquer deposits. However, the proposed additives not only inhibit but also act as a detergent in removing any varnish or lacquer deposits which might be present on the lubricating surfaces prior to the use of these additives in the lubricating oil. In this way, an engine which has lost its power and efficiency by reason of the increased resistance, due to a varnish and lacquer formation, may be restored to its normal operation through the use of a lubricating oil containing the proposed additives. As an explanation for the detergent action of these additives it has been suggested that, due to the high operating temperatures of the engines, the additive breaks down to the heavy metal phosphate or phosphite which is in itself an excellent detergent. Whatever the explanation may be, it has been found that an engine lubricated with a compounded oil as described is not troubled with any varnish or lacquer formation on its piston or cylinder walls.

Another feature of the present invention is the combination of the previously described additives with a corrosion inhibitor from the class of sulphurized fatty materials and the incorporation of small proportions of this combination in a lubricating oil. This particular class of compounds has already been acknowledged as possessing excellent anti-corrosion properties per se, and, when used in combination with the proposed additives of the present invention, these properties are not diminished but rather are added to the effective properties of the other additive. As was previously discussed above, the combination of two or more improving agents does not necessarily imply an additive effect and, in most cases, tends to destroy the improving qualities of the individual agents.

Among the particularly effective sulphurized fatty materials found suitable for the purposes of this invention are those sulphurized fatty materials formed by the sulphurization of non-glyceride fats, such as lanolin and sperm oil, or mixtures thereof. The amount of sulphurized compound added to a lubricating oil in combination with the other additive is usually within the range of 0.05 to 5.0% by weight, and preferably around 3.0%, depending upon the type of lubricating oil used.

These sulphurized fatty materials may be prepared in accordance with the copending application of Edwin C. Knowles and Frederic C. McCoy, Serial Nos. 358,876 now issued as Pat. No. 2,289,437 of July 14, 1942, 358,877 now issued as Pat. No. 2,289,438 of July 14, 1942, and 358,878, wherein a light-colored, sulphurized fatty material is prepared by the direct addition of sulphur to the fatty material at approximately 300° F. in the presence of water and under pressure of hydrogen sulphide. This pressure, which is at least 50 pounds per square inch, is maintained until all free sulphur has entered into combina-

tion and lasts usually from one-half to three hours. The sulphurized products formed by this process are directly soluble in lubricating oil and possess the added advantage in that the reaction product is a light-colored compound as against the usual dark-colored sulphurized compounds.

As illustrative of the unusual corrosion inhibiting properties of a lubricating oil containing either or both of the aforementioned additives, the results of the following empirical test are presented. A copper-lead bearing specimen, incased in a special non-wear bushing and rotatably mounted on a stainless steel shaft, was immersed in a glass pot of the oil to be tested. The tested oil was heated to a controlled temperature of either 250° F. or 350° F. and continuously circulated between the bearing specimen and the shaft for periods of time varying from two to ten hours. The bearing specimen was weighed before the test and at two-hour intervals and the loss in weight recorded in milligrams. The reference oil which was used throughout this test was a solvent-refined dewaxed Mid-Continent lubricating oil distillate of an S. A. E. 30 grade.

To this reference oil was added varying proportions of the additives of the present invention, taken individually and in combination, and the results compared. The results of two runs at 250° F. and 350° F., respectively are presented:

Corrosion test (250° F.)—copper lead bearings

[Bearing weight loss, mgs.]

Oil tested	2 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.
Ref. oil	9, 12	16, 19	22, 25	27, 31	34, 38
Ref. oil + 0.5% calcium isoamyl octyl ortho phosphate	2, 3	5, 6	7, 9	9, 11	10, 13
Ref. oil + 3.0% sulphurized non-glyceride fat	10, 10	11, 14	14, 16	16, 17	18, 19
Ref. oil + 3.0% sulphurized non-glyceride fat + 0.25% calcium isoamyl octyl ortho phosphate	3, 9	6, 13	9, 15	10, 17	11, 18
Ref. oil + 3.0% sulphurized non-glyceride fat + 0.5% calcium isoamyl octyl orthophosphate	7, 4	10, 6	11, 9	11, 10	11, 13
Ref. oil + 3.0% sulphurized non-glyceride fat + 0.25% calcium octyl pyro phosphate					16, 18

Corrosion test (350° F.)—copper lead bearings

[Bearing weight loss, mgs.]

Oil tested	2 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.
Ref. oil	10, 10	46, 43	72, 68	93, 88	133, 105
Ref. oil + 0.5% calcium isoamyl octyl ortho phosphate	27, 34	40, 36	51, 63	60, 83	67, 98
Ref. oil + 3.0% sulphurized non-glyceride fat	3, 3	4, 4	5, 4	6, 5	11, 5
Ref. oil + 3.0% sulphurized non-glyceride fat + 0.25% calcium isoamyl octyl ortho phosphate	1, 1	5, 5	6, 7	7, 8	9, 9
Ref. oil + 3.0% sulphurized non-glyceride fat + 0.5% calcium isoamyl octyl ortho phosphate	4	4	5	5	5
Ref. oil + 3.0% sulphurized non-glyceride fat + 0.25% calcium octyl pyro phosphate					8, 10

A further illustration of the corrosion inhibiting properties of the additives of the present invention was demonstrated by practical tests in a standard Plymouth engine equipped with special coarse structure copper-lead bearings which were chosen for this test because of the larger weight losses experienced under normal operation. This test was carried out by running the

engine for twenty-four hours at 3000 R. P. M. with three-quarter open throttle developing about thirty-four brake horsepower with the crankcase oil temperature maintained at 300° F. by means of an external heat exchanger with an external pump, and with a water jacket temperature of 212° F. The bearings were disassembled, cleaned and weighed before and after each run and the results tabulated as the percentage weight loss difference between the experimental oil and the reference oil. The reference oil in this test was a solvent-refined dewaxed Mid-Continent lubricating oil distillate of S. A. E. 30 grade and was compared to the same oil containing 3.0% sulphurized non-glyceride fat and 0.5% calcium isoamyl octyl ortho phosphate. The results obtained show 78% less bearing weight loss with the compounded oil than with the reference oil taken on an average of two test runs.

In order to illustrate the aforementioned detergent properties of the additives of the present invention, e. g. the ability of the compounded oil to remove a deposit of varnish and lacquer from the surfaces of an engine piston and cylinder, a test was devised which simulated as closely as possible the actual operating conditions of an internal combustion engine. This test was conducted on a single cylinder standard Lauson engine and the results obtained evaluated by visual inspection according to a classification of bad, fair and good. A heavy varnish deposit was obtained upon the piston of the Lauson engine by utilizing a solvent-refined, dewaxed Mid-Continent lubricating oil of an S. A. E. 10 grade, and running the engine at 1800 R. P. M. with a jacket temperature of 212° F., a crankcase temperature of 300° F., and with a crankcase ventilation of 0.4 cubic feet of air per minute for twenty-four hours. Then, without cleaning the piston, the oil was changed to the compounded oil containing the proposed additives and the engine operated at 1800 R. P. M., with a jacket temperature of 315° F., a crankcase temperature of 200° F., and with no crankcase ventilation for twenty-four hours. At the end of the twenty-four hour period the engine was dismantled, the condition of the piston noted, and the oil classified. The following results were obtained with a reference oil of the solvent-refined, dewaxed Mid-Continent lubricating oil of S. A. E. 30 grade, together with this reference oil compounded with the proposed additives:

Lauson detergency test

Oil tested	Rating	Remarks
Reference oil	Bad...	Heavy varnish deposit.
Reference oil + 3.0% sulphurized non-glyceride fat + 0.5% calcium isoamyl octyl ortho phosphate	Fair...	Light varnish film.

The effect of the proposed additives in reducing oil ring sludge is shown by the results of a so-called oil ring sludge test. In this test a CFR Diesel engine was operated for thirty-six hours at 1200 R. P. M., with a jacket temperature of 210° F. and a rich fuel mixture fed at the rate of 20 cc. per minute to aggravate sludge formation. The runs from the test were first made by using a reference oil, such as a solvent-refined, dewaxed Mid-Continent lubricating oil S. A. E. 30 grade, and then, upon the same reference oil, compounded with varying proportions of the proposed additives. At the completion of each run the oil rings were taken out and weighed, and the results of the test tabulated as the percentage

improvement of the compounded oils over the reference oil as follows:

Oil ring sludging test

Reference oil + 0.5% calcium isoamyl octyl ortho phosphate.	40% less oil ring sludge than reference oil.
Reference oil + 3% sulphurized non-glyceride fat + 0.5% calcium isoamyl octyl ortho phosphate.	19% less oil ring sludge than reference oil.
Reference oil + 0.5% calcium octyl pyro phosphate.	32% less oil ring sludge than reference oil.

As a final test to indicate the effectiveness of the compounded oil proposed by the present invention, a special endurance test was devised to test the suitability of the compounded oil. The particular endurance test which was used was a so-called caterpillar endurance test, which has been described in the Diesel Lubricant Test Manual, Laboratory test No. 1, put out by the Caterpillar Tractor Company. This test was carried out in a single cylinder Diesel engine operating at 900 R. P. M., with a water jacket temperature of 175° F., running continuously for 1000 hours, or until rings are stuck as indicated by the increase in blowby, and the crankcase oil drained every sixty hours and fresh oil added thereto.

In the present instance the reference oil used was a solvent-refined, dewaxed Mid-Continent lube oil of S. A. E. 30 grade. The test was carried out only to 600 hours, at which time a stuck ring was noted, and therefore all the tests were based upon a 600 hour period.

Caterpillar endurance test (600 hours)

Oil tested	Bearing weight loss	Remarks
Reference oil + 3.0% sulphurized non-glyceride fat.	Grams 0.975	No. 4 compression ring stuck, oil ring slots beginning to collect deposits, and piston partially coated with dark brown varnish deposit.
Reference oil + 3.0% sulphurized non-glyceride fat + 0.5% calcium isoamyl octyl ortho phosphate.	0.985	Oil rings free, pistons clean, filter virtually free of deposits, and oil ring slots free of deposits. Run was still in progress.

Obviously many modifications and variations of the invention may be used without departing from the spirit and scope thereof and only such limitations as are indicated in the following claims should be imposed.

I claim:

1. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein a small proportion of polyvalent metal salt of an organic ester of a phosphorus acid, said organic ester being selected from the group consisting of alkyl and naphthenyl esters, together with a small proportion of a sulphurized fatty material.

2. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein a small proportion of polyvalent metal salt of an organic ester of a phosphorus acid, said organic ester being selected from the group consisting of alkyl and naphthenyl esters, together with a sulphurized non-glyceride fat.

3. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein 0.05-5.0%, by weight, of polyvalent metal salt of an organic ester of a phosphorus acid, said organic ester being selected from the group consisting of alkyl and naphthenyl esters, together with 0.05-5.0%, by weight, of a sulphurized non-glyceride fat.

4. An improved lubricating oil according to claim 3, wherein the polyvalent metal salt of an organic ester of a phosphorus acid is calcium isoamyl-octyl-ortho phosphate.

5. An improved lubricating oil according to claim 3, wherein the polyvalent metal salt of an organic ester of a phosphorus acid is calcium octyl-pyro-phosphate.

6. An improved lubricating oil adapted for use in internal combustion engines, comprising a major proportion of a lubricating oil and a minor proportion of a combination of a polyvalent metal salt of an alkyl ester of a phosphorus acid and a sulfurized fatty material.

7. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein a small proportion of a combination of a polyvalent metal salt and an organic ester of a phosphorus acid, said organic ester being selected from the group consisting of alkyl and naphthenyl esters, said polyvalent metal being selected from the group consisting of calcium, magnesium, barium, tin, antimony, cobalt, aluminum, cadmium and zinc, and a sulfurized fatty material.

8. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein 0.05-5.0% by weight of a polyvalent metal salt of an alkyl ester of a phosphorus acid, and 0.05-5.0% by weight of a sulfurized non-glyceride fat.

9. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein a small proportion of a combination of a polyvalent metal salt of an alkyl ester of phosphoric acid and a sulfurized non-glyceride fat.

10. An improved lubricating oil adapted for use in internal combustion engines, comprising a lubricating oil having incorporated therein a small proportion of a combination of a polyvalent metal salt of an alkyl ester of phosphorous acid and a sulfurized non-glyceride fat.

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