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LUBRICATING COMPOSITION

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This invention relates to lubricants, and it com-
prises, as an improved lubricant composition,
petroleum lubricating oil to which has been added
a small amount of a sulfurized monoester of a
fatty acid, advantageously sulfurized sperm oil,
of an oil-soluble ester of an acid of phosphorus,
advantageously tricresyl phosphate and of a high
molecular weight aliphatic monohydric alcohol
such as cetyl alcohol or like fatty alcohol, this
combination of improvement agents dissolved in
the petroleum oil improving the lubricating qual-
ities of said oil; all as more fully hereinafter set
forth and as claimed.

The present application is a continuation-in-
part of my prior and copending application Serial
No. 212,393, filed June 7, 1938; now Patent No.
2,179,067, dated November 7, 1939.

In that prior application, I have claimed im-
proved lubricants adapted for use as a crank case
lubricant in internal combustion engines compris-
ing a petroleum lubricating oil having incorpo-
rated therein small amounts of a sulfurized mono-
ester of a fatty acid and of an oil-soluble ester of
an acid of phosphorus, specifically sulfurized
sperm oil and tricresyl phosphate, with or without
butyl stearate.

The present application is directed to other
lubricants containing a plurality of improvement
agents, particularly those containing combina-
tions of chlorinated paraffin wax, sulfurized sperm
oil and tricresyl phosphate to improve the oiliness
and extreme pressure characteristics of the min-
eral lubricating oil.

As shown in my prior application Serial No.
212,393, it is difficult from a practical standpoint
to produce improved lubricants containing a plu-
rality of improvement agents which will satis-
factorily meet all the lubricating requirements of
the modern machines and engines. From a prac-
tical standpoint, due consideration must be given
to each and every factor, starting as far back as
the refining of the lubricating oil itself.

Modern methods of refining lubricating oils
have resulted in the production of lubricants hav-
ing very advantageous and desirable characteris-
tics. Pennsylvania crudes and other highly par-
affinic crudes have long been regarded as excep-
tionally advantageous as stocks for the prepara-
tion of lubricants, because of their favorable vis-
cosity characteristics, their stability and other

properties. Other stocks can now by means of
solvent extraction methods and other treating
methods, including refining with aluminum chlo-
ride, be treated to produce lubricants comparable
with those obtained from Pennsylvania crudes.
Even Pennsylvania crudes are sometimes them-
selves subjected to drastic refining; one of the
finest lubricating oils now on the market com-
prises Pennsylvania residual oil refined by means
of aluminum chloride.

Such highly refined oils demand a premium and
are highly advantageous for use in many internal
combustion engines, even of such design as to im-
pose severe burdens upon lubricants. These oils
represent a marked advance over oils available
from similar stocks before the development of
such refining methods, and, as has been indicated,
they are superior lubricants for many purposes.

However, the present trend in design of internal
combustion engines, especially "high output" air-
craft engines, Diesel engines and the like, has pre-
sented new and different problems to the producer
of lubricants. As the ordinary oils of commerce
have improved in character, the engine designers
have been encouraged toward designs which im-
pose more and more severe burdens upon lubri-
cants. The whole problem is infinitely compli-
cated; many oils commercially sold must be avail-
able for use in a variety of engines of quite dif-
ferent design, while others must be made satis-
factory for use in particular internal combustion
engines in the lubrication of which difficult and
specific problems arise. As the necessity for and
tendency toward engines of high performance
have increased, engine designs have been produced
which tax or exceed the capabilities of the very
best and most highly refined petroleum lubricat-
ing oils.

Thus, in recent high-output aircraft engines
and Diesel engines much higher unit loads are
imposed upon the bearings than has been true in
the past. These engines also run at very high
operating temperatures; among other effects, the
cylinder walls of such engines are maintained at
temperatures higher than was true in older de-
signs. Inasmuch as any crank-case lubricant
also lubricates the cylinder walls of the engine,
that lubricant is subjected on such cylinder walls
to the extremely high temperatures maintained
there, with the result that after a short time de-

posits are formed around the piston rings. Deposition of carbon and sludging take place, causing the piston rings to stick, and resulting in loss of pressure in the combustion chamber and excessive wear of piston rings, cylinders and cylinder walls.

For various reasons there is also a growing tendency to employ special metal alloys for various parts of internal combustion engines. These alloys are frequently of such character as not only present a corrosion problem, but also to promote deterioration of the oils. For example, bearings of the cadmium-silver, cadmium-nickel and copper-lead types, particularly when subjected to high temperatures and high bearing pressures, give rise to difficult corrosion problems which are not always obviated by the use of otherwise desirable, highly refined oils. Entirely aside from bearings, certain engine designs also include alloy parts which are maintained in contact with the crank-case lubricant at extremely high temperatures. For example, in one type of high-output aviation engine, there are provided exhaust-valve guides made of a high-copper bronze alloy, these guides being in contact with the crank-case lubricant. By virtue of their proximity to the exhaust gases, these guides are subjected to temperatures high enough to be termed "frying" temperatures; in excess of 600° F. They are not only subjected to a severe tendency to corrosion under such conditions, but their copper content probably aids in promoting general deterioration of the lubricant, thereby tending to decrease the efficiency of the oil at other points in the engine.

It may also be mentioned at this point that inasmuch as operating temperatures vary, even for a given engine, over a considerably wide range, the lubricant employed must be such as to withstand the severe conditions imposed upon it both at high temperatures and at low temperatures.

Moreover, due to the zeal for saving weight and space in engine and power-transmission designs generally, the designers have produced lighter and smaller bearings, gears and the like; in such designs considerable increases in unit loads are encountered, imposing added burdens upon the lubricant. Petroleum lubricating oils in general require improvement in order to meet the requirements of such loads, the increased operating temperatures resulting therefrom, and to cut down the increased wear also occasioned thereby.

Inasmuch as refining methods employed in the production of lubricating oils have already been carried about as far as it is practicable to carry refining, a solution of the problems introduced by such designs must be sought through other means. Consequently, there have been developed a number of "addition agents" intended to improve the performance of petroleum lubricating oils under various conditions and for various purposes when added thereto. Among these agents may be listed "mild extreme-pressure" or "EP" agents, "oiliness" agents, "anti-corrosion" agents and the like. The utilities of these compounds considered individually have been investigated in the laboratories and under service conditions, in many cases with quite satisfactory results insofar as individual and isolated specific operating problems are concerned. Nevertheless, from a practical standpoint, the problem of producing a lubricant suitable for use in modern machine designs of the character indicated is far from complete solution.

There are several reasons why this is true. For example, lubricants in service in high-output engines usually encounter not one but all or most of the difficulties and conditions indicated hereinabove. It might appear to be a simple matter to add to the oil a collection of individual agents, each selected for its specific purpose, and each present in amount sufficient to effect that purpose, but the problem is not so simple. In the first place it is usually found that mixtures of addition agents of various types do not respond in a normal and expected manner when considered in the light of the performances of such agents used individually. The effects are not always additive; frequently an agent known to be effective when used alone for one purpose may lose its utility in the presence of other types of agents. No general prediction as to the behavior of compounded oils containing two or more addition agents is safe.

Moreover, the question of quantity is of the utmost importance. An agent effective, for example, to contribute the required load-bearing or corrosion-inhibiting characteristics to a given oil, in order for that oil to be used under given conditions, must frequently be added to the oil in a very definite amount; and that amount is often so great that other undesirable effects are produced. An agent which, when used in small quantities, assists in overcoming a given corrosion problem, may, if used in quantities sufficient to have the desired effect at one point in the engine, cause undesirable "over-corrosion" in other parts of the same engine. A sufficient quantity of a mild extreme-pressure agent to give an oil desired load-bearing characteristics may also result in a definite and undesirable tendency toward corrosion. Relatively large amounts of any of these agents may cause sludging. An oil so compounded as to be effective to carry high bearing loads and to reduce bearing wear at low temperatures may be unsatisfactory for operation at high temperatures, and vice versa.

The problem is considerably complicated and heightened by the fact that a great many of the known addition agents for various purposes are of very limited solubility in petroleum oils, and this is especially the case with respect to the more highly refined and highly paraffinic oils. Certainly highly refined oils will not dissolve sufficient amounts of an individual addition agent to give the oil the desired lubricating value necessary under given operating conditions.

It has been my experience that there is no single addition agent which, when added to petroleum lubricating oils, especially highly refined and highly paraffinic lubricating oils, in amounts which can be tolerated in such oils, will render such oils entirely effective as lubricants for high-output engines of the character indicated, and capable of being employed under the varying operating conditions normally to be expected in such use.

In my copending prior applications Serial No. 60,355, filed Jan. 22, 1936 (now Patent 2,179,060), Serial No. 60,357, filed Jan. 22, 1936 (now Patent 2,179,061), Serial No. 108,305, filed Oct. 29, 1936 (now Patent 2,179,065), and Serial No. 108,306, filed Oct. 29, 1936 (now Patent 2,179,066), all of which patents issued November 7, 1939, and in copending prior joint applications of myself and T. L. Cantrell Serial No. 103,050, filed September 28, 1936 (now Patent 2,179,063) and Serial No. 103,051, filed September 28, 1936 (now Patent

2,179,064), which also issued November 7, 1939, there is described and claimed improvement of petroleum lubricating oils for extreme pressure purposes by incorporating therein sulfurized mono-esters of fatty acids, such as sulfurized sperm oil. Sperm oil, unlike the usual fatty oils, is composed mainly of oils which are not glycerides, which are not tri-esters of glycerine. In sperm oil the contained esters are mono-esters of fatty acids and alcohols of relatively high molecular weight. As set forth in said prior applications, I have found that sulfurized sperm oil, made by heating sperm oil with sulfur, is a useful addition to lubricating oils in proportions varying from 0.1 to 30 per cent by weight, in accordance with the desired service for the oil or lubricant.

However, while refined and carefully prepared sulfurized sperm oils have advantages as addition agents for petroleum lubricating oils in reducing bearing corrosion and in increasing the pressure-bearing properties of the compounded oils, comparatively large amounts of sulfurized sperm oil are sometimes found to induce sludging effects in the oil. Moreover, amounts of sulfurized sperm oil sufficient to contribute the desired load-bearing properties to an oil when added thereto, sometimes produce undesirable corrosion effects at other points in the engine maintained at temperatures in excess of bearing temperatures, as for example when brought into contact with copper alloys at excessively high temperatures, such as have been referred to hereinabove in connection with the copper-alloy exhaust-valve parts of certain aviation engines. I have found that very small amounts of sulfurized sperm oil, down to as little as 0.02 per cent by weight of the composition, are effective when used in combination with certain other addition agents, as set forth herein, in preparing compounded lubricants for service in such engines.

Tri-cresyl phosphate and certain other oil-soluble phosphorus esters, when used alone as addition agents for petroleum lubricating oils, are known to contribute mild extreme-pressure characteristics; oils containing such esters are thereby adapted to carry higher bearing loads. Tri-cresyl phosphate is one of the cheapest and most available of this class of agents. However, several factors limit the usefulness of tri-cresyl phosphate, when added alone to lubricating oils intended for internal combustion engines. Tri-cresyl phosphate is not very soluble in oils ordinarily used for crank-case lubrication, especially with respect to highly refined, highly paraffinic oils, and if present in amounts much over 1 per cent by weight, frequently imparts an undesirable haze or muddiness to the oil. This effect is not always apparent at the time of addition, but may appear upon storage of the treated oil, or after the oil has been in use for some time. The amount of tri-cresyl phosphate which can be permanently dissolved in oil of this character is sufficient to impart some degree of "EP" characteristics, that is to say, to increase the load-bearing capacity of the oil to some extent, but is insufficient for an oil which is to be subjected to high bearing loads, say of the order of from 8,000 to 18,000 pounds per square inch, especially at high bearing speeds. Tri-cresyl phosphate, when employed as the sole addition agent to a petroleum oil, is not especially useful in obviating the tendency toward corrosion of sensitive alloy bearings at high operating temperatures, nor does it represent a satisfactory agent for preventing deteriora-

tion of petroleum oils at high temperatures. I have found that tri-cresyl phosphate is an efficient anti-ring-sticking agent for petroleum lubricating oils, and that, at low operating speeds and at low temperatures, it is useful as an extreme-pressure agent. However, tri-cresyl phosphate, if present in such amounts as to be effective alone for the purpose of contributing the desired extreme-pressure characteristics, has shown undesirable effects; there is frequently a definite tendency toward sludging. In some cases, particularly when water is present, an acid corrosion effect is observed, possibly due to decomposition of the tri-cresyl phosphate.

I have discovered that I can impart to a lubricating oil properties sufficient to enable it to be used with satisfactory results for lubrication of high performance engines of the character set forth above, by adding to the oil both sulfurized sperm oil, or other composition containing a sulfurized mono-ester of a fatty acid, and an oil-soluble ester of an acid of phosphorus, such as tri-cresyl phosphate. By limiting the total amount of the combined addition agents thus employed, I find that I am able to secure the desired characteristics necessary for satisfactory performance, while avoiding the disadvantages which are incurred when relatively large amounts of these two agents are employed alone.

For engines in which high bearing pressures and temperatures require oils having marked load-bearing capacity and corrosion-inhibiting tendencies (with respect to sensitive alloy bearings) I prefer to employ these agents alone, without the use of other agents, and that is particularly true where there are no other serious corrosion factors to be met. In special cases, where the oil must come in contact with copper-alloy parts at extremely high temperatures, I have found it advisable to reduce the amounts of these agents and to compensate for this reduction by adding certain oiliness agents other than sulfurized sperm oil, preferably neutral in character, such as butyl stearate, refined sperm oil, benzyl naphthenate, benzyl stearate and the like. Many oiliness agents are available for this purpose and may be used more or less interchangeably. Thus other fatty oils may be used in place of refined sperm oil, although I have found that fatty oils containing substantial amounts of free fatty acids or glycerides are less desirable than sperm oil, which is substantially free from both fatty acids and glycerides.

While free fatty acids have been advocated for use as oiliness agents, I have found that in modern engine designs (involving high bearing speeds and temperatures and the use of corrosion-sensitive alloys of the so-called cadmium-copper-nickel-silicon group) these acids do not actually function as such. The corrosion effects induced by this type of agent under such conditions destroy the "oiliness" effect; the compounded lubricant is less "oily," in actual service, than is true of the petroleum lubricating oil alone. Consequently, notwithstanding any usage by others, the term "oiliness agent" as used herein does not include free fatty acids.

Aside from sulfurized sperm oil and the like, the oiliness agents I prefer are neutral esters of fatty acids, for example butyl stearate, isopropyl stearate, benzyl stearate, methyl oleate, glycol oleate, benzyl naphthenate, and refined sperm oil (unsulfurized) itself. Thus, I have found butyl stearate exceptionally attractive and useful, as it

serves to promote oiliness and pressure-bearing properties, causes little or no trouble from corrosion or sludging effects, and is a good solvent. It is a satisfactory oiliness agent for my purposes and shows a marked tendency, when used in conjunction with the other agents referred to, to reduce the temperature rise in operation of a given bearing over any given period, thereby promoting the effectiveness of the phosphorus ester used in combination therewith.

I have found, also, that its presence tends to cause carbon deposited on the piston and on the rings in an engine to be softer and lighter in character, more easily removed from the cylinder, than the characteristic hard, flinty deposit developed from highly-refined oils. It tends to reduce bearing, piston and cylinder wear and not only compensates for reduction in the other addition agents present, but assists the other addition agents in the performance of their individual functions to a marked extent. The same effects are also characteristic of the other oiliness agents mentioned.

The results obtained by the use of my invention are singular and valuable. The beneficial effects of each addition agent taken alone are retained, while in addition each ingredient tends to obviate deleterious effects or deficiencies of the others. Moreover, the characteristics imparted to the oil by the addition of the two or more ingredients are better than the sum of the individual effects, and the compositions exhibit performances, without disadvantages, which cannot be obtained by using two or more agents individually.

For example, to illustrate a remarkable effect of the use of a mixture of limited amounts of sulfurized sperm oil and tri-cresyl phosphate, the following results are significant. Under standard test conditions, the addition of 1.6 per cent by weight of a well refined sulfurized sperm oil composition (containing about 50 per cent actual sulfurized sperm oil) will increase the load-bearing capacity of one commercial lubricating oil to 8,000 pounds per square inch. Tri-cresyl phosphate, when added to the same oil, in the amount of 1.6 per cent, will produce an undesirable haze and is rather unsuitable for use in such amount on that account; nevertheless this amount of tri-cresyl phosphate will increase the load-bearing capacity of the oil to 11,000 pounds per square inch in the identical testing method. Surprisingly, when the sulfurized sperm oil composition and tri-cresyl phosphate are both added to the same oil in total amounts not exceeding 1.6 per cent of the oil by weight, the load-bearing capacity of the oil is markedly increased, being in each case greater than 11,000 pounds per square inch. The addition of 0.8 per cent of the sulfurized sperm oil composition and 0.8 per cent of tri-cresyl phosphate to the same oil enables the oil to withstand a bearing pressure above 18,000 pounds per square inch. Moreover, the same test is also employed to give an indication of "oiliness," measured in terms of tendency of the bearings to rise in temperature under given load conditions. Mixtures of the sulfurized sperm oil composition and tri-cresyl phosphate, in the total amounts of 1.6 per cent, in all cases show lower rates of temperature rise than is true where 1.6 per cent of the sulfurized sperm oil composition alone or tri-cresyl phosphate alone is present in the composition. In all cases where the amount of tri-cresyl phosphate does not exceed 1 per

cent of the total compounded lubricant, the oil is clear and free from haze, and where neither the sulfurized sperm oil composition nor the tri-cresyl phosphate exceeds 1 per cent by weight of the total oil composition, the undesirable effects associated with the use of these materials in larger amounts are absent.

The sulfurized sperm oil used in carrying out the invention may be manufactured and refined in accordance with the teaching in my copending application Serial No. 103,050, filed September 28, 1936, and subsequently added to the lubricating oil base without dilution or, as taught in that application, the sperm oil after sulfurization may be diluted with a mineral oil and the intermediate product so obtained refined with acid and clay, after which the refined dilute sulfurized sperm oil may be added to the base oil. I find it advantageous to employ a product (so diluted) sufficiently refined to have a color of 5.0 or under (NPA Color Scale), and a neutralization number of 6.0 or lower. The amount of sulfur present should not exceed that required to satisfy the esters present in the sperm oil, and should not run more than 10 or 12 per cent by weight of the refined sperm oil present.

By way of example, in preparing a suitable highly refined composition containing sulfurized sperm oil, 8,057 pounds of a commercial sperm oil is charged into a direct-fired open-top grease kettle equipped with suitable cooling coils and the sperm oil is gradually heated to 340° F. in about 2 hours, while stirring. As the stirring is continued, 1,098 pounds of sulfur flour (approximately 1 pound of sulfur per gallon of sperm oil) are rapidly added to the preheated oil over a period of 30 minutes. As soon as the reaction becomes vigorous the heating is discontinued, but the heat of reaction quickly raises the temperature to between 360° and 385° F. where it is maintained for one hour by sufficient cooling. The hot sulfurized oil so prepared is then admixed with paraffinic mineral lubricating oil, of moderately low viscosity, preferably in an amount about equal to that of the sulfurized sperm oil.

To each 1000 gallons of the intermediate oil mixture so obtained, while at a temperature around 120° F., there is added 1000 pounds of 98 per cent sulfuric acid of ordinary commercial grade. The mixture is agitated for approximately an hour during which time the temperature rises to a maximum of 135° F. About five minutes before discontinuing agitation, there is added about three gallons of water, so as to agglomerate the very fine sludge particles and thus promote more rapid and effective separation in settling. The stratified acid sludge is withdrawn and removed, representing a loss of around 10 per cent of the intermediate composition being refined. The sour oil recovered is charged into a drum with a mechanical stirrer and heating coil, where it is heated to 270° F. There is then added over a period of 40 minutes a commercial acid-treated clay having a fineness between 200 and 300 mesh in the proportion of one thousand pounds to each one thousand gallons of sour oil charged. The heating is continued for 2 hours at 270° F. while the mixture is continuously stirred. Most of the undesirable deleterious impurities having then been adsorbed by the clay, the mixture is then pumped to a suitable filter, where the oil is separated from the excess clay and impurities. The following

characteristics are typical of the compositions so refined:

TABLE I

5	Gravity: °A. P. I.-----	18-25
	Viscosity, S. U. V.—	
	At 100° F.-----	500-1000
	At 210° F.-----	60-100
	Color, NPA-----	3-5
10	Sulfur, B: per cent-----	4-5.5
	Neutralization No.-----	3-6

It will be understood, however, that the operating details mentioned just above are given by way of example, and need not be adhered to in practice. Thus the method of refining may be varied, as for example, by omitting the acid-treating step entirely, and where the sulfurization of the sperm oil is very carefully controlled, and the color of the final product is not important, the refining steps may be omitted entirely.

As an alternative method, the refining of the sulfurized sperm oil may be effected by means of highly activated adsorbent clay, such as acid-treated clay, "Filtrol" or the like, without using acid. In such case, it is usually necessary to employ more clay than is used in the foregoing example.

In practicing one embodiment of my invention I incorporate a small amount of refined sulfurized sperm oil, for example in the form of a composition as described hereinabove in a petroleum oil together with a small amount of an oil-soluble ester of an acid of phosphorus, such for example, as tri-cresyl phosphate, tri-phenyl phosphate, tri-butyl phosphate, "lorol phosphate," di-butyl-mono-cresyl phosphate, di-lauryl-mono-cresyl phosphate, tri-(tri-tertiary-butyl phenyl) phosphite, tri-(di-tertiary-butyl para-cresyl) phosphite, tri-para-tertiary-aryl-phenyl phosphite, mono-cresyl-di-propyl phosphite, tri-xylene phosphite, and other alkyl, aryl, alkaryl and mixed alkyl-aryl esters of phosphorus acid and of phosphoric acid, or mixtures thereof.

The phosphates are ordinarily suitable, but where the oil is to be used in contact with silver-cadmium and like corrosion-sensitive bearing metals, especially at high temperatures, and wherever, for any reason, fully effective amounts of sulfurized sperm oil can not be used it is desirable to employ a phosphite ester. When the latter are sufficiently soluble and stable, as in the case of the highly alkylated phenyl phosphites, they may be used without the presence of a phosphate; in the case of tri-phenyl phosphite and other phosphites of similar high-phosphorus content, it is best to use a mixture of such ester and a phosphate ester, the amount of the phosphite ester being not in excess of one-third of the amount of the phosphate ester.

Ordinarily, I find it most advantageous to employ tri-cresyl phosphate in combination with sulfurized sperm oil, as the tri-cresyl phosphate is commercially available and I have found that it is particularly advantageous in overcoming ring-sticking when lubricants containing it are placed in use. Tri-cresyl phosphate also has certain advantages over other oil-soluble esters of phosphorus acids, particularly certain phosphites, in that it is relatively free from the tendency possessed by most phosphites to develop excessive amounts of insoluble matter or sludge, when in contact with certain metals, for example, the metals with which many container packages

are lined. When used in reasonably small amount tri-cresyl phosphate also possesses less tendency to form acid reaction products and sludge-like materials in the presence of water than is true of many of the other organic phosphorus compounds.

Another phosphate ester especially suitable for the purpose of my invention may be prepared by reacting a phenol-olefin condensation product with phosphorus oxychloride in the presence of a relatively small amount of phosphorus sesquisulfide, as set forth in the copending application of Cantrell and Stockhardt, Serial No. 215,920, filed June 25, 1938.

The petroleum lubricating oil which forms the base of my improved lubricant is chosen with a view toward the ultimate application of the lubricant. For instance, where lubrication of aircraft engines is contemplated the oil chosen is ordinarily a highly refined residual oil having an SAE rating of 60 or thereabouts, while for crank-case lubrication of other internal combustion engines the oil chosen may be any one of the distilled lubricating oils or blends at present in common use, conforming with the SAE classification.

In preparing internal combustion engine lubricants, I have found it advantageous to limit the total amount of addition agents to a figure not exceeding 2 per cent by weight of the lubricating composition, but this limit is not invariable. This is especially true where sulfurized sperm oil and tri-cresyl phosphate, or their equivalents, are employed, without the use of butyl stearate or other oiliness agent. And as a matter of fact it is also generally true where butyl stearate is also added but in the case of less effective oiliness agents, this amount may be somewhat exceeded, where the effectiveness of the particular oiliness agent employed is relatively low. I have found it advantageous to add sulfurized sperm oil in amounts ranging from 0.02 per cent to 1.0 per cent of the total composition, and to add tri-cresyl phosphate in amounts ranging between 0.5 and 1.5 per cent by weight of the total composition. Where other phosphorus esters are employed, the amount so used may be determined on the basis of the above figures, using enough of such other phosphorus ester to give a final phosphorus content within the range contributed by tri-cresyl phosphate when employed in the stated range of proportions. I have used butyl stearate and other oiliness agents in amounts ranging from 0.1 per cent to 5.0 per cent.

One of the most effective lubricants within the present invention is prepared by adding 0.8 per cent of tri-cresyl phosphate and 0.8 per cent of a sulfurized sperm oil composition containing approximately 50 per cent by weight of sulfurized sperm oil, prepared as set forth herein, no supplemental oiliness agent being employed in this instance.

The following description is illustrative of the benefits of the invention in actual practice.

In preparing a lubricant for crank-case lubrication of aviation engines operating at high temperatures and high pressures, I used as a base oil a highly refined Pennsylvania residual oil having an SAE classification number of 60. To this oil I added 0.8 per cent by weight of a refined composition containing about 50 per cent sulfurized sperm oil prepared in accordance with the foregoing description. I also added tri-cresyl phosphate in an amount corresponding to 0.8 per cent by weight of the original oil. The mixture con-

taining the base oil, sulfurized sperm oil and tricresyl phosphate was thoroughly mixed by stirring until the blend was entirely homogeneous and clear.

In the following tables, I give the results of various tests showing the improvements in lubricating properties attributable to the invention. In the tables the highly refined petroleum lubricating oil used as a base in compounding is referred to as base oil and the lubricating composition prepared according to the invention and having the specifications last given is referred to as compounded oil.

In Table II there is afforded a comparison between the load-carrying capacity of the base oil and that of the compounded oil, as shown by the Almen test.

TABLE II
Almen test

	Base oil	Compounded oil
Lever load, pounds.....	8	26
Journal speed, R. P. M.....	600	600
Rubbing speed, ft./min.....	40	40
Torque, lb. ft./10.....	12	22
Unit load, lb./sq. in.: Initial, °F.....	4,000	13,000
Final, °F.....	81	89
	105	180

It will be noted that the load-carrying capacity of the base oil is greatly increased by compounding with the additions of the invention. The maximum load carried by the oil under the conditions of the Almen test has been increased over threefold.

A test (sometimes designated hereinafter as "Bearing test No. 8") has been devised to evaluate lubricants with respect to their efficiency in lubricating a bearing under conditions of high bearing loads. The test is carried out in a standard Almen bearing testing machine modified by the provision of an auxiliary "load stabilizing" hydraulic pump so designed as to keep a constant supply of oil under the piston which transmits the load to the bearing. This modification permits a constant bearing load to be applied over a prolonged period of time. The test is carried out under the following conditions using a regular Almen pin and split bushing:

Journal speed, R. P. M.....	600
Bearing speed, ft./min.....	40
Quantity of oil, cc.....	20
Initial oil temp., °F.....	80

After the test specimen is assembled, 20 cc. of oil are added at the oil reservoir, the machine is started and the bearing run in at no load for thirty seconds. After the run-in period, two pound weights are added to the loading lever every ten seconds until a load of sixteen pounds is accumulated. The machine is run for fifteen minutes with the sixteen pound bearing load and a log is made of the temperature rise of the oil in the oil reservoir. This log is interpreted by noting the number of seconds required for the temperature to rise from 150° F. to 200° F.; from 160° F. to 210° F. and from 170° F. to 220° F. Minimum acceptable values have been arbitrarily set as 150, 200 and 250 seconds, respectively. The higher the values the better the efficiency of a given oil in cooling the bearing. After the sixteen pound load has been carried for fifteen minutes the bearing load is increased by adding two

pound weights to the lever every ten seconds until thirty-two pounds have been accumulated on the lever and carried for ten seconds. After this, the machine is ordinarily stopped and the test specimen inspected, although in some instances, the loading is continued past the thirty-two pound point until failure occurs.

While results from this test are not a substitute for actual field service tests, nevertheless I have found that this modified Almen test is extremely valuable in determining the relative qualities of various oils, and in predicting the performance of those oils under service conditions. In effect, it serves as a test of oiliness or lubricity under bearing pressures and temperatures over a rather wide range.

When the base oil referred to above was subjected to the modified Almen test just described, the bearing failed entirely during the initial loading period when 8 lbs. had been added to the lever, and before the first stage of the test could be completed; operation under a 16 lb. load could not therefore be determined by this method. The compounded oil, however, successfully passed this part of the test. The remaining data obtained in testing the compounded oil are given in Table III below.

TABLE III

Modified Almen test (Bearing test No. 8)

Heating rates, seconds:	
150-200° F.....	150
160-210° F.....	240
170-220° F.....	280
Maximum load, lbs. on lever arm.....	36+
Unit load, lbs./sq. in.....	18,000+

In order to obtain information as to the advantages of the compounded oil in comparison to the base oil when placed in actual service, a service test was devised as follows: A standard Waukesha fuel testing engine is coupled to a cradle-type electric dynamometer. This engine is of single-cylinder type having a bore of 3¼ inches, a stroke of 4½ inches, and a compression ratio of 4.7:1.0. In the test, the piston is of cast iron with four compression rings and one oil-control ring, all located above the wrist pin. At the start of the test, three liters of the oil to be tested are placed in the crank-case. The engine is then run for twenty-five hours at a speed of 900 R. P. M. with the spark and the air-fuel ratio adjusted to give maximum power. The coolant temperature is maintained at 350° F. At the completion of the test, the engine is stopped and dismantled and the piston is examined. The performance of the oil is then rated according to the condition of the piston, in keeping with the following scale, in which the rating number increases as the piston condition becomes worse:

Piston condition performance rating

- No. 1.—No ring stuck, and no heavy hard deposit.
- No. 2.—Top and/or oil ring stuck on a small part of its circumference.
- No. 3.—Top and/or oil ring completely stuck.
- No. 4.—Top and oil ring completely stuck, end ring partially stuck.
- No. 5.—Top, 2nd, and oil rings completely stuck.
- No. 6.—Condition No. 5 with 3rd and/or 4th ring partially stuck.

In Table IV below there are given the results of a service test made on the base oil and on the compounded oil, a comparison being afforded of the effect of the lubricant on the piston con-

dition and also of the characteristics of each lubricant before and after the service test.

TABLE IV
Service test

	Base oil	Compounded oil
Operating time, hours.....	25.....	25.....
Brake horsepower developed, average.....	3.09.....	3.25.....
Fuel used: Grade.....	Aviation gasoline octane rating 73.	Aviation gasoline octane rating 73.
Fuel consumption, pounds:		
Total.....	63.8.....	62.9.....
Per BHP per hour.....	0.825.....	0.773.....
Temp., average, °F.:.....		
Cooling liquid.....	350.....	350.....
Cylinder head.....	659.....	661.....
Crank-case oil.....	146.....	151.....
Piston condition, No.....	3.....	1.....

	Base oil		Compounded oil	
	Before test	After test	Before test	After test
Gravity, ° API.....	28.7	27.7	28.8	27.8
Viscosity, SUV:				
100° F.....	1,494	1,712	1,477	1,588
210° F.....	117	127	116	120
Viscosity index.....	104	103	102	101
Neutralization No.....	nil	0.30	0.12	0.24

It will be noted that the results of this service test show how many significant advantages of the compounded oil of the invention over the base oil; the horsepower developed is greater, fuel consumption lower, the piston condition is decidedly better in that there was no ring sticking when using the compounded oil as against two rings stuck with the base oil, and less than half the total amount of carbon is formed on the pistons. The compounded oil also stands up much better in service than does the base oil.

For the lubrication of certain engines, such as certain types of high-output aviation engines, it is sometimes unnecessary to provide a lubricating composition having a load bearing capacity as high as that of the specific example given hereinabove. The composition of that example may, of course, be employed in many such engines, but I have found that compositions containing as much as 0.8 per cent tri-cresyl phosphate and 0.4 per cent of sulfurized sperm oil may be unsuitable if at some point in a particular engine the lubricant is subjected to contact with certain alloys, especially copper alloys, at extremely high temperatures. I have referred above to such a condition in connection with the exhaust-valve parts of a well known aviation engine. For the lubrication of an engine of this particular type, I have found it desirable and advantageous to employ lubricant compositions containing reduced amounts of tri-cresyl phosphate or the like and extremely small amounts of a sulfurized ester or mixture of esters, such as sulfurized sperm oil, together with a neutral oiliness agent, preferably butyl stearate. This combination, in the proportions indicated, is remarkably satisfactory and the results obtained by its use could not be predicted from consideration of the effects of the individual addition agents considered alone.

To illustrate this type of compound more specifically, I have prepared such a compounded oil from an aluminum-chloride refined Pennsylvania residual oil of SAE 60 classification.

To this oil I added, in one instance, 1 per cent

by volume of an inhibitor containing 33 per cent by weight of butyl stearate (technical grade), 58 per cent by weight of a commercial well-refined grade of tri-cresyl phosphate and 9 per cent by weight of a sulfurized sperm oil composition consisting of a mixture of equal parts of sulfurized sperm oil and highly refined lubricating oil of low viscosity, said mixture having been acid-treated at 260° to 275° F., using 2 pounds of acid-treated clay per gallon.

The proportions of the three addition agents contained in this inhibitor mixture I have found to be most advantageous. The addition of 1 per cent by volume of the mixture to the oil referred to above resulted in a composition containing approximately 0.38 per cent by weight of butyl stearate, 0.67 per cent by weight of tri-cresyl phosphate and between 0.05 and 0.06 per cent by weight of highly refined sulfurized sperm oil.

In this specific example, although the amount of sulfurized sperm oil and tri-cresyl phosphate are comparatively low, there is a definite improvement in the pressure-carrying characteristics of the oil. This is due to a combination of the effects of the three agents, the total effect being greater than the sum of the effects of the individual agents when added alone. The small amount of sulfurized sperm oil is effective in producing a very slight but effective coating on copper and other alloys with which the oil is brought into contact at high temperatures, this coating having the effect of preventing more serious corrosion.

The small amount of sulfurized sperm oil, in addition to providing an anti-corrosion effect, is extremely effective, especially at high temperatures, and, even in the small amount referred to, in contributing load-carrying capacity and reducing bearing wear, it is also effective in preventing undesirable corrosion of alloy bearings. It will, of course, be obvious that, if such corrosion develops, then no amount of extreme pressure agent will be effective.

If the amount of tri-cresyl phosphate is increased, without the presence of a small amount of the sperm oil, to such extent as to obtain the same load-bearing characteristics, the resultant compositions exhibit an undesirable tendency to develop sludge and produce corrosion effects. The same is true if the tri-cresyl phosphate is eliminated and the amount of sulfurized sperm oil increased, although the types of corrosion and sludging thus encountered are different. Both sulfurized sperm oil and tri-cresyl phosphate, when used in larger amounts appear to develop, under certain conditions, solid deposits, while under other conditions tri-cresyl phosphate frequently produces an acid etching effect, especially where water is present.

The butyl stearate and tri-cresyl phosphate used together promote oiliness and increased pressure, bearing properties, and the sum of the effects of these two compounds cannot be attributed to either one alone.

This oil has been found extremely satisfactory in actual service tests and represents a practical solution of an extremely difficult and important lubricating problem. Whereas the oil alone, when subjected to the service test referred to hereinabove, gave a No. 6 piston condition, the compounded oil of this particular example, when subjected to the same test, resulted in a No. 1 piston condition. The oil alone when subjected to the modified Almen test referred to herein-

above failed upon loading to a total of 8 lbs. in 2 lb. increments, 10 seconds apart, whereas the compounded oil carried a load of 16 pounds for a period of 900 seconds, thereby demonstrating adequate pressure-bearing properties. Accelerated oxidation tests in which the oil alone and the oil composition of this example, respectively, were maintained in bubbling contact with high-copper bronze at a temperature of 572° F. for an extended period of time showed definite advantages in favor of the compounded oil, with respect to corrosion of copper alloys at high temperatures.

These tests, of course, are valuable as control methods and in developing particular compositions for a given purpose. In the last analysis, service tests, under actual service conditions, must govern. Subjected to these tests, the various compositions of my invention, when prepared and employed in accordance with the principles set forth herein, have proved themselves satisfactory lubricants even under the drastic conditions referred to hereinabove.

My invention is not limited to lubricants of the character and for the purposes specifically described hereinabove, but may be applied to the manufacture of lubricants for various purposes, particularly those intended to be used under conditions imposing excessive burdens on uncompounded petroleum lubricants. Thus, I have found that in accordance with my invention it is possible to prepare improved gear lubricants, more specifically lubricants for the transmission gears of automotive vehicles and the like. In preparing gear lubricants, the base oil will ordinarily comprise an oil of the character generally employed for such purposes. I have successfully employed solvent-refined residual Mid-Continent lubricant oils, having viscosities of from 50 to 250 seconds at 210° F. Such oils will ordinarily carry from 6 to 8 pounds in the standard Almen test and from 8 to 16 pounds in the standard Timken test.

The addition agents which I have found most suitable for gear lubricants comprise sulfurized sperm oil, tri-cresyl phosphate or an equivalent oil-soluble phosphorus ester, and chlorinated paraffin wax. Ordinarily I employ any two of these three types of agents, although all three may be used where desired.

In using sulfurized sperm oil and chlorinated paraffin wax in combination, I ordinarily prefer to employ from 5 to 10 per cent of sulfurized sperm oil (or double that amount of the diluted refined sperm oil referred to hereinabove) and from 1 to 10 per cent of chlorinated paraffin wax, the percentage being stated in terms of the base oil employed. Oils so compounded will carry from 16 to 30 pounds in the Almen test and from 37 to 60 pounds in the Timken test.

Mixtures of the base oil referred to with from 1 to 5 per cent of tri-cresyl phosphate and from 5 to 10 per cent of chlorinated wax will carry from 16 to 20 pounds in the Almen test and from 27 to 60 pounds in the Timken test. Compounded oils prepared by adding from 1 to 5 per cent tri-cresyl phosphate and from 5 to 10 per cent of sperm oil to the base oil referred to will carry in excess of 30 pounds in the Almen test and from 30 to 42 pounds in the Timken test.

It should be noted at this point that tri-cresyl phosphate does not act as an oiliness agent at low pressures; it is used primarily to increase the load-bearing capacity of the oil. Chlorinated wax and sulfurized sperm oil both give

greater oiliness at low pressures, while sulfurized sperm oil also gives greater oiliness at high pressures. By using the combinations referred to hereinabove, it is possible to prepare oils which exhibit improved results over a wide range of bearing temperatures and pressures, whereas with any one of the individual addition agents alone, the improved properties are obtained in a restricted range only. Moreover, for such purposes, larger amounts of addition agents may be employed than is true of crank case lubricants.

However, crank case lubricants such as aviation oils, motor oils, etc. are an important part of the present invention. As shown ante, aviation oils containing relatively small amounts of tri-cresyl phosphate and sulfurized sperm oil, together with an additional oiliness agent have many advantages. My improved lubricants having the stated advantages are not limited to the specific combination or illustrations given ante.

For instance, other additional oiliness agents are employed in lieu of the butyl stearate. In fact, I have found generally that fatty alcohols may be advantageously substituted for the neutral fatty esters, as the additional oiliness agent. In such embodiments of my invention, fatty alcohols such as cetyl, lauryl, stearyl and other high molecular weight aliphatic monohydric alcohols are used. These fatty alcohols are mild but stable oiliness agents. Also, they serve as an oxidation inhibitor at high temperature tending to prevent the oxidation imparted by the rest of the components. These fatty alcohols in combination with the tri-cresyl phosphate and sulfurized sperm oil yield a very effective mixture for improving mineral lubricating oils, particularly aviation oils.

Further, in such combinations, part or all of the tri-cresyl phosphate may be replaced with phosphite esters. Lubricants in which part of the tri-cresyl phosphate has been replaced with alkylated-phenyl phosphites are advantageous. In making such lubricants, it is advantageous to employ alkylated-phenyl phosphites derived from alkylated phenols having anti-oxidant properties and prepared by the method set forth in the copending application Serial No. 99,662 of Cantrell and Turner.

In making such improved lubricants, it is advantageous to first blend together the several improvement agents, namely, the fatty alcohol, tri-cresyl phosphate, alkylated-phenyl phosphites and sulfurized sperm oil and then add this mixture to the mineral lubricating oil. An advantageous inhibitor composition for this purpose is one containing 37 per cent by weight of a commercial, well refined grade of tri-cresyl phosphate, 25 per cent of cetyl alcohol, 23 per cent of alkylated phenyl phosphites and 15 per cent of a sulfurized sperm oil composition consisting of a mixture of equal parts of sulfurized sperm oil and highly refined lubricating oil of low viscosity, said mixture having been clay treated at 260° to 275° F. using two pounds of acid-treated clay per gallon.

By adding 1 per cent by volume of the foregoing inhibitor composition to an aluminum-chloride refined Pennsylvania residual oil of SAE 60 classification, I obtained an improved lubricating oil containing approximately 0.42 per cent by weight of tri-cresyl phosphate, 0.28 per cent by weight of cetyl alcohol, 0.26 per cent by weight of alkylated phenyl phosphites and 0.08 per cent by weight of highly refined sulfurized sperm oil.

This improved lubricating oil is particularly useful in lubricating aviation motors. The finished aviation oil has a resistance to oxidation and to sludging equal to or better than that of the base oil.

Other improved lubricants may be produced by adding this inhibitor composition to various mineral lubricating oils. In making some lubricants, as high as 5 per cent of the inhibitor composition may be added. Likewise, similar inhibitor compositions containing other fatty alcohols such as lauryl or stearyl alcohols may be employed in making my improved lubricants. The use of fatty alcohols as the additional oiliness agent renders it feasible to prepare lubricants containing up to 1.5 per cent tri-cresyl phosphate and 1.0 per cent of sulfurized sperm oil. These alcohols in combination with the other components give good stable lubricants. However, smaller amounts of tri-cresyl phosphate and sulfurized sperm oil are usually sufficient to give all the improvements desired. For many purposes those containing as little as 0.25 per cent of tri-cresyl phosphate and 0.01 per cent of sulfurized sperm oil are effective when from 0.1 to 5.0 per cent of a fatty alcohol is also present. Also, the total amount of phosphate and phosphite esters is usually below 1.0 per cent. The usual range of the phosphite is between 0.1 and 1.0 per cent. In many cases, the total amount of all added improvement agents is also less than 1 per cent as is evident from the examples given ante.

It will be obvious to those skilled in the art that while I have set forth hereinabove various examples of my invention, my invention is not to be construed as limited to the details of such illustrative examples but may be variously embodied and practiced within the scope of the claims hereinafter made.

What I claim is:

1. An improved lubricant adapted for use as a crank case lubricant in internal combustion engines operated at high pressures and high temperatures comprising a petroleum lubricating oil having incorporated therein from 0.01 to 1.0 per

cent of a sulfurized monoester of a high molecular weight fatty acid and from 0.25 to 1.5 per cent of tri-cresyl phosphate, and from 0.1 to 5.0 per cent of a monohydric, high molecular weight fatty alcohol.

2. The improved lubricant of claim 1 wherein part of the tri-cresyl phosphate is replaced with an alkylated phenyl phosphite.

3. The improved lubricant of claim 1 wherein said fatty alcohol is cetyl alcohol.

4. An improved lubricant adapted for use as a crank case lubricant in internal combustion engines operated at high pressures and high temperatures comprising a petroleum lubricating oil having incorporated therein 0.08 per cent of refined sulfurized sperm oil, 0.42 per cent of tri-cresyl phosphate, 0.26 per cent of an alkylated phenyl phosphite and 0.28 per cent of cetyl alcohol by weight on the lubricating oil.

5. An improved lubricant adapted for use as a crank case lubricant in internal combustion engines operated at high pressures and high temperatures comprising a major amount of hydrocarbon lubricating oil and minor amounts of sulfurized sperm oil and tri-cresyl phosphate, together with an additional oiliness agent, said additional oiliness agent being a high molecular weight aliphatic monohydric alcohol.

6. An improved lubricant adapted for use as a crank case lubricant in internal combustion engines operated at high pressures and temperatures comprising a petroleum lubricating oil having incorporated therein from 0.01 to 1.0 per cent of a sulfurized monoester of a fatty acid having a high molecular weight, and from 0.25 to 1.5 per cent of an oil-soluble ester of an acid of phosphorus, and from 0.1 to 5.0 per cent of a monohydric, high molecular weight fatty alcohol.

7. The improved lubricant of claim 6 wherein said fatty alcohol is cetyl alcohol.

8. The improved lubricant of claim 6 wherein said fatty alcohol is lauryl alcohol.

9. The improved lubricant of claim 6 wherein said fatty alcohol is stearyl alcohol.

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