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PHOSPHONIC ACIDS

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This invention relates primarily to the manu-
facture of additives for lubricating oils, and the
particular object is to produce soaps or salts for
addition to lubricating oils having high deter-
gent characteristics for the elimination or pre-
vention of the formation of gummy, resinous,
and varnish-like materials that tend to form
in severe service internal combustion engines
such as Diesel engines and to deposit upon pis-
tons, piston rings and the like. Other objects
of the invention include easy production of ad-
ditive materials employed in mineral lubricating
oils to produce lubricants of the mentioned type.
Another object is to produce such lubricants
with high film-strength characteristics. An-
other important object is to furnish suitable
processes and materials for producing motor lu-
bricating oils of the indicated type from lubri-
cating oils of high viscosity index as represented
by the so-called "highly paraffinic" lubricating
oils, and also from lubricating oils of low vis-
cosity index. Subject matter disclosed herein
but not claimed is claimed in my companion
application Serial No. 333,605, filed May 6, 1940,
entitled Method of producing lubricating oil.

Not all mineral lubricating oils as they are
initially refined under modern refining methods
are wholly adapted to some of the use for which
they are intended, and apparently no such lu-
bricating oil is adapted for use under severe
service conditions such as use in Diesel engines
and high out-put aviation engines. Such oils
need modification, as by addition of modifying
agents. They need modification to increase their
film-strength and also to reduce their tendency
to deposit gummy, resinous, and varnish-like ma-
terial in the engine, particularly upon the pis-
tons and rings as above indicated. Most lubri-
cating oils, including the oils of high viscosity
index (namely the so-called "highly paraffinic"
mineral lubricating oils) require additives to
adapt them to severe service uses in order to
increase their film-strength and to overcome ex-
cessive tendencies towards deposits in the engine
as mentioned. This applies not only to paraf-
finic type oils but also to naphthenic type or so-
called Western or asphalt base oils. More re-
cently it has been particularly desired to adapt
oils of high viscosity index to Diesel engine uses
and other severe service uses. The term "vis-

cosity index" is well understood in the arts and
is defined in Chemical and Metallurgical Engi-
neering, vol. 36 (1929) page 618, in an article
by Dean and Davis. Quite commonly, where ad-
ditives have been introduced into lubricating
oils to attain these ends, corrosive conditions
have been developed in the engine probably by
catalytic influences of the additive. This has
been especially noticeable where highly corro-
sion-sensitive bearings have been employed in
Diesel engines. The result has often been that
such bearings have failed. For example, in the
case of copper-lead bearings acidic conditions
which probably are due to oxidation of the min-
eral oil have developed that resulted in the
leaching-out of lead from the copper-lead bear-
ings thereby leaving a damaged bearing surface.
Similar results have been encountered with cad-
mium-silver bearings and other bearings of this
corrosion-sensitive classification.

The invention

By the present invention the objectionable
features above described as existing in the men-
tioned lubricating oils apparently have been
overcome. The invention resides primarily in
oil-soluble salts (or "soaps") of phosphonic acids
produced by phosphorizing the so-called highly
paraffinic mineral lubricating oil fractions (high
V. I. oils), or other hydrocarbons such as naph-
thenic lubricating oils, paraffin wax, petrola-
tum, kerosene, gasoline, hydrocarbon deriva-
tives thereof such as halogenated or oxidized
paraffin wax or lubricating oil or other hydro-
carbon fraction, and other hydrocarbons or
derivatives from any other source; and then
oxidizing or air-blowing the resultant phos-
phorized materials to produce phosphonic
acids from which the salts are formed. The
invention further resides in those materials for
the incorporation into such mineral lubricating
oils which are represented by calcium salts of
such phosphonic acids, or substantially equally
oil-soluble salts of such phosphonic acids of
which salts or soaps formed with another alka-
line earth metal such as magnesium or barium,
or other oil-soluble metal soap such as those of
lead, zinc, aluminum, sodium, potassium, caesium,
cerium and the other more common metals in-

cluding manganese, iron, cobalt, nickel, cadmium, silver, tin, bismuth, chromium, titanium, vanadium, mercury, molybdenum and the like, or soaps of organic or nitrogen bases.

The invention applies particularly to such oils where the proportion of the soap is in the order of about one-half per cent to about 3% or in quantity sufficient to produce the desired detergent characteristics and at the same time not impart to the oil any appreciable viscosity increase.

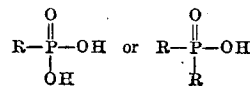
I have discovered that the phosphonic acidic materials themselves without saponification impart very high film-strength properties when used in similar proportions, and can be used alone or in conjunction with the soaps, and the invention extends also to these materials and their use in oils. The invention also comprises the methods of manufacture disclosed.

I have also discovered that the use of oil-soluble phosphonic salts or soaps of the type described when used in proportions around 1% based on the oil have the property of controlling the deposition of gummy, resinous, and varnish-like or lacquer-like materials upon the walls of pistons and about the rings and similar parts of internal combustion engines including diesel engines and other severe service engines. I have also discovered that these salts exert no appreciable catalytic influence towards the oxidation of lubricating oils and the formation of corrosive acids as is sometimes the case when soaps of other forms of acids are employed, such as carboxylic acids. Also soaps of the present type possess characteristics of maintaining non-corrosive conditions insofar as their effect on highly sensitive bearings and the like is concerned. This may be due to the fact that the metal element of the salt or soap may combine with any corrosive acids that might possibly form and thereby liberate the non-corrosive phosphonic acids which in turn appear to exert corrosion-inhibiting influences kindred to corrosion-inhibiting influences exerted by the phosphonic salts or soaps themselves. Or possibly, there is no decomposition of the phosphonic salts or soaps and they maintain their original form which continuously exerts said influences tending to inhibit development of corrosive conditions.

Phosphonation

The materials particularly used under this form of the invention are obtained from phosphorizing mineral lubricating oil fractions of so-called highly-paraffinic character or of high viscosity index. According to the best modern authorities on the constitution of mineral lubricating oil of this type, the molecules are not entirely aliphatic or chain compounds but are mixed or complex molecules containing aromatic or naphthenic rings protected by aliphatic or paraffinic side chains which may in themselves be straight chains or branched chains. Or such oils may be mixtures of molecules wherein aromatic or benzene rings are protected by aliphatic chains, and wherein naphthene rings are protected by aliphatic chains. Naphthenic type lubricating oils may be used, and also other hydrocarbons such as paraffin wax and the like as above mentioned. On phosphorizing these materials the phosphorus grouping apparently enters more readily to replace a hydrogen atom connected to one of the carbons of the aliphatic chain. This phosphorus grouping apparently may be connected either to an end carbon of the

chain portion of the molecule or to an intermediate carbon of said chain portion, and the phosphorus grouping of the resultant phosphonic acids apparently has the arrangement:



However, while there seems to be ample evidence that this is the structure, I nevertheless do not wish to be bound in all events by this theory. It is possible also that a portion of the total phosphorus may be attached to naphthenic rings, or to aromatic rings, when such are present.

Other hydrocarbons such as wax, gasoline, kerosene, gas oil, solvent extract from lubricating oil, coal tar distillate fractions, and hydrocarbon derivatives such as chlorinated or oxidized or otherwise modified hydrocarbons also may be similarly phosphorized with the production of similar useful compounds. Halogenation or oxidation may facilitate phosphonation or subsequent reactions. If oxidized starting materials are employed and they contain carboxylic acids, phosphonation should be complete enough to reduce all the acids before air-blowing, or the carboxylic acids may be removed before phosphonation as by selective solvent extraction, because the acids represent the objectionable type of material which it is sought to avoid in the present product.

In phosphorizing mineral lubricating oils, preparatory to oxidizing the phosphorized materials to yield the phosphonic acids, I have employed different procedures. According to one procedure the oil itself is heated to incipient "cracking" or decomposition and yellow phosphorus lumps are added with heating at appropriate temperatures such as up to about 600° F. until the phosphorizing reaction is complete. (Yellow phosphorus is the commercial term for white phosphorus which ordinarily contains small quantities of red phosphorus sufficient to give it a yellow color.) In this instance, a nitrogen, carbon dioxide or other inert atmosphere may be employed for safety purposes. According to another operation the mineral oil is first chlorinated to facilitate subsequent phosphorination. This may be done by bubbling a chlorine gas therethrough until the weight is increased by chlorine addition to an extent of perhaps 10% but preferably less, e. g. 2%. This material after a suitable washing is then phosphorized by heating for appropriate periods to incipient "cracking" or decomposition with addition of yellow phosphorus lumps until suitable phosphorination is produced. In this case lower temperatures such as a maximum of about 475° F. will suffice.

Oxidation

Following phosphorization for an appropriate time, for example one to three hours, the charge is cooled to about 200° F. for example, and air then passed therethrough at a slow enough rate to prevent temperature rise much above 250° F. When the oxidation reaction ceases to promote temperature increase, further air-blowing may or may not be resorted to, but if continued for the purpose of insuring sufficient or further oxidation the air-blowing may be extended for a suitable time, for example about one hour, at a higher temperature, for example at about 300° F. In

all cases, air-blowing should be carried out in a manner to attain sufficient oxidation of the phosphorus in the phosphonated oil, but should not be severe enough to oxidize more than minute quantities of the unphosphorized oil molecules. Formation of carboxylic acids by oxidation of the oil hydrocarbons is to be avoided as far as possible.

Saponification

When suitable oxidation of the original phosphorized material has been accomplished to insure production of the desired phosphonic acids, the charge is then mingled with a suitable alkaline earth metal hydroxide, such as calcium hydroxide, in the presence of diluting quantities of water, and the batch heated at a temperature around or somewhat above the boiling point of water for a time to effect saponification or conversion of the phosphonic acids into the calcium soap or salt, which material after filtering and washing is ready for incorporation into an appropriate mineral lubricating oil such as the high viscosity index or low viscosity index oils herein described, which oil in any given instance may or may not be of the same type as that which is phosphorized.

Examples

One specific method for the preparation of calcium phosphonates as herein described was as follows:

A paraffinic oil which was a highly solvent-refined lubricating oil of SAE 20 grade having 89 V. I., was heated to 300° F. and four separate five per cent additions (20% total) by weight of yellow phosphorus were made while heating from 300° F. to 400° F. Heating was then continued until the temperature reached the boiling point of the oil (600° F. to 650° F.) and the temperature of the oil was held at that point for one-half to one hour. The oil was heated at all times in a nitrogen atmosphere. The oil was then cooled to 200° F. and a stream of air was passed through the oil at a rate slow enough to prevent temperature rise above 250° F. After air-blowing caused no further evolution of heat, the oil was cooled, washed free of water-soluble acids, and the calcium soap was prepared by heating the resulting phosphonic acids with calcium hydroxide at 300° F. for one-half hour. The batch was filtered at 300° F. for removal of solids. This resulted in about 4% soap in about 96% unmodified oil. The same method was used to produce a similar product from a Western naphthenic lubricating oil having a viscosity of 600 seconds Saybolt Universal at 100° F.

Another method which was employed is as follows:

Nine quarts of said SAE 20 grade oil having a V. I. of 89, were chlorinated at 150° F. to 170° F. by bubbling a rapid stream of chlorine through the oil. The process was continued until 2.0% of chlorine had been absorbed as judged by the increase in weight of the charge. The chlorinated oil was then heated and stirred with 2% of yellow phosphorus. The temperature was raised to 475° F. and held at that point for three hours. (In another instance the temperature was raised to about 625° F. which insured removal from the product of the trace of chlorine retained when a temperature of only 475° F. was used.) The total charge was cooled to 200° F. and a rapid stream of air passed through the oil until heat evolution ceased (approximately 15 minutes), the temperature being held in the

meantime to a degree below 210° F. by use of cooling water. The charge was then filtered through a filter precoated with a fine diatomaceous earth. A small sample was then water washed, and the acid number found to be 8.05. The total charge was then again air-blown for one hour at 200° F. to 210° F. to insure complete oxidation of the phosphorus, after which the acid number of a small, water-washed sample was found to be 8.25. The whole charge was then washed with an equal volume of water, and the wash water drawn off.

The charge was then heated and stirred for one hour with 200 grams of calcium hydroxide and 300 ml. of water at 200° F. The water was evaporated off by final heating to 230° F. The charge was cooled, 200 ml. of ethyl alcohol was added to insure complete saponification, and the heating and stirring was continued for one hour until the temperature reached 300° F. The total charge was then filtered as above.

The filtered oil tested as follows:

Soap number.....	8.4 mg. KOH/g. oil
Phosphorus.....	0.25%
Sulfate ash.....	1.36%
Soap number, calculated	
from ash.....	11.4 mg. KOH/g. oil
Soap number, calculated	
from phosphorus.....	9.0 mg. KOH/g. oil

This signifies about 10% soap in about 90% of unmodified oil.

This same process may be used to treat naphthenic base oils as above described to produce corresponding products. Also all these procedures are appropriate for the treatment of the other hydrocarbons mentioned to yield similar useful products.

To indicate desirable variations of the methods above outlined, a continuous method may be employed wherein the oil charge is placed in the mixer and the required amount of the above-described yellow phosphorus stirred into the batch at a temperature above the melting point of the phosphorus (e. g. at about 215° F.), and the mixed charge then run continuously through a heating coil and heated in a range between 200° F. and 300° F. or at about 700° F. Such a heated charge is then passed from the heating coil through a cooling coil, and then into the top of a closed chamber and oxidized by continuously passing a stream of air up through the incoming charge of phosphonated oil. The air-blowing is preferably accompanied at a temperature not lower than 150° F. in order to avoid a reaction rate which is too slow and preferably at a temperature not above 250° F. in order to avoid undesirable color intensification of the hydrocarbon which would take place at higher temperatures. The oxidized oil and oxidation products are withdrawn from the bottom of the oxidizing chamber and passed into a saponification vessel.

If desired water may have been added to the charge undergoing oxidation in amounts ranging from 0.1% to 10% by volume, or water may be added to the charge after it enters the saponifier, or the oxidized charge may be settled and the clear oil separated from the sludge and recycled into the original charge. In the latter case the sludge is then passed into the saponifier.

In the saponifier a quantity of dry hydrated lime, or hydrated lime mixed with water especially when no water enters with the charge into the saponifier, is stirred into the oil and

maintained in contact therewith at suitable temperature and pressure and for a time to effect neutralization by the lime to produce calcium soaps. For example, one hour's contact time at 210° F., or ten minutes' contact at 260° F., both at atmospheric pressure, have been found satisfactory, additional water being supplied if required.

Instead of separating the clear oil from the sludge and saponifying only the sludge, or saponifying the whole oxidized charge, the clear oil may be separated from the sludge and itself saponified separately from the sludge. The acids retained in the clear oil make very desirable phosphonates and there is an advantage in separating oil from the sludge due to avoidance of emulsification difficulties in some instances.

By these procedures a concentration as high as 15% of oil-soluble calcium salts of the phosphonic acids can be obtained. By passing the saponified charge through an elongated horizontal saponifier saponification may be effected continuously, and the stream may then be passed through a drier if desired for removal of water by evaporation, or the stream may be passed through a vacuum still. This vacuum still may also be employed to increase the concentration by removal of any desired proportion of unmodified oil to leave an oil residuum of the desired soap concentration, the overhead being returned to the initial charging stream.

The amount of yellow phosphorus has been varied from about 0.5% to about 20%, but most desirable conditions apparently have been obtained when using phosphorus concentrations between about 2% and 10% based upon the original charge. Phosphonation has been effected at temperatures as high as 900° F. with contact time as low as about two minutes. Practical conditions appear to be to phosphonate in a range between about 500° F. to 700° F. at a gauge pressure of about 50 lb./sq. in. for at least two minutes and preferably about five minutes or somewhat more.

As to the saponification, both batch processes and continuous processes have been successfully employed with the direct production of concentrates ranging from 4% to 25%, the higher percentage having been obtained by employment of the vacuum still to reduce the unconverted oil content while operating by the batch method.

The various salts or soaps produced by methods herein given may be readily incorporated into suitable mineral lubricating oils by mere agitation with slight warming if required. Ordinarily about 1% to 1.5% of the salt will be employed in the oil. However, as conditions vary percentages perhaps as low as 0.25% to 0.5% may be used and higher percentages up to 2% or perhaps 3% may be employed. Larger percentages are of doubtful practical value and merely increase the cost, but unless very large do not materially increase the viscosity of the product over that of the original mineral lubricating oil.

A lubricating base oil particularly desired for addition of these soaps thereto is one of highly paraffinic type produced by modern dewaxing and heavy solvent-refining treatments to yield a viscosity index of from about 80 (or 75) to 100 or higher. Also naphthenic base oils may be used such as the Western oil of 600 viscosity at 100° F. above mentioned as a starting material for the formation of phosphonic soaps, or a 700 viscosity oil or the like.

Oils which have been used in practicing this invention and products therefrom possess the following specifications:

	Oil A (77.9 V. I. base oil)		Oil B (90 V. I. base oil)			Oil C naphthenic	
	Base oil	Base oil + about 1% soap	Base oil	Base oil + about 1% soap	Base oil + 1.5% soap	Oil	Oil + 1.5% soap
Viscosity Index—Dean and Davis	77.9	79.0	89.4	88.9	90.6	13.1	10.0
Viscosity gravity constant	0.818	0.824	0.810	0.810	0.812	0.878	0.879
Gravity, °A. P. I. at 60° F.	27.5	26.9	29.4	29.3	29.1	20.2	19.9
Viscosity Saybolt Univ. sec. at—							
100° F.	563.2	549.6	347.4	359.2	350.2	727.2	764.6
210° F.	63.2	62.1	54.0	54.5	54.3	59.8	60.5
Flash point, ° F.							
C. O. C.	465	445	445	430	445	390	385
Fire Point, ° F.	520	525	510	505	510	435	440
Pour Point, ° F.	5	5	5	0	10	-10	-5
Sulfate ash	0.0	0.15	0.0	0.16	0.26	0.0	0.25
Soap No.	0.0	1.0	0.0	0.99			
Phosphorus	0.0	0.025	0.0	0.02			
Chlorine	0.0	Trace	0.0	0.0			
Carbon residue			0.04	0.22			
Color, NPA		8+	4.5	8+	4.5	3+	6+
Acid. No., 95% alcohol method			0.04	0.12	0.6		

The presence of lower viscosity oil in concentrate added to highly V. I. oils serves to produce drop in viscosity and flash.

The above described mineral lubricating oils containing calcium phosphonates produced by the methods above described were tested on a Falex film strength testing machine with the results given in the following table, and the 90 V. I. oil with and without about 0.7% of the free phosphonic acids produced by the first method also was tested for film strength with the results appearing in the following table:

Results of Falex tests

Tests on the well known "Falex" tester of the Faville-Le Vally Corporation of Chicago, Illinois, are as follows:

Jaw pressures	90 V. I. oil	Torque—in. lb.		
		90 V. I. oil plus 0.3% calcium soap of phosphonic acids made from unchlorinated oil	90 V. I. oil plus 0.7% phosphonic acids made from unchlorinated oil (acid No. 1.0)	90 V. I. oil plus 1% calcium soap of phosphonic acids made from chlorinated oils
200	6	5	5	5
300	9	7	7	7
400	12	10	9	9
500	14	12	13	12
600	16	14	15	14
700	19	17	18	17
800	21	19	20	20
900	25	21	24	22
1000	29	25	28	24
1100	Failure	27	32	26
1200		30	36	27
1300		35	39	29
1400		Failure	43	Failure
1500			48	
1600			51	
1700			54	
1800			55	
1900			63	
2000			Failure	

The oil from 77.9 V. I. oil and containing about 1% of calcium salts (produced by the first method) was run in a Diesel engine for 100 hours and gave exceptionally clean pistons and rings. Only a slight discoloration due to varnish deposits was found on the piston, and only slight deposits around and behind the rings were found.

No ring quadrants were stuck and there was no bearing corrosion. The same oil was tested for corrosion on sensitive bearings of the copper-lead type by oxidizing for about 100 hours and then subjecting the bearings to an augmented corrosion test with said oxidized oil. No corrosion was developed in 16 hours. The same oil containing 1.5% of the calcium soap produced even cleaner pistons. However, the base oil (without soap addition) stuck the rings at 39 hours in a similar engine run. The same base oil on the same kind of corrosion test with 1% of a calcium carboxylic acid soap showed heavy corrosion at the end of four hours.

The 90 V. I. oil containing about 1% soap when run in an ordinary internal combustion engine of the automobile type showed an exceptionally clean piston with unusually clean, free rings after a run of 100 hours.

These oils were prepared and tested both where they contained and where they did not contain as an oxidation inhibitor about 1% of a phenol extract fraction obtained from the original base oils themselves. The phenol extract obtained in producing the oils by a well-understood method was in turn re-extracted with phenol containing about 20% water to recover about 15% to 20% of the initial extract. This re-extract possessed a lower A. P. I. gravity (i. e. heavier) than the whole extract. This extract fraction will also tend to act as a solubilizer for sludges and the like, but in many cases this function is not sufficiently valuable to offset increased tendencies toward carbon deposit and the like.

The oil indicated in the third column under "Oil B" in the first table and containing 1.5% soap, which was made by the continuous process described above, was run 500 hours in a Diesel engine, resulting in exceptionally clean pistons and rings with no lacquer or varnish deposit on pistons or skirts, and only traces of carbon and lacquer in ring grooves.

When these oils were subjected to an oxidation test similar to the Indiana test but modified to approximate motor conditions (the oils having about 1% of calcium soap of the present invention) they yielded the following acid numbers:

	Contain- ing 1% extract	No ex- tract
Acid number increase after—		
24 hr. oxidation, mg. KOH/g.-----	0.15	0.10
48 hr. oxidation, mg. KOH/g.-----	0.30	0.20
96 hr. oxidation, mg. KOH/g.-----	0.67	0.71

These results may be contrasted with the same oils containing equivalent amounts of calcium soap of carboxylic acids which showed acid numbers of 0.92 mg. KOH/g. after 24 hours, 2.14 after 48 hours, and 5.52 after 96 hours.

As indicated, similar oils have been used where in the same high viscosity index base lubricating oils were employed with the same amounts of calcium soaps of the phosphonic acids described, but without the extract fraction as an oxidation inhibitor. The oils were not substantially different except for slight changes in the viscosity index and viscosity gravity constant and a somewhat higher color. An extract fraction in the low V. I. (naphthenic oils) is ordinarily not required since they already contain kindred constituents.

In connection with high V. I. oils a further advantage is found in the fact that these phosphonic acid soaps do not precipitate from the

oils or from oil concentrates even after long standing in storage or in the laboratory, as is a common tendency with high V. I. oils containing other soaps. In other words, they do not cloud. There is no gelling tendency, and the soaps are sufficiently soluble in the high viscosity index oil described that concentrates containing as high as 20% to 25% soap or even more may be prepared and shipped or stored. Another advantage of these soaps and oils containing these soaps, is that they do not hydrolyze, and where moisture conditions are encountered in practical engine uses the presence of the moisture does not affect the soap nor cause separation nor gelling nor emulsification. Similarly, where the phosphonic acids themselves are added to the oils as film-strength or oiliness agents, no objectionable results are encountered upon storage or standing or use in the presence of moisture and the like.

Phosphonic acids, anhydrides and soaps

In addition to producing phosphonic acids or their anhydrides and their soaps from naphthenic base oils and from high V. I. paraffinic oils in the order of 80 to 90 V. I., I have also produced such acids and their anhydrides and their soaps from oils having a viscosity index of about 100. These various oils have ranged from 20 SAE grade to 50 SAE, and concentrates containing 15% and more of the oil-soluble soap have been produced directly. In addition to treating lubricating oils, whether modified or by halogenation or oxidation or not, I have also produced highly satisfactory phosphonic acids and their soaps from wax-oil slurries produced in the de-waxing of lubricating oils, and from deoiled water-white paraffinic wax obtained from solvent-refining of slack wax, and the like. These materials may or may not have been modified as by halogenation or by oxidation to facilitate phosphonation where advantageous or desired. The mentioned anhydrides may be formed in the absence of water.

The phosphonic acids and anhydrides which have been produced by the above described methods have contained 16 or more carbon atoms per molecule. To insure adequate oil-solubility of their soaps such acids should contain at least about 10 carbon atoms per molecule. This permits use even of acids from materials as light as kerosene and gasoline as previously indicated. In blending the phosphonates with the oils, the soap addition has generally been based on the sulfate ash produced. It may vary from a calcium sulfate ash of about 0.1% to about 0.6%. This will vary the soap content in the finished oil from about 0.25% to about 3%, the lower the molecular weight of the acids (lower number of carbons per molecule) the greater will be the calcium content and the higher the calcium sulfate ash test. Ordinarily, in the order of about 0.75% to 1.5% of the soap will be adequate.

In addition to using calcium soaps it will be appropriate, at least for some uses, to employ magnesium soaps or barium soaps, i. e., the alkaline earth metal soaps. The other alkaline earth metal soaps and the light metal soaps such as aluminum and zinc, and likewise the alkali metal soaps may also be used. Similarly, other oil-soluble metal soaps or organic or nitrogen base soaps may be used as stated above. However, I prefer for most practical Diesel engine purposes the calcium soaps here described, or barium soaps, and in general, I prefer to employ around

1% to 1.5% of soaps from those acids produced from lubricating oil fractions of the type indicated.

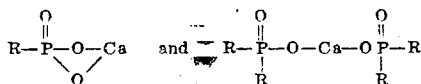
The general ratio of calcium to phosphorus in the calcium soaps produced according to this invention is around 1 to 3. Ignition of these calcium soaps leaves an ash of various calcium phosphates, and analysis shows that over 85% of the ash can be accounted for from calcium and phosphate content by ascribing the formula $\text{Ca}_2\text{P}_2\text{O}_7$ to the ash. Long saponification of the acids shows the acid number to be substantially equal to the saponification number by the A. S. T. M. method. These soaps are stable at temperatures as high as 800° F. when heated with the oil, and no cloudiness or inorganic precipitation is thus formed. The soaps are non-catalytic toward oil oxidation and do not become catalytic upon the addition of other metal catalysts. The use of these soaps in oils as indicated indicates remarkable corrosion inhibiting properties for alloy bearings of the copper-lead and cadmium-silver type now being used in Diesel engines and the like. For example, a paraffinic lubricating oil of about 90 V. I. has shown harmful corrosion when oxidized to an acid number of around 1.0 mg. KOH per gram of oil. When adding calcium phosphonates of this invention to the same lubricating oil, the oil was found to be non-corrosive to such bearings when oxidized to an acid number of above 1.0, including ranges up to 2.2 acid number where employing 1.5% of the soap to yield a sulfate ash of 0.25.

As to the nature of the phosphorus compounds formed there is evidence that phosphonic acids are produced having a molecular weight in the general range of 400 to 500. Apparently traces of compounds of the type

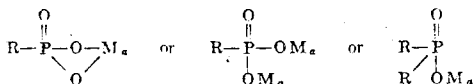


are formed. These may be very desirable oxidation inhibitors but on the other hand they may be objectionable in the combustion chamber where lead gasolines are used due to the tendencies to form P_2O_5 and thereby form objectionable lead phosphates. It is to be noted that most of the P_2O_5 formed in the phosphorizing operation will have been blown out and recovered in the oxidizing stage. The remainder is removed by filtration as the insoluble salt after saponification.

The calcium soaps produced apparently are of the form



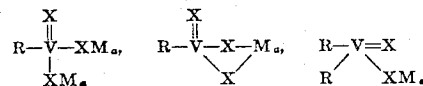
Thus the general soap structures as related to any appropriate metal or other base will possess one or more of the following forms:



where R is any hydrocarbon radical or derivative thereof, and M is a metal or organic base material having alkaline properties, a being an integer or fraction according to the valence of the metal or organic base.

Similarly, sulfur or selenium may be substituted for oxygen. Also arsenic may be substituted for phosphorus for many uses, suitable

processes being employed to produce the acids and their soaps. Thus, the soaps or salts used are of the following types:



where R is any hydrocarbon radical or derivative thereof, V is arsenic or phosphorus, X is oxygen, sulfur or selenium, M is a metal or organic base material having alkaline properties, and a represents a fraction or an integer according to the valence of M. The invention also extends to these features.

The arsenic, sulfur and selenium compounds mentioned may be more or less readily prepared. Arsenic compounds, e. g. arsenonic acid, may be made in much the same way as the phosphonic acids by heating the hydrocarbon with arsenic in corresponding temperature ranges up to perhaps 700° F., and the arsenated hydrocarbon then blown as described for the phosphonated hydrocarbon. The soap will then be prepared as previously described. Instead of blowing to form the acidic materials by oxidation, thio-acids or seleno-acids may be made by mixing a calculated amount of sulfur or selenium with the phosphonated or arsenated hydrocarbon and heating below temperatures at which the arsenic or selenium would replace hydrogen in the hydrocarbon molecule. Such a temperature would be for example about 300° F. or below but high enough for the reaction to proceed.

As indicated in the table above showing "Results of the Falex tests" the phosphonic acids themselves as here disclosed impart high film-strength to lubricating oils. Along this line, a valuable acid fraction having high film-strength characteristics was obtained by extracting a phosphorized oil which had been oxidized to form phosphonic material, in the absence of moisture, the extract being made with a solution of 50% methyl ethyl ketone and 50% methyl alcohol. The extracted material, which may initially have been in the form of an anhydride in the absence of water was separated by the evaporation of solvent on a hot plate by heating to 300° F. A viscous oily liquid remained having an acid number and a saponification number of 40. The material may have been a kind of polymer. When 1% of this was added to a 90 V. I. oil, the oil resisted failure until a jaw pressure of 2950 was reached, compared to failure value of about 1200 for the uncompounded oil.

These last mentioned materials, the various acids and the anhydrides herein disclosed, and the soaps, as well as the oils produced and the various processes described, all constitute portions of the invention, as do other modifications thereof which will be understood by those skilled in the art.

Thus, other acids suitable for the production of soaps according to this invention may be prepared by reacting the mineral oil fraction with 20% phosphorus trichloride and 20% aluminum chloride at a temperature slightly under about 200° F. with refluxing for 8 to 10 hours or until evolution of HCl ceased. The mass then hydrolyzed with hot water and the aluminum chloride washed free. The batch containing the excess oil is then air-blown (as above) to convert the phosphorus compounds into phosphonic acids which may be converted into soaps as above described in connection with the other methods.

I claim:

1. A method for producing phosphonic acids comprising heating a mineral oil to incipient cracking in the presence of phosphorus to cause phosphorus to enter the hydrocarbon molecule, and air blowing the phosphorized hydrocarbon to yield phosphonic acids.
2. A method comprising heating a normally non-gaseous petroleum hydrocarbon with phosphorus at a temperature within the range of about 200° F. to 800° F. to cause phosphorus to enter the molecule, air blowing the phosphorized hydrocarbon within a temperature range of about 150° F. to 250° F. to yield phosphonic acids.
3. The preparation of phosphonic acids and their anhydrides by admixture of phosphorus with a petroleum hydrocarbon at elevated temperature to cause the phosphorus to react with the hydrocarbon and oxidation of the resulting mixture by contact with oxygen.
4. Preparation of phosphonic acids and their anhydrides where petroleum oil and about 2% by weight of phosphorus are mixed at temperatures of 200° F. to 230° F., passed through a heater at about 700° F. with about five minutes contact time, and the resulting product air blown at temperatures approximating 150° F. to 200° F.
5. The method comprising heating a normally non-gaseous petroleum hydrocarbon at an incipient cracking temperature with a small proportion of an agent of the class consisting of phosphorus and arsenic to effect chemical combination with hydrocarbon, and reacting such modified hydrocarbon at elevated temperature between about 150° F. and 250° F. with an agent from the class consisting of oxygen, sulfur and selenium to form acidic materials.

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