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STABILIZED HYDROCARBON COMPOSITION

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This invention relates, as indicated, to the stabilization of hydrocarbon compositions. The term "hydrocarbon compositions," as used herein, is intended to include liquid compositions which are essentially derivatives of petroleum, naturally occurring oils of the type represented by animal, vegetable and marine oils, and derivatives of the same.

More specifically, this invention relates to the stabilization of hydrocarbon compositions such as lubricants which are usually essentially mineral oil. This invention also is applicable to the stabilization of lighter fractions of petroleum such as are used as fuels.

It is well known that liquid hydrocarbon compositions of the character above identified are subject to deterioration as by oxidation and polymerization, for example but not by way of limitation, during storage and handling and are also subject to deterioration which proceeds at a more rapid rate during use of these compositions.

For example, the various oils mentioned above and the lighter fractions used as fuels have a tendency, on storage, to oxidize, polymerize, or otherwise deteriorate to form gums and the like; and when such compositions are used, particularly under conditions of high temperature, deterioration proceeds at a more rapid rate to the production of gums, sludges and other oxidation and/or polymerization products. This deterioration is manifested by discoloration of the liquid hydrocarbon body; the generation within the body of flocculant material; the precipitation from the body of the more serious types of deterioration products, such as sludge; and the deposit of varnish- or shellac-like deposits on metallic surfaces with which the compositions come in contact during use.

Liquid hydrocarbon compositions, such as refined mineral oil, when employed for use as lubricants in internal combustion engines, whether of the ignition or Diesel type, are generally subject to the various conditions above-named which tend to cause deterioration of such oil composition. Oxidation and/or sludging of liquid hydrocarbon compositions employed as lubricants in such engines is usually accelerated by the relatively high temperatures to which such compositions are subjected. This is particularly true in engines of the Diesel type in which the operating temperatures are generally somewhat higher than those in the so-called ignition type.

It is a principal object of our invention, therefore, to provide for the stabilization of compositions of the character defined in order to reduce the tendency of the same to decompose, particularly in the manner indicated.

It will also be observed that the addition agents employed for the prescribed purpose are, in themselves, new compositions of matter.

Other objects of our invention will appear as the description proceeds.

Broadly stated, this invention comprises the stabilization of liquid hydrocarbon compositions of the character previously identified, by the inclusion therein of a minor proportion of oil-soluble phosphorus-bearing products resulting from the reaction of phosphorus tri-chloride (PCl_3) with a compound of the class consisting of lactic acid, esters of lactic acid and salts of lactic acid.

As hereinafter more fully explained, the stabilization of certain types of liquid hydrocarbon compositions and especially when the same are used for certain specific purposes, may be effected by the inclusion therein of certain derivatives of the aforesaid reaction product or products or portions thereof, which derivatives may be prepared, for example, by halogenation and/or treatment with an alkali or other base to form a salt, or ester-salt.

The following are illustrative of specific embodiments of our invention:

A material, which, for purposes of convenience in referring to the same herein, we shall designate as P. M. L., is prepared by the reaction of methyl lactate with PCl_3. The relative proportions of methyl lactate and PCl_3 used in the preparation of P. M. L. are given in the following table, as well as the properties of the end product.

P. M. L.

Methyl lactate	104 parts by weight.
PCl_3	45 parts by weight.
Weight of product	74.5 parts by weight.
Weight of material removed by distillation	31.8 parts by weight.
Yield	65%.
Average mol. wt	312.
Boiling point	230° C.
Melting point	Liquid at room temperature.
Sp. gr. at 20° C	1.252.
Ref. index at 26° C	1.4365.
Color	Light yellow.
Phosphorus	10.9%.
Chlorine	1.12%.
Acid number	415.

Soluble to extent of about 1% in Penna. 150 (S. U. S. at 100° F.) neutral.
Completely miscible with water and ethyl alcohol.

The methyl lactate is placed in a reaction vessel equipped with an agitator and reflux condenser. The vessel and agitator are preferably of glass or enamel. The PCl_3 is added slowly and the temperature of the reactants maintained below 60° C. during the addition of the PCl_3. The mixture is stirred continuously during the addition of the PCl_3. The temperature of the reactants may be controlled by the rate of the addition of the PCl_3. After the addition of the PCl_3 is complete, the mixture is agitated until the temperature begins to decrease, indicating that the PCl_3 has reacted to some extent with the methyl lactate. The slow addition of PCl_3 accompanied by stirring until a decrease in temperature is noted insures against loss of PCl_3

whose boiling point is 76° C. and also gives a higher yield than when these precautions are not taken. After the temperature of the reactants has begun to drop, heat is applied and the temperature of the reactants is raised to 120° C. This temperature is maintained for 3 hours. A slight reaction is apparent until the mixture has been heated at 120° C. for about 2 hours and 45 minutes. The mixture is stirred continuously all during the time of adding the PCl_3, while the temperature is maintained at 120° C.

After completion of the reaction between the methyl lactate and PCl_3, i. e., after the mixture has been maintained at a temperature of 120° C. for about 3 hours, the end product may either be used as such as a stabilizing addition agent for liquid hydrocarbon compositions or the end product may be distilled at atmospheric pressure and all of the material which distills over at 130° C. or less may be discarded. Whether the end product as produced or the refined end product derived by removal of the more volatile products is used depends largely upon the use for which the ultimate composition containing the stabilizing addition agent is designed. In general, the less volatile part of the reaction product, or that part which contains combined phosphorus, is preferred for our purpose.

We believe the reaction produces two general types of compounds:

(*a*) Chlorine-containing compounds, for example, the type in which chlorine has been substituted for the hydroxyl group of the hydroxy-ester; and

(*b*) Phosphorus-containing compounds, for example, the type in which the hydroxyl group has lost hydrogen (which forms HCl with chlorine removed from the PCl_3) so that the oxygen of the hydroxyl group becomes attached to a phosphorus atom.

For example, in the reaction of methyl lactate with PCl_3, part (*a*) would be principally the methyl ester of chlor propionic acid and part (*b*) principally esters of phosphorous acid such as $P(OC_2H_4COOCH_3)_3$ and $POH(OC_2H_4COOCH_3)_2$. It appears that the constituents of the reaction product described as part (*b*) are responsible for the stabilizing effect when the product is used in accordance with our invention. However, for most purposes, part (*a*) is not deleterious, and for some purposes may even be advantageously included. Part (*a*) is, in general, more volatile than part (*b*) and may, therefore, be easily separated from the latter by distillation at atmospheric or sub-atmospheric pressure.

The specific properties given in the table above are those for the refined materials.

The following table gives the results obtained by the addition of minor amounts of P. M. L. (the refined material) to several different representative commercial oils, and oils treated with other addition agents.

Ex. No.	Composition					Oxidation test								Corrosion test (lead-bronze)
						Conradson carbon		Viscosity S. U. S. at 210° F.			Naphtha insoluble			
	Hexachlor diphenyl oxide	Ortho dichlor benzene	Methyl stearate	Butyl stearate	Percent P.M.L.	Original	At 48 hours	Original	At 48 hours	Percent viscosity increase	Hours for 10 mg.	Hours for 100 mg.	Milligrams at 48 hours	
NAPHTHENIC BASE ACID TREATED S. A. E. 30 DIESEL OIL														
1	Untreated					.08	2.15	54.9	70.9	29.2	14	34	249	−.24
2					.03	.08	.88	54.7	60.4	10.4	28.5	*b*	29	−.26
MID-CONTINENT S. A. E. 30 MOTOR OIL														
3	Untreated					.32	1.67	63.1	74.4	17.9	13.5	44	121	−.18
4					.03	.43	1.27	63.9	69.0	7.1	32.5	*b*	42	−.02
5					.06	.43	1.61	67.1	71.0	5.9	28.5	*b*	56	−.06
6	.30	.30				.68	1.82	63.6	73.1	16.0	17.0	46	111	−.51
7	.30	.30			.06	.57	1.28	63.1	68.3	8.2	37.0	*b*	34	−.12
8	.50	.50	.25	.25		.41	2.05	61.6	72.2	17.2	13.0	45	118	−.02
9	.50	.50	.25	.25	.03	.78	1.18	62.1	69.0	11.1	35.0	*b*	40	−.06
COMMERCIAL S. A. E. 10 MOTOR OIL HAVING A V. I. OF 67														
10	Untreated					.09	2.81	42.8	48.2	12.6	7.0	24.5	375	−.22
11					.03	.04	1.20	42.7	45.5	6.5	19.5	41.5	160	−.07
12	.30	.30				.03	3.12	42.9	48.9	14.0	5.0	20.0	414	−.26
13	.30	.30			.06	.01	1.54	42.8	45.9	7.3	19.0	40.0	189	−.09
PENNSYLVANIA S. A. E. 40 MOTOR OIL														
14	Untreated					1.25	3.52	82.7	104.0	26.3	*a*	*b*	5	−.08
15					.03	1.46	2.51	83.0	95.7	15.3	*a*	*b*	2	−.46
16					.06	1.51	2.51	83.0	95.8	15.4	*a*	*b*	2	−.38
17	.30	.30				1.67	3.54	82.3	104.0	26.5	*a*	*b*	3	−.38
18	.30	.30			.06	1.24	2.32	81.4	94.0	15.5	*a*	*b*	0.7	−.09
19	.50	.50	.25	.25		1.19	2.80	79.6	98.9	24.2	*a*	*b*	6	−.35
20	.50	.50	.25	.25	.03	1.40	2.60	81.9	94.9	15.8	*a*	*b*	0.6	−.10
PENNSYLVANIA S. A. E. 10 MOTOR OIL														
21	Untreated					.23	.94	47.1	49.8	5.7	25.0	*b*	45	−1.15
22					.03	.16	.45	46.5	47.8	2.8	*a*(64.0)	*b*	2	−.84
23					.06	.30	.50	46.3	47.6	2.8	*a*	*b*	3	−.31
24	.30	.30				.15	1.40	46.3	50.6	9.3	22.0	*b*	65	−1.40
25	.30	.30			.06	.20	.75	46.9	48.7	3.8	38.5	*b*	17	−.05
26	.50	.50	.25	.25		.21	1.19	46.5	50.0	7.5	23.0	*b*	85	−1.40
27	.50	.50	.25	.25	.03	.21	.81	47.3	49.1	3.8	39.0	*b*	19	−.17
28		*.75				.13	1.13	47.3	50.8	7.4	23.0	*b*	45	−1.15
29		*.75			.03	.19	8.7	46.6	49.0	5.1	34.0	*b*	39	−.07

*Methyldichlorstearate.
a=did not produce 10 mg. in 48 hours.
b=did not produce 100 mg. in 48 hours.

The determinations which appear in the foregoing table, such as, for example, Conradson carbon, viscosity determinations and naphtha insoluble were determined on samples prepared by an oxidation test procedure which is in every respect similar to that prescribed by the Standard of Indiana oxidation test, excepting that a piece of iron wire is submerged in the oil during the test.

The data given in the column headed "Corrosion" has been determined in accordance with the standard Shell corrosion test using lead bronze as the metal.

A series of tests substantially duplicating those given in the foregoing table but employing the unrefined P. M. L., i. e., the product immediately resulting from the reaction between methyl lactate and PCl_3 and without distilling off any of the end product as hereinbefore specified, were run with substantially the same results as those given in the foregoing table. It would appear, therefore, that it is not necessary for most uses to refine the P. M. L. before it is used as an addition agent.

The esters which are suitable for use as one of the components of the reaction with PCl_3 in the preparation of the stabilizing addition agent of our invention, may, for example, be any of the esters produced by reacting any of the alcohols, and preferably any of the mono- or di-hydroxy low molecular weight alcohols, such as any of the following:

Methyl alcohol
Ethyl alcohol
Propyl alcohol
Butyl alcohol
Ethylene glycol
Propylene glycol
Trimethylene glycol
Cyclohexanol
Benzyl alcohol
Furfuryl alcohol

with lactic acid.

We have found the methyl ester to be preferable for our purpose in most cases.

Very small amounts are effective, in most cases less than one percent, and usually a fraction of 1%, e. g. from about 0.001 to about 0.2%. For use in mineral lubricating oil (e. g. a motor oil for automobile, aviation, or Diesel engines) amounts from about 0.01% to about 0.1% are suitable, and usually about 0.03% is preferable.

As indicated above, our invention also contemplates the use of oil-soluble derivatives of the reaction products above identified. (In this connection we are more particularly concerned with the phosphorus-containing constituents of the PCl_3 reaction product.) Such derivatives include the oil-soluble salts and ester-salts, which may be produced by substituting a metal or basic radicle for one or more of the alcohol-derived radicles of the ester. This is conveniently accomplished by partly or completely saponifying the PCl_3 reaction product with an alkali (e. g. sodium, potassium, ammonium, or substituted ammonium, hydroxides) in aqueous solution. Similar salts and ester-salts of metals other than the alkali metals may be formed directly by reacting the ester with the metallic base, or more readily by double-decomposition of the alkali salt (or ester-salt) with a salt of the other metal.

Our invention also contemplates the employment as a stabilizing agent of a reaction product of PCl_3 which may be prepared by either of the following methods, viz:

(a) Reacting PCl_3 with a mixture of different esters of lactic acid or a mixture of lactic acid with one or more esters of lactic acid;

(b) Reacting PCl_3 with one or two molecules of lactic acid or lactic acid ester per molecule of PCl_3 and then completing the reaction with another reactant of the class consisting of lactic acid and its esters, different from that which was initially employed.

The reacton products thus prepared are especially desirable for use for certain purposes on account of their complexity.

The effectiveness of P. M. L. in improving the properties of a lubricating composition for use in internal combustion engines with particular regard to the stability of the lubricant during use has been demonstrated by tests conducted on a liquid-cooled single cylinder 4-cycle gasoline engine rated at 2½ h.p. at 1800 R. P. M. This engine was run at 1600 R. P. M. under a load of 2 h.p. for a period of 100 hours for each test. The cooling fluid temperature was maintained at 250° F. and the temperature of the lubricant in the crankcase at 225° F. The air-fuel ratio was adjusted to maintain a value of 12.7 to 1.

In the first test, a S. A. E. 20 motor oil having a viscosity index of about 105 was employed as the lubricant and in a second test, the same oil to which .03% of P. M. L. was added was employed as a lubricant. The engine was fitted with new pistons and rings before the start of each test and after completion of the first test, the engine was taken down, thoroughly cleaned and fitted with a new piston and rings.

At the conclusion of the first test, nearly the entire skirt of the piston was very black, while at the end of the second test, the skirt showed only light deposits of dark brown material. The inside of the piston skirt at the end of the first test showed a light shellac-like deposit with a dark brown deposit on the vertical ribs, while the inside of the piston skirt at the end of the second test showed no discoloration.

The oil remaining in the engine at the completion of each test was analyzed with the following findings:

	Without inhibitor	With inhibitor
Viscosity S. U. S. at 210° F.:		
Original	56.9	58.0
Final	64.5	64.4
Percent increase	13.3	11.1
Conradson Carbon:		
Original	0.72	0.68
Final	1.40	0.82
Acid Number:		
Original	0.06	0.10
Final	0.28	0.19

From the foregoing, it will be observed that we have provided an inhibitor for liquid hydrocarbons, particularly mineral oils used as lubricants, and that such inhibitor is in itself a new composition of matter.

The liquid hydrocarbon compositions which may be stabilized by the use of the addition agents hereinbefore specified need not be pure hydrocarbons but may contain other addition agents of the type commonly employed in hydrocarbons of the class specified above. In other words, when the hydrocarbon being stabilized is a mineral lubricating oil, it may advantageously contain other addition agents such as extreme pressure addition agents on the order of halogen, phosphorus and/or sulfur compounds, as well as

corrosion inhibitors, such as phosphorus compounds, etc. and other additions commonly employed, such as pour-point depressors and the like.

When a lighter fraction, as above indicated, is stabilized, the addition agents commonly employed in such lighter fractions may also be present, as for example, the various "dopes" commonly employed in Diesel fuels and anti-knock compounds commonly employed in gasolines such as tetraethyl lead, iron carbonyl, etc.

In general, the addition agents of this invention will not be found incompatible with commonly employed anti-oxidants such as are used in gasolines and the like.

There may, however, be certain of these other addition agents which might be found incompatible with the addition agents of the present invention and in such cases, of course, the incompatible addition agent, whatever it may be, should be omitted, since it will usually be found that a compatible addition agent for the desired purpose will be available among others of those available.

Among the other addition agents with which the compounds of the present invention may be employed to advantage, as above stated, are the extreme pressure addition agents, such as the halogen, phosphorus and/or sulfur-containing compounds.

In general, we have found that the addition agents of the present invention do not detrimentally affect the extreme pressure characteristics of a mineral lubricating oil, for example, which characteristics are the result of the presence therein of the extreme pressure addition agents above-named. Moreover, where the addition agents of the present invention have been tested in lubricating compositions which also contain certain other addition agents, the extreme pressure characteristics of the resultant composition has been somewhat improved and such improvement has been traceable to the presence therein of the compounds of the present invention.

Throughout the foregoing specification and in the appended claims, reference is made to "oil-soluble" and by such term, as used herein, it is intended to indicate the ability of the addition agent to form not only true solutions with the oil to which the same are added, but also the ability to form therewith any form of substantially permanently homogeneous composition.

With certain of the more difficultly soluble addition agents to which this application relates, it may be advantageous to employ a mutual solvent as one means for increasing the "oil-solubility" of the addition agents and to also incorporate the addition agents in the oil base by special homogenizing apparatus, such as for example, that described in Cornell Patent No. 2,042,880.

Irrespective, therefore, of the manner in which the addition agent is incorporated in the liquid hydrocarbon, either as a true solution or a permanently stable homogeneous mixture, these various expedients are intended to be included by the term "oil-soluble," as employed herein. Furthermore, those addition agents which are not "oil-soluble" to any extent and which may not be incorporated in such a way as to effect any improvement in the oil, will obviously be excluded by the term "oil-soluble," as employed in the specification and in the claims.

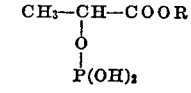
In general, the addition agents prepared in the manner specified will be sufficiently non-volatile so as to find usefulness for the purposes specified. In cases, however, where high temperatures are encountered, it will be best to select those which will neither substantially evaporate from the liquid hydrocarbon and those which will not be decomposed by the temperatures which the composition encounters in use. These limiting factors which must obviously be observed in the selection of any addition agent for use in liquid hydrocarbons are, therefore, intended to be included by the definition "stable" wherever used herein.

In the foregoing specification, reference has been made to optimum percentages within which the addition agents may be employed. It is within the contemplation of our invention, however, to admix the addition agents with the specified liquid hydrocarbons up to the limit of their solubility. This may be done advantageously in making concentrates, for example, to be blended with bodies of the same or different liquid hydrocarbons. In other words, the concentrate formed by dissolving the addition agent in a particular hydrocarbon may be dissolved or admixed with another hydrocarbon. In this way advantages of increased solubility may be realized as well as other advantages flowing from the combination of the constituent named. For example, it is within the contemplation of our invention to add to a light hydrocarbon fraction such as gasoline or Diesel fuel, minor amounts of a heavier liquid hydrocarbon such as refined mineral lubricating oil to which has been added a minor amount of the addition agents which characterize the present invention. Such combination, i. e., a major proportion of gaosline to which has been added a minor amount of a mineral oil of lubricating viscosity for internal combustion engine use, along with a minor amount of the addition agents which characterize the present invention, produces a fuel for internal combustion engines which is particularly desirable for use on account of the nature of the deposits left by the fuel in the combustion chamber, as well as the general performance of the fuel.

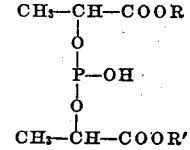
For proper results, when the compounded relatively heavier liquid hydrocarbon is essentially mineral oil having a viscosity of from about 50 to about 250 seconds Saybolt Universal at 100° F., such composition should be added to the usually lighter hydrocarbon fuel of the type boiling within the gasoline range in quantities varying from .05% to 1.50% by volume. The amount of compounded heavier hydrocarbon added to the lighter hydrocarbon fuel for optimum results will be found to be in the vicinity of .30%, i. e., in the range of from about 0.15% to 0.60%.

It will be observed that the addition agents of our invention may be classified for convenience as follows:

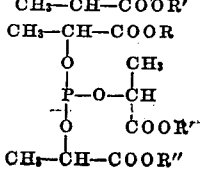
1.



2.



3.



Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the materials employed, provided the ingredients stated by any of the following claims or the equivalent of such stated ingredients be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. A lubricating composition comprising a major proportion of mineral oil, the properties of which affecting its use as a lubricant are improved by the inclusion therein of a minor proportion of an oil-soluble, phosphorus-containing product resulting from the reaction of PCl_3 with a compound of the class consisting of lactic acid, esters of lactic acid and salts of lactic acid.

2. A lubricating composition comprising a major proportion of mineral oil, the properties of which affecting its use as a lubricant are improved by the inclusion therein of a minor proportion of an oil-soluble, phosphorus-containing product resulting from the reaction of PCl_3 with lactic acid.

3. A lubricating composition comprising a major proportion of mineral oil, the properties of which affecting its use as a lubricant are improved by the inclusion therein of a minor proportion of an oil-soluble, phosphorus-containing product resulting from the reaction of PCl_3 with an ester of lactic acid.

4. A lubricating composition comprising a major proportion of mineral oil, the properties of which affecting its use as a lubricant are improved by the inclusion therein of a minor proportion of an oil-soluble, phosphorus-containing product resulting from the reaction of PCl_3 with a salt of lactic acid.

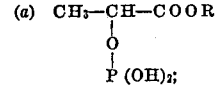
5. A composition of matter comprising at least 90% of a petroleum hydrocarbon and a minor amount on the order of .001% to about 1% of an oil-soluble, phosphorus-containing product resulting from the reaction of PCl_3 with a compound of the class consisting of lactic acid, esters of lactic acid and salts of lactic acid.

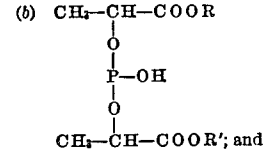
6. A composition of matter comprising at least 90% of a mineral lubricating oil of the type used in the crankcase of internal combustion engines and a minor amount on the order of .001% to about 1% of an oil-soluble, phopshorus-containing product resulting from the reaction of PCl_3 with a compound of the class consisting of lactic acid, esters of lactic acid and salts of lactic acid.

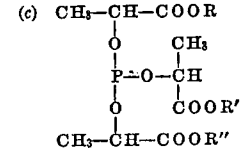
7. A lubricating composition comprising a major proportion of mineral lubricating oil of the type used in the crankcase of internal combustion engines and from about .001% to about 0.2% of a product resulting from the reaction of PCl_3 with methyl lactate.

8. As a new composition of matter, a lubricating oil composition containing a minor amount of an oil-soluble salt derived from the product of the reaction of PCl_3 with methyl lactate.

9. A composition of matter comprising a major proportion of a liquid hydrocarbon having included therein a minor proportion of an oil-soluble compound of the class consisting of:

(a)


(b)


(c)


where, R, R' and R'' are selected from the class consisting of an organic radicle, a metal, a metallic radicle and hydrogen.

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