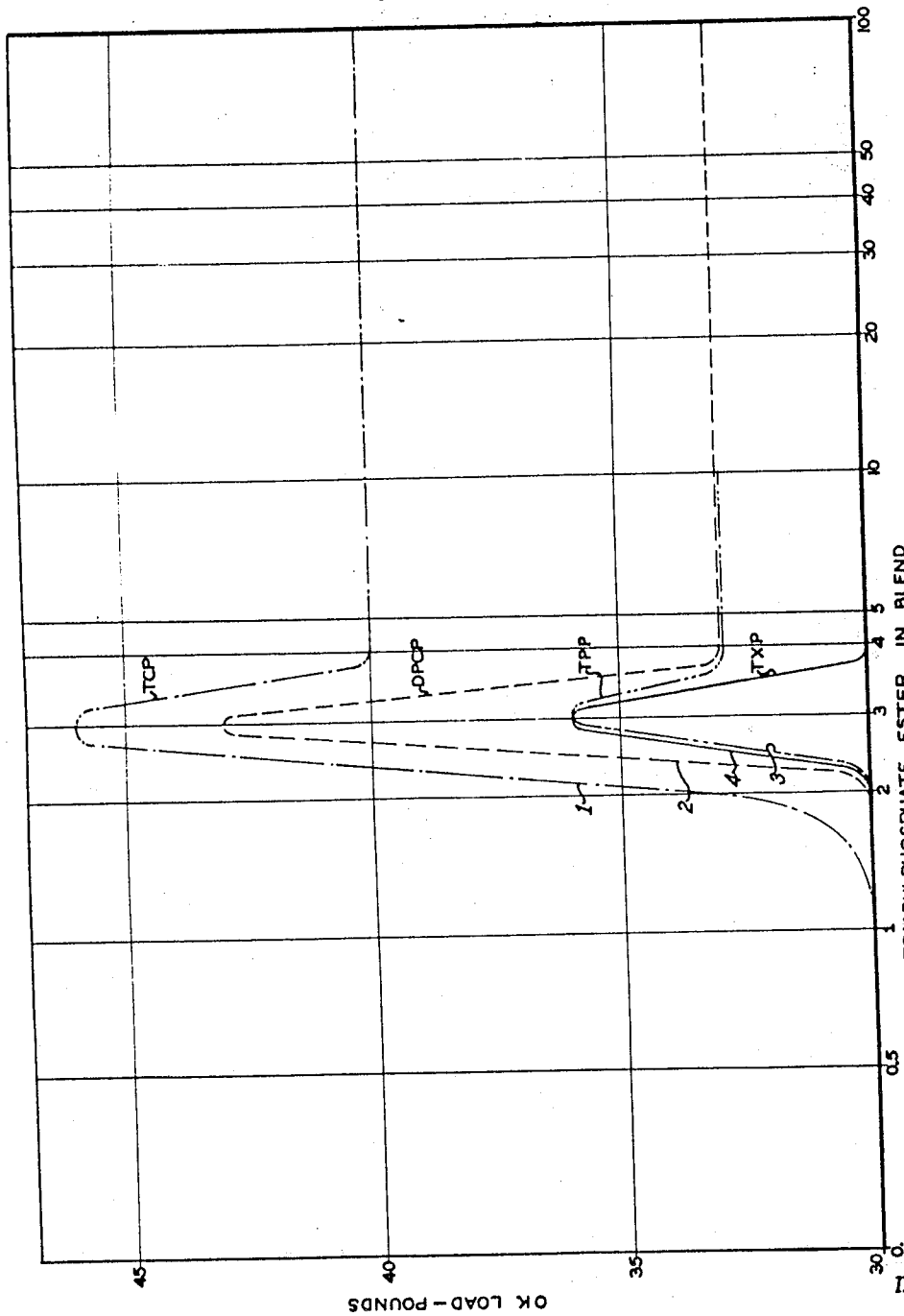
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FIRE RESISTANT-EXTREME PRESSURE AND HYDROLYSIS RESISTANT LUBRICANT COMPRISING POLYCHLORINATED DIPHENYL AND TRIARYL PHOSPHATES

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TIMKEN MACHINE TESTS ON TETRACHLOROOIPHENYL AND TRIARYLPHOSPHATE ESTER BLENDS

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FIRE RESISTANT-EXTREME PRESSURE AND HYDROLYSIS RESISTANT LUBRICANT COMPRISING POLYCHLORINATED DIPHENYL AND TRIARYL PHOSPHATES

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This invention relates to a non-flammable lubricant having improved extreme pressure and non-sludging characteristics. While it has many lubricant applications, it is particularly useful as a lubricant for turbines as well as reduction gearing for turbines, lubrication of gas compressors, and other extreme pressure, and non-flammable, fire-resistant uses. Other useful applications are as hydraulic fluid and heat transfer fluid.

The lubricant hereof comprises a poly-chlorinated diphenyl as the main component, containing from about 0.5 to 5%, preferably about 2 to 4%, of a phosphoric ester. The composition further usually includes additives for imparting improved non-foaming, viscosity index improving, anti-rust and anti-oxidant characteristics.

In general aspect this invention is to specific improvement over such non-flammable oils commonly used in the art, comprising polychlorinated diphenyl and triaryl phosphates usually blended in proportions of 20/80 to 80/20. While such lubricants are used for their fire-resistant properties as turbine oils, they are corrosive and sludge-forming when subject to the standard ASTM.D.943 Turbine Oil oxidation stability tests, properties which are cured in the present invention.

Accordingly to the present invention, it is found that the reduction of the phosphoric ester to the critical range of the 0.5 to 5% of the mixture with poly-chlorinated diphenyl, in the presence of usual oxidation or rust inhibitors, forms a far superior lubricant to the composition stated in respect to corrosion resistance and sludge formation, and indeed this lubricant readily passes the ASTM.D. 943 minimum test standards for turbine oils.

Surprisingly, moreover, in the preferred narrower range of 2 to 4% of aryl phosphoric ester to poly-chlorinated diphenyl, the lubricant acquires markedly superior extreme pressure characteristics and, in fact, the curves shown in the drawing herewith reach a maximum peak at about a 3% phosphoric ester content in the lubricant. That 3% peak is shown to be variable in extreme pressure values only with the character of the phosphoric ester, but not essentially with the quantity thereof present in the lubricant. There is apparent synergistic cooperation between the phosphoric ester and the poly-chlorinated diphenyl component in the quantity stated. The surprisingly high extreme pressure results are obtained in the narrower 2 to 4% range stated; but improved resistance to increase in acidity and sludge formation during long oxidation, according to the said ASTM test, is in the larger quantity 0.5 to 5% range stated.

The poly-chlorinated diphenyl may be tri-chlorinated diphenyl, tetra-chlorinated diphenyl or penta-chlorinated diphenyl or mixtures thereof.

The phosphoric ester may be any liquid trihydrocarbyl ester of ortho phosphoric acid of the formula

$$(RO)_3 \equiv P = O$$

wherein R is monocarbocyclic aryl such as phenyl, tolyl, xylenyl, cumenyl, ethyl phenyl, as well as mixed types wherein the hydrocarbon components of the ester as defined may be mixed. I prefer the phosphoric esters of monocarbocyclic aryl and aryls having lower alkyl substituents wherein the alkyl is methyl or ethyl. Typically,

preferred phosphoric esters are triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, phenyl discresyl phosphate and diphenyl cresyl phosphate, and the like.

Other valuable properties are imparted to the lubricant by the optional addition of certain additives. Typical additives are foam inhibitors, rust inhibitors, anti-oxidants and viscosity index improvers. These are usually used in quantities from 0 to 3%, such as from 0.1 to 3% by weight, except that the viscosity index improver would be used in quantity up to 10%, such as from 2 to 10%.

Accordingly, the composition of this invention comprises 0.5 to 5% of phosphoric ester, optionally further containing an additive of the character stated, and the balance being polychlorinated diphenyl.

It is known in the art to use foam inhibitors such as polymethoxy silane or poly-phenoxy silane of a molecular weight in the range of about 2,000 to 10,000, such additives having a very short life tending to precipitate out of the oil upon the filter or to be absorbed by sludge and dusts entering the system. It is preferred to use alpha-chloro-naphthalene in the quantity range stated, preferably about 0.5 to 3%. This defoaming material greatly reduces the foaming tendency even over large temperature ranges and what foam forms under accelerated tests is quite unstable and will quickly break.

As anti-oxidant it is preferred to use higher alkyl phenols, typically ditertiary butyl phenol or ditertiary butyl cresol, usually used in quantity from about 0.05 to 3%, preferably about 0.5 to 1%.

As rust inhibitor, alkaline earth metal sulfonate, for instance calcium sulfonate, may be used. Alternately, or combined with said calcium sulfonate, a higher alkyl or alkenyl succinic acid, preferably having from 16 to 20 carbon atoms, typically octadecenyl-succinic acid, may be used as rust inhibitor. Such rust inhibitors are in quantity of up to 1% and are preferably used in quantity of 0.01 to 0.5% or more.

For improving the viscosity index, I prefer to use a lower alkyl such as 1 to 5 carbon atoms polymerized lower alkyl acrylic or methacrylic ester such as polymethyl acrylate, polybutyl acrylate, polymethyl methacrylate or polybutyl methacrylate having from 5,000 to 15,000 molecular weight, a typical example of which is poly-butyl acrylate of molecular weight of about 10,000. Such viscosity index improver is usually added in quantity of about 2 to 10%, preferably about 4 to 6%.

To illustrate the synergistic effect upon the extreme pressure properties of a small quantity of a phosphate ester in a poly-chloro diphenyl lubricant, several tests were performed in a Timken machine and the film strength was measured for a series of lubricant blends as described above, all comprising triaryl phosphate esters mixed with tetra-chloro diphenyl in the critical quantity range of 1 to 5% by weight, and the film strength was plotted to obtain a series of curves shown in the attached drawing. These several phosphate esters tested were: (1) tricresyl phosphate, (2) diphenyl cresyl phosphate, (3) triphenyl phosphate, and (4) trixylenyl phosphate. The actual test method is identified as Fed. method Std. 791a, No. 650. The tricresyl phosphate was superior, as the curves show with diphenyl cresyl coming next.

Additional Timken machine tests upon blends with other poly-chlorinated diphenyls were conducted and the film strength is recorded in Table I. The specific identity of the compositions 2, 3, 4 and 5 are set forth under corresponding positions 2, 3, 4 and 5 of Table II below. These compositions were particularly included in this test to illustrate that other additives present for other purposes such as anti-oxidant, rust inhibitor, or viscosity index improver have no significant effect upon the extreme pressure properties.

TABLE I.—TIMKEN MACHINE TESTS (FED. METHOD STD. 791A, NO. 6505)

	O.K. load, lbs.	Rupture of the film, lbs.
Composition No.:		
2	30	33
3	40	43
4	46	50
5	40	43
100% tetrachlorinated diphenyl	30	33
99% tetrachlorinated diphenyl, 1% tricresylphosphate	30	33
98% tetrachlorinated diphenyl, 2% tricresylphosphate	33	36
97% tetrachlorinated diphenyl, 3% tricresylphosphate	46	50
96% tetrachlorinated diphenyl, 4% tricresylphosphate	40	43
95% tetrachlorinated diphenyl, 5% tricresylphosphate	40	43
90% tetrachlorinated diphenyl, 10% tricresylphosphate	40	43
80% tetrachlorinated diphenyl, 20% tricresylphosphate	40	43
100% tricresylphosphate	40	43
99% tetrachlorinated diphenyl, 1% trixylenylphosphate	30	33
98% tetrachlorinated diphenyl, 2% trixylenylphosphate	30	33
97% tetrachlorinated diphenyl, 3% trixylenylphosphate	36	40
96% tetrachlorinated diphenyl, 4% trixylenylphosphate	30	33
95% tetrachlorinated diphenyl, 5% trixylenylphosphate	30	33
100% trixylenylphosphate	30	33
99% tetrachlorinated diphenyl, 1% diphenylcresylphosphate	30	33
98% tetrachlorinated diphenyl, 2% diphenylcresylphosphate	30	33
97% tetrachlorinated diphenyl, 3% diphenylcresylphosphate	43	46
96% tetrachlorinated diphenyl, 4% diphenylcresylphosphate	33	36
95% tetrachlorinated diphenyl, 5% diphenylcresylphosphate	33	36
100% diphenylcresylphosphate	33	36
98% tetrachlorinated diphenyl, 2% triphenylphosphate	30	33
97% tetrachlorinated diphenyl, 3% triphenylphosphate	36	40
96% tetrachlorinated diphenyl, 4% triphenylphosphate	33	36
90% tetrachlorinated diphenyl, 10% triphenylphosphate	33	36
57% trichlorinated diphenyl, 40% pentachlorinated diphenyl, 3% tricresylphosphate	46	50
50% trichlorinated diphenyl, 50% pentachlorinated diphenyl	30	33

It is quite surprising that each of these materials in the quantity range stated shows much increased film strength in the minor quantity range of ester in the blend. The actual film strengths vary somewhat, one phosphoric ester from the next, but all seem to show a peak of effectiveness in concentration of about 3%, tapering off to a plateau between about 2 and 4%, as illustrated in the curves. For this reason applicant prefers in this sub-group of triaryl phosphates to use a concentration in the range of 2 to 4%, the concentration of 3% being vastly superior as an unusual peak in each of the curves illustrating the extreme pressure effect maximum at this concentration.

The following eighteen examples set forth in tabular form illustrate the effect of the low concentration, 0.5 to 5%, of the phosphate ester to resist corrosion and sludge formation, in some contrast to higher concentration in the poly-chlorinated diphenyl base when subject to the standard ASTM.D.943 Turbine Oil oxidation stability test.

That oxidation stability test consists of bubbling oxygen into a selected quantity of oil containing polished corrodible metals, in this case a coil of polished copper and steel, and measuring the acidity developed in the oil, the corrosion of the metal, and the quantity of sludge developed. Table II sets forth the actual compositions tested, and Table III sets forth the results of the tests. Certain of the compositions, it will be noted, which are identified in Table II below contain 1-mono-chloro naphthalene as a foaming agent. The actual foaming test results are set forth in Table IV below.

TABLE II.—IDENTIFICATION OF COMPOSITIONS (PERCENT WEIGHT)

Components	Number																	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Trichlorinated diphenyle												50	91.4		40.4	39.4	38.4	39.4
Tetrachlorinated diphenyle	74.4	84.4	89.4	91.4	95	91.4	91.4	90.4	90.4	91.4	91.4			90.9	50.0	50.0	50.0	50.0
Pentachlorinated diphenyle												41.4						
Tricresylphosphate	20		5	3	5						3	3	3	3	3	3	3	
Trixylenylphosphate		10																3
Diphenylcresyl phosphate										3								
Tributylphosphate						3		4										
Octyldiphenyl phosphate							3		4									
1-mono chloro naphtalene														0.5	1.0	2.0	3.0	2.0
Di-tert butyl paracresol	0.5	0.5	0.5	0.5		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Calcium petroleum sulfonate	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1	0.1	0.1	0.1
Octa decenyl succinic acid											0.05							
Butyl polyacrylate (M.W. 10,000)	5.0	5.0	5.0	5.0		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

TABLE III.—ASTM TEST D.943/54

Composition No.	Neutral number before test	Neutral number after 500 h	Neutral number after 1,000 h	Neutral number after 2,000 h	Iron and copper coils	Sludge or deposits
1	0.05		0.39	0.70	Corrosion	Sludge.
2	0.10	0.50	0.82	1.05	do	Do.
3	0.05		0.17	0.39	No corrosion	Very little sl.
4	0.04		0.14	0.29	do	No sludge.
5	0.05		0.20	0.52	Rusted iron	Do.
6	0.06	0.87	1.02	1.77	do	Sludge.
7	0.08	0.74	0.95	1.21	do	Do.
8	0.07	0.92	1.11	1.92	do	Do.
9	0.08	0.82	0.99	1.42	do	Do.
10	0.09		0.25	0.51	No corrosion	Little sludge.
11	0.12		0.27	0.43	do	No sludge.
12	0.05		0.16	0.32	do	Do.
13	0.05		0.14	0.32	do	Do.
16	0.06		0.16	0.35	do	Do.
17	0.06		0.20	0.41	do	Very little sl.
18	0.12		0.24	0.60	do	No sludge.

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TABLE IV.—FOAMING TEST ASTM D.892/58 T

Composition No.*	Foaming tendency, ml. foam after 5 minutes bubbling at—			Foam stability, ml. foam after 10 minutes rest at—		
	75° F.	200° F.	75° F.*	75° F.	200° F.	75° F.*
4	610	530	530	480	10	200
14	490	280	570	Traces	10	200
15	150	100	200	0	0	0
16	90	70	102	0	0	0
17	150	143	171	0	0	0

*After the 200° F. test.

It will be observed that above the 5% upper quantity limit of phosphoric acid the oil will deposit sludge despite the presence of anti-oxidant and will develop corrosive acidity despite the use of rust inhibitors.

As the tables show, the phosphate esters in the limited quantity are non-corrosive and do not deposit sludge. Moreover, they exhibit superior extreme pressure characteristics with respect to compositions of the art having higher quantities of phosphate esters. The triaryl phosphoric esters, for extreme pressure purposes, exhibit a striking maximum at around 3% as shown in the attached curves.

Certain modifications will occur to those skilled in the art and, accordingly, it is intended that the description be regarded as illustrative and not limiting except as defined in the claims attached hereto.

What is claimed is:

1. A fire resistant, substantially non-sludging, substantially non-corrosive fluid consisting essentially of polychlorinated diphenyl containing about .5 to 5% by weight of a tri-monocarbocyclic aryl phosphoric acid ester and stabilizing amounts of an antioxidant and of a rust inhibitor.

2. The product as defined in claim 1 wherein the tri-monocarbocyclic aryl radical is a member of the group consisting of phenyl, cresyl and xylenyl.

3. The composition as defined in claim 1 wherein the phosphate ester is tri-cresyl phosphate limited for extreme pressure properties to a quantity in the range of 2 to 4%.

4. The composition of claim 1 containing alpha chloronaphthalene as an anti-foaming agent in quantity of 0.5 to 3% by weight.

5. The composition of claim 1 containing as a rust inhibitor a small quantity of a compound of the group consisting of an alkaline earth metal sulfonate, a higher alkyl succinic acid and mixtures thereof.

6. The composition of claim 1 containing as a viscosity index improver a polymer of the group consisting of poly lower alkyl acrylates and poly lower alkyl methacrylates in quantity of from 2 to 8% by weight.

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