United States Patent

Street

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[54] SYNERGISTIC FUNCTIONAL FLUID COMPOSITIONS

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 739,912, June 17, 1968, abandoned, which is a continuation of Ser. No. 497,195, Oct. 18, 1965, abandoned.

[52] **U.S. Cl.** **252/49.9,** 252/78

[51] **Int. Cl.** **C10m 1/46,** C10m 1/30

[58] **Field of Search** 252/49.8, 49.9, 58, 78

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[57] **ABSTRACT**

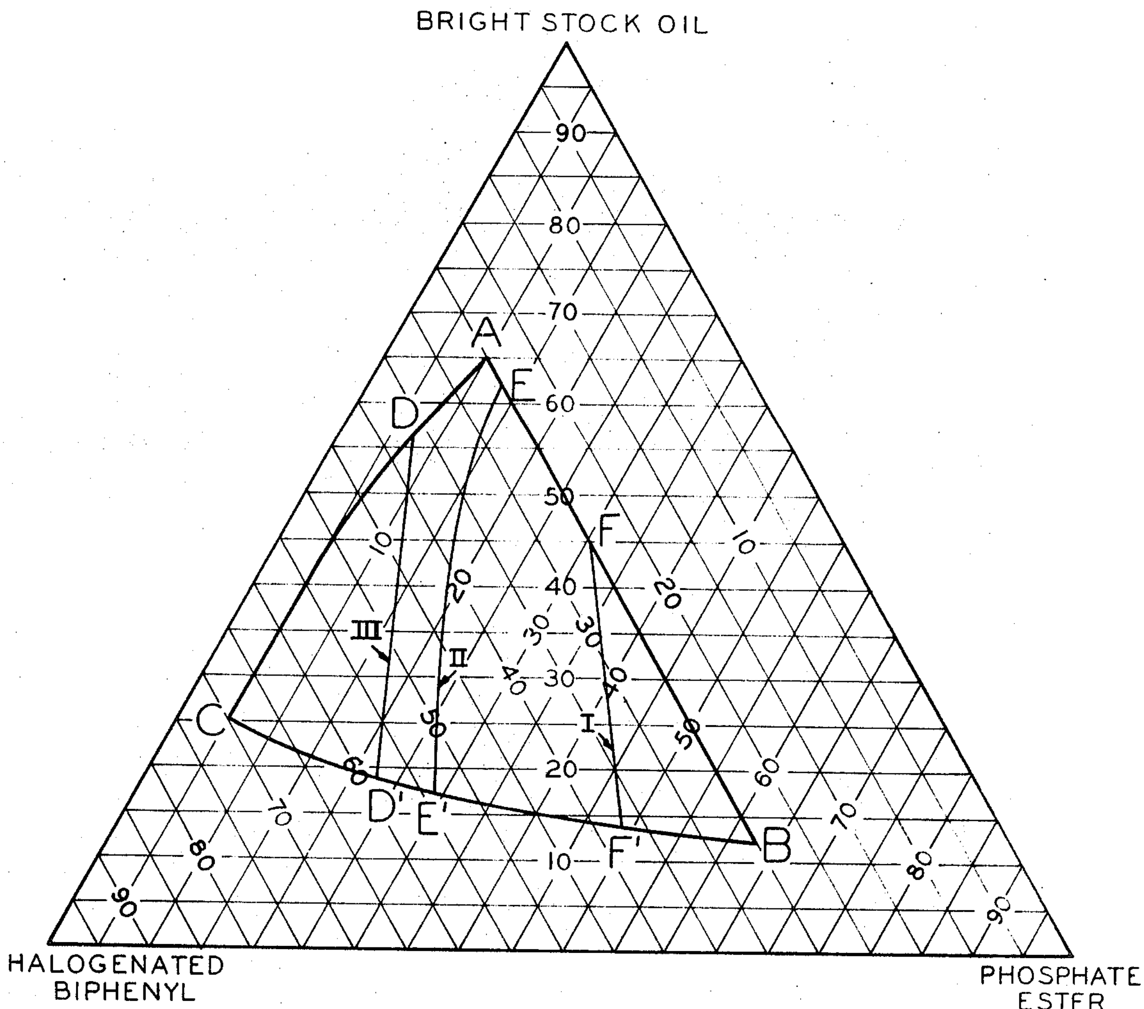
Functional fluid compositions comprising at least one halogenated compound, certain phosphate esters and certain bright stock petroleum fractions which have excellent lubricity, fire-resistance, and homogeneity and are particularly useful as lubricants and hydraulic fluids.

16 Claims, 2 Drawing Figures

I - ISOOCTYL DIPHENYL PHOSPHATE

II - TRICESYL PHOSPHATE

III - CRESYL DIPHENYL PHOSPHATE



BRIGHT STOCK OIL/PHOSPHATE ESTER/HALOGENATED BIPHENYL WEIGHT %

FIG. 1

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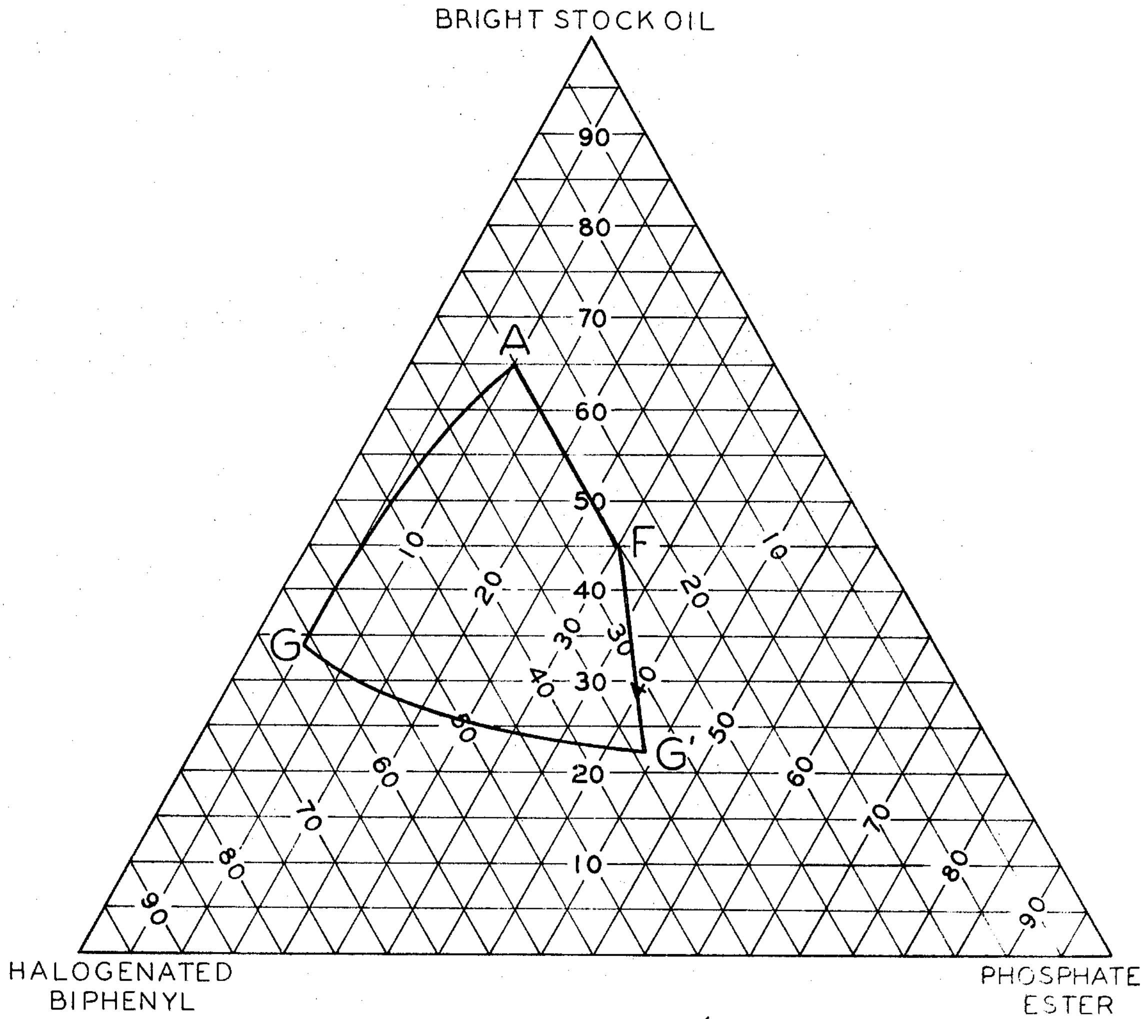

BRIGHT STOCK OIL/PHOSPHATE ESTER/HALOGENATED BIPHENYL

FIG. 2

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SYNERGISTIC FUNCTIONAL FLUID COMPOSITIONS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 739,912 filed June 17, 1968, which in turn is a continuation of application Ser. No. 497,195 filed Oct. 18, 1965 both of which applications are now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to functional fluid compositions comprising (1) petroleum bright stock, (2) at least one phosphate ester and (3) at least one halogenated hydrocarbon wherein (1), (2), and (3) are present in certain critical proportions to provide a unique combination of lubricity, fire-resistance and homogeneity.

2. Description of the Prior Art

Many different types of materials are utilized as functional fluids and functional fluids are used in many different types of applications. Such fluids have been used as electronic coolants, atomic reactor coolants, diffusion pump fluids, synthetic lubricants, damping fluids, bases for greases, force transmission fluids (hydraulic fluids) and as filter mediums for air conditioning systems. Because of the wide variety of applications and the varied conditions under which functional fluids are utilized, the properties desired in a good functional fluid necessarily vary with the particular application in which it is to be utilized with each individual application requiring a functional fluid having a specific class of properties.

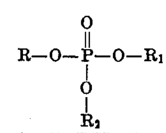
Of the foregoing, the use of functional fluids as lubricants and hydraulic fluids, particularly industrial lubricants and hydraulic fluids, has posed a difficult area of application. Increasing demands to improve the safety of industrial manufacturing as a whole has caused the extended use of fire-resistant fluids, e.g., fire-resistant lubricants and fire-resistant hydraulic fluids in a wide range of industries. The term "fire-resistant fluid" as used herein means a fluid of such chemical composition and physical characteristics that it will resist the propagation of flame under certain conditions hereinafter defined. At present there are four major classes of hydraulic fluids used in industrial hydraulic systems, which are petroleum oils, water/glycol solutions, water-in-oil emulsions and completely synthetic types. It is well known in the art that the ability of the fluid to resist flame propagation is one of degree. Fluids of the four types mentioned have varying degrees of fire-resistance and are used in applications according to the severity of the conditions, taking into account such factors as degree of danger from fire, operating temperature, being loads and cost. Many synthetic fluids such as the aryl phosphate esters offer a high degree of fire resistance and are usually employed when the danger from fire is great. The cost of synthetic fluids has restricted their use to the most severe conditions. The water containing fluids, while offering an acceptable degree of fire resistance at low cost, are not desirable in systems operating at high temperatures or where good lubricity of the fluid is required or where danger from fire is great.

Petroleum oils, while offering good lubricity, are the least fire resistant but are used in many applications having a marginal fire hazard due to their low cost and general availability. Previous attempts to render petroleum oil more fire resistant by incorporating therein known fire-resistant compounds such as phosphate esters have not produced fluids having a generally acceptable combination of lubricity, fire resistance and homogeneity. Numerous proposals have been made for correcting one or another of these properties, but correction of one property is usually effected at the expense of another property. For example, the incorporation of alkyl phosphate esters in petroleum to improve fire resistance results in fluids of marginal hydrolytic stability. The aryl phosphate esters, while providing superior fire resistance and hydrolytic stability, can only be added in small amounts due to the limited miscibility of the esters in petroleum oils and such amounts are ineffective in producing any significant increase in fire resistance. Also, previously, aliphatic and olefinic chlorinated hydrocarbons have been combined with mineral oil to improve fire resistance; however, they have required either the use of only minor amounts of mineral oil thus not achieving economical fire-resistant compositions or the use of significant amounts of corrosion inhibitor because such chlorinated hydrocarbons tend to be corrosive to metals. The combination of approximately equal amounts of aryl phosphate esters and chlorinated hydrocarbons yields a fluid with good flame resistance and fair lubricity, but requires the addition of VI improvers to obtain a satisfactory viscosity index.

Low-cost, fire-resistant, homogenous petroleum-containing fluids overcoming the problems of the prior art fluids have now been discovered which not only provide superior lubricating capability but also a surprising degree of fire resistance at reasonable costs. It is therefore, an object of this invention to provide a fire-resistant petroleum-containing fluid having a unique combination of lubricity, fire-resistance and homogeneity. Another object of this invention is to provide a reasonably low cost petroleum-containing hydraulic fluid having superior fire resistance. Still another object of this invention is to provide a fire-resistant fluid having superior lubricity. Other objects will become apparent from the following description of the invention.

SUMMARY OF THE INVENTION

According to this invention, there are provided compositions useful as functional fluids which are comprised of (1) a petroleum bright stock oil having a viscosity range of from about 150 to about 250 SSU at 210° F., (2) a phosphate ester selected from the group consisting of an ester represented by the formula



where R, R_1, and R_2 are each selected from the group consisting of phenyl radicals, substituted phenyl radicals and alkyl C_{2-18} radicals provided that not more than one of R, R_1, and R_2 is an alkyl radical, and mixtures thereof, and (3) halogenated compounds selected from the group consisting of halogenated benzenes, naphthalenes, biphenyls, terphenyls, perhalodienes and perhalocyclodienes having not less than four nor more than eight carbon atoms. The term "halogens" and "-halogenated" as employed in the specification and claims are intended to refer to one or more of the group consisting of chlorine, bromine and fluorine.

DESCRIPTION OF PREFERRED EMBODIMENTS

1. Bright Stocks

The bright stocks useful in the compositions of this invention are those known in the art as conventionally refined of solvent extracted. In the refining of mineral oils, the crude oils are subjected to a first distillation under ordinary pressures to remove the low boilers, and a second steam distillation to remove heavy oil and waxy fractions. The residue from the steam distillation is known as "steam refined stock" or "-cylinder oil." This material is subsequently deasphalted and dewaxed and treated with solvents and clays to produce the product known as "bright stock."

The bright stocks are most generally used as heavy gear lubricants, and for blending with neutral oils for automatic engine lubricants. While the bright stocks can have a viscosity in the range of from about 50 to about 300 SSU at 210° F., those which are useful in the compositions of the present invention have viscosities in the range of about 150 to 250 SSU at 210° F., and preferably in the range of 200 to 220 SSU at 210° F.

The bright stocks are not to be confused with the lower viscosity mineral oils, which generally have viscosities in the range of 45 to 120 SSU at 210° F., as shown below.

Viscosity Ranges of SAE Grade Oils

	Centistokes (CS)	Saybolt Seconds (550)
SAE 20	5.59 to 9.36	45 to 57
SAE 30	9.36 to 12.58	57 to 69
SAE 40	12.58 to 16.26	69 to 83
SAE 50	16.26 to 21.94	83 to 107
SAE 90	14.24 to 25.0	75 to 120

2. Phosphate Esters

Phosphate esters useful in compositions of this invention are the alkyl diaryl and the tri-aryl phosphate esters which may contain substituted and unsubstituted phenyl radicals. Such substituents can be alkyl C_{1-4} radicals, chlorine, bromine or fluorine and haloalkyl C_{1-4} radicals. In the case of alkyl or haloalkyl substituted phenyl radicals up to three positions on the ring can be occupied whereas as many as four positions can be substituted by chlorine, bromine or fluorine. Typical examples of alkyl diaryl phosphate esters useful in compositions of this invention are ethyl diphenyl phosphate, propyl diphenyl phosphate, butyl diphenyl phosphate, pentyl diphenyl phosphate, hexyl diphenyl phosphate, octyl diphenyl phosphate, nonyl diphenyl phosphate, tridecyl diphenyl phosphate, dodecyl diphenyl phosphate, octadecyl diphenyl phosphate, pentadecyl diphenyl phosphate, preferably osooctyl diphenyl phosphate and 2-ethylhexyl diphenyl phosphate.

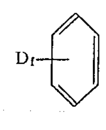
Typical examples of triaryl phosphate esters include triphenyl phosphate tris-m-difluorophenyl phosphate, cresyl diphenyl phosphate, tricresyl phosphate, m-chlorophenyl dicresyl phosphate, m-chlorophenyl diphenyl phosphate, o-xenyl diphenyl phosphate, trixenyl phosphate, m-chlorophenyl diphenyl phosphate, perfluoromethylphenyl diphenyl phosphate, e, m-fluorophenyl diphenyl phosphate, tris-m-butylphenyl phosphate and bromophenyl diphenyl phosphate.

The phosphate ester components of compositions of this invention can also be a mixture of esters comprising at least one ester represented by Formula I above and at least one other phosphate ester which can be either trialkyl or dialkyl aryl provided the resulting mixture contains an alkyl ester group to aryl ester group ratio which does not exceed 1.5 to 1 respectively. For example, a composition of this invention can be prepared wherein the phosphate ester component is a mixture of tris-n-butyl phosphate and isooctyl diphenyl phosphate in a weight ratio of 1 to 2 respectively. Such a mixture of phosphate esters provides an alkyl group to aryl group ratio of slightly less than 1.5 to 1 respectively. These same exemplary esters, when employed in a weight ratio of 1 to 4 respectively, would provide an alkyl group to aryl group ratio of slightly less than 1 to 1 with the aryl groups slightly in excess.

Typical dialkyl aryl esters which can be used in admixture with the above-described esters are dipropyl phenyl phosphate, di-n-butyl phenyl phosphate, di-tert.-butyl cresyl phosphate, di-n-butyl chlorophenyl phosphate, dipentyl phenyl phosphate, diethyl bromophenyl phosphate, dioctyl phenyl phosphate, dioctyl cresyl phosphate, didecyl phenyl phosphate and dioctadecyl phenyl phosphate. The aryl group of the dialkyl aryl phosphates may contain one or two substituent groups on the aryl nucleus selected from methyl and halide radicals. Typical alkyl phosphates which can be used are tri-n-propyl phosphate, tri-tert.-butyl phosphate tri-isobutyl phosphate, tri-2-ethylhexyl phosphate, tricapryl phosphate, tridecyl phosphate, tris-tridecyl phosphate and trioctadecyl phosphate, tris (m-tert-butyl phenyl) phosphate, 2,3,5-triethylphenyl dixenyl phosphate.

3. Halogenated Compounds

the halobenzenes useful in compositions of this invention are those represented by the formula



where D is selected from the group consisting of chlorine, bromine and fluorine, and *f* is an integer from 2 to 4.

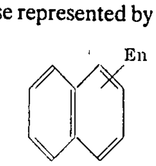
Typical examples of halobenzenes useful in compositions of this invention are o-dibromobenzene, 1-bromo-3-chlorobenzene, 1,3-dichloro-5-bromobenzene, 1,3-difluoro-5-bromobenzene, 1-fluoro-3-chloro-5-bromobenzene, 1,2,3,4-tetrafluorobenzene, 1,3-dibromo-3,5-dichlorobenzene, 1,3-dibromo-4,6-difluorobenzene, trifluorobenzene and preferably m-dibromobenzene. Also useful are mixtures in all proportions of halobenzenes containing the same or different halogens. For example, a mixture of m-dibromobenzene and 1,2,4-trichlorobenzene can be used as the halogenated hydrocarbon in the compositions of this invention. In addition, mixtures of chlorobenzenes are particularly useful in compositions of this invention. Such mixtures can contain by weight from about 40 percent to about 80 percent tetrachlorobenzene and from about 20 percent to about 80 percent trichlorobenzene. Such mixtures can also contain pentachlorobenzene in small amounts ranging up to about 20 percent by weight. Exemplary mixtures of tri- and tetrachlorobenzenes are as follows:

	Component	Weight %
A	1,2,3,4-tetrachlorobenzene	40–50
	1,2,4,5-tetrachlorobenzene	4–10
	1,2,4-trichlorobenzene	25–35
	1,2,3-trichlorobenzene	0–3
	pentachlorobenzene	10–20
B	1,2,3,4-tetrachlorobenzene	26–29
	1,2,4,5-tetrachlorobenzene	3
	trichlorobenzene	58.5
	pentachlorobenzene	5.5
C	1,2,3,4-tetrachlorobenzene	26.9
	1,2,4,5-tetrachlorobenzene	2.6
	1,2,4-trichlorobenzene	53.5
	1,2,3-trichlorobenzene	9.7
	pentachlorobenzene	5.3
	impurities	2.0

Because of solubility characteristics the 1,2,4,5-isomer of tetrachlorobenzene is not normally employed in large amounts. In addition, such mixtures of tri- and tetrachlorobenzenes are normally employed in amounts of up to about 50 percent of the total composition for most uses although amounts up to about 75 percent can be used when operating temperatures remain above 140° C.

The perhalodienes and perhalocyclodienes useful in this invention are those compounds having at least four and not more than eight carbon atoms in the molecule. Typical perhalodienes are perchlorobutadiene, perbromobutadiene, perfluorobutadiene, perchloropentadiene, perfluoropentadiene, perbromopentadiene, perchlorohexadiene, perbromohexadiene, perchloroheptadiene, perchlorooctadiene, perbromooctadiene and perfluorooctadiene. Perchlorobutadiene is preferred. Typical perhalocyclodienes are perchlorocyclobutadiene, perfluorocyclobutadiene, perchlorocyclopentadiene, perbromocyclopentadiene, perfluorocyclopentadiene, perchlorocyclohexadiene, perbromocyclohexadiene, perchlorocycloheptadiene, perchlorocyclooctadiene and perfluorocyclooctadiene.

The halogenated naphthalenes useful in compositions of this invention are those represented by the formula



wherein E is a halogen selected from the group consisting of chlorine, bromine and fluorine and *n* is an integer from 1 to 8. Typical halogenated naphthalenes are 1-chloronaphthalene, 1,4-dichloronaphthalene, 1,5-dichloronaphthalene, 1,3,5-trichloronaphthalene, hexachloronaphthalene, octachloronaphthalene, 1-bromonaphthalene, 1,3-dibromonaphthalene, 1,5-dibromonaphthalene, 1,3,5-tribromonaphthalene, hexabromonaphthalene, octabromonaphthalene, 1-fluoronaphthalene, 1,4-difluoronaphthalene, 1,3,5-trifluoronaphthalene and octafluoronaphthalene.

Also within the scope of this invention are halogenated naphthalenes containing more than one specie of halogen in the same molecule and mixtures of one or more of halogenated naphthalenes wherein the combined halogen content represents a degree of substitution of from one to eight halogen atoms.

The halogenated biphenyl and terphenyl compounds useful in compositions of this invention can contain chlorine fluorine or bromine or combinations thereof in amounts corresponding to mono-, in the case of bromine only, di-, tri-, tetra-, penta- and hexahalobiphenyl. Typical of such biphenyl compounds are the chlorinated biphenyls commercially available as products containing 32 percent, 42 percent, 48 percent, 45 percent, and 60 percent by weight of combined chlorine and chlorinated terphenyls containing from about 20 percent to about 70 percent by weight of combined chlorine. The expression halogenated biphenyl or terphenyl containing a stated percentage of combined halogen is used herein as including the directly halogenated products, halogenated products containing more than one specie of halogen in the same molecule and blends of one or more of such halogenated products whereby the halogen content is broadly within the range of about 30 percent to 60 percent, preferably within the range of about 30 percent to 42 percent by weight. Halogenated quaterphenyl may also be present in small amounts up to about 5 percent by weight. Such minor amounts of halogenated quaterphenyl do not significantly alter the characteristics of the compositions of this invention.

Compositions of this invention in general terms contain, by weight, from about 12 percent to about 65 percent bright stock, from about 5 percent to about 63 percent phosphate ester and from about 25 percent to about 70 percent halogenated compound with each component present within their respective ranges so that the total of the three components is 100 percent. The compositions of this invention can be more readily determined by reference to FIG. I which shows the weight percent of components (1), (2), and (3) required to produce the compositions of this invention. Thus, while the components (1), (2), and (3) used to provide the compositions of this invention can be combined in a fairly wide range of proportions, the unique combination of homogeneity, fire resistance and synergistic lubricity characteristic of such compositions is only obtained when such components are present in certain amounts which are defined by the area within the curve ABC of FIG. I.

While homogeneity at a temperature of at least about 150° F. is obtained when employing any phosphate described above in any amount included in the area defined by the curve ABC in FIG. I, functional fluids are desirably homogeneous at room temperature, i.e., about 70° F. When using phosphate esters having less than about 10 alkyl carbon atoms in the molecule, however, the amounts of such esters must be further limited within the area defined by the curve ABC of FIG. I in order to provide compositions which are homogeneous at room temperature. More specifically, in such phosphate esters the alkyl carbons can be located in a single ester group, distributed among aryl ester groups as substituents on the aryl nucleus or divided between aryl substituents and alkyl ester groups. Maximum concentrations of typical phosphate esters having less than 10 alkyl carbon atoms and providing compositions homogeneous at 70° F. are illustrated by lines I, isoctyl diphenyl phosphate, II, tricresyl phosphate, III, cresyl diphenyl phosphate, in FIG. I, which lines are 70° F. isotherms indicating maximum weight percent amounts of such esters. Thus, the compositions of this invention which are homogenous at 70° F. and which contain isooctyl diphenyl phosphate, tricresyl phosphate and cresyl diphenyl phosphate are defined by the area within the curves AFF'C, AEE'C and DD'C, respectively.

It has also been discovered that the components (1), (2), and (3) above, when combined in certain proportions, produce functional fluids having surprisingly small rates of change of viscosity with change of temperature, which property is highly desirable in fluids employed as lubricants and as hydraulic fluids. This property is highly unexpected in view of the relatively high rates of change of viscosity with temperature found in some of the individual components.

Thus preferred compositions of this invention which have a small rate of change of viscosity with change of temperature as indicated by viscosity index are those containing (*1a*) bright stocks having a viscosity index of at least about 90, preferably about 95 and a viscosity in the range of from about 150 to about 250 SSU at 210° F., (*2a*) phosphate esters as described hereinabove in Formula I with the exception that the alkyl and haloalkyl substituents on the aryl radicals can contain no more than 1 carbon atom and (*3a*) at least one halogenated compound containing from about 30 percent to about 50 percent combined halogen by weight. Thus, preferred compositions of this invention contain from about 22 percent to about 65 percent bright stocks, from about 5 percent to about 44 percent phosphate ester and from about 25 percent to about 70 percent halogenated compound. These preferred compositions of this invention can be more readily determined by reference to FIG. II which shows the weight percent of components (*1a*), (*2a*), and (*3a*) required to produce preferred compositions of this invention. Thus, preferred compositions of this invention having the combined properties of fire resistance, synergistic lubricity, homogeneity and good viscosity characteristics are obtained only when such components are present in certain critical amounts which are defined by the area within the curve AFG'G of FIG. II.

Preferred compositions of this invention include those which contain, by weight, from about 25 percent to about 45 percent of a bright stock having a viscosity in the range of from about 150 to 250 SSU at 210° F. and a viscosity index of at least about 90, from about 10 percent to about 15 percent of an alkyl C_{2-18}-diaryl phosphate and from about 40 percent to about 60 percent of a chlorinated biphenyl containing from about 30 percent to about 54 percent, by weight, combined chlorine.

When triaryl phosphate esters are employed, preferred compositions having weight percent proportions of (*1a*), (*2a*), and (*3a*) within the are of the curve AFG'G of FIG. II have a viscosity index rating of at least about +20 and when alkyl diaryl phosphate esters are employed viscosity index ratings of at least about +35 are obtained. Viscosity measurements of illustrative preferred compositions of this invention were made according to ASTM Method D-445-54T using a Cannon-Fenske modified Ostwald viscometer and are set forth in Table I below in centistoke units. The viscosity indices appearing in Table I were determined according to ASTM Method D567-53. The amounts of each component listed in Table I are in weight percent of the final composition.

TABLE I

Component	Viscosity, cs. 100° F.	Viscosity, cs. 210° F.	Viscosity index
(a) Bright stock oil 200 SSU at 210° F	848	42.0	+94
(b) Chlorinated biphenyl, 42 percent Cl	17.0	2.45	−215
(c) Chlorinated biphenyl, 48 percent Cl	44.06	3.20	−625
(d) Isooctyl diphenyl phosphate	11.29	2.65	+68
(e) Tricresyl phosphate	28.32	3.98	−25
(f) 2-ethylhexyl dicresyl phosphate	15.94	3.06	+25

Table I—Continued

No.	Weight percent of components (a)	(b)	(c)	(d)	(e)	(f)	Viscosity (cs.) measured 100 F.	210° F.	VI	Viscosity (cs.) calculated 100° F.	210 F.	VI
1	25.5	49.5		25.0			36.22	4.99	+49.5	28	3.9	−38
2	31.0	56.0		13.0			49.01	5.92	+56.5	35	4.3	−55
3	35.0	60.0		5.0			61.64	6.74	+56.0	43	4.7	−57
4	60.0	25.0		15.0			144.8	13.15	+92	120	10.3	+66
5	25.5		49.5	25.0			50.37	5.85	+45	49	4.9	−69
6	25.5	49.5			25.0		54.20	5.80	+22	37	4.3	−81
7	31.0	59.0			10.0		59.42	6.37	+42	40	4.5	−70
8	36.0	47.0			17.0		75.52	7.50	+54.5	50	5.3	−9
9	25.5	49.5				25.0	44.25	5.38	+37	30.8	4.0	−62

As indicated in Table I, surprisingly and unpredictably high viscosity indices are obtained with the preferred compositions of this invention in view of the extremely low viscosity indices of the components making up the major weight percent amounts of the compositions, and in view of the low viscosity indices calculated according to the procedure given in ASTM D-341-43. Also, it is to be noted that these relatively high readings were obtained without the use of viscosity index improvers. Commonly used viscosity index improvers such as the methacrylates and polyalkylacrylates are known to possess inferior shear stability which is imparted to the base fluid to which they are added. Thus, yet another advantage is seen in the preferred compositions of this invention in that good viscosity characteristics are obtained without sacrificing the shear stability of the fluid by the use of viscosity index improvers. In some instances, however, it may be desirable to add viscosity index improvers when a higher viscosity index is more important than shear stability.

The shear stability of one preferred composition of the present invention was determined by means of a Raytheon sonic oscillator, Model DF-101, wherein the composition was maintained at about 100° F. for a period of 2 hours under irradiation while samples were taken at intervals over a 2-hour period. The test was repeated with a hydraulic fluid of the prior art which contained a VI improver. The fluid compositions, and the results of the test, were as follows:

Fluid 1. Composition of the present invention
38.5% Bright stock, 200 SSU at 212° F.
47.5% Chlorinated diphenyl (42% Cl)
14% isooctyl diphenyl phosphate

Fluid 2. Example of prior art
45% Tricresyl phosphate
52.5% Chlorinated diphenyl (48% Cl)
2.5% Polyalkyl methacrylate—petroleum oil V.I. improver (Acryloid 710, a product of the Rohm and Haas Co., Philadelphia, Penn.)

Sonic Shear Test Results [1]

Irradiation time, min	15	30	60	90	120
Percent viscosity loss:					
Fluid 1	0.40	0.56	0.63	0.71	0.79
Fluid 2	16.1	17.6	19.6	21.0	22.0

[1] ASTM Procedure, vol. 1, October 1961, p. 1160 "Proposed Method of Test for Shear Stability of Polymer-Cutting Oils."

It is clearly evident from the above data that the fluid compositions of the present invention is considerably more shear stable than the fluid of the prior art.

Another of the unique features of the compositions of this invention is that while each of the components of such compositions has fairly good lubricating ability, the compositions defined by the area within the curve ABD of FIG. I possess greater lubricating ability than any of such components. The surprising synergistic lubricating properties found in the compositions of this invention are demonstrated by the data contained in Tables II and III below. These data were obtained using a "Timken Extreme Pressure Lubricant Testing Machine," which is a machine designed to determine the ability of a lubricant to prevent a test block from being seized or abraded by a rotating, tapered roller bearing (test cup) under a known load. The test block and test cup are in lubricated contact with each other during a test period of ten minutes during which time the bearing is rotated at 810 R.P.M. under a known load. After the test period the machine is stopped and the test block inspected. A new test block and test cup is installed and if no evidence of seizure or abrasion is found on the previously used test block, the test is repeated with a 5-pound increase in load. The procedure is repeated until damage to the test block is observed. If seizure or abrasion is observed on the first run, the test is repeated with five pound incremental decreases in the load until no damage to the test block is observed. The highest load run without observing damage to the test block is reported as the maximum load, in pounds. Table II, below, contains the data thus obtained when individual components of the compositions of this invention were employed as the lubricant. In Table III, data are presented from test runs employing typical examples of compositions of this invention. In each instance except Test Composition No. 4, a Mid-Continent bright stock oil having a viscosity of 200 SSU at 210° F. was used. In Test Composition No. 4 a Mid-Continent bright stock oil having a viscosity of 220 SSU at 210° F. was employed.

TABLE II

Component	Maximum Load (Lbs.)
a) Bright stock oil	20
b) Chlorinated biphenyl (42% combined chlorine	45
b') Chlorinated biphenyl (42% combined chlorine)*	40
c) Chlorinated biphenyl (48% combined chlorine)	35
d) Tricresyl phosphate	45
e) Isooctyl diphenyl phosphate	45
f) 2-Ethylhexyl diphenyl phosphate	45
g) Mixture of Tri- and Tetrachlorobenzene (Approx. 50/50)	45

* Contains, by weight, 23% chlorinated terphenyl and 2% chlorinated quaterphenyl.

TABLE III

Test compositions	Weight percent of components a	b	b'	c	d	e	f	g	Acceptable load limit (pounds)
1	40	46				14			55
2	40	46			14				55
3	30		60				10		50
4	40		46			14			55
5	25	50				25			65
6	40			35		25			60
7	25				5			70	50
8	65				10			25	50
9	14					48		38	55
10	65	12.5			10			12.5	50
11	14	19				48		19	55
12	35	20				25		20	60
13	[1] 40	46			14				50
14		85				15			40
15		75				25			45
16	75					25			[2] 25
17	50					50			[2] 25
18	25					75			[2] 25
19	75	25							45
20	50	50							55
21	25	75							55
22	10	50			40				40
23	15	60			25				40

[1] 155 SSU at 210° F. viscosity.
[2] Composition was non-homogeneous at test temperature.

The data contained in Table III is divided into three areas as follows:

Samples 1–13: three component compositions included within the scope of this invention,

Samples 14–21: two component compositions not included within the scope of this invention,

Samples 22,23: three component compositions not included within the scope of the present invention.

A comparison of the test data presented in Tables II and III clearly show the following:

1. the maximum load carrying ability of the individual components in Table II ranges from 20 to 45 pounds,

2. the maximum load carrying ability of two component mixtures according to samples 14–21 (Table III) range from 25 to 55 pounds,

3. the maximum load carrying ability of the three component mixtures included within the scope of the instant invention as exemplified by samples 1–13 (Table III) range from 50 to 65 pounds.

4. the maximum load carrying ability of typical three component mixtures lying outside the limits of the present invention (samples 22 and 23 of Table III) is significantly less than that of the compositions of this invention.

From a comparison of Items (2) and (3) above, it is evident that a synergistic effect equivalent to at least an additional 10 psig or about a 20 percent increase in load bearing capacity is obtained with the three component mixtures defined by the present invention, and that the high load carrying capacity of these compositions could not be predicted on the basis of the single fluid or two component fluid test results.

Another property of the unique compositions of this invention is their outstanding fire resistance even though they contain significant amounts of flammable bright stock. To illustrate the fire resistance of the compositions of this invention their typical properties and the properties of other commercially used fire-resistant hydraulic fluids are set forth in Table IV below. The test procedures used to measure the various properties of the fluids of this invention and those used as comparisons are as follows:

Viscosity	ASTMD–445–61
High Pressure Spray Test	AMS–3150C

Two tests were used for the measurement of the fire-resistance of the instant fluids since there is no single test that can be used to evaluate all types of fluids under all expected use conditions. The degree of fire-resistance in any given test is influenced by the characteristics of the fluid, the physical state of the fluid and many other factors. One of the tests was designed to simulate conditions resulting from a broken line spraying hydraulic fluid into various sources of ignition and is known as the "High-Pressure Spray Test." An additional test often used, which is a smaller scale test, is the Molten-Metal Pour Test. In this test the fluid under evaluation is dropped from a medicine dropper or poured from a calibrated test tube onto the surface of molten aluminum alloy which has been heated to about 1,250° F. If spontaneous ignition does not occur, a spark is placed in the vapors to determine if they can be ignited.

TABLE IV.—FIRE-RESISTANCE TESTS

No.	Composition components	Weight percent of components	Viscosity. cs.. at— 40° F.	100° F.	210° F.	High pressure spray test	Molten Aluminum test. 1.250° F.
1	Bright stock 200 SSU at 210° F. Chlorinated biphenyl 42% combined chlorine. Isooctyl diphenyl phosphate	40.0 46.0 14.0	930	70.6	7.8	Does not flash up to 6 ft. from orfice. At 6 ft. flames carry about 6 inches from tip of torch.	(1) Does not burn without spark (2) Flashes with a spark but is self extinguishing until half of fluid is vaporized then flashes and burns to completion.
2	Bright stock 200 SSU at 210° F. Chlorinated biphenyl 42% combined chlorine. Isooctyl diphenyl phosphate	25 61.0 14.0	532	39.5	5.1	Does not flash up to 6 ft. from orfice. At 6 ft. flames carry about 6 inches from tip of torch.	(1) Does not burn without spark. (2) Flashes with a spark but is self extinguishing until half of fluid is vaporized then flashes and burns to completion.
3	Water/oil emulsion: Water Oil	 40 60	1,100	130	19.5	Does not flash up to 6 ft. from orifice. At 6 ft. flames carry 4 to 6 inches from tip of torch.	(1) Burns to completion without spark after water boils off. (2) Burns to completion with spark after water boils off.
4	Water/glycol solution: Water Glycol	 40 60	300	60	14	Does not flash up to 6 ft. from orifice. At 6 ft. from orifice flames carry 4 to 6 inches from tip of torch.	(1) Burns to completion without spark after water boils off. (2) Burns to completion with a spark after water boils off.
5	Chlorinated biphenyl. 48% combined chlorine. Chlorinated biphenyl. 42% combined chlorine.	67 33	4,000	30	2.85	No flashes up to 6 ft. from orifice. At 6 ft. flames carry about 6 in. from tip of torch.	(1) Does not flash or burn without a spark. (2) Flashes with a spark but is self extinguishing.
6	Triaryl phosphate	100	450	32	4.2	Occasional flashing at about 4½ ft. from orifice with flames carrying about 2 ft. from tip of torch.	(1) Does not flash or burn without a spark. (2) Flashes with a spark but is self extinguishing.
7	Premium petroleum oil hydraulic fluid.	100	500	48	6.7	Fluid ignited 12 inches from orifice with continuous flames carrying 10 ft. from tip of torch.	Ignites without a spark and burns to completion.

In addition to the above, the compositions of this invention are not prone to foaming and any foam formed is not stable. Furthermore, the claimed compositions have good stability, even at temperatures of 250° F. and in the presence of air, and are essentially noncorrosive to metals such as aluminum, aluminum bronze alloy, iron, silver and titanium. A further advantage of the instant compositions is their outstanding hydrolytic stability.

As a result of the excellent physical properties of the fluids particularly described in the proceeding examples, improved hydraulic pressure devices can be prepared in accordance with this invention which comprise in combination a fluid chamber and an actuating fluid in said chamber, said fluid comprising one of the compositions hereinbefore described. In such a hydraulic apparatus wherein a movable member is actuated by the above-described functional fluids, performance characteristics are obtainable which are superior to those heretofore obtainable.

Because of the excellent fire-resistance of the compositions of this invention and good lubricity, they can be utilized in those hydraulic systems wherein power must be transmitted and the frictional parts of the system lubricated by the hydraulic fluid utilized. Thus, the novel functional fluids of this invention find utility in the transmission of power in a hydraulic system having a pump therein supplying the power for the system. In such a system, the parts which are so lubricated include the frictional surfaces of the source of power, namely the pump, valves, operating pistons and cylinders, fluid motors, and in some cases, for machine tools, the ways, tables and slides. The hydraulic system may be of either the constant volume or the variable volume type.

The pumps may be of various types, including the piston-type pump, more particularly the variable-stroke piston pump, the variable-discharge of variable displacement piston pump, radial-piston pump, axial-piston pump, in which a pivoted cylinder block is adjusted at various angles with the piston assembly, for example, the Vickers Axial-Piston Pump, or in which the mechanism which drives the pistons is set at an angle adjustable with the cylinder block; gear-type pump, which may be spur, helical or herringbone gears, variations of internal gears, or a screw pump; or vane pumps. The valves may be stop valves, reversing valves, pilot valves, throttling valves, sequence valves or relief valves. Fluid motors are usually constant or variable discharge piston pumps caused to rotate by the pressure of the hydraulic fluid of the system with the power supplied by the pump power source. Such a hydraulic motor may be used in connection with a variable-discharge pump to form a variable speed transmission.

In addition to the above, compositions of this invention can be utilized as gear lubricants in mechanical power trains. Mild mineral oil E.P. gear lubricants currently employed commercially provide ratings within the ranges of 45 to 65 pounds when tested by the Timken Extreme Pressure Lubricant Testing Machine described above and typical para-ffinic petroleum oil employed as a gear lubricant having a viscosity of about 300 SSU at 100° F. provide ratings in the range of only 10 to 20 pounds. Accordingly, in view of the high ratings reported in Table III (50 to 65 pounds), compositions of this invention can be used alone or in combination with lubricant adjuvants as lubricants in automotive and other mobile equipment power trains. Also, compositions of this invention are heavier than water thus making their use as gear lubricants even more desirable in applications such as in sheet metal rolling mill power trains where water contamination is likely. This property allows water contamination to be more easily removed by flotation of the water and renders such water contamination less harmful than in prior lubricants containing mineral oil.

The compositions of this invention can also contain dyes, pour point depressants, antioxidants, viscosity index improvers, such as polyalkylacrylates and polyalkylmethacrylates, anti-rust agents, hydrolytic stabilizers and the like where ever desired for special use requirements.

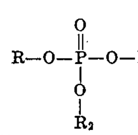
While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

What is claimed is:

1. A composition comprising a mixture of

1. a bright stock having a viscosity in the range of from about 150 to about 250 SSU at 210° F.,

2. a phosphate ester selected from the group consisting of an ester represented by the formula



where R, R_1, and R_2 are each selected from the group consisting of phenyl, alkyl C_{2-18} radicals, and phenyl radicals substituted with halogen, alkyl C_{1-4} radicals, or haloalkyl C_{1-4} radicals, provided not more than one of R, R_1, and R_2 is alkyl, and mixtures thereof, and,

3. halogenated biphenyls containing from about 30 percent to about 60 percent by weight halogen and mixtures thereof, wherein the amounts of (1), (2), and (3) are within the area defined by the curve ABC of FIG. I.

2. A composition of claim 1 where the halogenated compound is chlorinated biphenyl containing from about 30 percent to about 60 percent by weight combined chlorine.

3. A composition of claim 1 where the phosphate ester is an alkyl diaryl phosphate.

4. A composition of claim 3 where the phosphate ester is selected from the group consisting of 2-ethyl-hexyl diphenyl phosphate, isooctyl diphenyl phosphate, and cresyl diphenyl phosphate.

5. In the method of operating a hydraulic pressure device wherein a displacing force is transmitted to a displaceable member by means of a hydraulic fluid, the improvement which comprises employing as said hydraulic fluid a composition of claim 1.

6. A composition comprising a mixture by weight of from about 25 percent to about 45 percent of a bright stock having a viscosity in the range of from about 150 to 250 SSU at 210° F. and a viscosity index of at least about 90, from about 10 percent to about 15 percent of an alkyl C_{2-18} diaryl phosphate and from about 40 percent to about 60 percent of a chlorinated biphenyl containing from about 30 percent to about 54 percent, by weight, combined chlorine.

7. A composition of claim 6 where the bright stock has a viscosity in the range of from about 200 to 220 SSU at 210° F. and a viscosity index of at least about 95.

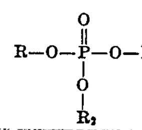
8. A composition of claim 6 where the phosphate ester is selected from the group consisting of isooctyl diphenyl phosphate and ethyl hexyl diphenyl phosphate.

9. In the method of operating a hydraulic pressure device wherein a displacing force is transmitted to a displaceable member by means of a hydraulic fluid, the improvement which comprises employing as said hydraulic fluid a composition of claim 6.

10. A composition comprising a mixture of

1. bright stock having a viscosity in the range of from about 150 to 250 SSU at 210° F.,

2. a mixture of phosphate esters comprising (i) at least one ester represented by the formula



where R, R_1, and R_2 are each selected from the group consisting of phenyl, alkyl C_{2-18} radicals, and phenyl radicals substituted with halogen, alkyl C_{1-4} radicals, or haloalkyl C_{1-4} radicals, provided not more than one of R, R_1, and R_2 are alkyl and (ii) at least one ester selected from the group consisting of trialkyl C_{2-18} phosphates and idalkyl C_{2-18} aryl phosphates, the maximum ratio of alkyl ester groups to aryl ester groups being about 1.5 to 1 respectively; and

3. halogenated biphenyls containing from about 30 percent to about 60 percent by weight halogen and mixtures thereof,

wherein the amounts of (1), (2), and (3) are within the area defined by the curve ABC of FIG. 1.

11. A composition of claim 10 where the bright stock has a viscosity in the range of from about 200 to 220 SSU at 210° F.

12. A composition of claim 10 where the mixtures of phosphate esters comprises at least one alkyl diaryl phosphate and at least one trialkyl phosphate.

13. A composition of claim 17 where the mixture of phosphate esters comprises at least one triaryl phosphate and at least one trialkyl phosphate.

14. A composition of claim 10 where the halogenated compound is chlorinated biphenyl containing from about 30 percent to about 60 percent, by weight, combined chlorine.

15. In the method of operating a hydraulic pressure device wherein a displacing force is transmitted to a displaceable member by means of a hydraulic fluid, the improvement which comprises employing as said hydraulic fluid a composition of claim 10.

16. A composition comprising, by weight, about 40 percent bright stock having a viscosity of about 200 SSU at 210° F., about 14 percent isooctyl diphenyl phosphate and about 46 percent chlorinated biphenyl containing about 42 percent chlorine.

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