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INHIBITION OF CORROSION OF HYDRAULIC FLUIDS

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12 Claims. (Cl. 252—75)

This invention relates to compositions and to hydraulic fluids containing phosphinates, and is particularly concerned with improved phosphinate-containing compositions and hydraulic fluids, which are inhibited against corrosion of certain metals, particularly iron.

In the copending application of Robert S. McCord, Serial No. 334,588, filed December 30, 1963, is disclosed novel hydraulic fluids containing a phosphinate as a major component, and designed for operation at high temperatures in the hydraulic systems of modern aircraft, particularly supersonic aircraft. Such hydraulic fluids have many advantages over prior art hydraulic fluids employed in hydraulic systems of aircraft, particularly high stability and high fire resistance. Although the phosphinate component, specifically the aryl dialkly phosphate, of the hydraulic fluids described in the above copending application, or mixtures of such phosphinate with thickeners, such as described in the above application, and forming the improved hydraulic fluids thereof, are suitable for use with and are substantially non-corrosive to many metals and alloys such as aluminum, titanium, silver and certain types of steels, e.g., 18–8 stainless steels, such phosphinates or mixtures thereof with thickeners corrode certain metals such as low carbon steels. Such low carbon steels are exemplary of the types of steel often used for construction of pumps employed in hydraulic systems of aircraft.

It is accordingly an object of the invention to inhibit corrosion of metals such as iron by compositions containing organic phosphates.

Another object is to provide hydraulic fluids containing organic phosphates as a major component, and which have substantially reduced corrosiveness on metals such as iron, especially low carbon steels, and particularly at high temperatures, e.g., of the order of about 400°F.

Another object of the invention is the provision of improved hydraulic fluids containing an aryl dialkyl phosphinate as a major component, and a suitable thickener, and inhibited against attack of metals such as iron, particularly low carbon steels, by incorporation of an effective inhibitor.

A still further object of the invention is to provide novel hydraulic fluids containing an aryl dialkyl phosphinate, preferably phenyl di n-butyl phosphinate, as a major component, and a suitable thickener, e.g., a polyalkyl methacrylate, effective to increase substantially the viscosity index of said phosphate, and providing a thermally stable and fire resistant hydraulic fluid operable at high temperatures in the range of about 400° to about 500° F., said hydraulic fluids having an additive incorporated therein inhibiting or substantially reducing attack of such hydraulic fluids on iron, particularly low carbon steels, especially at high temperatures of the order of about 400° F.

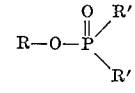
Other objects and advantages will be in part apparent and in part obvious from the following description of the invention.

The term "iron" employed in the specification and claims, unless otherwise indicated, is intended to denote and include iron and steels, particularly low carbon steels.

I have found that by addition of a small or minor amount of 2-iodobiphenyl to an organic phosphinate, particularly an aryl dialkyl phosphinate, or to a composition containing such phosphinate in admixture with other materials, the resulting phosphinate material or composition containing the same, unexpectedly exhibits substantially reduced corrosion on iron, particularly low carbon steels, as compared to the phosphinate or phosphinate-containing composition in the absence of such additive. The invention principles are particularly applicable to the phosphinate-containing mixtures forming the hydraulic fluids described in the above copending application, preferably employing an aryl dialkyl phosphinate as a major component and including a minor proportion of a suitable thickener. Of particular significance, such corrosion inhibition is attained substantially without adversely affecting the important functional properties of the above-noted hydraulic fluids, in the absence of such additive.

The addition of hexaphenyl di tin to the above-described phosphinate-containing compositions or hydraulic fluids to inhibit attack of such compositions on iron is described in the above copending application of Robert S. McCord. However, as a further feature of this invention, it has been found surprisingly that the incorporation of a small amount of hexaphenyl di tin, together with 2-iodobiphenyl, into the composition or hydraulic fluids containing the above-noted organic phosphinate, remarkably reduces corrosion of the composition on iron, particularly low carbon steels, to a greatly reduced value much below the reduction in corrosion achieved by the use of 2- iodobiphenyl or hexaphenyl di tin separately. Thus, it has been found that whereas the incorporation of 2-iodobiphenyl or hexaphenyl di tin separately into a composition or into hydraulic fluids containing the above-described phosphinates, particularly aryl dialkyl phosphinate, reduces corrosion on iron, particularly low carbon steels, to about one-tenth of the corrosive attack by such composition in the absence of either 2-iodobiphenyl or hexaphenyl di tin, the combination of 2-iodobiphenyl and hexaphenyl di tin functions synergistically in such phosphinate-containing compositions or hydraulic fluids to reduce dramatically corrosion thereof on iron or low carbon steels, e.g., down to as little as $\frac{1}{100}$ of the corrosion to which such metal is subjected in the absence of both such additives.

The hydraulic fluids described and claimed in the above copending application contain monoaryl dialkyl phosphinates having the general formula.



where R is aryl, e.g., phenyl or naphthyl, and R′ is an alkyl group of from 4 to 8 carbon atoms, preferably an alkyl group of from 4 to 6 carbon atoms. Thus, the alkyl groups can be butyl, pentyl, hexyl, heptyl and octyl. Also, branched chain alkyl groups can be employed. In this respect, aryl dialkyl phosphinates can be employed wherein the alkyl groups are secondary and tertiary butyl, neopentyl, branched chain hexyls and heptyls, and also branched chain octyl groups, such as isooctyl. Preferably, aryl dialkyl phosphinates are employed wherein the alkyl groups are straight-chain alkyls. The two alkyl groups in the phosphinates may be the same or different.

In the process of manufacture of the above monoaryl dialkyl phosphinates the final reaction product contains, in addition to the desired aryl dialkyl phosphinate, small amounts of other side reaction products, including phosphonates and phosphine oxides. Thus, for example, in the preparation of phenyl di n-butyl phosphinate for use in hydraulic fluids, according to the invention, by practice of the above process a mixture of products is formed composed of about 70% to 80% of the phenyl di n-butyl

phosphinate, about 10% to 15% of disphenyl n-butane phosphinate, and about 10% to about 15% of tri n-butyl phosphine oxide. This impure material itself is substantially as suitable as the purified aryl dialkyl phosphinate. To obtain a purer material, the above mixture may be distilled to increase the amount of phosphinate and reduce the amounts of the above-noted side-reaction products. Thus, the above-described mixture may be distilled to obtain a composition composed of about 87% of the phenyl di n-butyl phosphinate, about 7% diphenyl n-butane phosphonate, and about 6% tri-n-butyl phosphine oxide. Hence, the term "aryl dialkyl phosphinate" employed herein and in the claims is intended to denote either the pure compound or an impure mixture containing a major proportion of aryl dialkyl phosphinate.

If desired, a single one of the above-defined phosphinates can be employed in the hydraulic fluid or a mixture of such phosphinates can be employed. The preferred aryldialkyl phosphinate is phenyl di n-butyl phosphinate.

According to the above application, a minor amount of a compatible thickener or thickening agent is employed in conjunction with the aryl dialkyl phosphinates in order to provide a hydraulic fluid having proper viscosity characteristics at hydraulic fluid operating temperatures of the order of 400° to 550° F., a minimum increase in viscosity at low temperature and a high viscosity index. Thus, such thickener should be effective to increase the viscosity index of the phosphinate-containing hydraulic fluid to at least 75, e.g., in the range of about 75 to about 150, with the resulting fluid containing the thickener having a viscosity at low temperature down to about —40° F. not in excess of about 14,000 centistokes. The thickener should also have high thermal stability at temperature of at least 400° F., and provide a hydraulic fluid having high fire resistance. Examples of suitable thickeners for this purpose include the polyalkyl methacrylates, the polyalkylene glycols, the polyurethanes and the methyl phenyl silicone polymers, in the order of preference named.

The polyalkyl methacrylates employed are generally those resulting from the polymerization of alkyl methacrylates in which the alkyl groups can have an average of from about 3 to 10 carbon atoms. Preferably, the alkyl groups of the methacrylate can vary from about 4 to about 8 carbon atoms. The poly n-butyl methacrylate is preferred for use with the preferred phosphinate material, i.e., phenyl dibutyl phosphinate. The average molecular weight of the polyalkyl methacrylate can range from about 7,000 to about 12,000. Another suitable thickener are the high molecular weight polyalkylene glycols. Suitable materials of this type are those in which the alkylene groups contain from 2 to 3 carbon atoms. Thus, specific examples of such polyalkylene glycols are the high molecular weight polypropylene glycols, polyisopropylene glycols, and copolymers such as the ethylene glycol, isopropylene glycol copolymer. Such high molecular weight polyalkylene glycols are characterized by having a range of viscosity of about 1,400 to about 23,000 centistokes at 100° F. Also suitable as thickeners are the urethane polymer liquids. These may be urethane polyether or urethane polyester materials. Another thickener which can be added to the above aryl dialkyl phosphinate are the liquid methyl phenyl silicone polymers, preferably of high molecular weight and characterized by having a viscosity, e.g., in the range of about 450 to about 575 centistokes at 100° F. The polymers of this type most useful in the hydraulic fluids of the above application are those having a high phenyl to methyl ratio, e.g., of at least about 1:1 and which may be about 2:1, or higher.

Usually a minor proportion, and generally from about 0.5% to about 10% by weight of the thickener, based on the weight of the total composition, produces the desired effectiveness in the aryl dialkyl phosphinate base stock. In preferred practice, a proportion of about 1% to about 5% by weight of thickener is employed.

The entire description of the phosphinates and the hydraulic fluids containing such phosphinates in the above-noted copending application is incorporated herein by reference.

The development of suitable inhibitors against attack of the above-described phosphinates on iron, and which are compatible and suitable for use with such phosphinates, and particularly for incorporation in the above-described hydraulic fluids containing such phosphinates as an essential component has been complex. The difficulties in developing suitable additives for this purpose, and particularly for use with such hydraulic fluids, are the requirements that such additives must be compatible with or soluble in such phosphinate-containing compositions or hydraulic fluids over a broad temperature range, the additives should not cause undesirable gelation of these compositions tending, for example, to transform such compositions or fluids into a thixotropic material, and should not have any adverse side effects or side reactions on the components of these compositions, particularly the organic phosphinates, specifically the aryl dialkyl phosphinate component thereof. Also, the inhibitor should not to operate to increase corrosion on the metals which are not normally affected by the phosphinate-containing material, and also the volatility of the additive should be low enough so that the inhibitor is not volatilized at the higher temperatures of operation. Further, for preferred use in the above-described hydraulic fluids which are intended for operation at high temperatures in the range of 400° to 550° F., it is necessary that such additives have good thermal stability at temperature of at least about 400° F., preferably in the range of about 400° to about 550° F., and fire resistance.

The above-described 2-iodobiphenyl, or combination of 2-iodobiphenyl and hexaphenyl di tin, in addition to possessing high inhibiting effectiveness of the attack of the above organic phosphinates on iron, also possess substantially all of the above characteristics.

The amount of 2-iodobiphenyl, or a combination of 2-iodobiphenyl and hexaphenyl di tin, incorporated into the organic phosphinate-containing material, preferably the above-described hydraulic fluid, to achieve the above-described inhibiting effectiveness, generally can range from about 0.01% to about 3%, preferably from about 0.01% to about 1%, by weight of the composition. The use of about 0.5% by weight of 2-iodobiphenyl, or a combination of 0.5% by weight of 2-iodobiphenyl and 0.5% by weight of hexaphenyl di tin, has been found particularly satisfactory. Where a combination of 2-iodobiphenyl and hexaphenyl di tin is employed, it is preferred to employ approximately equal amounts of each additive, the total amount of both employed being within the aforementioned general and preferred ranges. However, if desired, a larger amount of one, e.g., 2-iodobiphenyl, or the other, can be employed in such additive mixture, the relative amounts of such compounds present being such that preferably the above-noted synergistic effect is obtained.

Although an amount of additive material greater than 3% can be employed, where such amount of additive is soluble in the base phosphinate material, such larger amounts usually do not materially enhance the effectiveness of the additive. Amounts of additive smaller than 0.01% by weight generally are of reduced effectiveness in producing the desired inhibition of corrosion according to the invention.

The following are examples of practice according to the invention:

EXAMPLE 1

The following compositions were prepared by dissolving in each case the indicated amount of inhibitor in the indicated amount of phosphinate.

Composition A

	Percent by weight
Phenyl di n-butyl phosphinate	99.5
2-iodobiphenyl	0.5

Composition B

Phenyl di n-butyl phosphinate	99.0
2-iodobiphenyl	0.5
Hexaphenyl di tin	0.5
	100.0

Each of Compositions A and B, and a control consisting of phenyl di n-butyl phosphinate alone in the absence of any inhibitor, was tested for corrosion on iron in the form of a low carbon steel, as follows: 1" x 1" x .032" thick samples of a mild carbon steel meeting the requirements of Federal Specification QQ–S–636 were immersed respectively in each of the fluid Compositions A and B, and in the control, and such fluids heated to 400° F. for 24 hours. The specimens were then removed from the fluids and cooled, and the change in appearance of the fluids and the respective samples, and the weight loss of each metal sample determined.

The results of these tests showed that substantial corrosion of the iron sample occurred in the control fluid not containing the invention inhibitor. Thus, the iron sample immersed in such fluid had a weight loss of 7.0 mg./cm.^{2}, and the appearance of the surface of the sample was rough and discolored. The control fluid had changed in appearance to an opaque black sediment-containing fluid due to such corrosion of the iron sample.

On the other hand, the tests showed that the iron sample contacted with fluid Composition A containing the invention inhibitor 2-iodobiphenyl had substantially reduced corrosion. Thus, weight loss tests of the iron sample contacted with Composition A showed reduction of corrosion of such sample to about one-tenth of the corrosion of the iron sample contacted with the control fluid as described above. Fluid Composition A following treatment, although darkened to some extent, was essentially clear in appearance, with substantially no sludge formation visible.

With respect to the corrosion tests employing Composition B, containing the combination of 2-iodobiphenyl and hexaphenyl di tin as additive, the amount of corrosion of the iron sample was reduced significantly below the above-noted small amount of corrosion of the iron contacted with Composition A. Thus, weight loss determination of the iron sample contacted with Composition B showed corrosion of the iron sample was reduced to about 1/100 of the corrosion of the iron sample contacted with the control fluid, as compared to about 1/10 for the iron sample contacted with Composition A as noted above.

EXAMPLE 2

The following compositions are prepared by dissolving in each case the indicated amount of inhibitor in the indicated amount of phosphinate and polyalkyl methacrylate or polyalkylene glycol thickener forming a hydraulic fluid, Composition C being the control.

Composition C

	Percent by weight
Phenyl di n-butyl phosphinate	94
A mixture of 30% by weight of a poly n-butyl methacrylate having an average molecular weight of 7,900, and 70% by weight of an organic phosphate ester as a carrier and solvent, marketed as Acryloid R–3876X by Rohm & Haas Co.	6
	100

Composition D

Phenyl di n-butyl phosphinate	93.5
Acryloid R–3876X	6.0
2-iodobiphenyl	0.5
	100.0

Composition E

Phenyl di n-butyl phosphinate	93.0
Acryloid R–3876X	6.0
2-iodobiphenyl	0.5
Hexaphenyl di tin	0.5
	100.0

Composition F

Phenyl di n-butyl phosphinate	93.5
Acryloid R–3876X	6.0
2-iodobiphenyl	0.3
Hexaphenyl di tin	0.2
	100.0

Composition G

	Percent by weight
Phenyl di n-butyl phosphinate	97.5
High molecular weight polyalkylene glycol, believed to be an ethylene glycol, isopropylene glycol copolymer having a viscosity of 2,620 centistokes at 210° F. and 19,500 centistokes at 100° F., marketed as Union Carbide Chemical Company's #75–H–90,000	2.0
2-iodobiphenyl	0.5
	100.0

Composition H

Phenyl di n-butyl phosphinate	97.0
#75–H–90,000 (Union Carbide)	2.0
2-iodobiphenyl	0.5
Hexaphenyl di tin	0.5
	100.0

Each of the hydraulic fluid Compositions C, D, E, F, G and H is tested for corrosion on iron by procedure similar to that set forth in Example 1 above.

The results are similar to those obtained in Example 1. Thus, Composition C, the control, containing no inhibitor according to the invention, causes substantial corrosion of the iron practically to the same extent as did the control in Example 1, whereas Compositions D and G, hydraulic fluids containing phosphinate, thickener and invention inhibitor 2-iodobiphenyl, substantially reduced corrosion on the iron samples essentially to the same extent as did Composition A of Example 1. Similarly as in the case of Composition B of Example 1, Compositions E, F and H each greatly reduced corrosion of the iron samples contacted therewith below the corrosion of the iron samples contacted with each of Compositions D and G, as in the case of Composition B of Example 1.

Hence, it is apparent that the presence of the thickener in the phosphinate-containing hydraulic fluids of Compositions C to H have substantially no effect on the function of the invention inhibitors in the inhibited hydraulic fluids of the invention for inhibiting corrosion of iron.

EXAMPLE 3

The following formulations are prepared.

Composition J

	Percent by weight
Phenyl di n-butyl phosphinate	99
2-iodobiphenyl	1
	100

Composition K

Phenyl di n-butyl phosphinate	98
2-iodobiphenyl	2
	100

Composition L

Phenyl di n-butyl phosphinate	98.5
2-iodobiphenyl	1.0
Hexaphenyl di tin	0.5
	100.0

Inhibition of corrosion on iron samples is obtained using Compositions J and K, with highly reduced corrosion on iron particularly realized using Composition L. However, better results are obtainable employing compositions containing amounts of inhibitors not above about 1%.

EXAMPLE 4

The following are additional examples of inhibited phosphinate-containing compositions according to the invention.

Composition M

	Percent by weight
Phenyl di n-pentyl phosphinate	96.8
A poly n-hexyl methacrylate having an average molecular weight of about 8,000 to about 10,000	3.0
2-iodobiphenyl	0.2
	100.0

Composition N

Phenyl di n-hexyl phosphinate	93.5
A polypropylene glycol	6.0
2-iodobiphenyl	0.5
	100.0

Composition O

Phenyl di neopentyl phosphinate	99
2-iodobiphenyl	1
	100

Composition P

Phenyl di isooctyl phosphinate	94.4
A urethane polymer liquid	5.0
2-iodobiphenyl	0.3
Hexaphenyl di tin	0.3
	100.0

Composition Q

Naphthyl di n-butyl phosphinate	96.5
A poly n-butyl methacrylate having an average molecular weight of about 8,000	3.0
2-iodobiphenyl	0.5
	100.0

Composition R

Phenyl di n-butyl phosphinate	94.5
Methyl phenyl silicone polymer marketed as DC710 by Dow Corning Co. and believed to be a high molecular weight polymer having a high phenyl to methyl ratio	5.0
2-iodobiphenyl	0.5
	100.0

Composition S

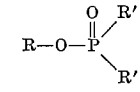
Naphthyl di neopentyl phosphinate	93.2
A poly n-butyl methacrylate having an average molecular weight of about 8,000	6.0
2-iodobiphenyl	0.4
Hexaphenyl di tin	0.4
	100.0

From the foregoing, it is seen that the invention provides phosphinate-containing compositions and valuable phosphinate-containing hydraulic fluids which are inhibited against attack of iron, particularly low carbon steels, and certain of which are especially effective in greatly reducing corrosion of iron or low carbon steels, important metals of construction of components of aircraft hydraulic systems, and which are subject to substantial corrosion in the presence of such uninhibited phosphinate-containing compositions and hydraulic fluids.

While I have described particular embodiments of my invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention, as set forth in the appended claims.

I claim:

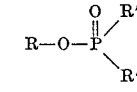
1. A hydraulic fluid consisting essentially of an aryl dialkyl phosphinate having the formula



where R is an aryl group selected from the class consisting of phenyl and naphthyl, and R′ is an alkyl group containing from 4 to 8 carbon atoms, and about 0.01% to about 3% of 2-iodobiphenyl by weight of said composition as a corrosion inhibitor.

2. A hydraulic fluid as defined in claim **1**, wherein said phosphinate is phenyl di n-butyl phosphinate.

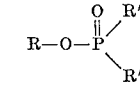
3. A hydraulic fluid consisting essentially of an aryl dialkyl phosphinate having the formula



where R is an aryl group selected from the class consisting of phenyl and naphthyl, and R′ is an alkyl group containing from 4 to 8 carbon atoms, and about 0.01% to about 3% of a combination of approximately equal amounts of 2-iodobiphenyl and hexaphenyl di tin by weight of said composition as a corrosion inhibitor.

4. A hydraulic fluid as defined in claim **3**, wherein said phosphinate is phenyl di n-butyl phosphinate.

5. A hydraulic fluid consisting essentially of an aryl dialkyl phosphinate having the formula



where R is an aryl group selected from the class consisting of phenyl and naphthyl, and R′ is an alkyl group containing from 4 to 8 carbon atoms, and from about 0.5% to about 10% by weight of a material selected from the group consisting of polyalkyl methacrylates wherein the alkyl groups contain an average of from about 3 to 10 carbon atoms, and having an average molecular weight ranging from about 7,000 to about 12,000, high molecular weight polyalkylene glycols, wherein the alkylene groups contain from 2 to 3 carbon atoms, and having a range of viscosity of about 1,400 to about 23,000 centistokes at 100° F., urethane polymer liquids and high molecular weight methyl phenyl silicone polymers having a viscosity in the range of about 450 to about 575 centistokes at 100° F., said material being compatible with said phosphinate and effective to increase the viscosity index to at least 75, and about 0.01% to about 3% by weight of said composition of 2-iodobiphenyl as additive to inhibit corrosion of iron by said hydraulic fluid.

6. A hydraulic fluid as defined in claim **5**, wherein said material is a polyalkyl methacrylate having an average molecular weight ranging from about 7,000 to about 12,000.

7. A hydraulic fluid as defined in claim **5**, wherein said material is a high molecular weight polyalkylene glycol

having a range of viscosity of about 1,400 to about 23,000 centistokes at 100° F.

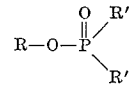
8. A fire-resistant hydraulic fluid consisting essentially of phenyl di n-butyl phosphinate, about 0.5% to about 10% by weight of polybutyl methacrylate having an average molecular weight range from about 7,000 to about 12,000, and about 0.01% to about 3% by weight of 2-iodobiphenyl.

9. A fire-resistant hydraulic fluid consisting essentially of phenyl di n-butyl phosphinate, about 0.5% to about 10% by weight of polybutyl methacrylate having an average molecular weight range from about 7,000 to about 12,000, and about 0.01% to about 3% by weight of a combination of approximately equal amounts of 2-iodobiphenyl and hexaphenyl di tin.

10. A fire-resistant hydraulic fluid consisting essentially of phenyl di n-butyl phosphinate, about 0.5% to about 10% by weight of a high molecular weight polyalkylene glycol wherein the alkylene groups contain from 2 to 3 carbon atoms, and having a range of viscosity of about 1,400 to about 23,000 centistokes at 100° F., and about 0.01% to about 3% by weight of 2-iodobiphenyl.

11. A fire-resistant hydraulic fluid consisting essentially of phenyl di n-butyl phosphinate, about 0.5% to about 10% by weight of a high molecular weight polyalkylene glycol wherein the alkylene groups contain from 2 to 3 carbon atoms, and having a range of viscosity of about 1,400 to about 23,000 centistokes at 100° F. and about 0.01% to about 3% by weight of a combination of approximately equal amounts of 2-iodobiphenyl and hexaphenyl di tin.

12. A hydraulic fluid consisting essentially of an aryl dialkyl phosphinate having the formula



where R is an aryl group selected from the class consisting of phenyl and naphthyl, and R′ is an alkyl group containing from 4 to 8 carbon atoms, and from about 0.5% to about 10% by weight of a polyalkyl methacrylate wherein the alkyl groups contain an average of from about 3 to 10 carbon atoms, and having an average molecular weight ranging from about 7,000 to about 12,000, said polyalkyl methacrylate being compatible with said phosphinate and effective to increase the viscosity index to at least 75, and about 0.01% to about 3% by weight of said composition of a combination of approximately equal amounts of 2-iodobiphenyl and heaxphenyl di tin as additive to inhibit corrosion of iron by said hydraulic fluid.

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