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LUBRICANT COMPOSITION

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This invention relates to antirust compositions. More particularly, this invention is concerned with vapor space corrosion inhibition with oils and other substrates containing certain amines and phenols.

It is well known that the rusting of ferrous metal surfaces is a common problem in the field of lubrication. Accordingly, a large amount of research effort has developed a great many additives which, when present in lubricants in small amounts, inhibit corrosion of the surfaces with which the oil comes into contact. Reference to many of these inhibitors is found in a book by Putilova et al., *Metallic Corrosion Inhibitors*, Pergamon Press, 1960. Although these known inhibitors are successful in reducing or eliminating corrosion of metal in contact with the liquid, they are generally ineffective for reducing corrosion in the vapor space above the fluid. These preservative oils are adequate only as long as a continuous oil film of appreciable thickness is maintained. However, serious rusting problems have been encountered in certain infrequently operated or stored equipment, especially when the humidity is high. For instance, a large amount of agricultural machinery is in operation only during certain seasons of the year. Fruit picking and packing equipment may be idle for most of the year; for example, processing equipment in a winery may be in operation only a few weeks annually. Snow removal equipment must be in storage throughout the summer. Both new and used cars may remain for months in dealers' lots with infrequent operation. It is apparent that although known inhibitors would prevent rusting of the metal surfaces in contact with the lubricating oil, corrosion could occur freely in the space above the oil level. The present invention obviates this problem.

It is an object of this invention to provide compositions for reducing vapor space corrosion. It is a further object of this invention to provide a lubricant for machinery and equipment which is infrequently used, or is in storage. Another object of the invention is to provide a lubricant for preventing vapor space corrosion in systems where water may be present in the oil, such as steam turbines and systems employing water-containing hydraulic fluids. Other objects will become apparent from the following discussion of the invention.

It has now been discovered that oils containing certain low-molecular-weight amines and phenols provide excellent corrosion inhibition for ferrous metals not in contact with the fluid lubricant. In accord with the invention, lubricating oils contain from about 0.02 to 5% by weight, preferably 0.05 to 2%, and more especially 0.1 to 1% of each of a phenol and an amine as defined below. The amines used in the invention are mono-

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diamines having from 4 to 8, preferably 4 to 7, and still more preferably 4 to 6 carbon atoms per molecule. Examples of amines to be used in combination with phenols include butylamine, pentylamine, hexylamine, cyclohexylamine, methyl piperazine, N,N'-dimethyl piperazine, N,N'-dimethyl-1,3-propanediamine, and pyridine. The phenols used in lubricants of the invention are substituted with alkyl groups having 0 to 10, preferably 1 to 8, and more especially 4 to 8 carbon atoms. The number of carbon atoms in the total of the alkyl substituents on any phenol is not more than 10, and is favorably 1 to 8, preferably 4 to 8, especially 4. Examples of suitable phenols are cresol, xlenol, tert-butyl phenol, di-tert-butyl phenol, 2,6-di-tert-butyl-4-methylphenol, and isooctyl phenol. Although vapor space inhibition properties are obtained when each of the components is present in amounts within the range specified above, excellent results are in general obtained when the mole ratio of amine to phenol is approximately 1.

As mentioned above, the defined amines and phenols must be used in combination to achieve significant rust protection in the vapor space above the oil. As is apparent from the data in Tables 1 and 2 below, the individual amines and phenols are less effective as vapor space corrosion inhibitors. The mechanism of corrosion protection by the combination of the amines and phenols of the invention is not completely understood; one possible explanation is that the amines and phenols are present individually in the vapor space but combine to form a weak salt on the surface of the metal in contact with the vapor space. This salt may then inhibit corrosion of the metal surface. Although combinations of phenols and amines of higher molecular weights are known to produce contact rust inhibition (i.e., to prevent corrosion of metal in contact with the liquid), the present mixtures of low-molecular-weight compounds do not necessarily possess this property. Indeed, other known corrosion inhibitors may be added to the mixtures of the invention to provide increased contact rust inhibition, if desired.

The outstanding vapor space rust inhibition properties of the combinations of amines and phenols of the invention are illustrated by means of the following examples and tables, which are intended to exemplify but not to limit the invention.

Example I

A freshly polished and cleaned mild steel plate (1 mm. x 23 mm.) was suspended in the upper part of a loosely stoppered 250-ml Erlenmeyer flask containing 10 ml. of distilled water and 5 ml. of vapor-space inhibiting oil. The flask was placed in a heated oil bath to a depth of 5 cm. The time for rust to appear at a given temperature was then noted. The base oil used for all of the compositions in the table was a mixture of 68% w. high-VI mineral oil having a Saybolt Universal Viscosity of 500 seconds at 100° F. and 32% w. high-VI mineral oil having a Saybolt Universal Viscosity of 250 seconds at 100° F. The results of tests with various amines, phenols, and combinations thereof are tabulated below.

TABLE I.—VAPOR SPACE RUST INHIBITION TESTS

Additive	Concentration of additive in weight percent	Time before appearance of rust	
		100° F. (Days)	150° F. (Hours)
None		1 to 2	1 to 2
Cresol	0.25		2 to 3
Cresol	0.50	4	2 to 3
tert-Butyl phenol	0.25		1 to 2
Di-tert-butyl phenol	0.25		1 to 2
Ionol (2,6-di-tert-butyl-4-methylphenol)	0.25		1
Hexylamine	0.25	5	6
Octylamine	0.25		2
Octylamine	0.50	5	2
2-methyl piperazine	0.25		1
Cresol and hexylamine	0.25	15	>24
Cresol and hexylamine	0.50	15	
Cresol and octylamine	0.25	9	>24
Cresol and octylamine	0.50	>18	>24
Cresol and octylamine	0.25		22
Cresol and 2-methyl piperazine	0.25		18
tert-Butyl phenol and hexylamine	0.25		22
tert-Butyl phenol and octylamine	0.25		22
tert-Butyl phenol and octylamine	0.50		22
tert-Butyl phenol and 2-methyl piperazine	0.25		>24
Di-tert-butyl phenol and hexylamine	0.25	10	>24
Di-tert-butyl phenol and octylamine	0.25	11	20
Di-tert-butyl phenol and 2-methyl piperazine	0.25		>40
Ionol and hexylamine	0.25	4	24
Ionol and octylamine	0.25	>18	20
Ionol and octylamine	0.50		20
Ionol and octylamine	0.50		

Thus it is apparent from the above data that the amine and phenol additives of the invention coact to produce vapor space protection which is superior to that of the individual components. The following example further illustrates the advantage of compositions of the invention.

Example II

Tests were conducted at ambient temperature, 150° and 210° F. to determine the temperature range of effectiveness of various VSI agents. The ambient temperature test, designated as Test A, was conducted outdoors at temperatures ranging from about 5° F. to 55° F. A freshly polished and cleaned mild steel plate 5 x 7.5 x 0.3 cm. was rested against the interior side of a covered one-quart glass jar. The plate was held in place with a small glass cylinder, the bottom of the plate resting in the oil-water layers to a depth of about 1 cm. A mild steel block 1.8 x 1.8 x 0.6 cm. was suspended about 5 cm. from the perforated plastic cover of the jar with a platinum wire. The duration of the test was 43 days. The faces of the block and the underside of the plate are rated in Table II below.

In Test B, a freshly polished and cleaned mild steel block 1.8 x 1.8 x 0.6 cm. was suspended in the upper part of a loosely covered 250 ml. Erlenmeyer flask containing 10 ml. of distilled water and 15 ml. of VSI oil. The metal block was suspended with a platinum wire. The flask was immersed to a depth of 5 cm. in a constant-temperature bath at 150° or 210° F. The time for rust to appear at each condition is recorded in Table II below. The base stock was the same as that used in Example I. In the table below each additive, whether alone or in combination with another, is present in the amount of 0.25% w. The results are tabulated in Table II.

TABLE II.—VAPOR SPACE RUST INHIBITION TESTS

Additive	Test A		Test B	
	Specimen condition		Hours before rust appears on block	
	Ambient temperature		150° F.	210° F.
None	{Block: Lt. rust. Plate: Med. rust.		½	½
Hexylamine	{Block: Trace rust. Plate: Perfect.		5	1
Cyclohexylamine	{Block: Trace rust. Plate: Trace rust.		<20	
2-methylpiperazine	{Block: Trace rust. Plate: Trace rust.		2	1
Hexylamine plus 2-methyl piperazine			2	
tert-Butylaminoethanol			2	
2-methyl piperazine plus tert-butyl aminoethanol			3	
N,N'-dimethyl piperazine			1	
Cresol			1	
tert-Butyl phenol	{Block: Trace rust. Plate: Trace rust.		2	½
Di-tert-butyl phenol	{Block: Trace rust. Plate: Lt. rust.		2	½
Octylphenol			1	
tert-Butyl phenol plus 2-methyl piperazine	{Block: Perfect. Plate: Perfect.		>24	>24
tert-Butyl phenol plus hexylamine			<20	
Di-tert-butyl phenol plus hexylamine			20	
Di-tert-butyl phenol plus 2-methyl piperazine	{Block: Trace rust. Plate: Perfect.		>24	20
tert-Butyl phenol plus cyclohexylamine			>20	
Di-tert-butyl phenol plus cyclohexylamine			20	
Octylphenol plus 2-methyl piperazine			20	
Octylphenol plus hexylamine			20	
Octylphenol plus cyclohexylamine			20	

It is apparent from the data in Table II that the compositions of the invention are effective over a considerable temperature range, which is surprising in view of the extremely low partial pressures of the additive above the oil at low temperatures. The combinations of 2-methyl piperazine with tert-butyl phenol and 2-methyl piperazine with di-tert-butylphenol are particularly successful in this regard.

Example III

Tert-butyl phenol and 2-methyl piperazine were added to a water-oil emulsion containing about 60% w. high-VI oil and about 40% w. water. The emulsion was stabilized with glycerol monooleate. The concentrations of tert-butyl phenol and 2-methyl piperazine were about 0.50% w. each, basis oil phase. A test was conducted in accord with procedure B in Example II, at 150° F. Rust did not appear on the block for over 24 hours after the start of the test. Thus the additives of the invention are also suitable for vapor space corrosion inhibition in systems employing oil-water emulsions for, e.g., hydraulic fluids, wherein serious corrosion problems have been known to occur.

The additives of the invention may be advantageously used in a wide variety of petroleum fractions and other organic and inorganic, preferably organic, liquid and semi-solid substrates. The amine-phenol additive package is effective in gasoline, fuel oil, printing ink, paints and lacquers, greases, paraffin waxes, vegetable waxes, asphalts, etc. The inhibitor combination may be added as a package to the above-mentioned substrates; weight ratios of amine to phenol may vary from about 1/0.01 to 0.01/1, and are preferably between 1/0.05 and 0.05/1.

When the amine-phenol combination is used in a preservative lubricating oil, the oil may be obtained from paraffinic, naphthenic asphaltic, or mixed base crude oil, or mixtures thereof. The viscosity of these oils may vary over a wide range, for example, from 50 Saybolt seconds at 100° F. to 100 Saybolt seconds at 210° F. Emulsions of water in mineral oil, the oil comprising the continuous phase, are also excellent base fluids for additives of the invention. The amine-phenol combinations of the invention are also contemplated for use in synthetic lubricants, such as polymerized olefins, polyalkylene glycols, polyphenyl ethers, methyl and phenyl silicone polymers, and organic esters, e.g., 2-ethylhexyl sebacate, C₄-C₁₀ acid esters of pentaerythritol or dipentaerythritol. Synthetic lubricants containing amines and phenols of the invention would be particularly useful for, e.g., vapor space corrosion protection for stored aircraft.

In addition to the additives of the invention, the claimed compositions may contain other agents such as antioxidants, contact corrosion inhibitors, color stabilizers, metal deactivators, pour point and viscosity index modifiers, antifoam agents, etc.

I claim as my invention:

1. A composition comprising a major proportion of an organic substrate and from about 0.02 to 5% by weight of each of

- (1) an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and
- (2) a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms.

2. The composition of claim 1 where the amine is 2-methyl piperazine.

3. A lubricating composition comprising a major proportion of a mineral lubricating oil and from about 0.02 to 5% by weight of each of

- (1) an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and
- (2) a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms.

4. A composition comprising a major proportion of a

mineral lubricating oil and from about 0.02 to 5% by weight of each of

- (1) an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule, and
- (2) a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms.

5. The composition of claim 4 wherein the phenol is selected from the group consisting of tert-butyl phenol and di-tert-butyl phenol.

6. A composition comprising a major proportion of a mineral lubricating oil and from about 0.02 to 5% by weight of an amine selected from the group consisting of butylamine, hexylamine, cyclohexylamine, methyl piperazine, N,N'-dimethyl piperazine, pyridine, and N,N'-dimethyl-1,3-propanediamine, and from about 0.02 to 5% by weight of a phenol selected from the group consisting of cresol, xyleneol, tert-butyl phenol, di-tert-butyl phenol, 2,6-di-tert-butyl-4-methyl phenol, and isooctyl phenol.

7. A composition comprising a major proportion of a mineral lubricating oil and from about 0.02 to 5% of each of 2-methyl piperazine and tert-butyl phenol.

8. A composition comprising a major proportion of a water-in-mineral oil emulsion and from about 0.02 to 5% by weight of each of

- (1) an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and
- (2) a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms.

9. A composition comprising a major proportion of a hydrocarbon fuel and from about 0.02 to 5% by weight of each of

- (1) an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and
- (2) a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms.

10. A composition comprising a major proportion of a grease and from about 0.02 to 5% by weight of each of

- (1) an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and
- (2) a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms.

11. An additive package for inhibiting vapor space corrosion which comprises an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms, the weight ratio of amine to phenol being from 1/0.01 to 0.01/1.

12. An additive package for inhibiting vapor space corrosion which comprises an amine selected from the group consisting of monoamines and diamines having from 4 to 6 carbon atoms per molecule and a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms, the weight ratio of amine to phenol being from 1/0.01 to 0.01/1.

13. An additive package for inhibiting vapor space corrosion which comprises an amine selected from the group consisting of monoamines and diamines having from 4 to 8 carbon atoms per molecule and a phenol substituted with alkyl groups which have a total of from 0 to 10 carbon atoms, the weight ratio of amine to phenol being from 1/0.05 to 0.05/1.

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