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CORROSION INHIBITING COMPOSITIONS

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This invention relates to petroleum base compositions which may be applied as coatings to metal surfaces to provide for corrosion inhibition of the metal surfaces, through the vapors produced by the compositions or by contact of the compositions with the metal surfaces.

The prevention of corrosion of metal surfaces and weight loss therefrom has been a considerable problem particularly when such surfaces are exposed to the elements including rain, snow, and high humidity. In addition, acidic atmospheric conditions have to a large extent aggravated the corrosion problem. These problems of corrosion are of primary importance not only in the ferrous metals field, but also of considerable importance for many of the non-ferrous metals.

It has been desirable to apply to metal surfaces some quickly and easily applied and readily removed coating which gives good corrosion protection. It has also been desirable that the coating be of such a nature that the applied material is not undesirable or detrimental when the treated article is put to its intended use, or when corrosion protection is no longer of prime concern.

Previously proposed special wrappings and packaging treatments with dehumidification are costly and difficult. Slushing compounds such as heavy oils and greases have been employed but the applied products are often unsightly, are difficult and expensive to remove, and are not completely satisfactory in preventing corrosion under many conditions. Furthermore, such slushing compounds ordinarily must be applied to bone-dry metal surfaces. Coating formulations embodying organic amides and inorganic metal nitrites have been employed. Other formulations containing ammonium derivatives, ureas, and the like have also been employed. Coatings embodying either of these last aforementioned materials have not been sufficiently satisfactory inasmuch as many of them produce rapid and disastrous weight loss on many non-ferrous metals, especially on copper, brass, zinc, and cadmium, or they are not of sufficient strength or volatility to efficiently inhibit corrosion. It has been found also that many formulations incorporating ammonium salts are not completely soluble in hydrocarbon vehicles at practical working concentrations. Further, compositions, which cause excessive weight loss on copper and brass especially, exclude a large portion of the metals industry field, inasmuch as many finished metallic products contain combinations of ferrous metals and non-ferrous metals.

It is also desirable to have available a corrosion inhibiting additive which is not only soluble in hydrocarbon solvents such as benzene and toluene, but has a relatively good solubility in water. Many paints and coating compositions comprise an aqueous solvent and a corrosion inhibitor that can be dissolved therein would be highly useful.

An object of the present invention is to provide a corrosion inhibiting additive capable of being dissolved in both hydrocarbon solvents and water comprising the reaction product of a mixture of caproic and caprylic acids and a cyclic amine.

Another object of this invention is to provide a corrosion inhibiting additive of controlled alkalinity and moderate vapor pressure, and capable of being dissolved in hydrocarbon solvents and in water, comprising the reaction product of at least 9 weight percent of caproic acid and the balance being at least 75 weight percent of caprylic acid, from 80 to 135 parts of dicyclohexylamine per 100 parts of the acids, and from 0.1 to 45 parts of alpha-methyl benzylamine.

Another object of this invention is to provide a highly effective corrosion inhibiting composition comprising a major proportion of a petroleum base vehicle, and a minor proportion of the reaction product of a cycloaliphatic amine, a methylbenzylamine and a mixture of caproic and caprylic acids.

A further object of this invention is to provide a highly effective corrosion inhibiting composition comprising a major proportion of a petroleum base vehicle, a minor proportion of the reaction product of a cycloaliphatic amine, a mixture of caproic and caprylic acids, methylbenzylamine and hydrophilic wetting agent.

Other objects will in part be obvious and will in part appear hereinafter.

This invention is based upon the discovery that a certain combination of amines reacted with suitable acids exhibits synergistic corrosion inhibiting characteristics whereby it is highly effective in the vapor phase, in the liquid contact phase, and, produces no deleterious effects on ferrous metals, copper, brass, and alloys and combinations of copper, brass, and ferrous metals.

In particular, it has been discovered that the reaction product of a cycloaliphatic amine, particularly dicyclohexylamine, methylbenzylamine and a mixture of caproic and caprylic acids will dissolve both in hydrocarbons and in water, and imparts exceptional corrosion inhibiting properties to oleaginous liquids, paints and aqueous coating compositions. From 15 to 0.1 parts of this reaction product, and preferably at least 2 parts, admixed with an oleaginous liquid to give 100 parts by weight of a composition, provides an excellent protective coating material. The composition should comprise at least 75 parts by weight of the oleaginous liquid and preferably from 80 to 98 parts thereof. From 10 to 0.1 parts, and preferably from 5 to 0.5 parts, of an oil soluble hydrophilic wetting agent may be present to enable the composition to be applied to damp or wet metal surfaces.

We have discovered that the reaction product of substantially equimolar parts of caprylic acid and dicyclohexylamine is relatively insoluble in water. The solubility of the dicyclohexylamine octoate reaction product is less than 1 part in 100 parts of water at 25° C. However, we have found that upon substituting caproic acid for part of the caprylic acid, when the caproic acid reaches approximately 9% by weight of the acid mixture that the reaction product becomes quite water soluble, and that upon the caproic acid reaching, by weight, 15% of the mixture of acids, 10 grams of the dicyclohexylamine caproate-caprylate reaction product will dissolve in 90 grams of water. This effect is obtained when alpha-methyl benzylamine is substituted for up to half the weight of the dicyclohexylamine or when cyclohexylamine is substituted in whole or in part for the dicyclohexylamine. These compositions are all substantially completely soluble in hydrocarbon solvents such as toluene, benzene, and the like.

The following compositions of Examples I to IV illustrate the water solubility features of the invention:

EXAMPLE I

A mixture comprising 95 parts of dicyclohexylamine, 40 parts of alpha methylbenzylamine, 10 parts of caproic acid and 90 parts of caprylic acid was stirred at room temperature and it reacted to form a product in a few minutes. When ten grams of the reaction product was admixed with 90 grams of water at 25° C., 22% of the reaction product dissolved. When ten grams of a similar reaction product containing no caproic acid was admixed

with 90 grams of water it did not appreciably dissolve in the water.

EXAMPLE II

A mixture of 95 parts of dicyclohexylamine, 40 parts of alpha methylbenzylamine, 14 parts of caproic acid and 86 parts of caprylic acid was reacted as in Example I. When ten grams of this reaction product were placed in 90 grams of water at 25° C., 84.4% of the reaction product dissolved.

EXAMPLE III

The proportions of the reactants in Example II were varied to provide 12 grams of caproic acid and 88 grams of caprylic and the remaining ingredients being unchanged. When 10 grams of the reaction product was placed in 90 grams of water at 25° C., it dissolved to the extent of 68.8% by weight.

EXAMPLE IV

When the process of Example II was repeated with all the components being the same except for employing 15 grams of caproic acid and 85 grams of caprylic acid, 10 grams of the reaction product dissolved completely in 90 grams of water at room temperature.

The following general formulations are given as illustrative of this invention; in Examples V and VI, the components need merely be admixed and are ready for use.

EXAMPLE V

A. From 75 to 99.8 parts, by weight, of an oleaginous vehicle, such as petroleum oil, of a viscosity of 5 centipoises to 100 poises at 20° C.;

B. From 10 to 0.1 parts, by weight, of an oil soluble hydrophilic wetting agent such as petroleum sulfonates and sorbitan monolaurate; and

C. From 15 to 0.1 parts, by weight, of the reaction product of (*a*) from 80 to 135 parts of dicyclohexylamine, (*b*) from 45 to 0.1 parts of alpha-methyl-benzylamine, (*c*) from 91 to 75 parts of caprylic acid and (*d*) from 9 to 25 parts of caproic acid.

EXAMPLE VI

A. From 85 to 99.9 parts, by weight, of an oleaginous vehicle of a viscosity of 5 centipoises to 100 poises at 20° C.; and

B. From 15 to 0.1 parts, by weight, of the reaction product of (*a*) from 80 to 135 parts of dicyclohexylamine, (*b*) from 0.1 to 45 parts of alpha-methyl-benzylamine, (*c*) from 91 to 75 parts of caprylic acid and (*d*) from 9 to 25 parts of caproic acid.

Small amounts of the order of up to 10% of the weight of the composition may comprise other corrosion inhibiting additives such as phosphates (zinc phosphate), chromates (sodium chromate), and organic corrosion inhibitors (diisopropylamine nitrite), thickening agents such as polyisobutylene, and anti-oxidants such as dimethyltert-butyl phenol.

The oleaginous vehicle is preferably a relatively non-volatile material of a viscosity from 5 centipoises to 50 poises at 20° C. However, certain applications may require a vehicle of a viscosity from 1 centipoise through 100 poises. Suitable oleaginous vehicles are petroleum hydrocarbon oils, and particularly oils of a viscosity of 5 poises to 25 poises at 100° F., vegetable oils such as castor oil, and synthetic oils such as long chain esters of dibasic acids for example bis(2-ethyl-hexyl) sebacates and the like sold in the trade as Ucon fluids.

Numerous oil soluble hydrophilic wetting agents may be employed in preparing the compositions. Petroleum sulfonates or mahogany soaps of which sodium and barium mahogany sulfonates are examples, are quite satisfactory. Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monooleate and sorbitan polyoxyethylene derivatives, such as those sorbitan monopalmitate polyoxyethylenes sold as Tween 40 and Tween 80, are other examples of suitable wetting agents.

The reaction product may comprise (1) 100 parts by weight of a mixture of the monocarboxylic fatty acids composed of at least 9 parts of caproic acid and at least 75 parts of caprylic acid; (2) from 80 to 135 parts by weight of dicyclohexylamine or cyclohexylamine, or mixtures of the two; and (3) from 0.1 to 45 parts by weight of alpha-methylbenzylamine, the total of (2) and (3) being from 80.1 to 150 parts. Particularly good results are had using 25 to 15 parts of caproic acid and from 75 to 85 parts of caprylic acid.

The alpha methylbenzylamine performs an important function in the additive component for vapor phase protection applications. A series of five separate reaction products was prepared in which constant proportions comprising 15 parts of caproic acid and 85 parts of caprylic acid were employed, while a total of 125 parts of dicyclohexylamine and alpha methylbenzylamine were employed, the latter varying from all dicyclohexylamine to all alpha-methylbenzylamine. A small quantity of several grams each of the five reaction products was placed in glass cylinders 8 inches tall and 2½ inches in diameter with a tapered neck which was closed with a cap. After a sample was put in a glass cylinder, an alkaline indicator strip was placed at the neck and capped. The time for the vapors to reach the neck and charge the indicator was noted as well as the pH of the vapor. A low alkaline pH of about 8 is most desirable since higher alkalinity will result in corrosion of metals. Also slow volatilization of the alkaline vapors is desired for long effective life of the composition in service. However, an extremely slow vapor evolution is not adequate to provide good corrosion protection. The following table indicates the results of these tests:

Table I

	Ratio of Dicyclohexyl-amine/Methyl-benzylamine	Time	pH
1	125/0	3′4″	8
2	110/15	2′52″	8
3	95/30	1′37″	8
4	80/45	1′6″	8
5	0/125	⅒″	10

Composition 5 is essentially useless because of its excessive vaporization rate and excessive alkalinity. Compositions 3 and 4 bore excellent pH values and desirable rates of vapor evolution. Compositions 1 and 2 evolve alkaline vapors rather slowly and would not be acceptable for many applications.

Alpha methylbenzylamine also improves the effect of the compositions on copper and copper base alloys. At least three parts of alpha-methylbenzylamine per one hundred parts of dicyclohexylamine will prevent a copper reaction from occurring.

The reaction product may be prepared and then dissolved in a small amount of xylol or kerosene or other organic solvent and then added to the oleaginous vehicle. For ease of production the reaction product may be made by adding the caprylic and caproic acids, dicyclohexylamine and alpha-methylbenzylamine directly to the oleaginous vehicle. Stirring or agitation of the mixture then completes the reaction and disperses the reaction product throughout the vehicle. The oleaginous vehicle, the hydrophilic wetting agent, the dicyclohexylamine, the alpha-methylbenzylamine, the caprylic acid and the caproic acid may be admixed together in any order.

Jet engine fuels that are stable and non-corrosive when stored in steel drums may be prepared from kerosene and a quantity of the reaction product of from 0.5% to 0.1% in weight admixed therein.

The composition comprising the additives in oils may be applied to metal members by dipping, brushing, spraying or roller coating. After a brief drainage, a thin

covering film of the composition will be present to protect the metal surface. The metal to be treated may be damp or wet with water, and quite cold, but the composition will displace the moisture readily from its surface.

The composition may be placed in close proximity to the metal member, the metal member is then packaged or enclosed so that the package situation or enclosure contains the metal member and a quantity of the compounded oleaginous material. The vapors produced by the composition will afford highly effective corrosion protection to the metal members.

The reaction product compositions of the present invention are highly suited for incorporation in amounts of up to 15% into fluid compositions comprising substantial proportions of water and aqueous media (from 10% to 90%) as one component and oleaginous fluids both synthetic and natural. Thus, for example, hydraulic fluids comprising aqueous emulsions of petroleum oils or synthetic polyesters and "hydrolubes" which may comprise water, ethylene glycol and a high viscosity liquid such as phosphate ester, chlorinated biphenyl and polyglycol, each may be treated to incorporate from 0.1% to 15% or more, by weight of the corrosion inhibiting reaction product compositions of the present invention. The reaction product compositions will readily dissolve in the aqueous phase of the emulsions or the "hydrolubes" and confer corrosion resistance in the liquid phase as well as the vapor phase. When such treated emulsions and other aqueous phase hydraulic lubricants are employed as brake fluids and in hydraulic drive mechanisms they will impart excellent corrosion resistance to all portions of the apparatus exposed to the compositions and their vapors.

Numerous metal working lubricating compositions comprise a mixture or emulsion of (*a*) water or a water solution, often containing slurry of a solid lubricant or non-abrasive filler such as lithopone, and (*b*) a hydrocarbonaceous material such as oils and bitumens, as well as an emulsifier such as a cationic amine salt and an extreme pressure agent, for instance, a haloorganophosphate such as monobutyl trichloromethanephosphorate. The addition of the reaction products of the present invention to such aqueous metal lubricants in amounts of up to 15% will reduce rusting and corrosion of the metal while it is being machined, drawn or otherwise being worked and prevents corrosion while the metal is stored or further processed.

Sheet metal members, casting, wire strip, fabricated members, ship interiors, barrels, bearings, crankcases, are examples of products that may be treated. Barrels, crankcases, gear boxes, transmission cases or other enclosed objects as well as packaged or closed structures will be effectively protected by the oleaginous vehicle composition containing from 0.1 to 3% of the dicyclohexylamine - alpha - methylbenzylamine - caprylate - caproate product. Totally exposed members or members subjected to wet or highly humid conditions should be coated with compositions having from 3% to 15% of the dicyclohexylamine-alpha-methylbenzylamine octoate-caprylate and at least 3% of a suitable wetting agent.

Examples of metals which may be effectively protected comprise steel, cast iron, 12% chromium iron or other lower moderately stain resistant steels, copper, brass, and aluminum.

In all cases of application of a composition formulated with a petroleum oil base stock of 5 centipoises to 70 poises, a thin uniform unbroken coating was produced on all surfaces.

All coatings referred to in this specification can be readily wiped off or dissolved completely in a brief dip in a suitable solvent cleaner such as trichlorethylene.

It will be understood that this specification and examples are illustrative only and are not limiting of the invention.

We claim as our invention:

1. A corrosion inhibiting composition soluble in both liquid hydrocarbons and water consisting essentially of the amine salt reaction product consisting essentially of from 9 to 25 parts by weight of caproic acid, from 91 to 75 parts by weight of caprylic acid, the total of caproic and caprylic acid being 100 parts, and from 80 to 135 parts by weight of at least one cyclic amine selected from the group consisting of cyclohexylamine and dicyclohexylamine.

2. A corrosion inhibiting composition soluble in both liquid hydrocarbons and water consisting essentially of the amine salt reaction product consisting essentially of from 9 to 25 parts by weight of caproic acid, from 91 to 75 parts by weight of caprylic acid, the total of caproic and caprylic acid being 100 parts, from 0.1 to 45 parts by weight of alpha-methylbenzylamine, and from 80 to 135 parts by weight of dicyclohexylamine, the total of dicyclohexylamine and alpha-methylbenzylamine being from 80.1 to 150 parts by weight.

3. A corrosion inhibiting composition soluble in both liquid hydrocarbons and water consisting essentially of the amine salt reaction product consisting essentially of from 15 to 25 parts by weight of caproic acid, from 75 to 85 parts of caprylic acid, from 80 to 100 parts by weight of dicyclohexylamine and from 45 to 30 parts by weight of alpha-methylbenzylamine.

4. A corrosion inhiibting composition suitable for application to wet and damp metal surfaces, consisting essentially of from 85 to 99.9 parts by weight of an oleaginous vehicle of a viscosity of from 1 centipoise to 100 poises at 25° C., and from 15 to 0.1 parts by weight of the amine salt reaction product consisting essentially of from 9 to 25 parts by weight of caproic acid, from 91 to 75 parts by weight of caprylic acid, the total of caproic and caprylic acid being 100 parts, and from 80 to 135 parts by weight of at least one cyclic amine selected from the group consisting of cyclohexylamine and dicyclohexylamine.

5. A corrosion inhibiting composition suitable for application to wet and damp metal surfaces, consisting essentially of from 85 to 99.9 parts by weight of an oleaginous vehicle of a viscosity of from 1 centipoise to 100 poises at 25° C., and from 15 to 0.1 parts by weight of the amine salt reaction product consisting essentially of from 9 to 25 parts by weight of caproic acid, from 91 to 75 parts by weight of caprylic acid, the total of caproic and caprylic acids being 100 parts, from 0.1 to 45 parts by weight of alpha-methylbenzylamine, and from 80 to 135 parts by weight of dicyclohexylamine, the total of dicyclohexylamine and alpha-methylbenzylamine being from 80.1 to 150 parts by weight.

6. A corrosion inhibiting composition suitable for application to wet and damp metal surfaces, consisting essentially of from 85 to 99.9 parts by weight of an oleaginous vehicle of a viscosity of from 1 centipoise to 100 poises at 25° C., and from 15 to 0.1 parts by weight of the amine salt reaction product consisting essentially of from 15 to 25 parts by weight of caproic acid, from 75 to 85 parts of caprylic acid, from 80 to 100 parts by weight of dicyclohexylamine and from 45 to 30 parts by weight of alpha-methylbenzylamine.

7. A corrosion inhibiting composition suitable for application to wet and damp metal surfaces, consisting essentially of (A) from 75 to 99.9 parts by weight of an oleaginous vehicle of a viscosity of from 1 centipoise to 100 poises at 25° C., (B) from 15 to 0.1 parts by weight of the amine salt reaction product consisting essentially of from 9 to 25 parts by weight of caproic acid, from 91 to 75 parts by weight of caprylic acid, the total of caproic and caprylic acids being 100 parts, and from 80 to 135 parts by weight of at least on cyclic amine selected from the group consisting of cyclohexylamine and dicyclohexylamine, (C) and up to 10 parts by weight of a hydrophilic wetting agent.

8. A corrosion inhibited aqueous fluid composition

suitable for use as a hydraulic fluid consisting essentially of (*a*) from 85 to 99.9 parts by weight of a fluid comprising a substantial proportion of an aqueous media and the balance being an oleaginous material and (*b*) from 15% to 0.1% by weight of the amine salt reaction product consisting essentially of from 9 to 25 parts by weight of caproic acid, from 91 to 75 parts by weight of caprylic acid, the total of caproic and caprylic acids being 100 parts, and from 80 to 135 parts by weight of at least one cyclic amine selected from the group consisting of cyclohexylamine and dicyclohexylamine.

9. The aqueous fluid composition of claim 8 wherein the reaction product includes from 0.1 to 45 parts by weight of alpha-methylbenzylamine.

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