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VAPOR-PHASE CORROSION INHIBITION WITH A MIXTURE OF INHIBITORS

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This invention relates to corrosion inhibitors. More specifically, this invention relates to novel vapor-phase corrosion-inhibiting compositions and the techniques of utilization thereof.

The copending application Serial No. 124,727, filed October 31, 1949, now Patent No. 2,629, 649, describes and claims various vapor-phase corrosion inhibitors and the use thereof. The present invention deals with the discovery that certain combinations of these volatile corrosion inhibitors are especially useful and efficient.

It has now been found that a combination of an organic base nitrite salt and a weak organic acid salt of an amine is outstandingly effective as a vapor-phase corrosion inhibitor. More particularly, it has been found that under certain unusually severe corrosive conditions, the use of a given quantity of the above combination of corrosion inhibitors will afford better protection for materials against oxidative atmospheric corrosion by water vapor and air than will an equal quantity of either of the inhibitors utilized individually. An example of such severe corrosive conditions is found in the shipment, storage, handling and utilization of metal parts in Arctic climates, where the metal is exposed to extreme fluctuations in temperature and relative humidity.

The organic base nitrite salts which are useful in the above combinations are those salts of nitrous acid and an organic base which have a vapor pressure of at least 0.00002 mm. Hg at 21° C. and preferably greater than about 0.0001 mm. Hg at 21° C. The bases which will form such salts will usually be amines or nitrogen-containing compounds although non-nitrogenous bases, such as sulfonium, phosphonium and iodonium compounds have also been found to be effective. Examples of nitrogenous bases are primary amines, such as isopropylamine, cyclohexylamine, benzylamine, allylamine, etc.; secondary amines, such as diethyl or diisopropylamine, dicyclohexylamine, piperidine, morpholine, imidazolines, various thiazolines and the like; tertiary amines, such as trimethylamine, triisopropylamine and higher homologues thereof, N-methyl piperidine and various other alicyclic aralkyl, alkaryl, aryl, etc., tertiary amines; quaternary ammonium bases, such as tetramethyl ammonium hydroxide, trimethylbenzyl ammonium hydroxide and N-hydrocarbon pyridinium or quinolinium quaternary ammonium hydroxides having alkyl, cycloalkyl or aralkyl groups on the quaternary nitrogen atom.

The various hydrocarbon radicals or groups of the above amines may also contain stable and inert polar substituent atoms or radicals, such as ether, alcohol, free amino or nitro groups.

As will be readily recognized from the above, the important characteristic of the organic base is that it must have sufficient basicity to form a salt of nitrous acid, and the important characteristic of the nitrite salt is that it must have sufficient volatility to be effective in the vapor phase.

The second essential component of the compositions

of this invention is a weak organic acid salt of an amine. The amines which are suitable for forming these salts are essentially the same as those suitable for forming the above nitrite salts, with the additional limitation that there be not more than about 35 carbon atoms in such amines and preferably not more than about 25 carbon atoms. As before, the basicity must be sufficient to form a salt with the weak organic acid.

In general, best results will be obtained with the amine salts of organic acids wherein the acid has a dissociation constant between about 1×10^{-3} and 1×10^{-8}. Thus, suitable acids for forming such salts are the carboxylic acids, such as, for example, the fatty acids, lauric, stearic, n-butyric, palmitic, etc.; unsaturated acids such as oleic, maleic, fumaric and the like; dibasic acids, such as carbonic, oxalic, phthalic, malonic, succinic, pimelic, etc., and aromatic acids, such as benzoic and the like.

In order to obtain the additional corrosion-inhibiting protection available by the use of the present combination of salts, it is necessary that the weight ratio of the nitrite salt to the organic acid salt be maintained between about 20 and about 0.3. The most markedly increased corrosion inhibition occurs when said ratio is between about 5 and about 1.

The various techniques already known to those skilled in the art are effective in the utilization of the present mixture or combinations of volatile corrosion inhibitor salts. For example, within any enclosing means or container, corrosion of metal surfaces by moisture and air is prevented by the presence, in the enclosed gaseous atmosphere, of extremely small amounts of the vapors from the above compositions. These compositions may be originally introduced as a solid, liquid, or vapor, in a solution, or as an emulsion or dispersion, etc., just so long as the inhibitor vapors may diffuse throughout the atmosphere in contact with the metal to be protected.

In a preferred embodiment of the instant invention, the vapor-phase inhibitor combinations are coated upon, or impregnated within, a solid sheet or packaging material such as paper, cardboard, cloth, or various fibrous or porous materials, metal foil, plastic films or sheets, and the like, which may be used for packaging metallic objects. In such cases between about 0.01 and about 5 grams of the inhibitor combination per square foot of wrapping material will usually be satisfactory. It should be obvious, however, that under extreme conditions smaller amounts may suffice or greater amounts may be required.

Although not necessary for the complete understanding and successful practice of this invention, the following examples are presented to show the surprising results which may be attained by the use of the present invention. It is emphasized that these examples are merely illustrative, and the invention should in no way be construed as limited thereby.

Example I

Pieces of kraft wrapping paper 24 inches square were impregnated with various vapor-phase corrosion inhibitors and placed in the bottom of glass reagent bottles, along with ½ gram of water. The bottles were each closed with a stopper having a single hole through which a 4½ inch length of mild steel rod was inserted in such a manner that one end of the rod was exposed to the atmosphere within the bottle, and the other end was exposed to the atmosphere outside of the bottle. The bottle was partially immersed in a controlled temperature bath of 54° C. for about four hours, after which that portion of the steel rod exposed to the atmosphere

within the bottle was inspected for corrosion. Results were as follows:

Vapor-Phase Corrosion Inhibitor	Concentration, gm./sq. ft. of paper	Percent of Surface Rusted
Control (unimpregnated paper)		[1] 100
Dicyclohexylamine nitrite	1.0	[1] 38
Dicyclohexylamine fumarate	1.0	80
Dicyclohexylamine nitrite plus Dicyclohexylamine fumarate	0.7 / 0.3	[1] 2
Dicyclohexylamine palmitate	1.0	60
Dicyclohexylamine nitrite plus Dicyclohexylamine palmitate	0.7 / 0.3	[1] 3

[1] Average of two runs.

Example II

Clean air at a controlled rate of about 120 cc. (S. T. P.) per minute was bubbled through distilled water and then successively passed through four glass tubes, each 5 inches long and 31 mm. inside diameter. The first two tubes served as spray traps for entrained liquid. The third tube was lined with paper impregnated with a vapor-phase corrosion inhibitor at a concentration of 1 gram per square foot of paper. The fourth tube contained a hollow tubular specimen of polished SAE 1020 steel, through the center of which specimen cold water was continuously circulated. The equipment was placed in an oven maintained at 100° F., and the air stream was at approximately the same temperature. After 20 hours the results observed were as follows:

Vapor-Phase Corrosion Inhibitor	Concentration in gm./sq. ft. of paper	Percent of Surface Rusted
Dicyclohexylammonium nitrite	1.0	35
Dicyclohexylammonium nitrite plus Dicyclohexylammonium stearate	0.7 / 0.3	25

Example III

The procedure of Example II was repeated except that the air was not purified and that the duration of the test was only 6 hours. The results were as follows:

Vapor-Phase Corrosion Inhibitor	Concentration in gm./sq. ft. of paper	Percent of Surface Rusted
Dicyclohexylammonium nitrite	1.0	38
Dicyclohexylammonium nitrite plus Dicyclohexylammonium oleate	0.7 / 0.3	1

Example IV

When the procedure of Example II is repeated using diisopropylammonium nitrite, stearate and oleate salts, substantially similar results are obtained.

From the results in the above examples, it may be seen that the organic base nitrite salts are better than the weak inorganic acid salts of amines when used individually. However, when a portion (particularly a minor portion) of the nitrite salt is replaced by the less effective weak organic acid salt, the combination becomes much more effective.

The invention claimed is:

1. A wrapping material comprising paper having physically associated therewith an effective corrosion inhibiting amount of a mixture of dicyclohexyl ammonium nitrite and dicyclohexyl ammonium fumarate, the weight ratio of said nitrite to said fumarate being between about 5 and about 1.

2. A substantially solid inactive packaging material having physically associated therewith a mixture of a secondary cycloalkyl ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C. and a carboxylic acid salt of a cycloalkyl amine, said carboxylic acid being a hydrocarbon carboxylic acid having between one and two carboxyl radicals, containing less than 19 carbon atoms per molecule and having a dissociation constant between about 10^{-3} and 10^{-8}, said amine containing not more than about 25 carbon atoms, the weight ratio of said nitrite salt to said carboxylic acid salt being between about 20 and about 0.3.

3. A corrosion-inhibiting composition of matter comprising a mixture of dicyclohexyl ammonium nitrite and dicyclohexyl ammonium fumarate, the weight ratio of said nitrite to said fumarate being between about 20 and about 0.3.

4. A corrosion-inhibiting composition of matter comprising a mixture of dicyclohexyl ammonium nitrite and dicyclohexyl ammonium palmitate, the weight ratio of said nitrite to said palmitate being between about 20 and about 0.3.

5. A corrosion-inhibiting composition of matter comprising a mixture of an aliphatic hydrocarbon ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C. and an aliphatic hydrocarbon ammonium maleate salt, the ammonium radical of said maleate salt containing not more than about 25 carbon atoms therein, the weight ratio of said nitrite to said maleate being between about 20 and about 0.3.

6. A corrosion-inhibiting composition of matter comprising a mixture of an aliphatic hydrocarbon ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C. and an aliphatic hydrocarbon ammonium salt of a hydrocarbon carboxylic acid, the ammonium radical of said salt containing not more than 25 carbon atoms therein, the acid having from one to two carboxyl groups and less than 19 carbon atoms per molecule, and a dissociation constant between about 10^{-3} and 10^{-8}, the weight ratio of said nitrite to said carboxylic acid salt being between about 20 and about 0.3.

7. A corrison-inhibiting composition of matter comprising a dicycloalkyl ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C. and a fatty acid salt of a dicycloalkyl amine, said fatty acid containing less than 19 carbon atoms per molecule having a dissociation constant between about 10^{-3} and about 10^{-8}, said amine containing not more than about 25 carbon atoms, the weight ratio of the nitrite salt to the fatty acid salt being between about 20 and about 0.3.

8. A corrosion-inhibiting composition of matter comprising a non-aromatic hydrocarbon ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C. and a carboxylic acid salt of an amine, said carboxylic acid being a hydrocarbon carboxylic acid having between one and two carboxyl radicals, containing less than 19 carbon atoms per molecule and having a dissociation constant between about 10^{-3} and about 10^{-8}, said amine containing not more than about 25 carbon atoms, the weight ratio of said nitrite salt to said carboxylic acid salt being between about 20 and about 0.3.

9. A corrosion-inhibiting composition of matter comprising a nitrite salt of a secondary alkyl amine and a fumarate salt of the same amine, said nitrite salt having a vapor pressure of at least 0.00002 mm. Hg at 21° C., said amine containing not more than about 25 carbon atoms, the weight ratio of said nitrite to said fumarate being between about 20 and about 0.3.

10. A composition of matter comprising a dicycloalkyl ammonium nitrite salt having a vapor pressure of at least about 0.0001 mm. Hg at 21° C. and an aliphatic hydrocarbon dicarboxylic acid salt of a dicycloalkyl amine, said acid having a dissociation constant between about 10^{-3} and 10^{-8}, and containing less than 19 carbon atoms per molecule, said amine containing not more than 35 carbon atoms, and the weight ratio of said nitrite salt

to said carboxylic acid salt being between about 20 and about 0.3.

11. A composition of matter comprising a dicycloalkyl ammonium nitrite salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C. and an unsaturated aliphatic hydrocarbon dicarboxylic acid salt of a dicycloalkyl amine, said acid containing less than 19 carbon atoms per molecule and having a dissociation constant between about 10^{-3} and 10^{-8}, said amine containing not more than 35 carbon atoms, the weight ratio of said nitrite salt to said carboxylic acid salt being between about 20 and about 0.3.

12. A composition of matter comprising a dicycloalkyl ammonium nitrite salt having a vapor pressure of at least about 0.00002 mm. Hg at 21° C. and an unsaturated fatty acid salt of a dicycloalkyl amine, said acid containing less than 19 carbon atoms per molecule and having a dissociation constant between about 10^{-3} and 10^{-8}, said amine containing not more than about 35 carbon atoms per molecule, the weight ratio of said

nitrite salt to said carboxylic acid salt being between about 20 and about 0.3.

13. A composition of matter comprising dicyclohexyl ammonium nitrite and a saturated fatty acid salt of an amine, said acid containing less than 19 carbon atoms per molecule and having a dissociation constant between 10^{-3} and 10^{-8}, said amine containing not more than 35 carbon atoms per molecule, the weight ratio of said nitrite to said fatty acid salt being between about 20 and about 0.3.

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