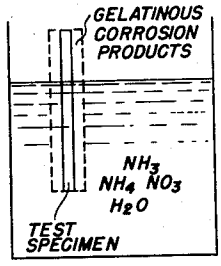
May 17, 1960 G. A. MARSH ET AL 2,936,884

CORROSION INHIBITION IN AQUEOUS AMMONIA-AMMONIUM NITRATE SYSTEMS

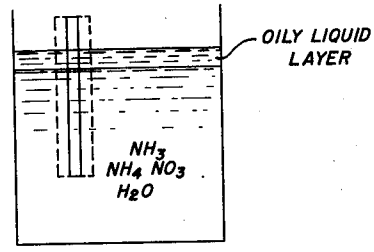
Filed May 20, 1958

CORROSION IN $H_2O - NH_3 - NH_4NO_3$ SYSTEM



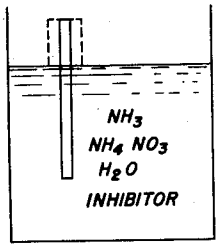
NO INHIBITOR

FIG. 1



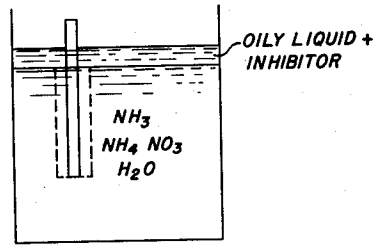
NO INHIBITOR
OILY LIQUID LAYER

FIG. 2



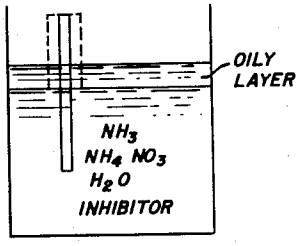
INHIBITED SOLUTION
NO OILY LAYER

FIG. 3



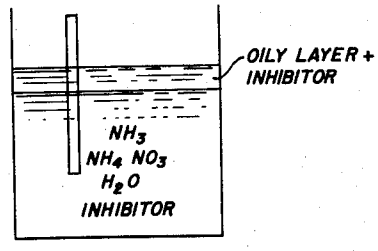
ONLY OILY LAYER
CONTAINS INHIBITOR

FIG. 4



INHIBITED SOLUTION
UNINHIBITED OILY LAYER

FIG. 5



BOTH SOLUTION AND
OILY LAYER CONTAIN
INHIBITOR

FIG. 6

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United States Patent Office 2,936,884 Patented May 17, 1960

2,936,884

CORROSION INHIBITION IN AQUEOUS AMMONIA-AMMONIUM NITRATE SYSTEMS

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Application May 20, 1958, Serial No. 736,616

17 Claims. (Cl. 206—84)

This invention relates to new and useful improvements in methods for preventing corrosion of ferrous metals by aqueous ammonia-ammonium nitrate systems and is more particularly concerned with a disposition of corrosion inhibitors which inhibits corrosion both below and above the liquid level.

Ammonia-ammonium nitrate systems containing water are utilized in the preparation of some types of liquid fertilizers for commercial use. Such systems present a severe corrosion problem for the apparatus in which they are handled. Ferrous metal processing equipment as well as tank cars and other types of metallic shipping containers are subjected to very rapid corrosion by the solutions far exceeding that encountered by ferrous metal in contact with an ordinary aqueous environment. A special corrosion problem occurs where a ferrous metal is in contact both with air or other oxidizing environment and the corrosive ammonia-ammonium nitrate solution, as when a ferrous metal container is only partly filled with the solution and has an air space above the liquid level. The type of oxidation which occurs in this environment is unique and requires a type of protection not needed in other corrosive environments and which is not suggested by previous investigators of corrosion. When a ferrous metal is placed in contact with an aqueous ammonia-ammonium nitrate solution which contains no corrosion inhibitor, the rate of corrosion is very rapid. The corrosion products which develop on the surface of the ferrous metal form a gel which adheres to the surface of the metal and grows rapidly in thickness as the corrosion of the metal surface proceeds. Thus, when a thin strip of iron or steel is placed in an aqueous ammonia-ammonium nitrate solution very thick layers of oxide gels develop on each side of the strip and within a few days exceed the volume of the metal strip. In fact, it has been noted in some cases that when a metal strip is placed in a small jar containing an aqueous ammonia-ammonium nitrate solution and allowed to corrode, the gelatinous corrosion products may fill the entire jar. The problem of corrosion in aqueous ammonia-ammonium nitrate solutions is only partially solved by the use of ordinary corrosion inhibitors. Inhibitors which are placed in the solution retard corrosion only in the liquid and have no effect on corrosion which occurs above the liquid level.

It is therefore one object of this invention to provide a means for inhibiting corrosion of ferrous metals by corrosive aqueous ammonium nitrate-ammonia solutions both in the air space above the liquid and on the portions of metal below the liquid level.

Another object of this invention is to provide an aqueous ammonia-ammonium nitrate solution in a ferrous metal container with inhibitors which inhibit the corrosion of ferrous metal both below and above the level of liquid in the container.

A feature of this invention is the provision of a ferrous metal container containing an aqueous ammonia-ammonium nitrate solution provided with a suitable corrosion inhibitor dissolved therein, and having a liquid layer floating on and substantially immiscible with the solution, in an amount sufficient to cover the surface of the solution, and having dissolved therein a corrosion inhibitor substantially insoluble in the solution, in an amount operable to inhibit corrosion of the walls of the container above the liquid level.

A further feature of this invention is the provision of a ferrous metal container containing an aqueous ammonia-ammonium nitrate solution having dissolved therein as a corrosion inhibitor a compound containing a sulfur-carbon-nitrogen linkage and having a mineral oil or other inert oleaginous liquid floating on the solution with a polar compound dissolved therein for inhibiting corrosion above the liquid level.

A still further feature of this invention is the provision of an improved method for inhibiting corrosion in aqueous ammonia-ammonium nitrate solutions by dissolving in the solution a corrosion inhibitor and placing on the surface of the solution an inert oleaginous liquid having a corrosion inhibitor dissolved therein to inhibit corrosion above the liquid level.

Other objects and features of this invention will become apparent from time to time throughout the specification and claims as hereinafter related.

In the accompanying drawings, to be taken as part of the specification, there are illustrated diagrammatically the results of a series of tests demonstrating this invention, in which drawings:

Fig. 1 is a diagrammatic view showing the extent of corrosion of a test specimen both below and above the liquid level in an aqueous ammonia-ammonium nitrate solution containing no inhibitor,

Fig. 2 is a diagrammatic view similar to Fig. 1 showing the extent of corrosion in a non-inhibited aqueous ammonia-ammonium nitrate solution having an oily liquid layer floating on the surface thereof,

Fig. 3 is a diagrammatic view showing the extent of corrosion of a test specimen in an aqueous ammonia-ammonium nitrate solution containing an inhibitor in said solution, but without the oily layer of Fig. 2,

Fig. 4 is a diagrammatic view similar to Fig. 3 showing the extent of corrosion of a test specimen in an aqueous ammonia-ammonium nitrate solution containing no inhibitor but having an oily liquid floating on and covering the surface of the solution and having an inhibitor dissolved therein,

Fig. 5 is a diagrammatic view similar to Fig. 3 showing the corrosion of a test specimen in an aqueous ammonia-ammonium nitrate solution containing a dissolved inhibitor and having an oily layer floating on and covering the surface thereof with no inhibitor in said layer, and

Fig. 6 is a diagrammatic view showing a test specimen in an aqueous ammonia-ammonium nitrate solution containing a dissolved inhibitor and provided with an oily layer floating on and covering the surface thereof with an inhibitor dissolved in said layer.

We have found that it is possible to inhibit very substantially the corrosion of ferrous metals by aqueous ammonia-ammonium nitrate solutions through the use of a single selected corrosion inhibitor where the metal has not been activated, i.e., has not been abraded or exposed to a strong acid or electrolytically coupled with a more active metal, to render the ferrous metal more easily corrodible in the presence of oxygen. Corrosion of ferrous metal in an unactivated state may be inhibited by a single selected corrosion inhibitor (e.g., 2-mercaptobenzothiazole) as long as the metal is completely immersed in the solution or the portion thereof above the liquid level is exposed to an oxygen-free atmosphere. If the ferrous metal is activated, it may still be inhibited

against corrosion by a single inhibitor in the solution, if it is completely immersed in the solution and the solution is totally deaerated or the portion of the metal above the liquid level is exposed to an oxygen-free atmosphere. If the solution is aerated and the ferrous metal is in an activated state, there are certain combinations of inhibitors which may be dissolved in the solution to inhibit corrosion, as long as the ferrous metal is totally immersed in the solution or the portion thereof which is exposed is in contact with an oxygen-free atmosphere. While these conditions for inhibiting corrosion of ferrous metals are of considerable theoretical interest, it is obvious that the conditions above enumerated are ones which are difficult to attain in practice and thus are not applicable to the inhibition of corrosion in aqueous ammonia-ammonium nitrate solutions under varying conditions.

The essence of our invention, therefore, resides in our discovery of a means to inhibit corrosion in aqueous ammonia-ammonium nitrate solutions regardless of the state of activation of the ferrous metal, the degree of aeration of the solution, or the presence of an oxygen-containing atmosphere in contact with a portion of the metal. We have found that the corrosion of ferrous metals by aqueous ammonia-ammonium nitrate solutions is unique. This corrosion takes place in the form of an oxidation at the surface of the metal, with the oxide forming a gel which adheres to the metal surface. The rate of oxidation is rapid and the gelatinous oxidation products build up to very substantial thicknesses before dropping from the metal. This form of corrosion and growth of gelatinous corrosion products occurs both below and above the liquid level. If a metal test specimen in the form of a rectangular strip is partially submerged in an aqueous ammonia-ammonium nitrate solution containing no corrosion inhibitor, as in Fig. 1, the gelatinous corrosion products which form may grow to a thickness several times that of the test specimen. If one or more inhibitors is added to the solution, as in Fig. 3, the formation of the gelatinous corrosion products is substantially completely inhibited and the corrosion of the metal surface is reduced to a very small fraction of that observed in the absence of an inhibitor. This inhibition of corrosion, however, takes place only below the liquid level. The portion of the test specimen protruding above the liquid level continues to develop gelatinous corrosion products thereon as shown in Fig. 3. If a layer of an inert oily liquid is placed on the surface of the solution, with no inhibitor in the solution but a suitable inhibitor dissolved in the oily layer, the growth of gelatinous corrosion products above the liquid layer is substantially completely inhibited while the gelatinous corrosion products continue to grow on the portion of the test specimen extending into the solution, as shown in Fig. 4. If an aqueous ammonia-ammonium nitrate solution is provided with an inhibitor and blanketed with an oily layer containing an inhibitor dissolved therein, as in Fig. 6, a test specimen placed in the solution and extending into the air space above will be completely free from the gelatinous corrosion products and will have a very low rate of corrosion of the metal surface. In Fig. 2, it is seen that the use of an oily layer on an aqueous ammonia-ammonium nitrate solution, with no inhibitor in the solution or the oily liquid layer, does not reduce the growth of gelatinous corrosion products on the test specimen. Likewise, the use of an oily liquid layer without an inhibitor on an aqueous ammonia-ammonium nitrate solution containing a dissolved inhibitor, as shown in Fig. 5, does not appreciably reduce the growth of gelatinous corrosion products above the liquid level.

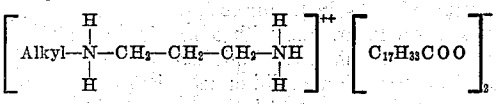
In carrying out this invention, the aqueous ammonia-ammonium nitrate solution which is to be stored in a ferrous metal container is provided with a suitable corrosion inhibitor (preferably in a concentration of about

0.01–0.2 wt. percent) which is soluble therein. Any corrosion inhibitor may be used which is soluble in water and which substantially mitigates corrosion by the solution. Compounds which are particularly useful in inhibiting corrosion by aqueous ammonia-ammonium nitrate solutions are mainly sulfur-containing compounds and preferably compounds containing a sulfur to carbon to nitrogen linkage. Any of the various sulfur compounds disclosed in U.S. Patent 2,238,651 to Frank G. Keenen may be used for inhibiting corrosion in the solution. These compounds include oxides of sulfur, metal sulfides, sulfur chlorides, sulfamide, sulfurous acid and metal sulfites, metal hyposulfites, metal thiosulfates, metal salts of polythionic acids, persulfuric acid and metal persulfates, metal sulfates and bisulfates. Organic compounds of sulfur which are particularly useful in inhibiting corrosion in aqueous ammonia-ammonium nitrate solution include mercaptans, mercaptals, hydrocarbon sulfides and disulfides, sulfoxides, sulfonium compounds, sulfur derivatives of hydroxy organic acids, sulfonic acids and derivatives thereof, thiosulfonates, thiocyanates, isothiocyanates, thiazoles, sulfur derivatives of carbonic acids, sulfur derivatives of carboxylic acids, and sulfur dye colors such as sulfogene compounds and the like. As pointed out above, the preferred inhibitors are ones which include a sulfur to carbon to nitrogen linkage and include specifically 2-mercaptobenzothiazole, ammonium thiocyanate, thiourea, sodium dimethyldithiocarbamate, trimethyl sulfonium nitrite, tetramethyl ammonium hydrosulfide, tetramethyl ammonium sulfide, and thioacetamide. These inhibitors may be used either singly in solution or in mixtures of two or more or in mixture with other corrosion inhibitors such as water-soluble metal nitrites, such as potassium nitrite, sodium nitrite, lithium nitrite, cesium nitrite, barium nitrite, and/or inorganic oxidizing agents for ferrous metals such as ammonium or alkali metal chromates or chlorates.

The oily layer which is floated on the surface of the aqueous ammonia-ammonium nitrate solution is chosen strictly for its physical properties and chemical inertness. The layer consists of a liquid which is lighter than the solution so that it may float on the solution and cover the entire surface thereof. The layer is of a liquid which is substantially immiscible with the solution and which is inert toward air, toward the solution, and toward the inhibitors which are used in the solution and in the layer. The immiscible liquid layer is preferably a hydrocarbon or other oily material and may be, for example, liquid propane or butane, naphtha such as rubber solvent, textile spirits, V.M. & P., Stoddard solvent, kerosene, fuel oils of any viscosity and of a petroleum origin, gas oils of a petroleum-derived nature, neutral lubricating stocks or any other hydrocarbon oil. Oily esters may be used provided that they are inert toward the solution. Synthetic lubricants which are lighter than the solution and immiscible therewith may be used. Such synthetic lubricants include the silicone oils, such as dimethyl silicone polymers, ester-type lubricants, such as diisooctylazelate, phosphate esters, such as tricresyl phosphate, and polyoxyalkylene glycols, such as polypropylene glycols of sufficiently high molecular weight to be water insoluble. Mineral oils such as a white oil are preferred. In the oily layer, there is dissolved an inhibitor in a concentration of 0.1–5 wt. percent, with a concentration of 0.5 to 1.0 wt. percent being preferred. The inhibitors which are used in the blanketing oily layer include any known corrosion inhibitors which are soluble in the liquid layer and which are substantially insoluble in the solution. These corrosion inhibitors include any of the well known polar-type oil-soluble inhibitors, as described in Industrial and Engineering Chemistry, 40, 2338–2347. Suitable inhibitors include C_6–C_{30} monocarboxylic acids, C_6–C_{30} hydrocarbyl primary, secondary, and tertiary amines, C_6–C_{30} alcohols, aliphatic and aromatic esters, including monoesters of glycols and glycerol, metal soaps of

C_6–C_{30} aliphatic and aromatic acids, metal petroleum sulfonates, fatty amides and nitriles, phenols, naphthols, and hydrocarbyl derivatives thereof, and ammonium and amine salts of C_6–C_{30} carboxylic acids.

Amine salts (or ammonium salts) of fatty acids of about 6–30 carbon atoms per molecule are particularly useful and preferred corrosion inhibitors for the oily layer. One of the most satisfactory amine salts is the dioleate of a fatty diamine produced by the Armour Chemical Division of Armour and Company under the trade name Duomeen T. Dioleate. Duomeen T. Dioleate is a monoalkyl-substituted trimethylene diamine dioleate, where the alkyl substituent is derived from tallow acids and consists mainly of C_{16} and C_{18} normal, saturated hydrocarbon chains, and C_{18} mono-unsaturated hydrocarbon chains. Compound is prepared by direct neutralization of Duomeen T (N-tallow-trimethylenediamine) with oleic acid. Ionically, Duomeen T. Dioleate has the following structural formula:



Hereinafter throughout the specification and claims, this compound (or mixture of compounds) will be referred to as N-tallow-trimethylenediaminedioleate or DTD. Other suitable oil-soluble ammonium and amine salts of fatty acids include ammonium oleate, ammonium stearate, ammonium palmitate, and trimethylamine oleate, triphenylamine oleate, stearylamine palmitate, oleylamine ricinoleate, stearylamine stearate, etc.

The oily liquid layer and corrosion inhibitor therefor may be added separately, or with the inhibitor dissolved in the oily liquid, and before, during, or after the addition of the water-soluble inhibitor to the aqueous ammonia-ammonium nitrate solution. Thus, any order and rate of addition of the individual ingredients or groups of ingredients may be followed by, with or without agitation of the solution. Preferably, the water-soluble inhibitor is added to a preformed solution of ammonia and ammonium nitrate in water, followed by the oily liquid containing a corrosion inhibitor dissolved therein.

A series of experiments was carried out, using the procedure described hereafter, for establishing the scope of this invention and the necessity of using the combination of inhibitors in the manner above described. A one pint glass jar was filled about half full of a solution consisting of ammonium nitrate, 60 wt. percent, ammonia, 24 wt. percent, and water, 16 wt. percent. The corrosivity of this solution was tested on a strip of cold-rolled mild steel. A strip of cold-rolled mild steel 6.5" x .625" x .05" (18 gauge) was cleaned by rubbing with steel wool and activated by being dipped in 15% HCl at 150° F. for 15 seconds. The solution in the jar was shaken until thoroughly aerated and cooled to reduce the vapor pressure as low as possible. The cleaned and activated steel strip was placed in the jar with approximately half of the strip extending above the liquid level. The jar was then closed and sealed with a lid enclosing an air space over the liquid. The solution was allowed to warm to room temperature and was maintained at room temperature for a period of two weeks. At the end of the two-week test period, the test specimen was observed for extent of corrosion and was removed from the jar and cleaned and measured for thickness to determine the extent of corrosion during the test period. The corrosion rates in this and other experiments are expressed in terms of mils per year or m.p.y. In this and other experiments the corrosion of the test specimen was measured below and above the liquid level. In this experiment, the test specimen developed a very heavy layer of gelatinous corrosion products as illustrated in Fig. 1 of the drawing. In fact, at the end of the test period the gelatinous corrosion products had become so bulky as to have broken partially away from the surface of the metal and collected in the bottom of the jar. When the test specimen was removed and cleaned and measured for extent of corrosion, it was found that below the liquid level the metal had corroded at a rate of 218 m.p.y., while above the liquid level the corrosion rate was 190 m.p.y.

EXAMPLE I

A series of experiments was carried out following the test procedure above-described, but using a corrosion inhibitor dissolved in the solution. The test specimens were maintained in the corrosive environment for a period of two weeks, were observed as to the type of corrosion which took place, and were measured for extent of corrosion below and above the liquid level as above-described. In one experiment, the aqueous ammonia-ammonium nitrate solution was inhibited by the addition of 2-mercaptobenzothiazole in a concentration of 0.12 wt. percent. The steel test specimen was almost completely free from corrosion products below the liquid level but developed a gelatinous growth of corrosion products above the liquid level as shown in Fig. 3 of the drawing. The rate of corrosion below the liquid level was 4.8 m.p.y. while the corrosion rate above the liquid level was 15 m.p.y. A second test sample was placed in an aqueous ammonia-ammonium nitrate solution containing 0.12 wt. percent ammonium thiocyanate as inhibitor. As in the preceding case, the corrosion was inhibited below the liquid level while growth of corrosion products above the liquid level was substantial. The rate of corrosion of the test specimen below the liquid level was 0 m.p.y. while the corrosion rate above the liquid level was 112 m.p.y. In a third experiment, the aqueous ammonia-ammonium nitrate solution was inhibited with 0.12 wt. percent of thiourea. Again, the corrosion of the test specimen was inhibited only below the liquid level, as in Fig. 3. The corrosion rate below the liquid level was measured and found to be 0 m.p.y. while the corrosion rate above the liquid level was 139 m.p.y.

EXAMPLE II

In another experiment, an aqueous ammonia-ammonium nitrate solution was prepared as in the preceding examples. This solution was placed in a jar and blanketed with a ½" layer of a white mineral oil. Neither the solution nor the mineral oil contained any inhibitor. A metal test specimen was cleaned and activated as described in the previous examples and was sealed in the jar, exposed half to liquid and half to air, for a period of two weeks. As in the preceding example, the solution was aerated and the space above the solution was filled with air. At the end of the test period, the test specimen was found to have developed a heavy layer of gelatinous corrosion products as illustrated in Fig. 2. When the test specimen was removed from the jar and cleaned and measured, it was found that the corrosion rate above the liquid level was 255 m.p.y. and below the liquid level was 225 m.p.y.

EXAMPLE III

A series of experiments was carried out as in Example I above using 2-mercaptobenzothiazole, ammonium thiocyanate, and thiourea, respectively, as corrosion inhibitors and each of the solutions was blanketed with a ½" layer of white mineral oil containing no dissolved corrosion inhibitor. The concentration of the inhibitors in the aqueous solution was 0.12 wt. percent as in Example I. In each of the three experiments, corrosion was substantially inhibited below the liquid level while there was a small amount of corrosion in the form of gelatinous corrosion products on the portions of the test specimens extending above the liquid level, as illustrated in Fig. 5. The test specimen in the solution inhibited with 2-mercaptobenzothiazole was corroded below the liquid level at a rate of 5.4 m.p.y. and above the liquid level at a

rate of 10.8 m.p.y. The test specimen in the solution inhibited with ammonium thiocyanate was corroded below the liquid level at a rate of 5.4 m.p.y. and above the liquid level at a rate of 11.4 m.p.y. The test specimen in the solution inhibited with thiourea was corroded above the liquid level at a rate of 7.2 m.p.y. and below the liquid level at a rate of 7 m.p.y.

EXAMPLE IV

Another experiment was carried out duplicating the conditions of Example II except that the mineral oil layer contained 1% by wt. of N-tallow-trimethylenediamine-dioleate (hereinafter referred to as DTD) as a corrosion inhibitor. The steel test specimen was cleaned and activated as in the previous examples and sealed in the glass jar half exposed to liquid and half to air. At the end of the two-week test period, the test specimen had corroded in the manner shown in Fig. 4 of the drawings. The corrosion rate above the liquid level was only 3.6 m.p.y. while the corrosion rule in the uninhibited liquid solution below the liquid level was 30 m.p.y.

EXAMPLE V

A series of three experiments was carried out using the inhibitors of Examples I and III and the inhibited oil layer of Example IV. In each experiment the steel specimen was cleaned and activated as in the preceding examples. The steel specimens were placed in the respective solutions half exposed to liquid and half to air and sealed for a period of two weeks. In each experiment, the specimens were substantially completely free from corrosion products and remained shiny. In the jar containing 2-mercaptobenzothiazole in the solution and DTD in the oil layer, the corrosion rate of the test specimen below the liquid level was 2.4 m.p.y. and above the liquid level was 3.6 m.p.y. In the test jar in which the solution was inhibited with ammonium thiocyanate and the oil layer with DTD, the corrosion rate of the test specimen below the liquid level was 3.6 m.p.y. and above the liquid level was 6 m.p.y. In the test jar in which the solution was inhibited with thiourea and the oil layer with DTD, the corrosion rate below the liquid level was 3 m.p.y. and above the liquid level was 6 m.p.y.

The above experiments demonstrate the fact that the corrosion of ferrous metals, such as iron and steel, in aqueous ammonia-ammonium nitrate solutions takes place as illustrated in the drawings. When a metal strip is exposed to an aqueous ammonia-ammonium nitrate solution containing no corrosion inhibitor, a heavy growth of gelatinous corrosion product takes place as shown in Fig. 1. The addition of an oily layer without any inhibitor does not reduce the rate of corrosion in either the liquid or the air space above the liquid. The addition of corrosion inhibitors in the aqueous ammona-ammonium nitrate solution inhibits corrosion below the liquid level but has no effect on corrosion of metal in the air space above the liquid. The use of a non-inhibited oil layer on an inhibited solution does not inhibit completely the corrosion in the air space above the liquid. The use of an inhibited oil layer on an aqueous ammonia-ammonium nitrate solution containing no dissolved inhibitor inhibits corrosion in the air space above the liquid but does not completely inhibit corrosion in the liquid. It is only when a corrosion inhibitor is used in the solution and in the oily layer floating on the solution that corrosion is inhibited substantially completely both in the liquid and in the air space above the liquid.

EXAMPLE VI

In another series of three experiments, the effect of a combination of inhibitors in the aqueous ammonia-ammonium nitrate solution was evaluated, without an oil layer, with a non-inhibited oil layer, and with an oil layer inhibited with 1% by wt. of DTD. In each experiment the aqueous ammonia-ammonium nitrate solution was inhibited with 0.06 wt. percent 2-mercaptobenzothiazole and 0.06 wt. percent sodium chromate. In the experiments without an oil layer and with a non-inhibited oil layer, the corrosion below the liquid level was inhibited but a gelatinous growth of corrosion products occurred above the liquid level. Without an oil layer, the corrosion rate below the liquid level was 1.2 m.p.y. and above the liquid level was 15 m.p.y. With a non-inhibited oil layer, the corrosion rate below the liquid level was 0 and above the liquid level was 15.6 m.p.y. In the experiment with 2-mercaptobenzothiazole and sodium chromate in solution and 1% by wt. of DTD in a ½" white oil layer floating on the solution, the growth of gelatinous corrosion products was inhibited both below and above the liquid level. The corrosion rate below the liquid level was 3 m.p.y. and above the liquid level was 5.4 m.p.y.

EXAMPLE VII

In another series of three experiments the effect of a combination of three inhibitors in the aqueous solution was evaluated. As in Example VI, one experiment was without an oil layer, one with a non-inhibited oil layer, and one with an oil layer inhibited with 1% by wt. of DTD. The corrosion inhibitor used in the aqueous ammonia-ammonium nitrate solution in each of these experiments was 0.04 wt. percent 2-mercaptobenzothiazole, 0.04 wt. percent sodium nitrite, and 0.04 wt. percent potassium chlorate. As in the other experiments, the solution was aerated and the test specimens were exposed to the aerated solution and to air in the space above the solution. As in Example VI, the experiments using no oil layer and using an inhibited oil layer were substantially identical in result. The growth of gelatinous corrosion product below the liquid level was substantially completely inhibited while corrosion products formed on the test specimens in the air space above the liquid. In the experiment using no mineral oil layer on the solution, the rate of corrosion above the liquid level was 14.4 m.p.y. and below the liquid level was 3 m.p.y. In the experiment using a non-inhibited oil layer on the inhibited solution, the corrosion rate above the liquid level was 13.8 m.p.y. and below the liquid level was 3.6 m.p.y. In the third experiment, in which a ½" mineral oil layer containing 1 wt. percent of DTD was floated on the aqueous ammonia-ammonium nitrate solution containing 2-mercaptobenzothiazole, sodium nitrite, and potassium chlorate as corrosion inhibitors, the test specimen was substantially free of gelatinous corrosion products both below and above the liquid level. The test specimen remained shiny and was only slightly corroded. Above the liquid level the rate of corrosion was 5.4 m.p.y. while below the liquid level the rate of corrosion was 1.2 m.p.y.

EXAMPLE VIII

In another series of two experiments the effect of other inhibitors in the oil layer was investigated. In one experiment, 1 wt. percent of sodium ethylene diamine sulfonate was dissolved in mineral oil and applied as a ½" layer over a non-inhibited aqueous ammonia-ammonium nitrate solution. The steel test specimen was cleaned and activated and otherwise tested and measured as in the preceding examples. The growth of corrosion products on the test specimen above the liquid level was reduced by about 70% while the growth of gelatinous corrosion products on the test specimen below the liquid level was approximately the same as in the experiment where no oil layer was used. The corrosion rate above the liquid level was 48 m.p.y. and below the liquid level was 193 m.p.y.

In the second experiment, 1 wt. percent of glyceryl monooleate was dissolved in mineral oil and applied to a non-inhibited aqueous ammonia-ammonium nitrate solution as a ½" layer. The growth of corrosion products below the liquid level was very great while corrosion was substantially inhibited (reduced by 80%) above the

liquid level. The corrosion rate above the liquid level was 27 m.p.y. and below the liquid level was 190 m.p.y.

EXAMPLE IX

In another series of two experiments the effect of the inhibitors of Example VIII in the oil layer was evaluated in connection with the mixed inhibitors of Example VII in the aqueous solution. In one experiment the aqueous solution was provided with 0.04 wt. percent of 2-mercaptobenzothiazole, .04 wt. percent of sodium nitrite, and 0.04 wt. percent of potassium chlorate. The solution was blanketed with a ½" layer of mineral oil containing 1% by wt. of sodium ethylene diamine sulfonate. The test specimen was cleaned and activated as in the previous experiments. At the end of the two-week test period, the test specimen remained shiny and free from growth of gelatinous corrosion products. The corrosion rate both above and below the liquid level was 3.6 m.p.y.

In the second experiment an aqueous ammonia-ammonium nitrate solution was provided with 0.04 wt. percent of 2-mercaptobenzothiazole, 0.04 wt. percent of sodium nitrite, and 0.04 wt. percent of potassium chlorate, and was blanketed with a ½" layer of white mineral oil containing 1 wt. percent of glyceryl monooleate. The test specimen was cleaned and activated as in the previous examples. At the end of the two-week test period, the test specimen was substantially free of corrosion products and remained shiny. The corrosion rate of the test specimen above the liquid level was 6 m.p.y. and below the liquid level was 0.6 m.p.y.

EXAMPLE X

In another experiment, a silicone oil (dimethylsilicone polymer) was substituted for the mineral oil layer of Example VI. The aqueous solution contained 0.06 wt. percent 2-mercaptobenzothiazole and 0.06 wt. percent sodium chromate, while the silicone oil contained 1.0 wt. percent of DTD. The corrosion in the liquid was substantially completely inhibited while the corrosion above the liquid level was reduced by about 30%.

EXAMPLE XI

In two other experiments the conditions of Example V were duplicated, substituting another synthetic lubricant for the mineral oil layer. In one experiment the solution contained 0.12% 2-mercaptobenzothiazole and the oily layer consisted of di-isooctylazelate containing 1% of DTD. Corrosion in the liquid was substantially completely inhibited. Corrosion above the liquid level was reduced by about 75%. In the other experiment the solution contained 0.12% 2-mercaptobenzothiazole and the oily layer consisted of UCON LB 550 X (polypropylene glycol having a viscosity of 550 SUS at 100° F.) containing 1% of DTD. Corrosion in the liquid was substantially completely inhibited. Corrosion above the liquid level was reduced by about 60%.

EXAMPLE XII

The procedure of Example V is followed substituting corrosion inhibitors in the solution and in the mineral oil layer as indicated in Table I. In each case the concentration of inhibitor in the soluition is 0.12 wt. percent and in the mineral oil layer is 1%.

Table I

Inhibitor in Solution	Inhibitor in Mineral Oil
2-mercaptobenzothiazole.	Ammonium oleate.
Ammonium thiocyanate.	Ethylenediamine dipalmitate.
Thiourea.	Dodecanol.
Dimethylsulfide.	DTD.
Thioacetamide.	2-ethylhexylhexanoate.
Tetramethylammonium sulfide.	Octadecylphenol.
Sodium dimethyldithiocarbamate.	Stearonitrile.
Thiourea.	Triethylaminehexanoate.

With the use of each of the above pairs of inhibitors corrosion above and below the liquid level is reduced by more than 75%.

From the above examples, it is seen that protection against corrosion by aqueous ammonia-ammonium nitrate solutions, both below and above the liquid level may be accomplished by incorporating in the aqueous solution any suitable corrosion inhibitor in an amount sufficient to inhibit corrosion of the ferrous metal container below the liquid level and by blanketing the surface of the liquid with an oily layer containing a suitable corrosion inhibitor dissolved therein in an amount sufficient to inhibit corrosion of the ferrous metal container in the air space above the liquid level.

While we have described this invention fully and completely as required by the patent statutes, including several preferred embodiments of the invention, it is to be understood that within the scope of the appended claims, this invention may be practiced otherwise than as specifically described.

This application is a continuation-in-part of our copending application Serial No. 539,690, filed October 10, 1955.

What is claimed is:

1. In combination, a ferrous metal container containing (A) an aqueous ammonium nitrate solution containing dissolved ammonia and normally corrosive to ferrous metals, said solution containing a corrosion inhibitor dissolved therein in an amount operable to inhibit corrosion of the walls of the container in contact with the solution, and (B) a liquid layer floating on and substantially immiscible with said solution in an amount sufficient to cover the surface of said solution, said liquid layer being of a material liquid at ambient temperatures, immiscible with, inert toward, and less dense than said solution, and said liquid layer having dissolved therein a corrosion inhibitor substantially insoluble in said solution in an amount operable to inhibit corrosion of the walls of the container above the liquid level.

2. A combination as defined in claim 1 in which the liquid layer is of the group consisting of hydrocarbons and synthetic lubricants.

3. A combination as defined in claim 1 in which the inhibitor in the aqueous solution includes at least one sulfur-containing compound.

4. A combination as defined in claim 1 in which the inhibitor in the aqueous solution includes at least one compound having a sulfur to carbon to nitrogen linkage.

5. A combination as defined in claim 1 in which the inhibitor in the floating liquid layer is an oil-soluble polar compound.

6. A combination as defined in claim 1 in which the inhibitor in the aqueous solution is present in a concentration of about 0.01–0.2 wt. percent and the inhibitor in the floating layer is present in a concentration of about 0.1–5.0 wt. percent.

7. A combination as defined in claim 6 in which the inhibitor in the aqueous solution includes at least one compound having a sulfur to carbon to nitrogen linkage.

8. A combination as defined in claim 7 in which the inhibitor in the floating layer is a nitrogenous salt of a fatty acid of at least 6 carbon atoms per molecule.

9. A combination as defined in claim 7 in which the inhibitor in the aqueous solution is 2-mercaptobenzothiazole.

10. A combination as defined in claim 7 in which the inhibitor in the aqueous solution is ammonium thiocyanate.

11. A combination as defined in claim 7 in which the inhibitor in the aqueous solution is thiourea.

12. In combination, a ferrous metal container containing (A) an aqueous ammonium nitrate solution containing dissolved ammonia and normally corrosive to ferrous metals, said solution containing at least 0.01 wt. percent of 2-mercaptobenzothiazole dissolved therein to

inhibit corrosion of the walls of the container in contact with the solution, and (B) a layer of mineral oil floating on and covering the surface of said solution, and said mineral oil having dissolved therein at least 0.1 wt. percent of a polar compound to inhibit corrosion of the walls of said container above the liquid level.

13. In combination, a ferrous metal container containing (A) an aqueous ammonium nitrate solution containing dissolved ammonia and normally corrosive to ferrous metals, said solution containing at least 0.01 wt. percent of 2-mercaptobenzothiazole dissolved therein to inhibit corrosion of the walls of the container in contact with the solution, and (B) a layer of an oleaginous synthetic lubricant immiscible with water, floating on and covering the surface of said solution, and said synthetic lubricant having dissolved therein at least 0.1 wt. percent of a polar compound to inhibit corrosion of the walls of said container above the liquid level.

14. A combination as defined in claim 13 in which the oleaginous synthetic lubricant is a stable organic ester.

15. A combination as defined in claim 13 in which the synthetic lubricant is a liquid oleaginous polyoxyalkylene glycol.

16. In combination, a ferrous metal container containing (A) an aqueous ammonium nitrate solution containing dissolved ammonia and normally corrosive to ferrous metals, said solution containing a small amount of 2-mercaptobenzothiazole, a water-soluble metal nitrite, and an oxidizing agent for ferrous metals, sufficient to inhibit corrosion of the walls of the container in contact with the solution, and (B) a layer of mineral oil having dissolved therein a nitrogenous salt of a fatty acid of at least 6 carbon atoms per molecule in an amount sufficient to inhibit corrosion of the walls of said container above the liquid level.

17. A combination as defined in claim 16 in which the metal nitrite used is an alkali metal nitrite, the oxidizing agent used is of the group consisting of ammonium and alkali metal chlorates and chromates, and the nitrogenous salt of a fatty acid is N-tallow-trimethylenediaminedioleate.

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