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PREVENTING CORROSION OF METALS IN AQUEOUS SYSTEMS

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This invention relates to methods of preventing corrosion of metals in contact with aqueous systems and more particularly to prevention of corrosion of automobile radiators.

The invention is applicable broadly to various types of metals such as iron, steel, copper, brass, solder, and even aluminum under some circumstances. When these various metals are in contact with aqueous systems, particularly at a slightly elevated temperature and when the water or aqueous solution contains dissolved air, these various metals are subject to corrosion as by oxidation or electrolytic action. This is particularly true in cooling radiators of automobiles and other vehicles or engines where hot water is subjected to forced circulation through the radiator and a certain amount of air is dissolved in the water at intervals, particularly when the radiator is allowed to cool down. The invention is also applicable to other aqueous systems such as hot water and steam heating systems, hydraulic presses, elevators, etc., as well as to cutting oil emulsions or solutions, and the like.

Broadly, the invention comprises dissolving in the water or aqueous solution in contact with the metal, a small amount of a basic organic compound of the onium base type. By this term is meant organic bases in which monovalent organic radicals are connected to an inorganic element to which, in turn, an OH radical is attached but to which no hydrogen atoms are attached. These onium bases may be considered to have the type formula R_nXOH in which R_n are organic radicals not necessarily the same and X is one of the various onium base elements such as nitrogen, arsenic, phosphorus, sulfur, iodine, and various metals, for example, tin, bismuth, antimony and other elements capable of forming onium compounds. The subscript "n" represents one less than the valence of X. Thus the compounds used in the present invention will be usually either tertiary or quaternary hydroxides, depending upon the valence of the onium base element.

The substituted radicals to be combined with the onium base element may be any organic radicals and may comprise either the same or different members in the same series, as methyl, ethyl, etc., or in different series, as alkyl, aryl, alcohols, or mixed or substituted groups. Also tertiary heterocyclic onium base compounds are suitable, for example, those of the pyridin type having a nitrogen atom in the ring, and the homologs of such compounds. The chief requirement is that all hydrogen atoms originally connected directly with the onium base element should be completely substituted by organic radicals.

Tetramethyl ammonium hydroxide is one of these onium bases which has proved successful; other examples are: Tetraethyl ammonium hydroxide, tetraethanol ammonium hydroxide, diethyl-monomethyl sulfonium hydroxide, trimethyl tin hydroxide (this may be called trimethyl stannonium hydroxide), and triphenyl tin hydroxide.

These onium bases have relatively high dissociation constants of the order of those of the alkali hydroxides and it is believed that they are particularly adapted for preventing corrosion of aqueous systems because they are strong bases of a predominantly organic nature and have less tendency to cause electrolytic corrosion than do the strong inorganic bases, such as caustic soda and the like. On the other hand, they have the advantage over many organic compounds in that they are, for the most part, very soluble in water and hence a small amount thereof is quickly and uniformly dispersed throughout the entire aqueous system and comes into intimate contact with any metallic surfaces immersed therein.

Instead of using the onium bases themselves, in other words, the hydroxides, it is possible under some circumstances to use weak salts and esters thereof, such as carbonate, acetate, stearate, etc., which may hydrolyze sufficiently under the conditions of use in order to liberate a small amount of free onium base.

These onium bases may be used by either dissolving directly in the aqueous system a small amount of the compounds themselves, many of which are solids (such as tetramethyl ammonium hydroxide which has a melting point of 62°), or they may be dissolved in a suitable amount of a solvent for said compounds, such as water, alcohol, etc., to prepare a concentrated (e. g. 5 or 10%) stock solution, and then a small amount of this solution added at will to the aqueous system in which the metals are to be protected against corrosion.

The onium base may also be used in emulsions, particularly of the oil-in-water type, not only to inhibit corrosion of metals in contact therewith, but also to stabilize the emulsion by neutralizing any traces of acid. Water-soluble anti-freeze agents such as alcohol, glycol, glycerine, etc., or various other addition agents, e. g. alkylolamines, may be dissolved in the aqueous system if desired. The presence of inorganic salts, such as sodium chloride, calcium chloride, etc., in the aqueous

system, does not prevent the effectiveness of the onium base as a corrosion inhibitor.

The amount of onium base to be used may vary over a fairly wide range depending upon the type of materials in question and the severity of the conditions, such as temperature and pressure, contact with air, etc., under which they are to be used. Generally, however, from 0.01 to 1 or 2% is sufficient, and for most ordinary purposes, such as in automobile radiators, 0.1 or 0.2% is sufficient. It is possible that under conditions where organic or inorganic acids may be formed during use it may be desirable to either use a much larger initial quantity of onium base or else to add small amounts at various intervals in order to maintain a small amount present at all times.

For the sake of illustration, a number of examples are given herewith.

Example 1

4 iron wire nails were placed in each one of 4 small glasses containing respectively plain water, a weak solution of baking soda, a weak solution (about 0.5%) of tetramethyl ammonium hydroxide, and a weak solution and suspension of hydrated lime. These were allowed to stand at room temperature and after 4 hours it was observed that all of the nails had become rusty and the water had become red, except in the glass containing the onium base solution where the nail was still bright and the water was clear. After 4 days the results were practically the same except that the rusting had progressed considerably further giving a very thick coating of loose rust deposit on the 3 nails, whereas the nail immersed in the onium base solution still remained shiny and bright over the entire submerged surface, a small amount of rusting appearing only at the surface of the solution where it came into contact with the air.

Example 2

2 samples of iron (50×25×3 mm.) were immersed for 141 hours at 180° F. in plain water and in water containing 0.2% of tetramethyl ammonium hydroxide respectively. The onium base reduced the corrosion from 136.9 mg. to 1.7 mg.

Example 3

Similar corrosion tests were made with brass specimens and it was found that the onium base reduced the corrosion from 4.9 to 0.9 mg.

Example 4

Similar corrosion tests were made with iron specimens immersed in a solution containing 57.5% water and 42.5% glycerin containing 0.2% of two different corrosion inhibitors. With tetramethyl ammonium hydroxide as the inhibitor, the corrosion loss was 20.0 mg. whereas with an inhibitor comprising equal parts of urea and tertiary butyl phenol the loss was 22.7 mg.

Example 5

2 strips of copper were subjected to the same test conditions as in Example 4, the tetramethyl ammonium hydroxide showing a loss of only 4.6 mg. compared to 24.5 mg. for the other inhibitor (the mixture of urea and tertiary butyl phenol).

Example 6

A specimen of iron was subjected to a similar corrosion test by immersion in an aqueous solution containing 50% of triethanolamine and 0.2% of tetramethyl ammonium hydroxide. The corrosion loss was 1.3 mg. which shows in comparison with the data obtained in Example 2 that the onium base protected the iron in the aqueous solution of triethanolamine just as well as it did in the plain water.

Example 7

A small amount of a soluble oil comprising about 70% of a 100 sec. viscosity pale oil, 20% of petroleum sulfonates, 4 or 5% of rosin, ½% of caustic soda and 2 or 3% of water was emulsified in a large volume of water containing about 0.5% tetramethyl ammonium hydroxide.

The above data are especially pertinent in view of another series of tests which indicated that although 0.1% of tertiary butyl phenol and of urea separately inhibited the corrosion of aluminum and brass, neither of them had any effect on the corrosion of copper and both of them very greatly accelerated the corrosion of iron.

The above examples show the wide adaptability of these onium bases for preventing corrosion of metals in various aqueous systems, indicating that usually only a very small amount is effective and that in many instances the onium base is distinctly superior to other types of inhibitors.

These bases may be used in conjunction with other inhibitors such as urea, test-butyl phenol, pyridine bases, etc., with antifreeze agents, pickling compounds, emulsions, etc.

It is not intended that the invention be limited to the specific examples given nor to any theory advanced as to the operation of the invention, but it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. The method of preventing corrosion of metals in aqueous systems which comprises dispersing in said aqueous systems a small amount of an organic compound having the general formula R_nXY in which R_n represents monovalent organic radicals, the subscript "n" is a numeral one less than the valence of X, X is an inorganic element capable of forming an onium compound and which is capable of having a hydroxyl group directly connected thereto, and Y is a radical selected from the group consisting of hydroxyl and inorganic and organic radicals capable of forming weak or at least partially hydrolyzable salts and esters respectively with the positive radical of the onium compound.

2. Process according to claim 1 in which X is an element selected from the group consisting of nitrogen, arsenic, phosphorus, sulfur, iodine, tin, bismuth and antimony.

3. An aqueous medium adapted to prevent corrosion of metals in contact therewith, said medium having dissolved therein about 0.01 to 2.0% of an organic compound having the general formula R_nXY in which R_n represents monovalent organic radicals, the subscript "n" is a numeral one less than the valence of X, X is an inorganic element capable of forming an onium compound and which is capable of having a hydroxyl group directly connected thereto, and Y is a radical selected from the group consisting of hydroxyl and inorganic and organic radicals capable of forming weak or at least partially hydrolyzable salts and esters respectively with the positive radical of the onium compound.

4. Composition according to claim 3 containing a substantial proportion of a water-soluble aliphatic mono- or poly-hydroxy alcohol.

5. The method of preventing corrosion in auto-

mobile radiators and other aqueous systems, which comprises dispersing in said aqueous systems a small amount of tetra-alkyl ammonium hydroxide.

6. Process according to claim 5, in which about 0.2% of tetramethyl ammonium hydroxide is used.

7. An automobile radiator cooling liquid containing a major proportion of water and about 0.1% of tetramethyl ammonium hydroxide.

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