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[54] METHOD OF INHIBITING CORROSION

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[51] Int. Cl. **A01n 9/24**

[58] Field of Search **71/83, 65, 84, 117,**
71/113, 116; 252/389

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[57] ABSTRACT

The combination of boric acid or a soluble salt thereof and a halophenoxyalkanoic acid or salt thereof is effective to inhibit corrosion of ferrous metals when in contact with aqueous fluids containing said combination. The inhibitory composition is particularly useful in inhibiting the corrosion of metal in contact with herbicidal compositions of which the active ingredient is halophenoxy-alkanoic acid or salt, especially when the composition also includes a corrosive chelating agent, e.g., citric acid, tartaric acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid or the like.

1 Claim, No Drawings

METHOD OF INHIBITING CORROSION**BACKGROUND OF THE INVENTION**

Various borate salts, alone or in combination with other known inhibitors, are known to be effective corrosion inhibitors in aqueous and nonaqueous media.

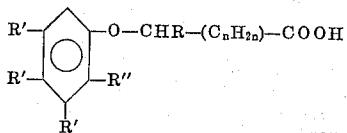
The halophenoxyalkanoic acids and their salts have not heretofore been recognized as corrosion inhibitors and, in fact, exhibit little or no inhibitory action when used alone in the compositions described herein.

SUMMARY OF THE INVENTION

It has now been discovered that the combination of boric acid and halophenoxyalkanoic acid, or the soluble salts thereof, is an effective corrosion inhibitor for protecting ferrous metals in aqueous media. By the term "boric acid" we mean to include all the common acids of boron, e.g., ortho-, meta-, tetra- and pentaboric acid and the like.

DETAILED DESCRIPTION

The halophenoxyalkanoic acids of special interest are those of the formula



wherein R is H or alkyl, each R' and R'' independently is H, halogen or alkyl and n is an integer 0-16, at least one of R and R'' being H, and at least one of R' and R'' being halogen, the total number of carbon atoms in the group $-\text{CHR}-(\text{C}_n\text{H}_{2n})-\text{COOH}$ being two to about 18.

Particularly preferred acids are those of the above formula wherein at least two of R' and R'' are Cl, any others being H or CH_3 , R is H or CH_3 and n is 0. Illustrative suitable acids include p-chlorophenoxyacetic, p-iodophenoxyacetic, 2(3,5-dichlorophenoxy)-propionic, 2,4,5-trichlorophenoxyacetic, 2(p-bromophenoxy)-valeric, 2-bromo-4-methylphenoxyacetic, 2(4,5-dichlorophenoxy)-butyric, 2(3-bromo-4-sec. butylphenoxy)-caproic, 2(3,5-difluoro-5-isopropylphenoxy)-butyric, 2-methyl-4-bromo-5-chlorophenoxyacetic and 2(2,3,4,5-tetrachlorophenoxy)-acetic acids and the like.

While the inhibitor combination of the invention is of some value in acidic solutions, it is much more effective at higher pH values, i.e., in neutral or, preferably, alkaline solutions. This, of course, means that both the boric acid and the halophenoxyalkanoic acid are usually used in the salt form rather than the free acid. The identity of the cation of the salt is unimportant so long as the salt has adequate solubility in the aqueous medium to be inhibited. Ordinarily the alkali metal, ammonium and amine salts are preferred, though others, particularly the alkaline earth metal salts, are also useful. The amine salts are often preferred because of their high solubility, especially when the aqueous medium to be inhibited contains other amine salts. Suitable amines include the primary, secondary and tertiary alkyl- and alkanolamines, such as mono-, di- and trimethyl-, ethyl-, butyl-, ethanol-, propanol- and butanolamines, dimethylethanolamine, butyl-diethanolamine and the like.

An area of special utility for the inhibitor composition of the invention is in the inhibition of the corro-

siveness of herbicidal compositions based on the halophenoxyalkanoic acids and salts of such acids. Such compositions are often corrosive to metal containers in which they are prepared, shipped or stored or to the tanks, pumps, etc. of the equipment with which they are applied to the vegetation to be controlled. This corrosiveness is often engendered or enhanced by the presence of chelating agents that are commonly used to sequester undesirable cations, thus reducing discoloration, precipitation or other undesirable effects of such ions. Among the commonly used chelating agents are citric acid, tartaric acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, etc., and the soluble salts of such acids. Since such herbicidal compositions consist essentially of one component of the present inhibitor combination, the combination can be conveniently formed in situ by adding thereto a small amount of the second component, i.e., the boric acid or salt. Effectively, the inhibitor combination is formed in and is present in a very large excess of the halophenoxyalkanoic acid component and thus inhibits the corrosiveness of the latter and of any corrosive chelating agent that is present. Such inhibition is particularly surprising because neither component of the inhibitor combination when used alone will effectively inhibit the corrosiveness of such chelating agents in aqueous media.

The amount of inhibitor used and the proportions of the two components therein are not critical and may be varied widely. Less than 1% by weight, based on the aqueous medium to be inhibited, of each component or of the combination is usually sufficient to markedly inhibit the corrosiveness of the medium. Ordinarily amounts in excess of about 5% contribute little additional inhibition, though larger amounts may be used if desired. For many purposes it is sufficient to use as little as about 0.1% of each component in the aqueous medium.

The practice of the invention is illustrated by the following examples.

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EXAMPLE 1

A 40 percent by weight aqueous solution of the dimethylamine salt of 2,4-dichlorophenoxyacetic acid containing 3 percent, by weight, of citric acid was highly corrosive to ferrous metal tanks, drums and cans. The addition thereto of 2 percent, by weight, of H_3BO_3 and adjustment of the pH to 7.4-7.8 by addition of dimethylamine substantially eliminated the discoloration of the material and the corrosion of ferrous metals in contact therewith. Various steel drum stocks, cold rolled can stock, zinc phosphated steel and iron phosphated steel were also tested in contact with the inhibited composition and found not to be significantly corroded under normal storage conditions.

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EXAMPLE 2

When the experiments of Example 1 were repeated except that the halophenoxyalkanoic acid was 2-methyl-4-chlorophenoxyacetic acid, in a concentration of 4 lb. per gal. acid equivalent, excellent corrosion inhibition was obtained.

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EXAMPLE 3

The corrosiveness of various solutions toward ordinary drum steel was estimated by applying a variable E.M.F. to the steel in contact with the solution and plotting the resultant current. The resulting graphs

show little or no current at potentials of -0.7 volt or less (relative to a standard calomel electrode). Between -0.7 and about -0.4 the current went through a peak, the height of which was indicative of corrosiveness, and then dropped to near zero at more positive voltages. The following are illustrative of typical tests made by this method.

A. A 3 percent aqueous solution of citric acid was neutralized with dimethylamine to a pH of 7.7. Varying amounts of an inhibitor consisting of a 1:1 molar complex of H_3BO_3 with 2,4-dichlorophenoxyacetic acid were then added and the peak current noted. Results were as follows:

Inhibitor, Normality	Current, m.a.
0	7.3
0.01	5.6
0.05	3.3
0.07	2.3
0.32	0.01

B. An aqueous solution of citric acid (1.5 percent) and boric acid (2 percent) was tested with various concentrations of 2,4-dichlorophenoxyacetic acid, all formulations being neutralized to pH 7.0 with dimethylamine. Results were as follows:

2,4-D, % by wt.	Current, m.a.
0	0.88
1	0.67
3.5	0.01

C. A series of halophenoxyalkanoic acids were tested under the same conditions, i.e., in 0.323 molal aqueous solutions containing 3 percent citric acid and 2 percent boric acid and neutralized to pH 7.7 with dimethylamine. Results were as follows:

Acid	Current, m.a.
4-Bromophenoxyacetic	<0.01
2-Methyl-4-bromophenoxyacetic	0.01
2-Methyl-4-Chlorophenoxyacetic	0.09
2,4-Dibromophenoxyacetic	0.04
2,4-Dichlorophenoxyacetic	0.01
2-Methyl-4-fluorophenoxyacetic	0.55

D. To show the substantial equivalence of various cations in the invention, tests were made with an aqueous solution of 3 percent citric acid, 2 percent boric

acid and 7 percent 2-methyl-4-chlorophenoxyacetic, all neutralized with various bases as indicated.

Cation	Current, m.a.
Dimethylamine, Blank (no methyl-chlorophenoxyacetic acid)	8.8
Dimethylamine	2.4
Triethanolamine	3.5
Sodium	2.1

EXAMPLE 4

An aerosol window cleaner composition consisting essentially of a surfactant dissolved in aqueous isopropanol with small amounts of NH_3 and glycol ethers and pressurized with isobutane was found to be corrosive to the steel aerosol container. Addition of various amounts of sodium nitrite, a widely used corrosion inhibitor, failed to inhibit the corrosion. Addition of 0.5 percent by weight of a 1:1 molar complex of H_3BO_3 and 2,4-dichlorophenoxyacetic acid resulted in substantially complete inhibition of corrosion throughout a test period of one month at 100°F.

As illustrated in Example 4, the inhibitor composition of the invention is of general utility in corrosive aqueous solutions. For such general use it is convenient to prepare inhibitor concentrates consisting essentially of a boric acid and a halophenoxyalkanoic acid, as hereinbefore defined. While the most economical and effective concentrate is the 1:1 molar complex of the two components, as little as 1 percent or less of either component significantly enhances the activity of the other so that concentrates may vary in weight ratio of components from about 1:99 to about 99:1, though a ratio higher than about 10:1 of borate to phenoxy acid is not ordinarily preferred.

We claim:

1. The method of inhibiting the corrosiveness of an aqueous solution of a herbicidal halophenoxyalkanoic acid or salt thereof and a corrosive chelating agent comprising dissolving in said solution a corrosion inhibiting amount not exceeding about 5 percent of boric acid or salt thereof.

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