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[54] **SULFONIUM COMPOUND AS A CORROSION INHIBITOR IN AQUEOUS ACID**

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[58] **Field of Search** ..... 252/151, 395, 87, 252/181; 260/607 B

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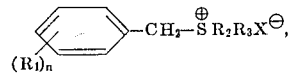
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[57] **ABSTRACT**

Alkylbenzyldialkysulfonium salts are discovered to be useful corrosion inhibitors in aqueous acid solutions. Said sulfonium salts have the formula



wherein n is 1 or 2; R_1 is an alkyl radical with the aggregate carbon content of R_1 being from 6 to about 24 carbon atoms; R_2 and R_3 are alkyl radicals and X^- is an anion. The novel inhibitors are useful at very low concentrations even in the presence of ferric ions. E.g., an aqueous solution of ethylenediaminetetracetic acid as the ammonium salt at pH 5 and initially 3×10^{-4}M. in p-dodecylbenzyldimethylsulfonium chloride is illustrative of the inhibited solutions disclosed.

16 Claims, No Drawings

SULFONIUM COMPOUND AS A CORROSION INHIBITOR IN AQUEOUS ACID

BACKGROUND OF THE INVENTION

Iron oxide encrustations, commonly known as rust or iron oxide scale, frequently form on ferrous metal surfaces. Such surface deposits are objectionable on ferrous articles which are scheduled to be refinished (e.g. sheet steel) and are particularly troublesome when located on the surfaces of tubing and other conduits (e.g., boiling tubing, heat exchangers, connecting piping, and the like) wherein the deposits can restrict flow and interfere with heat exchange.

Various methods of removing such surface deposits have been devised, a common one being to contact the ferrous surface with an aqueous acidic cleaning solution (e.g. aqueous HCl) and thereby dissolve and remove the iron oxide encrustations from the surface. An iron salt typically results from this operation, the specific salt depending upon the acidic cleaning medium used. E.g., $FeCl_3$ and/or $FeCl_2$ are formed when HCl is used.

Such iron salts are generally soluble to at least a limited extent in the cleaning media. Ferric ions thus result.

Corrosion of ferrous metal surfaces in contact with aqueous acids is known. It is also known that the presence of ferric ion causes severe corrosion problems of ferrous metal surfaces during the above mentioned acid cleaning process. Namely, the cleaning solution attacks (corrodes) the freshly cleaned metal surface with the attendant loss of metal. In the presence of oxygen, ferric ions are continually regenerated accentuating the problem.

Many compounds have been included as corrosion inhibitors in such cleaning solutions but their effectiveness in the presence of ferric ion is generally nonexistent or quite low.

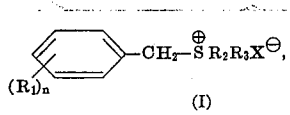
Similarly, the corrosion of other common construction metals (and metal alloys) in contact with aqueous acid solution is a definite problem. E.g., in the abovementioned process of cleaning ferrous metal surfaces with acid solutions, other metals may be present as an integral part of the system being cleaned (e.g. copper, copper alloys, zinc, zinc alloys, stainless steels, etc), which may be similarly corroded.

It is therefore an object of this invention to inhibit the acid induced corrosion of metal surfaces, particularly ferrous and cuprous metal surfaces, in contact with aqueous acid solutions.

Another object of this invention is to inhibit acid induced corrosion of ferrous metal surfaces even in the presence of ferric ions.

SUMMARY OF THE INVENTION

It has now been discovered that alkylbenzyldialkylsulfonium salts are unusually effective in inhibiting the corrosion of metals, particularly ferrous and cuprous metals, in contact with aqueous acid solutions. Said sulfonium salts are represented by the formula



(I)

wherein n is 1 or 2 (preferably 1); R_1 is an alkyl radical with the aggregate carbon content of the R_1 radical(s) being from 6 to 24 carbon atoms; R_1 is preferably a C_8 to C_{18} alkyl radical and is most preferably a linear or substantially linear C_8 to C_{18} alkyl radical; R_2 and R_3 are each independently alkyl radicals of from 1 to about 18 carbon atoms and are preferably alkyl radicals of from 1 to 4 carbon atoms; and X^- is an anion. The position(s) of R_1 on the aromatic ring is not critical and thus may be ortho, meta or para; the monosubstituted para moieties being currently preferred. The subject class of inhibitors are effective at low concentrations (e.g. 2×10^{-4} moles/liter) and are surprisingly effective even in the presence of ferric ions. Thus, the above-described ferric ion corrosion problem experienced during the cleaning ferrous metal surfaces can be substantially reduced if not eliminated by incorporating into the acidic cleaning solution a small but sufficient amount of said sulfonium salts to produce the desired inhibition effect.

Examples of suitable sulfonium salts defined by I include those having the following values for R_1–R_3 and X^-

TABLE I

R_1	R_2	R_3	X^-
4-n-C_6H_{13}	CH_3	CH_3	Cl
2-CH_3; 4-C_5H_{11}	C_2H_5	C_8H_{17}	HSO_4
4-n-C_6H_{13}	C_4H_9	C_4H_9	NO_3
3-n-C_6H_{13}	CH_3	$C_{12}H_{25}$	Cl
4-n-C_7H_{15}	C_2H_5	C_4H_9	Br
4-n-C_7H_{15}	CH_3	$C_{18}H_{37}$	HSO_4
4-i-C_8H_{17}	CH_3	C_2H_5	I
3-n-C_8H_{17}	C_2H_5	C_2H_5	NO_3
4-n-C_8H_{17}	C_4H_9	C_4H_9	I
2-C_2H_5; 4-C_6H_{13}	CH_3	C_5H_{11}	NO_3
3-C_4H_9; 5-C_4H_9	C_2H_5	C_2H_5	I
4-n-$C_{12}H_{25}$	C_3H_7	C_3H_7	tosylate
3-n-$C_{12}H_{25}$	CH_3	C_4H_9	Br
4-n-$C_{12}H_{25}$	C_4H_9	C_4H_9	I
4-n-$C_{12}H_{25}$	C_6H_{13}	C_6H_{13}	NO_3
2-CH_3; 4-i-$C_{12}H_{25}$	CH_3	CH_3	H_2PO_4
3-n-$C_{18}H_{37}$	CH_3	CH_3	Br
4-n-$C_{18}H_{37}$	CH_3	C_3H_7	Cl
4-n-$C_{20}H_{41}$	CH_3	CH_3	Cl

The above examples are meant to be merely illustrative of the well known class of compounds defined by I. The remaining compounds defined by I will be readily apparent to one skilled in the art. Mixtures of sulfonium salts can likewise be used. The choice of anion, X^-, is not critical and may be varied to convenience; e.g. the anion is generally chosen to be the same as the acid in solution. The anion may be selected by the method of preparing the sulfonium salt or by ion exchange means. Examples of suitable anions include chloride, bromide, iodide, nitrate, bisulfate, tosylate, acetate, benzoate, dihydrogen phosphate, and the like.

The acid solutions suitable for use herein are aqueous solutions of non-oxidizing inorganic acids, such as HF, HCl, H_2SO_4, H_3PO_4, etc., and mixtures thereof (oxidizing inorganic acids include HNO_3, $HClO_4$, CrO_3, etc); or aqueous solutions of organic acids, such as formic acid acetic acid, sulfamic acid, hydroxy acetic, citric acid, etc., and mixtures thereof; or are aqueous solutions of known chelating agents, such as ethylenediaminetetracetic acid, hereafter EDTA (and the ammonium, amine, or alkali metal salts of EDTA), and other like polyaminepolycarboxylic acids and the like; and mixtures of such aqueous acid solutions. The most common cleaning solutions are aqueous solutions of HCl and aqueous solutions of EDTA and amine or al-

kali metal salts of EDTA. The acid solutions may be buffered to maintain a desired pH level with conventional buffering agents, such as citric acid, acetic acid, and salts thereof. The pH values of acid cleaning solutions typically range from 1 to 5 for aqueous solutions of organic acids, and from pH 2–5 for aqueous solutions of chelating agents, such as the EDTA type cleaning solutions. The normality of cleaning solutions using inorganic acids are typically greater than 1.

The concentration of sulfonium salt used in the acid solutions may vary depending upon the particular salt, the particular metal and the degree of corrosion inhibition desired. Typically, concentrations of from about 1×10^{-6} to about 0.1 moles of sulfonium salt per liter of solution are sufficient and concentrations of from about 1×10^{-4} to 0.01 moles/liter are generally preferred.

SPECIFIC EMBODIMENTS

The following examples further illustrate the invention.

GENERAL PROCEDURE

Coupons of carbon steel (having 98.7% Fe; 0.3% Mn; and 0.05% C.) having approximately 40 square centimeters of surface area were (a) scrubbed thoroughly with a soap-filled pad of steel wool in warm water, (b) rinsed with water, (c) washed with acetone, (d) pickled for 5 minutes in 10% aqueous HCl, (e) dried in air, and (f) weighed. The coupons thus prepared were then suspended from glass hooks in a stirred acid cleaning solution at 25°C. or 50°C. for normally 16 hours; the coupons being completely immersed in the solution. The coupons were then removed from the acid solutions, washed with soap and warm water, rinsed, dried and weighed. The weight loss resulting from such treatment is a measure of corrosion. The weight loss rate (WLR), having the units lbs./ft^2/day is determined as follows:

$$WLR = \frac{(49.15)\ (\text{weight loss in gm.})}{(\text{original weight in gm.})\ (SF)\ (\text{time})},$$

wherein (a) 49.15 is a conversion factor for converting gm./cm.^{2}/hr. to lbs./ft.^{2}/day; (b) SF = strip factor = average ratio of surface area (cm.^{2}) to weight (gm.); and (c) the time is measured in hours.

The effectiveness of the sulfonium salts was determined by comparing the WLR of a cleaning solution containing the sulfonium salts (WLR (test)) against the WLR of an identical cleaning solution without the sulfonium salts (WLR (blank)). The comparative data is reported as the "Percent Protection" which is calculated as follows:

$$\text{Percent Protection} = \frac{WLR\ (\text{blank}) - WLR\ (\text{test})}{WLR\ (\text{blank})} \times 100.$$

The sulfonium salts were evaluated in three representative acid cleaning solutions. Solution "A" was a 3.8 percent by weight, total weight basis, aqueous solution of an ammonium salt of ethylenediaminetetracetic acid buffered at a pH OF 5 with citric acid and contained 0.10 percent by weight, total weight basis, of Fe^{+3} (added as $FeNH_4(SO_4)_2 \cdot 12\ H_2O$). Solution "B" was a 10 percent by weight, total weight basis, aqueous solution of HCl, and 0.10 percent by weight of Fe^{+3} (added as $FeCl_3$). Solution "C" was a 10 percent by weight, total weight basis, aqueous solution of H_2SO_4 and 0.1 percent by weight of FE^{+3} (added as $FeNH_4(SO_4)_2 \cdot 12\ H_2O$).

The results of several experiments using solution "A" are tabulated in Table II below. The concentration of the sulfonium salt is reported in millimoles per liter. The neutralizing anion, X^-, in each case was chloride.

TABLE II

Ex.	R_1	R_2	R_3	Conc.	Temp. (° C.)	WLR (test)	Percent protection
1	p-n-C_8H_{17}	CH_3	CH_3	0.69	50	0.0054	89
2	p-n-$C_{12}H_{25}$	CH_3	CH_3	0.20	25	0.0020	95
3	p-n-$C_{12}H_{25}$	CH_3	CH_3	0.30	50	0.0090	82
4	p-n-$C_{12}H_{25}$	CH_3	n-C_4H_9	0.40	25	0.0039	90
5	p-$C_{17}H_{35}$	CH_3	CH_3	0.30	50	0.020	61

In Examples 2–4, the R_1 radical was actually a mixture of C_8–C_{18} alkyl radicals with $C_{12}H_{25}$ being the predominant species.

In like manner, a p-n-dodecylbenzyldimethylsulfonium chloride was evaluated as an inhibitor in solutions "B" and "C". The results are tabulated in Table III below. The concentration of the sulfonium salt in solution is reported as millimoles per liter.

TABLE III

Ex.	Solution	Inhibitor Conc.	Temp. (°C.)	WLR (test)	Percent Protection
6	B	0.20	25	0.020	52
7	B	0.39	50	0.021	89
8	C	0.39	25	0.0065	81

In other experiments, test solution "A" containing p-n-dodecylbenzyldimethylsulfonium chloride as the inhibitor was evaluated in a "flow test" wherein the solution was pumped through steel pipes for 6 to 7 hours and the degree of corrosion determined as above. The steel pipes used in this test were sections cut from the same length of pipe and measured approximately 1 foot in length and 0.75 inch in inside diameter. The pipes were cleaned free of rust by use of a commercial cleaning solution quite similar to solution "A" except that no Fe^{+3} was added, and were scrubbed with soap and warm water, rinsed with water, rinsed with acetone, dried and weighed. After the flow test, the pipes were again scrubbed, rinsed with water, rinsed with acetone, dried and weighed. The "WLR" and "Percent Protection" were calculated as above. The results are summarized in Table IV below. The flow rate is measured in gallons/minute and the concentration of sulfonium salt (Conc.) is expressed as millimoles per liter.

TABLE IV

Ex.	Flow Rate	Temp. (°C.)	Inhibitor Conc.	WLR (test)	Percent Protection
9	0.2	25	0.39	0.011	89
10	0.2	50	0.39	0.016	81
11	0.2	65	0.56	0.014	86
12	5.0	25	0.39	0.0064	97
13	5.0	65	0.56	0.028	95
14	10.0	25	0.39	0.0064	99

In still other experiments, the subject sulfonium salts were evaluated as corrosion inhibitors in aqueous acid solutions which did not initially contain any significant amount of ferric ion. Examples 15 and 16 were conducted in 10 percent by weight, total weight basis, aqueous HCl solutions and Example 17 was conducted in a 10 percent by weight aqueous H_2SO_4 solution. In

each of Examples 15–17 the inhibitor was p-dodecylbenzyldimethylsulfonium chloride and the metal coupons and the testing procedure used were substantially the same as those described in Example 1. The results are tabulated in Table V below. The concentration (Conc.) of sulfonium salt is expressed in millimoles per liter.

TABLE V

Ex.	Inhibitor Conc.	Temp. °C.	WLR (test)	Percent Protection
15	0.28	25	0.0027	91
16	0.36	50	0.0047	98
17	0.30	25	0.0031	75

EXAMPLE 18

Using substantially the same procedure as Example 2, the corrosion of a copper alloy (78% Cu, 21% Zn, and 1% Sn) in contact with solution "A" at 25°C. was found to be inhibited by p-dodecylbenzyldimethylsulfonium chloride (Conc. of 0.4 millimoles/liter). WLR (test) equals 0.0003. Percent Protection = 96 percent

EXAMPLE 19

Using substantially the same procedure as Example 2, the corrosion of a ferrous metal coupon (having the aforesaid analysis) in contact with an aqueous 5 percent phosphoric acid solution at 25°C. was found to be inhibited by p-dodecylbenzyldimethylsulfonium chloride (Conc. of 0.4 millimoles/liter). WLR (test) = 0.003. Percent Protection = 63 percent.

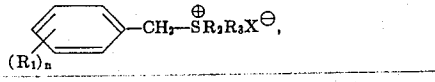
In the above examples, a thin, adherent, hydrophobic protective film was generally observed on the ferrous articles cleaned with the inhibited cleaning solutions. The film was predominantly a mixture of compounds of the formula



wherein R_1 had the designated meaning in the examples. E.g., coupons cleaned with the test solutions inhibited with p-dodecylbenzyldimethylsulfonium chloride were observed to have a protective film of (predominantly) (p,p'-bisdodecyl)bibenzyl and p-dodecyltoluene on their surface; such coupons were suspended over water in a closed vessel for 11 days and showed only small localized rust spots while coupons cleaned with the uninhibited solutions and concurrently aged over water were uniformly covered with red rust.

We claim:

1. An aqueous acidic cleaning solution of at least one non-oxidizing inorganic acid or organic acid or mixtures thereof having incorporated therein at least one sulfonium salt of the formula



wherein n is 1 or 2; each R_1 is independently an alkyl radical; the aggregate carbon content of said R_1 radicals being from 6 to about 24 carbon atoms; R_2 and R_3 are each independently alkyl radicals of from 1 to about 18 carbon atoms; and X^- is an anion; said sulfonium salt being present in an amount at least sufficient to inhibit the corrosion of ferrous metal in contact with said solution and ferric ions.

2. The composition defined by claim 1 wherein n is 1.

3. The composition defined by claim 2 wherein R_1 is a para substituent on the aromatic ring.

4. The composition defined by claim 1 wherein each R_1 is an alkyl radical of from 8 to 18 carbon atoms.

5. The composition defined by claim 1 wherein R_2 and R_3 are independently alkyl radicals of from 1 to 4 carbon atoms.

6. The composition defined by claim 1 wherein n is 1, R_1 is an alkyl radical of from 8 to 18 carbon atoms and R_2 and R_3 are each independently alkyl radicals of from 1 to 4 carbon atoms.

7. The composition defined by claim 1 wherein said acid solution is an aqueous solution of a non-oxidizing inorganic acid or a mixture of such acids.

8. The composition defined by claim 1 wherein said acid solution is an aqueous solution of an organic carboxylic or polycarboxylic acid or a mixture thereof.

9. The composition defined by claim 1 wherein said acid solution is an aqueous solution of a polyaminepolycarboxylic acid or an ammonium-, amine, or alkali metal salt thereof, or mixtures thereof.

10. The composition defined by claim 1 wherein said acid solution is an aqueous solution of at least one of HCl, H_2SO_4, ethylenediaminetetracetic acid (EDTA) or the ammonium-, amine- or alkali metal salt of EDTA.

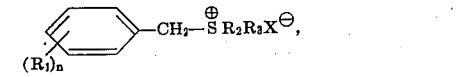
11. The composition defined by claim 1 wherein n is 1; R_1 is p-dodecyl; and R_2 and R_3 are each independently alkyl radicals of from 1 to 4 carbon atoms.

12. In the process of treating ferrous metal surfaces to remove iron oxide encrustations by treating said metal surface with an aqueous acid cleaning solution, the improvement of using the composition defined by claim 1 as said cleaning solution.

13. The composition defined by claim 10 wherein said acid solution is an aqueous solution of at least one of EDTA and an ammonium-, amine- or alkali metal salt of EDTA and wherein said solution is buffered to a pH of from 2 to 5.

14. The composition defined by claim 13 wherein n is 1; R_1 is an alkyl radical of from 8 to 18 carbon atoms; and R_2 and R_3 are each independently alkyl radicals of from 1 to 4 carbon atoms.

15. A process of inhibiting acid-induced and ferric ion-induced corrosion of metal surfaces in contact with an aqueous acid solution of at least one non-oxidizing inorganic acid or organic acid or mixtures thereof, the process comprising incorporating in said acid solution a small but corrosion-inhibiting amount of at least one sulfonium salt of the formula



wherein n is 1 or 2; each R_1 is independently an alkyl radical; the aggregate carbon content of said R_1 radicals being from 6 to about 24 carbon atoms; R_2 and R_3 are each independently alkyl radicals of from 1 to about 18 carbon atoms; and X^- is an anion.

16. The process defined by claim 15 wherein n is 1; R_1 is an alkyl radical of from 8 to 18 carbon atoms; and R_2 and R_3 are each independently alkyl radicals of from 1 to 4 carbon atoms.

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