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METHOD FOR INHIBITING CORROSION OF FERROUS METALS

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No Drawing. Filed Nov. 5, 1958, Ser. No. 771,975
9 Claims. (Cl. 252-135)

This invention relates to methods and compositions for inhibiting the corrosion of ferrous metals caused by caustic alkali solutions containing certain polyhydroxy sequestering compounds.

The use of caustic alkali solutions in industry is widespread. Such solutions are extensively used, for example, in those industries which wash large quantities of bottles and other glassware, metal surfaces, china, porcelain, enamelware, rubber, and similar surfaces. Among the problems faced by these industries was the deposition of unsightly films on articles such as bottles and glassware washed with caustic alkali solutions and the formation of hard adherent precipitates which formed on the surfaces of the equipment. This problem has been successfully solved by incorporating in the caustic alkali solution certain polyhydroxy sequestering and chelating agents which function to inhibit the formation of these films and precipitates.

Although the polyhydroxy sequestering agents referred to above successfully solved the problem of film and deposit formation, it has been found that the prolonged use of these compounds has created another problem, namely, the corrosion of ferrous metals such as the heat transfer elements which are in contact with the alkali solutions. In dilute and moderately concentrated solutions, i.e., in concentrations up to about 20%, caustic alkalis have no appreciable corrosive effect on iron and steel surfaces. On the contrary, such solutions have a passivating effect by reason of the formation of a dense oxide film on the surface which prevents or greatly reduces further corrosion. However, when the above mentioned sequestering agents are present in the alkali solution, this film is apparently dissolved or otherwise removed thus exposing a fresh surface and permitting corrosion to continue unabated.

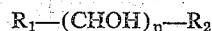
It has been discovered that the corrosive effect of aqueous solutions of caustic alkali containing a water soluble aliphatic saturated polyhydroxy sequestering compound which substantially inhibits the formation of unsightly films and hard adherent precipitates can be eliminated or substantially reduced by adding to the caustic alkali solution an inhibitor comprising a boron compound which on addition to a caustic alkali solution is capable of being converted to the alkali metal salt of boric acid, the weight ratio of the inhibitor to the sequestering compound being within the range from about 0.1 to about 3 or less, depending on the solubility of the inhibitor in the solution. Examples of such compounds are boric acid, the soluble metal salts and preferably the alkali metal salts thereof, and boron trioxide. Also included within the scope of the invention are compounds which are capable of hydrolyzing in alkaline solution to yield water soluble salts of boric acid, such as boric acid esters. It can be seen therefore that the inhibitor of the invention can also be described as a compound which yields borate ions in aqueous solution.

The fact that the inhibitors of the invention function in this manner to prevent corrosion of ferrous metals is quite unexpected. Although metal borates and particularly sodium borate have been used in the past as corrosion inhibitors, such use was predicated on the mildly alkaline nature of the salts. Thus by adding sodium borate, the corrosive action of weakly acidic waters is inhibited as a result of

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the increase in pH caused by the addition of the borate. In the present case, however, the inhibiting action of the boric acid and/or borates is definitely not due to the alkaline nature of these compounds. The solutions containing caustic alkali are already strongly alkaline and the increase in pH on the addition of the borate, if any, is negligible. The effectiveness of the borates in inhibiting corrosion by the caustic alkali solutions of the invention is surprising in view of the fact that other alkaline salts such as carbonates, phosphates, silicates, etc. which also effectively inhibit corrosion caused by mildly acidic solutions have no such effect when used in the caustic alkali solutions of the present invention.

The sequestering or chelating agents which are used in the invention may be generally described as aliphatic saturated polyhydroxy compounds. Included within this class are polyhydric alcohols, polyhydroxy monobasic acids and polyhydroxy dibasic acids. These compounds have the general formula



wherein n is an integer having a value of at least 3, and preferably 4-5, R_1 and R_2 are radicals selected from the group consisting of $-CH_2OH$ and $-COOH$. The preferred sequestering agents are sorbitol among the polyhydric alcohols, mucic and saccharic acids among the dibasic acids, and gluconic and glucoheptonic acids among the monobasic acids. If desired, the acids may be added as such to the alkali solutions where they are converted to the alkali metal salts, or alternatively, any derivative which provides ions of the acid, such as a salt thereof, can be used.

The hydroxy carboxylic acids are known to give the corresponding lactones when subjected to an intermolecular dehydration process. In an aqueous solution of a caustic alkali the lactones hydrolyze to give the alkali salts of the hydroxy carboxylic acid. Thus, it is possible to use lactones in place of these acids or the salts thereof and the description and the claims herein are intended to include the use of such lactones that are hydrolyzed in solution to salts of the hydroxy carboxylic acids.

The caustic alkali can be any alkali metal hydroxide and preferably either sodium or potassium hydroxide. These alkalis are commonly used in cleaning and etching solutions in concentrations of from about 0.25 to about 20% wt./vol., and preferably from about 3 to about 15% wt./vol., which are accordingly the preferred concentration limits of alkali in the present invention. (The designation percent wt./vol. is used herein and in the appended claims to designate grams per 100 ml. of final solution.)

With the above described concentration of caustic alkali, it is customary to use the polyhydroxy sequestering agents in concentrations of about 0.002-5% wt./vol. and preferably about 0.05-1.5% wt./vol. As is customary when selecting amounts of two or more ingredients over a relatively wide range, the amount of sequestering agent in the lower portion of the range is used when an amount of caustic is employed within the lower portion of its range. Similarly, when the amount of caustic is within the upper part of its range, the amount of sequestering agent is also in the upper part of its range, as will be apparent to one skilled in the art.

The inhibitor can be added to alkali solutions in the form of boric acid which of course reacts with the alkali present to form the alkali metal borate. Alternatively, any soluble metal salt of boric acid, preferably sodium borate or potassium borate, can also be used. The inhibitor is used in an amount which is roughly proportional to the amount of polyhydroxy sequestering agent present, the weight ratio of inhibitor to sequestering agent being in the range from about 0.1-3 and preferably from about

0.5 to 1.5. The upper ratio limit of 3 for the inhibitor is established by the fact that this quantity of inhibitor prevents substantially all corrosion in most cases and therefore need not be exceeded, although larger quantities of inhibitor are not detrimental. It should also be understood that in certain instances the solubility limit of the inhibitor in the solution may prevent establishing a weight ratio of inhibitor to sequestering agent as high as 3. In such cases the upper concentration limit of inhibitor corresponds to the level set by its solubility in the solution, i.e., the solution is saturated with respect to the inhibitor.

As examples of the invention a series of experiments were run under identical conditions using different alkali solutions in which the corrosive action of the solutions on a length of steel pipe was determined. In these experiments, a standard black steel nipple 5 inches long with a 1/2 inch nominal diameter was closed at one end with a rubber stopper and equipped with a snugly fitting electric heating element inside the pipe, separated from the rubber stopper by a glass bead. The pipe was then partially immersed in the test solutions in a vertical position and heat was supplied by means of the heating element for about four days (96 hrs.) during which time the solution was maintained at a constant level. All of the solutions tested contained 5% wt./vol. of sodium hydroxide. Some of the solutions contained in addition a polyhydroxy sequestering agent alone and in the additional presence of sodium borate. At the end of the experiment, the steel nipple was removed from the solution and after rinsing and removal of smut, the weight loss was determined. The results of these tests are given in Table I below.

Table I

Solution	Solution Containing—	Concentration, Percent Wt./Vol.	Average Weight Loss, mg. ²
1	Sodium hydroxide	5	49
2	Sodium hydroxide	5	228
3	Sodium gluconate	0.5	
	Sodium gluconate	0.5	
	Sodium gluconate	0.5	96
	Sodium gluconate	0.5	
4	Sodium gluconate	0.5	
	Sodium gluconate	0.5	237
	Sodium gluconate	0.5	
5	Sodium gluconate	0.5	
	Sodium gluconate	0.5	61
	Sodium gluconate	0.5	
6	Sodium gluconate	0.5	
	Sodium gluconate	0.5	222
	Sodium gluconate	0.5	
7	Sodium gluconate	0.5	
	Sodium gluconate	0.5	56
	Sodium gluconate	0.5	
	Sodium gluconate	0.5	

¹ As the anhydrous salt.

² Average of 4 tests.

The results of Table I clearly indicate that the addition of sodium gluconate, sodium glucoheptonate, or sorbitol, which are representative of the polyhydroxy sequestering agents used to prevent the formation of films and precipitates, increases the corrosive action of the solutions to mild steel which is in contact therewith. The results also indicate that this corrosion is greatly reduced if sodium borate is added to the solutions. Although only sodium borate was used in the tests reported above, equivalent results can be obtained using any other compound which yields borate ions in solution, such as boric acid or the salts thereof.

In another series of tests, a different test procedure was adopted. In these experiments, two steel electrodes were partially immersed in the test solutions and heated by means of an alternating electric current which was passed through the electrodes and the solution. After two hours of immersion, the weight loss of the electrodes was determined. Table II below summarizes the results of the tests using several sequestering and chelating agents in the presence and absence of sodium borate. Also included in Table II are the results of tests in which other sequestering agents (solutions 7-10 inclusive) not within the class of polyhydroxy compounds defined above were used together with sodium borate.

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Table II

Solution (containing 5% wt./vol. of NaOH)	Sequestering Agent, 0.55% wt./vol.	Average Weight Loss, mg.	
		No Inhibitor	0.5% wt./vol. Sodium Borate ¹
1	None	1.5	
2	Sodium gluconate	54.6	6.0
3	Sodium glucoheptonate	56.0	7.8
4	Sodium saccharate	66.9	9.6
5	Sodium mucate	37.8	6.5
6	Sorbitol	29.0	3.2
7	Pyrocatechol	52.4	55.8
8	Triethanolamine	56.7	54.9
9	Ethylenediaminetetra-acetic acid (sodium salt)	25.2	21.1
10	N-hydroxyethyl-ethylenediaminetriacetic acid (sodium salt)	26.1	23.8

¹ As the anhydrous salt.

The results of Table II again indicate that the addition of a sequestering agent to the caustic alkali solution increases the corrosion of ferrous metals in contact therewith. This is true of both the aliphatic polyhydroxy compounds (solutions 2-6) used in the invention as well as other well known sequestering agents (solutions 7-10). Surprisingly, however, the addition of sodium borate had little or no effect in reducing the corrosion caused by solutions containing these latter sequestering agents, whereas, in the case of the polyhydroxy compounds, the addition of sodium borate greatly reduced the corrosive effect of the solution.

In practicing the invention on a commercial scale, it is preferred to have solid compositions or liquid concentrates adapted to be dissolved in or diluted with water for use, for example, as cleaning solutions. Solid compositions of this type suitably may contain, by weight based on the total composition, about 50-98.9% of a caustic alkali, about 1-13% of a solid water soluble aliphatic saturated polyhydroxy sequestering compound, and about 0.1-38% of the inhibitor. A preferred solid composition of this type contains about 80-90% by weight of caustic alkali, about 1.5-8% of the sequestering compound, and about 0.8-12% of the inhibitor. The liquid concentrates may contain water and an amount of the solid compositions such that the caustic alkali concentration in the concentrate is above about 20% wt./vol. When dissolved in or diluted with water to give a suitable concentration of caustic alkali within the range from about 0.25 to about 20% wt./vol., the compositions described above will automatically have present amounts of sequestering compound and inhibitor within the operative ranges.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

What is claimed is:

1. The method of inhibiting corrosion of ferrous metals in contact with an aqueous solution containing from about 0.25 to about 20% wt./vol. of a caustic alkali and from about 0.002 to about 5% wt./vol. of a water-soluble aliphatic saturated polyhydroxy sequestering compound having the formula



where n is an integer having a value of 3-5, and R_1 and R_2 are radicals selected from the group consisting of $-\text{CH}_2\text{OH}$ and $-\text{COOH}$ which method comprises adding to said solution an inhibitor comprising a boron compound which on addition to a caustic alkali solution is capable of being converted to the alkali metal salt of boric acid, the weight ratio of said inhibitor to said se-

questering compound being between about 0.1 and about 3.0.

2. The method of claim 1 wherein said sequestering compound is selected from the class consisting of sorbitol, gluconic acid, glucoheptonic acid, saccharic acid, mucic acid, the water-soluble salts of said acids, and mixtures thereof.

3. The method of claim 1 in which the weight ratio of said inhibitor to said sequestering compound is within the range from about 0.5 to about 1.5.

4. The method of claim 1 in which said alkali is sodium hydroxide and said inhibitor is selected from the class consisting of boric acid, the water-soluble salts thereof, and boron compounds capable of hydrolyzing in alkaline solutions to yield water soluble salts of boric acid.

5. The method of claim 4 in which said sequestering compound provides gluconate ions.

6. The method of claim 4 in which said sequestering agent provides glucoheptonate ions.

7. The method of claim 4 in which said sequestering compound provides saccharate ions.

8. The method of claim 4 in which said sequestering compound provides mucate ions.

9. The method of claim 4 in which said sequestering compound is sorbitol.

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