

1

3,247,124

COMPOSITION AND METHOD OF INHIBITING CORROSION OF COPPER-CONTAINING METALS

Robert C. Kimble, John B. Braunwarth, and Louis A. Joo, Crystal Lake, Ill., assignors, by mesne assignments, to Union Oil Company of California, Los Angeles, Calif., a corporation of California

No Drawing. Filed July 11, 1962, Ser. No. 209,256

9 Claims. (Cl. 252-138)

This invention relates to a method for inhibiting corrosive attack upon copper alloys contacted by aerated, aqueous detergent solutions, and to a novel detergent composition.

Copper alloys such as brasses and bronzes usually display high resistance to corrosive attack by water or aerated, aqueous salt solutions. Copper alloys which are highly resistant to corrosive attack, such as admiralty brass, nevertheless have been found to be rapidly corroded when contacted by aerated, aqueous solutions of commercial detergents. The art recognizes numerous organic compounds which can be used to inhibit the corrosion of metals subject to corrosive attack by aerated, aqueous solutions. Such inhibitors have been found to be generally ineffective, or only slightly effective, for inhibiting the corrosion of copper alloys contacted by aerated, aqueous solutions of commercial detergents.

It has been determined that this condition is due to the presence of builders in certain detergent formulations, these builders being alkali-metal polyphosphate salts, commonly sodium tripolyphosphate, sodium pyrophosphate, or sodium hexametaphosphate, or mixtures thereof. Normally, in the use of detergent compositions in machinery such as found in laundries or factories, coatings of corrosion products and other insolubles form a protective layer on metal surfaces. The presence of builders in detergents, however, prevents or removes this layer and promotes corrosion of the metallic surfaces. It has been found that such corrosion can be effectively inhibited by incorporating in the aqueous medium small amounts of naphthenic acids.

It is therefore an object of this invention to provide a novel method for inhibiting the corrosion of copper alloys contacted by aerated, aqueous, detergent solutions. Another object of this invention is to provide a novel detergent composition for use in apparatus fabricated at least in part of copper alloys. Other objects of this invention will become apparent from the following description.

In general, the naphthenic acids useful in this invention are obtained from petroleum, and preferably will have an average molecular weight of not less than about 250 and an acid number not greater than about 190. Still more preferably, the naphthenic acids will have a molecular weight of about 330 to about 415 and an acid number of about 122 to about 159. Such naphthenic acids, when used in the amount of about 0.005 to 0.1 percent by weight, in aerated, aqueous solutions of commercial detergents containing polyphosphate builders are effective for inhibiting corrosion of copper alloys contacted by such solutions.

Copper alloys having normally high corrosion resistance, which are readily attacked by aqueous, aerated, polyphosphate solutions include copper-zinc alloys containing 60-90% by weight of copper, such as gilding metal, commercial bronze, red brass, spring brass, common brass, muntz metals, and admiralty brass. Copper alloys containing minor amounts of metal such as zinc, lead, tin, aluminum, and nickel such as forging brass, architectural bronze, aluminum brass, naval brass, nickel-aluminum bronze, aluminum bronze, and cupronickel are also subject to corrosive attack and can be inhibited in accord-

2

ance with this invention. The alloys protected can also contain minor amounts of manganese, beryllium or phosphorus.

It has been found that the alkali-metal polyphosphate salts responsible for accelerated corrosive attack upon normally corrosion-resistant copper alloys are the pyrophosphate, tripolyphosphate, hypophosphate, hexametaphosphate, and trimetaphosphate salts. Of these, the pyrophosphate, tripolyphosphate, and hexametaphosphate salts of sodium are especially likely to be found in commercial detergents, and result in serious corrosion problems when such detergents are employed in apparatus fabricated of copper alloys.

The effectiveness of the method of this invention for inhibiting corrosion, as well as the ineffectiveness of a wide variety of chemically similar corrosion inhibitors of the prior art, for inhibiting the corrosion of copper alloys contacted by aerated, aqueous solutions of commercial detergents has been demonstrated experimentally.

First, a water solution of a commercial detergent composition containing mixed aryl alkyl sulfonates, sodium tripolyphosphate, sodium sulfate, and other components (0.5 gram detergent per 100 milliliters of water) was prepared and divided into a plurality of flasks. Sufficient amounts of various inhibitors were added to each flask to produce an inhibitor concentration of 0.1 gram per 100 milliliters of solution. Finally, two brass strips (1/2 inch by 3 inches) were immersed in the solutions in each flask, and air was bubbled through the solutions at a rate of 20-30 milliliters per minute for a period of 72 hours while the temperature was maintained at about 70° centigrade. Percent weight loss from the brass strips for each test are given in the following table.

Table I

Inhibitor:	Percent weight loss
Blank	1.60
Naphthenic acid No. 1	0.27
Naphthenic acid No. 2	0.045
Naphthenic acid No. 3	0.02
Phthalic anhydride	0.90
Tall oil fatty acid	0.68
Linoleic acid	0.73
Triethylene tetramine	1.59
Linseed oil fatty acid	0.73
Rosin acid	1.32
Pine oil	1.78
Lithium ricinoleate	0.95

The three naphthenic acids employed in the experiments reported in this specification are characterized as set forth in Table II.

Table II

Naphthenic acid	Mol. wt.	Acid number (mg. KOH/gram)	IBP (° F.) at 2 mm. Hg
Number 1	297	178	315
Number 2	330	159	287
Number 3	415	122	408

A further series of experiments was performed to establish that the effective agents causing the corrosion of normally corrosion-resistant copper alloys were polyphosphate builders usually employed in commercial detergents. These further experiments also establish that naphthenic acids when employed in the method of this invention are effective for inhibiting corrosion induced by the presence of polyphosphates in aerated aqueous solutions. The results of the experiments are set forth in Table III.

Table III

Detergent components	Component, wt. percent	Detergent, wt. percent	Inhibitor	Inhibitor, wt. percent	Percent wt. loss
DBSS ¹	100	0.5	-----	-----	-0.25
DBSS.....	40	0.5	-----	-----	-0.11
Sodium sulfate.....	60	-----	-----	-----	-----
DBSS.....	40	0.5	-----	-----	0.07
Sodium sulfate.....	40	-----	-----	-----	-----
Trisodium phosphate.....	40	-----	-----	-----	-----
DBSS.....	40	0.5	-----	-----	1.04
Sodium sulfate.....	20	-----	-----	-----	-----
Sodium pyrophosphate.....	40	-----	-----	-----	-----
DBSS.....	40	0.5	Naphthenic acid No. 1.	0.2	0.41
Sodium sulfate.....	40	-----	-----	-----	-----
Sodium pyrophosphate.....	40	-----	-----	-----	-----
DBSS.....	40	0.5	-----	-----	1.33
Sodium sulfate.....	20	-----	-----	-----	-----
Sodium tripolyphosphate.....	40	-----	-----	-----	-----
DBSS.....	40	0.5	Naphthenic acid No. 1.	0.2	0.28
Sodium sulfate.....	20	-----	-----	-----	-----
Sodium tripolyphosphate.....	40	-----	-----	-----	-----
Sodium pyrophosphate.....	100	0.5	-----	-----	1.75
Do.....	100	0.5	Naphthenic acid No. 1.	0.2	0.52
Sodium tripolyphosphate.....	100	0.5	-----	-----	1.64
Do.....	100	0.5	Naphthenic acid No. 1.	0.2	0.34

¹ Dodecylbenzene sodium sulfonate.

It will be noted that the naphthenic acids were not as effective in inhibiting corrosive attack upon copper alloys induced by the synthetic detergent compositions of Table III. This is believed to be because of the abnormally high concentration of polyphosphates in the compositions of Table III. In these experiments, the same procedure as described with reference to Table I were employed.

While the invention has been described with reference to commercial detergent solutions based upon alkaryl sodium sulfonates and including polyphosphate builders, the method of this invention is useful in inhibiting corrosion produced by and detergent composition which includes polyphosphate builders.

This invention also contemplates and includes detergent compositions per se which employ polyphosphate builders and which include a small but effective amount of naphthenic acids to inhibit corrosion of copper alloys which would otherwise occur when the detergent is placed in aqueous solution and contacts structures fabricated of copper alloys. Thus, the detergent compositions of this invention will include any of a wide variety of cationic, nonionic, or anionic detergents which include a minor but effective amount of polyphosphate builders, and a small amount of naphthenic acid inhibitor. Especially preferred compositions are detergents based upon alkaryl sodium sulfonates, and including minor amounts, usually in the range of about 5-20%, of polyphosphate builders such as the alkali-metal pyrophosphate, tripolyphosphate, hexametaphosphate, trimetaphosphate, and hypophosphate salts. Preferably, the builders will be the sodium salts such as sodium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate. A preferred detergent base is dodecylbenzene sodium sulfonate. The detergent composition will contain about 1-20% by weight, and preferably about 5% by weight, based upon the total weight of the detergent composition, of the aforedefined naphthenic acids.

A specific example of a detergent composition in accordance with this invention is as follows:

	Percent
Dodecylbenzene sodium sulfonate	75
Sodium sulfate	10
Sodium pyrophosphate	5
Sodium tripolyphosphate	5
Naphthenic acid No. 1	5

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of inhibiting the corrosion of copper-containing metals in contact with aqueous, aerated solutions of alkali-metal polyphosphate salts consisting essentially of adding to the solutions naphthenic acids characterized as having a molecular weight of at least about 297 and an

acid number not greater than about 178, said naphthenic acids comprising about 0.005 to 0.1% by weight of said solutions.

2. The method in accordance with claim 1 in which said alkali-metal polyphosphate salts are selected from the group consisting of sodium pyrophosphate, sodium tripolyphosphate, and sodium hexametaphosphate.

3. The method in accordance with claim 2 in which said solution is a detergent solution containing alkaryl sodium sulfonates.

4. The method in accordance with claim 3 in which said sulfonate is dodecylbenzene sodium sulfonate.

5. The method in accordance with claim 4 in which said naphthenic acids are characterized by an average molecular weight of about 330 to about 415, and an acid number of about 122 to 159.

6. A detergent composition consisting essentially of an alkaryl sodium sulfonate, effective amounts of alkali-metal polyphosphate builders to prevent the formation of insoluble soaps by metathesis in the solutions in which said composition is used and about 1-20% by weight of said composition of naphthenic acids characterized as having a molecular weight of at least about 297 and an acid number not greater than about 178.

7. The composition in accordance with claim 6 in which said alkali metal phosphate salts are selected from the group consisting of sodium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, and mixtures thereof.

8. A composition in accordance with claim 7 in which said sulfonate is dodecylbenzene sodium sulfonate.

9. The composition in accordance with claim 8 in which said naphthenic acids are characterized by an average molecular weight of about 330 to about 415, and an acid number of about 122 to 159.

References Cited by the Examiner

UNITED STATES PATENTS

2,068,979	1/1937	Fisher	252-389 XR
2,197,832	4/1940	Reiff	252-389
2,618,604	11/1952	Schaeffer	252-389
2,634,237	4/1953	Kopf	252-389 XR
2,861,954	11/1958	Ruff et al.	252-138 XR
2,903,431	9/1959	Ruff et al.	252-137 XR
2,954,347	9/1960	John et al.	252-138 XR
3,015,629	1/1962	Truitt	252-389 XR

OTHER REFERENCES

"NACE Technical Committee Reports," (publication 55-3), National Association of Corrosion Engineers (vol. 11, pp. 65 and 67).

JULIUS GREENWALD, *Primary Examiner*.

J. T. FEDIGAN, *Assistant Examiner*.