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[54] SYNERGISTIC COMBINATION FOR INHIBITING THE ATTACK OF ALKALINE SOLUTIONS ON ALKALI SENSITIVE SUBSTRATES

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[58] **Field of Search** 21/2.7; 134/2; 252/DIG. 11, 252/DIG. 10, 396, 389, 392, 156

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[57] **ABSTRACT**

Materials which are sensitive to the attack of alkaline solutions are protected by a synergistic combination of: (1) at least one metal ion selected from the group consisting of barium, calcium and strontium with (2) at least one surface-active agent selected from the group consisting of (A) alkyl glycosides having a formula corresponding to ROG_mH, wherein G is a glycosyl radical, R is an alkyl radical of six to 16 carbons connected to the number 1 carbon atom of glycosyl radical through the oxygen and m is an integer in the range of 1 to about 4, (B) ethylene oxide adducts of said alkyl glycosides containing up to two ethylene oxide units per glycosyl radical and (C) amino carboxylic acids having an alkyl radical of at least 10 carbons and metal salts of amino carboxylic acids in alkaline solutions used for cleaning. Optionally in certain applications, and essentially in other applications, a third element may be made a part of the synergistic combination, namely (3) a water soluble naphthalene derivative.

14 Claims, No Drawings

SYNERGISTIC COMBINATION FOR INHIBITING THE ATTACK OF ALKALINE SOLUTIONS ON ALKALI SENSITIVE SUBSTRATES

This invention relates to the protection of alkaline sensitive substrates from the attack of alkaline solutions. More particularly, this invention relates to the protection of alkaline sensitive substrates such as aluminum, zinc, tin, lead, alloys thereof and siliceous compositions from the attack of alkaline solutions by a synergistic combination of either (a) certain metal ions with particular surface-active agents included in the solutions, or (b) the same combination as in (a) supplemented by the inclusion of a water soluble naphthalene derivative.

Caustic and other alkaline solutions are highly corrosive to many surfaces, causing extreme pitting and dissolution of the surface of sensitive materials. This phenomenon presents serious limitations to fabricating equipment and fabricating procedures utilizing alkaline materials. Corrosion of surfaces by alkaline materials presents another serious limitation with respect to cleaning of such surfaces. For example, highly alkaline solutions have proved very effective for removing such soils as baked on food soils, oleoresinous films, fatty soils, oxidized hydrocarbons, waxy soils, carbonaceous soils and the like which are difficult to remove without using caustic or other highly alkaline solutions. The sensitivity of materials to alkaline attack presents problems in a wide spectrum of applications including the metal working industry, cleaning equipment in food processing installations, maintenance cleaning of transportation vehicles, dish washing and paint stripping operations.

Current methods for cleaning alkali sensitive materials have generally avoided the use of caustic or strong alkaline solutions in cleaning processes because of the disadvantages noted above. Solvents or emulsions have found limited use as cleaners; but, are generally not effective for many soils; do not produce surfaces suitable for subsequent finishing operations and present problems of toxicity and flammability. A great deal of research has been directed to the development of neutral or mildly alkaline solutions which offer detergent action. However, this detergent action is usually based on surfactants alone or in combination with sodium borate, which have proved ineffective for the more tenaciously held soils and are practical only for light duty cleaning operations.

Sodium silicate containing alkaline cleaners have probably been the most widely accepted materials for cleaning alkaline sensitive substrates such as aluminum; but, suffer from several limitations of which the most serious is the restriction on alkalinity. Inhibition of alkaline solution attack by sodium silicates appears to be effective only when the ratio of SiO_2/Na_2O is greater than one. The inhibiting effect occurs only at certain concentrations of sodium metasilicate when the ratio is equal to one. Therefore, the high alkalinity necessary for the removal of many soils cannot be used without attack of the substrate because ratios less than one are ineffective. Silicate containing cleaners also present rinsing problems by leaving deposits which cannot be removed except for drastic treatments such as hydrofluoric acid rinses. Furthermore, to achieve adequate cleaning, it has been found necessary to utilize long soaking periods or mechanical action to accomplish release of the soil.

Additives which have been tested and found unsatisfactory for inhibiting alkaline attack on sensitive substrates include glucose, guar gum, calcium lignosulfonate, chromates, naphthalene derivatives such as dihydroxynaphthalene, hydroxynaphthoic acid, and naphthoquinone.

Substrates which are particularly sensitive to attack or corrosion by alkaline solutions may be grouped in two classes. The first class consists of metals which form soluble reaction products with strongly alkaline solutions and include aluminum, zinc, lead, and tin as the more important examples. Aluminum is probably the most important metal of this group due to its extensive use in a wide variety of applications and the very rapid attack of alkaline solutions thereon. Alloys and other compositions containing major amounts of one or a mixture of these metals are also susceptible to alkaline attack and

included within this group. The second class of materials sensitive to alkaline solutions include those having silica as a major constituent. Examples of this group are glass, porcelain and over-glazes which form soluble silicate ions upon exposure to caustic solutions leading to dissolution of the surface.

It is an object of the present invention to clean alkaline sensitive materials with alkaline detergents without deleterious corrosion.

It is a further object of the present invention to inhibit the attack of very strong alkaline cleaners on aluminum, zinc, tin, lead, and siliceous surfaces to remove tenacious soils and coatings without damage to the substrate.

It is a further object of the present invention to permit the use of aluminum and zinc in applications where such metals could not previously be used because of the necessity for strong alkaline cleaning.

It is a further object of the present invention to provide a means for controlling the rate of the caustic attack on aluminum during etching and chemical milling operations.

We have discovered that the attack of strong alkaline solutions, particularly those containing caustic, on alkaline sensitive metals and siliceous compositions is substantially reduced by the synergistic combination of certain surfactants and specific metal cations, (and optionally, a water soluble naphthalene derivative). We have discovered that at least one metal ion selected from the group consisting of calcium, strontium and barium in combination with a surface-active agent selected from the group consisting of alkyl glycosides, ethylene oxide adducts of alkyl glycosides, and amphoteric surface-active agents containing one or more amine groups, one or more carboxyl groups and a hydrocarbon chain of at least 10 carbons substantially reduce the attack of caustic and other alkaline cleaners and sensitive metals.

The metal ion or a mixture of metal ions utilized in practicing the present invention may be supplied in the form of water soluble salts such as oxides, hydroxides, acetates or sulfates of the respective metal. The optimum concentration of the metal ion will vary with the concentration of the caustic, and the particular surfactant and cation employed, but generally molar concentrations on the order of 0.001 to 0.05 will be necessary to provide significant corrosion inhibiting action.

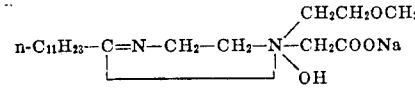
Only certain surfactants demonstrate the synergistic inhibition with the above metal cations to control the attack of alkaline solutions on sensitive metals and siliceous compositions.

One group of surface-active agents suitable for practicing the present invention include alkyl glycosides represented by the formula ROG_mH wherein G is a glycosyl radical, R is an alkyl radical of six to 16 carbons connected to the number 1 carbon atom of a glycosyl radical through an oxygen atom. The exact value of *m* varies between 1 and 10, the compound comprising a mixture of *m* values, the average of which will be less than 5. The alkyl radical may be straight or branched chain having six to 16 carbon atoms.

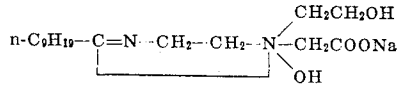
Examples of alkyl glycosides useful in practicing the present invention are hexyl glucoside, octyl glucoside, decyl glucoside, tetradecyl glucoside, hexadecyl glucoside and mixtures such as hexyl and octyl glucosides.

The present invention also contemplates using mixtures of alkyl glycosides such as octyl glucoside and octyl oligosaccharide.

A further embodiment of the present invention is the use of an amphoteric suitable for practicing the present invention and includes those containing one or two amine groups, one or two carboxylic acid groups, and having a carbon chain of at least 10 carbon atoms. Examples of these compounds include $t\text{-}C_{12}H_{25}NHCH_2CH(OH)CH_2CH_2COOH$; $n\text{-}C_{12}H_{25}NHCH_2CH_2COOH$; $t\text{-}C_{12}H_{25}NHCH_2CH_2COOH$; $t\text{-}C_{18}H_{37}NHCH_2CH_2COOH$; $n\text{-}C_{12}H_{25}N(CH_2CH_2COOH)_2$;



and



It is also contemplated that the amphoteric surfactant may be mixed with other surfactants such as one or more of the glycosides described hereinabove.

In practicing the present invention, the concentration of the surfactant in the alkaline solution is considered critical, for the synergistic effect of combining the surfactant and the alkaline earth metal ion is significant only when concentrations on the order of at least 0.03 weight percent are used.

It is well known that corrosion resistance of aluminum is affected by the thickness, degree of crystallinity and degree of hydration in oxide coatings thereon and that the resistance may be further modified by treatments with water, steam, solutions of electrolytes, electrolysis, and the like. The synergistic combination of the present invention provides a further inhibition of the attack of alkaline solutions upon oxide coated and pretreated aluminum surfaces.

The synergistic combination of the present invention may be utilized with solvents and/or other surface-active agents. It is frequently advantageous to include solvents in the alkaline solution to improve the cleaning action on certain dirts and some examples of suitable solvents are kerosene and the monobutyl ether of ethylene glycol.

The following examples are presented to demonstrate the several embodiments of the present invention and are not intended as limitations thereon. The values reported in mils per year were determined from weight loss of samples occurring during immersion in the respective solutions. In Examples I to IX, inclusive, all the samples of aluminum used were of the same roll of aluminum foil and its oxide coating had uniform thickness and chemical characteristics; this material was arbitrarily tagged as "Aluminum Foil No. 1." In Examples X–XII other samples of aluminum were used, they being arbitrarily tagged "Aluminum Foil Nos. 2 to 5," respectively.

EXAMPLE I

Samples of "Reynolds Wrap" aluminum foil having a purity of about 99.0 percent were weighed and immersed in sodium hydroxide solutions at 60° C. Table I reports the results of a test conducted with solutions of increasing alkalinity. This test demonstrates the synergistic effect of combinations of the present invention by first showing the drastic attack on aluminum caused by caustic, then showing the relatively little improvement caused by one or the other of the additives used in our invention, and finally showing how when both additives are present a tremendous improvement in resistance to attack on aluminum by caustic takes place.

TABLE I

Corrosion rate on aluminum in mils per year

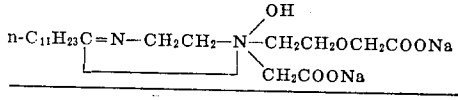
Percent NaOH	No additive	With 0.005 molar concentration of Ca^{++} (.028 wt. percent CaO	With 0.5 wt. percent n-octyl glucoside	With 0.005 molar Ca^{++} and 0.5 wt. percent n-octyl glucoside
0.5	36,000	21,000	6,500	<5
2.0	70,000	...	...	550
4.0	130,000	30,000	58,000	1,700

EXAMPLE II

Samples of Reynolds Wrap aluminum foil were weighed and immersed in an 0.5 percent sodium hydroxide solution at 60° C. modified as indicated in Table II. This sample demonstrates the various surfactants are far better inhibitors with the calcium ion than without. The first column shows that with just the surfactant present there is little or no corrosion inhibition. The second column shows that with the combination of the surfactant and the calcium ion a very marked improvement in corrosion inhibition takes place.

TABLE II

Rate of corrosion of aluminum by 0.5% NaOH solution in mils per year

Surfactant	0.5% surfactant	0.5% surfactant plus 0.005M Ca^{++}
None	36,000	21,000
n-$C_{8-10}H_{17-21}$ glucoside	6,500	<5
n-$C_{16}H_{33}$ glucoside	37,000	10
n-$C_{12}H_{25}$ oligosaccharide	39,000	20
n-$C_{12}H_{24}NHCH_2CH_2COOH$	34,000	13
	38,000	10

EXAMPLE III

A series of tests demonstrating the suitability of aminocarboxylic acids having an alkyl chain of at least 10 carbon atoms in practicing the present invention, and their desirability over similar compounds, was conducted by exposing samples of aluminum foil to 0.5 percent solutions of NaOH containing 0.028 weight percent CaO and 0.5 weight percent of various surfactants as indicated in Table III. The amphoteric surfactants of the present invention were utilized in test numbers 1 to 7, while the surfactants of tests 8–15 are included for comparison and test 16 was conducted without any surfactant. As can be seen, when the said amphoteric surfactants were employed a satisfactory resistance to corrosive attack took place, whereas when the other surfactants were employed the corrosive attack was excessive beyond normally acceptable limits.

TABLE III

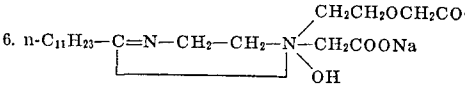
Surfactant composition	Corrosion
1. t-$C_{12}H_{25}NHCH_2CH(OH)CH_2CH_2COOH$	870
2. n-$C_{12}H_{25}NHCH_2CH_2COOH$	13
3. t-$C_{12}H_{25}NHCH_2CH_2COOH$	66
4. t-$C_{18-21}NHCH_2CH_2COOH$	6
5. n-$C_{12}H_{25}N(CH_2CH_2COOH)_2$	6
6. 	10

TABLE III—Continued

Surfactant composition	Corrosion [1]
7. n-C_9H_{19}-C(=N-CH_2-CH_2-N(CH_2CH_2OH)(CH_2COONa))-OH	800
8. NH_2CH_2COOH (glycine)	15,000
9. NH_2—$CH(CH_3)COOH$ (B-alanine)	15,000
10. $(CH_3)_2CHCH_2CH_2CH(NH_2)COOH$	23,000
11. n-$C_6H_{13}NHCH_2COOH$	3,300
12. n-$C_6H_{13}NHCH_2CH_2COOH$	18,000
13. t-$C_{12}H_{25}NH(CH_2CH_2O)_{15}SO_3Na$	11,000
14. n-C_7H_{15}-C(=N-CH_2-CH_2-N($CH_2CH_2OCH_2COONa$)(CH_2COONa))-OH	5,900
15. n-$C_{11}H_{23}$-C(=N-CH_2-CH_2-N(CH_2CH_2OH)($CH_2CH(OH)CH_2SO_3Na$))-OH	4,300
16. No surfactant	21,000

[1] Of Aluminum by 0.5% NaOH solution at 60° C. in mils per year.

EXAMPLE IV

A series of tests demonstrating the composition limits of alkyl glycosides was conducted by exposing samples of aluminum foil to solutions of 0.5 percent NaOH, 0.028 weight percent CaO and the various surfactants as indicated in Table IV, below. Tests 1 to 10 utilize surface-active agents of the present invention while tests 11 to 14 were run for comparative purposes. As will be noted, when the surfactants of the present invention were used a satisfactory resistance to corrosion took place, whereas with the other surfactants the corrosive attack was excessive beyond normally acceptable limits.

TABLE IV-A

Surfactant Composition *	Corrosion of Aluminum by 0.5% NaOH Solution at 60°C. in mils per year
1. n C_8H_{13} glucoside	830
2. n C_8H_{17} glucoside	<5
3. n $C_{10}H_{21}$ glucoside	<5
4. n $C_{14}H_{29}$ glucoside	<5
5. n $C_{16}H_{33}$ glucoside	10
6. n $C_{8-10}H_{17-21}$ oligosaccharide	700
7. n $C_{12}H_{25}$ oligosaccharide	20
8. n $C_{8-10}H_{17-21}$ glucosides + $C_{8-10}H_{17-21}$ oligosaccharides	<5
9. n C_8H_{17} glucoside adduct with 1 ethoxy unit	<5
10. n C_8H_{17} glucoside adduct with 2 ethoxy units	510
11. n C_4H_9 glucoside	17,000
12. n $C_{18}H_{37}$ oligosaccharide	1,700
13. n $C_{18}H_{37}$ glucoside + $C_{18}H_{37}$ oligosaccharide	6,300
14. glucose	4,200

*0.5 weight percent

TABLE IV-B

For further comparison, test nos. 1–18 in this table were run using other additives in lieu of the surfactant composition of the present invention as shown in Table IV-A. It will be seen that comparatively speaking, none of those additives provided satisfactory resistance to corrosive attack by alkali.

Additive	Mils per year
1. Gluconic acid	33,000
2. Nitrilo triacetic acid	53,000
3. Ethylene diamine tetracetic acid	61,000
4. Sodium lignosulfonate	4,300
5. Sorbitan monolaurate	33,000
6. Sorbitan monooleate	2,200
7. Sucrose monomyristate	17,000
8. Sucrose mono (hydrogenated tallow)	20,000
9. Sodium linear dodecyl benzene sulfonate	4,000
10. $nC_{15}H_{31}COOH$	32,000
11. Branched $C_8H_{17}C_6H_4O(CH_2CH_2O)_{12-15}H$	18,000
12. n-$C_{12}H_{25}O(CH_2CH_2O)_{10}CH_2CH_2COOH$	9,700
13. n-$C_{12}H_{25}O(CH_2CH_2O)_3SO_3Na$	19,000
14. Branched $C_9H_{19}C_6H_4O(CH_2CH_2O)_{10}$ phosphate	3,100
15. Ortho phenol phenol	18,000
16. Sorbitol	25,000
17. Mannitol	19,000
18. Sucrose	2,700

EXAMPLE V

The tests reported in Table V were conducted to demonstrate the effectiveness of calcium, strontium, and barium cations in practicing the present invention. Tests 1–3 are according to the present invention and the remaining tests are for comparative purposes only. These data indicate that of the many cations available, only calcium, strontium and barium are effective in accomplishing the synergistic results of the present invention.

TABLE V

Cation	Corrosion rate in mils per year on aluminum at 60° C. 0.5% NaOH, 0.5% A,* 0.005M cation	4.0% NaOH, 0.5% A,* 0.005M cation	0.1% NaOH, 0.1% A,* 0.001M cation
1. Calcium	<5	1,700	20
2. Strontium	940	860	
3. Barium	140	2,100	
4. None	6,500	58,000	8,700
5. Lithium	6,900		
6. Cesium	6,800		
7. Beryllium		51,000	8,300
8. Magnesium	11,000	79,000	9,000
9. Cerium	15,000		
10. Titanium	10,000		
11. Zirconium	16,000		
12. Chromium (ic)	27,000		
13. Iron (ic)	12,000		
14. Cobalt (ous)	9,100		
15. Copper (ic)	9,200		
16. Zinc	3,200	50,000	3,200
17. Cadmium	6,000	70,000	
18. Mercury (ic)		50,000	
19. Tin (ous)	20,000		

* A=n—$C_{8-10}H_{17-21}$ glucoside.

EXAMPLE VI

Tests were conducted on the substrates indentified in Table VI to demonstrate the improvements in corrosion resistance obtained by means of the present invention for materials other than aluminum. The samples were exposed to a 0.5% NaOH solution at 60° C. with corrosion values recorded as mils per year.

TABLE VI

Substrate	Corrosion rate in mils per year or aluminum in 0.5% NaOH at 60° C.			
	No additive	Plus surfactant [1]	Plus Ca^{++} [2]	Plus surfactant [1] and Ca^{++} [2]
Porcelain [3]	20	12	1.4	0.08
Window glass	4.3	...	...	0.41
Zinc [4]	60	40	...	<1
Tin	14	...	...	1.0
Lead	18	...	...	6.9

[1] Surfactant=0.5% n-C_{8-10} H_{17-21} glucoside.
[2] 0.005 M.
[3] Porcelain Enamel Steel Panel, Alkali Resistant Blue Ground Coat, Frit Nos. 1078/1081/1082 25/30/45, Chicago Vitreous Corp.
[4] Zinc Alloy-Zamak No. 3; 96/4/0.5 Zn/Al/Mg.

EXAMPLE VII

The tests reported in Table VII demonstrate the applicability of the present invention to various alkaline solutions other than NaOH and were conducted according to the procedure of Example 1.

TABLE VII

Alkali	Conc.	0.5% surf.	.005 molar concentration cation	Corrosion rate in mils per year of aluminum at 60° C.			
				No additive	With cation	With surf.	With surf. and cation
NaOH	0.5	A	Ca	36,000	21,000	6,500	<5
KOH	0.5	A	Ca	36,000	...	...	5
Na_2CO_3	0.5	B	Ca	6,700	6,200	8,000	<5
Sodium orthosilicate	0.5	A	Ba	13,000	...	10,000	<5

NOTE.—A=n-$C_{8-10}H_{17-21}$ glucoside. B=n-$C_{12}H_{25}N(CH_2CH_2COOH)_2$.

EXAMPLE VIII

Samples of aluminum foil were exposed at 60° C. to sodium hydroxide solutions of various degrees of alkalinity with different concentrations of the metal cation and surfactant to demonstrate the effectiveness of the present invention. In Tables VIII to XI, Surfactant A is a n-$C_{3-10}H_{17-21}$ glucoside and Surfactant B is n-$C_{12}H_{25}N(CH_2CH_2COOH)_2$. Table VIII illustrates the effect of various concentrations of the cation and surfactant on mild alkaline solutions.

TABLE VIII

% NaOH	Molar concentration and Cation	Weight % of Surfactant A	Corrosion Rate in mils per year
0.1	—	—	19,000
0.1	0.001 Ca	0.1 A	20
0.1	0.005 Ca	0.5 B	<5

Table IX reports the effect of increasing concentrations of the cation showing that a minimum amount is required under certain use conditions.

TABLE IX

% NaOH	Molar Concentration and Cation	Weight % of Surfactant A	Corrosion Rate in mils per year
0.5	—	—	36,000
0.5	—	0.1	36,000
0.5	0.0001 Ca	0.1	16,000
0.5	0.001 Ca	0.1	610
0.5	0.005 Ca	0.1	25

Table X illustrates the effects of increasing surfactant concentration showing that a minimum amount is required under certain use conditions.

TABLE X

% NaOH	Molar Concentration and Cation	Weight % of Surfactant A	Corrosion Rate in mils per year
0.5	0.005 Ca	—	21,000
0.5	0.005 Ca	0.01	18,000
0.5	0.005 Ca	0.03	5,000
0.5	0.005 Ca	0.1	25
0.5	0.01 Ca	1.0	7
0.5	0.05 Ca	5.0	69

Table XI illustrates that the present invention is effective even with relatively high concentrations of caustic in inhibiting its corrosive action on aluminum.

TABLE XI

% NaOH	Molar Concentration and Cation	Weight % of Surfactant A	Corrosion Rate in mils per year
4.0	—	—	130,000
4.0	0.005 Sr	—	98,000
4.0	0.005 Sr	0.1	900
4.0	0.05 Sr	0.1	1,900
10.0	—	—	223,000
10.0	0.005 Sr	0.5	1,800
10.0	0.005 Ca	0.5	67,000

EXAMPLE IX

Samples of Alclad Alloy 2024 and 3003 panels and sheets of aluminum foil (Reynolds Wrap) were divided into three corresponding groups. Mineral oil, triolein, milk, oleomargarine, and flour paste were used to soil each group of samples with each material applied to one sample in each group. The soiled samples were then oven dried at 180° to 200° C. and cleaned by immersion in a stirred solution containing 0.5 weight percent NaOH, 0.028 weight per cent CaO and 0.5 weight percent n-$C_{8-10}H_{17-21}$ glucoside at 60° C. for one-half hour. The soil was effectively removed from all samples during immersion and no significant corrosion of the samples occurred.

In Examples I–IX it was clearly demonstrated that the two-component synergistic combination of the present invention (the metal ion and the surfactant) performed uniquely and very satisfactorily. However, it was determined that on aluminum obtained from other sources, such as are represented by Aluminum Foil Nos. 2–5, inclusive, the same satisfactory corrosion inhibition did not take place with three of the specimens. To solve this problem we discovered that by the addition of a third component to the synergistic combination we obtained the same satisfactory level of performance, said third component being a water-soluble naphthalene derivative in the amount of 0.01 to 5.0 weight percent (based upon the final, total bath weight). Examples X–XII show this effect very clearly.

EXAMPLE X

In this example the two-component synergistic combination of this invention was used to compare the corrosion inhibition effect on the five different sources or specimens of aluminum foil. As will be seen from Table XII below, whereas the two-component composition performed well with Aluminum Foil Nos. 1 and 4, it performed poorly with Aluminum Foil Nos. 2, 3, and 5. The corrosive composition, containing the inhibitor, consisted of an aqueous solution of 0.5% NaOH and 0.055% $CaCl_2$ at 60° C.

TABLE XII

Aluminum Foil Sample[1]	Corrosion rate in mils per year	
	0.5% Surf. A[2]	0.1% Surf. A[2]
1	<5	25
2	290	—
3	550	>350
4	<5	60
5	>350	—

[1]Various lots from three suppliers; all found by atomic adsorption analysis to be about 99 percent aluminum with 0.4–0.9% Fe, 0.02–0.1% Cu, 0.01–0.03% Zn, and 0.01–0.03% Mn with traces of Si, Mg, and B.

[2]n-alkyl glucoside with 8–10 C alkyl group.

EXAMPLE XI

In Table XIII, which follows, using Aluminum Foil No. 3 (which caused the worst performance in Table XII above), it is demonstrated that only the three-component synergistic composition will work satisfactorily. Any combination of two of the three components will not perform satisfactorily. The data also show the minimum amounts of the composition necessary to obtain good performance. The corrosive composition used was an aqueous solution of 0.5% NaOH at 60°C.

TABLE XIII

Test No.	% Surfactant A	% Ca	% Ethyl Methyl Naphthalene Sulfonate	Corrosion Rate in mils per year
1	—	—	—	42,000
2	0.1	0.011	—	550
3	—	—	0.1	>350
4	—	0.011	0.1	>350
5	0.1	—	0.1	>350
6	0.1	0.011	0.01	200
7	0.1	0.011	.05	<5
8	0.1	0.011	.1	<5
9	0.1	0.011	5.0	<5

EXAMPLE XII

In Table XIV, which follows, the performance of various "third additives" are compared with the water-soluble naphthalene derivative to determine their relative effectiveness in the three-component synergistic composition. As will be seen, additives Nos. 2–7 of this invention performed well, whereas additives Nos. 8–18 performed poorly. The corrosive composition used was an aqueous solution of 0.5% NaOH with Surfactant A (of Table XII), $CaCl_2$, plus 0.1 percent of the third additive, at 60° C.

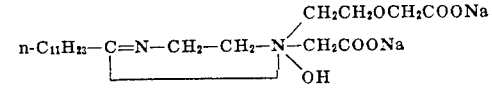
TABLE XIV[1]

Test No.	Additive	0.1% A, 0.011% $CaCl_2$	0.5% A, 0.055% $CaCl_2$
1	None	>350	>350
2	3 hydroxy 2 naphthoic acid	<5	<5
3	2,3 dihydroxy naphthalene		<5
4	Na isopropyl naphthalene sulfonates	<5	
5	Na dimethyl naphthalene sulfonate	<5	
6	Na methyl ethyl naphthalene sulfonate	<5	
7	Na methyl propyl naphthalene sulfonate	<5	
8	Naphthalene	>350	
9	Na xylene sulfonate	>350	
10	Na dodecyl benzene sulfonate		250
11	Na lignosulfonate	>350	
12	Na 2 mercapto benzothiazole		300
13	Octyl phenol		>350
14	Phthalic acid		>350
15	Citric acid		>350
16	Malic acid		>350
17	Glycolic acid		>350
18	Hydroxy propyl sorbitol		>350

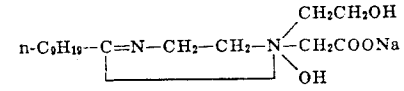
[1] >350 mils per year corresponds to disintegration of foil within 16-hour test period.

We claim

1. In a process of treating with an aqueous strong alkaline solution comprising 0.1 to 10 weight percent alkali, a material having a principal component selected from the group consisting of aluminum, zinc, tin, lead, alloys thereof, oxides of silicon and compounds containing oxides of silicon, the improvement of mixing with said aqueous solution a synergistic corrosion inhibitor combination comprising at least two components, (A) and (B), of which (A) is at least one metal ion selected from the group consisting of barium, calcium and strontium in a molar concentration of about 0.001 to about 0.5 and (B) is at least one surface active agent selected from the group consisting of alkyl oligosaccharides and a mixture of alkyl glucosides and alkyl oligosaccharides having a formula corresponding to ROG_mH, wherein G is a glycosyl radical, R is an alkyl radical of six to 18 carbons connected to the number one atom of the glycosyl radical and *m* is an integer from 1 to about 4, ethylene oxide adducts of said alkyl glucosides and oligosaccharides containing up to two ethoxy units per glycosyl unit, amino-carboxylic acids having an alkyl radical of at least 10 carbons, and being a compound selected from the group consisting of $t\text{-}C_{12}H_{25}NHCH_2\text{-}CH(OH)CH_2CH_2COOH$; $n\text{-}C_{12}H_{25}NHCH_2CH_2COOH$; $t\text{-}C_{12}H_{25}NHCH_2CH_2COOH$; $t\text{-}C_{18}H_{37}NHCH_2CH_2COOH$; $n\text{-}C_{12}H_{25}N(CH_2CH_2COOH)_2$;



and



and metal salts of said amino-carboxylic acids, in a concentration of about 0.01 to about 5 weight percent.

2. The improvement of claim 1 wherein said alkyl group of the glycosyl radical has 8 to 10 carbons.

3. The improvement of claim 1 wherein the alkyl glucosides and alkyl oligosaccharides contain one ethoxy unit per glycosyl unit.

4. The improvement of claim 1 wherein the alkyl glucosides and alkyl oligosaccharides contain two ethoxy units per glycosyl unit.

5. The improvement of claim 1 wherein said component is an oxide of silicon.

6. The improvement of claim 1 wherein (A) is a mixture of calcium and strontium ions.

7. The improvement of claim 1 wherein the synergistic corrosion inhibitor combination additionally is comprised of a third component, (C), which is a water-soluble naphthalene adduct.

8. The improvement of claim 7 wherein (C) is present in the amount of from 0.01 to 5.0 weight percent.

9. The improvement of claim 7 wherein (C) is ethyl methyl naphthalene sulfonate.

10. The improvement of claim 7 wherein (C) is 3 hydroxy 2 naphthoic acid.

11. The improvement of claim 7 wherein (C) is 2, 3 dihydroxy napthalene.

12. The improvement of claim 7 wherein (C) is the sodium salt of isopropyl naphthalene sulfonate.

13. The improvement of claim 7 wherein (C) is the sodium salt of dimethyl naphthalene sulfonate.

14. The improvement of claim 7 wherein (C) is the sodium salt of methyl propyl naphthalene sulfonate.

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