United States Patent Office

3,303,104

Patented Feb. 7, 1967

3,303,104

COMPOSITIONS CONTAINING DISCOLORATION INHIBITORS

Fred K. Rubin, Bronx, N.Y., assignor to Lever Brothers Company, New York, N.Y., a corporation of Maine

No Drawing. Filed Dec. 12, 1963, Ser. No. 329,958

18 Claims. (Cl. 252—99)

This invention relates to inhibitors suitable for retarding the discoloration of hard surfaces and more particularly, to synthetic detergent formulations suitable for dishwashing purposes and containing discoloration inhibitors.

Detergent compositions containing chlorinating compounds are now widely used for many cleansing applications. It has been observed that metallic surfaces such as gold, silver and platinum and non-metallic surfaces including chinaware, glass, porcelain and plastic surfaces such as are found inside automatic dishwashing machines become discolored when contacted with detergent formulations containing chlorinating agents in the presence of manganese ion (Mn^{++}) and particularly at elevated temperatures. Since the water of most communities contains manganese ion in concentrations high enough to cause discoloration of hard surfaces, it is apparent that a serious problem exists in this regard.

It is an object of this invention to prevent or diminish discoloration of hard surfaces caused by contact with halogenating agents in the presence of manganese ion.

Another object is to prevent the discoloration of metallic and non-metallic hard surfaces caused by contact with aqueous detergent compositions containing halogenating agents in the presence of manganese ion.

Still another object of this invention is to prepare dishwashing compositions suitable for washing dinner-ware decorated with a precious metal without discoloration of the metal.

An additional object is the preparation of compositions which may be added to aqueous detergent solutions containing halogenating agents to inhibit the discoloration of hard surfaces which come in contact with the detergent solution in the presence of manganese ion.

These and other objects and advantages are attained in accordance with the present invention by providing compositions containing discoloration inhibitors selected from the group consisting of (1) compounds furnishing gluconate ion in aqueous solution and certain combinations thereof with (2) cerium compounds or (3) certain inorganic persalts. These compositions prevent the discoloration of hard surfaces which would normally occur in the presence of halogenating agents and manganese ion.

The materials which inhibit the discoloration of hard surfaces when the latter are exposed to halogenating agents in aqueous solutions containing manganese ion are those which produce gluconate ion in aqueous solutions as well as compositions containing these compounds and other ingredients. The gluconate compounds which are employed in this invention are those materials which supply gluconate ion in aqueous solution. Examples of gluconate salts which can be used are alkali metal gluconates such as sodium and potassium, ammonium gluconate, gluconic acid, alpha-sodium glucoheptonate dihydrate, glucono-delta-lacetone, etc.

Those compounds which furnish cerium ion in aqueous solutions can be utilized in combination with compounds furnishing gluconate ion to prevent or inhibit discoloration of hard surfaces. Any cerium compound which fulfills the aforementioned requirement can be used. Examples of these compounds include cerium nitrate, cerium sulfate, cerium halides such as cerium chloride, etc.

It is preferred to use combinations of the gluconate and cerium inhibitors rather than the gluconate alone. It has been found that combinations of these materials are particularly effective in preventing discoloration. As pointed out more particularly in the following examples, combinations of, for example, cerium nitrate and sodium gluconate are considerably more effective as discoloration inhibitors than either of these compounds alone.

Furthermore, it has been discovered that combinations of gluconate salts such as sodium gluconate with water-soluble inorganic perborates and dipersulfates such as the alkali metal and ammonium salts thereof are also efficacious in preventing or retarding the discoloration of hard surfaces under the conditions described above. Examples of these inorganic materials include sodium perborate and ammonium dipersulfate [$(NH_4)_2S_2O_8$].

The proportions of discoloration inhibitor which can be employed in this invention depend upon a number of variables and can best be determined by those skilled in the art. Thus, the solubility of the inhibitor in aqueous solution is one factor and the level of manganese ion in the aqueous solution is still another factor in determining the requisite proportion of inhibitor to be employed. The amount of discoloration inhibitor which should be added to a composition is the amount which is sufficient to give the desired inhibition when the composition is used in its normal way such as for a dishwashing formulation.

It has been pointed out above that discoloration of hard surfaces occurs in the presence of manganese ion and only when certain halogenating compounds are present. The following halogenating compounds have been found to induce discoloration: sodium and potassium dichloroisocyanurate, dichloroisocyanuric acid, trichloroisocyanuric acid, dichlorodimethylhydantoin, N,N-dichloro-p-toluene-sulfonamide, sodium chlorite and chlorine. These compounds cause discoloration when used alone and when incorporated into detergent compositions. Elemental bromine has also been found to cause discoloration of hard surfaces. The aforementioned materials have the following common characteristics: they are all non-alkaline, inorganic and organic halogenating agents which discolor hard surfaces in the presence of manganese ion. In the absence of manganese ion or when these halogenating materials are removed from the aqueous solution it is observed that no discoloration occurs.

Alkaline-reacting chlorinating compounds such as hypochlorites, e.g., calcium and sodium hypochlorite, and chlorinated trisodium phosphate do not induce discoloration when added to aqueous solutions containing manganese ion unless condensed inorganic polyphosphates such as sodium tripolyphosphate are also present. These condensed polyphosphates do not discolor hard surfaces in the absence of halogenated agents even though manganese ion is present in the solution. Although highly alkaline detergent formulations will not ordinarily cause dis-

coloration even when halogenating materials are present, this does not hold true if the compositions contain condensed phosphates. In the latter case, it has been found necessary to add discoloration inhibitors.

The inhibitors of the invention can be admixed with the aforementioned halogenating agents and this combination added to aqueous solutions containing manganese ion to prevent discoloration of hard surfaces coming in contact with the solutions. Alternatively, the inhibitors can be utilized in various detergent formulations. Thus, the inhibitors are particularly useful when added to conventional synthetic detergent compositions of the type which contain one or more condensed polyphosphates as builders and one or more synthetic anionic and nonionic detergents.

As another alternative the inhibitor either alone or in admixture with an inert filler such as sodium sulfate may be packaged separately and introduced into the aqueous detergent solution prior to use thereof. Since local water conditions determine the extent of discoloration, this embodiment offers a more practical solution to the problem.

Examples of detergents which may be present in formulations in which the inhibitors of the invention are compatible include alkyl aryl sulfonates, alkyl aromatic sulfonic acids, esters of sulfuric acids with aliphatic alcohols of about 10–18 carbon atoms, sulfonated fatty oils, sulfated and sulfonated alkoxy derivatives and sulfuric acid esters of monoglycerides and glyceryl monoethers. The salts of these materials are ordinarily employed.

The inhibitors are also useful with nonionic detergents such as for example: alkylolamides of fatty acids, ethoxylated alcohols and thioalcohols, the nonionic detergents known as "Pluronics" which are polyoxypropylene polymers containing varying amounts of ethylene oxide present as polyoxyethylene chains, etc.

The detergent compositions can also contain builders, fillers, soil-suspending agents and other conventional detergent ingredients. The compositions may also be prepared by conventional methods, such as by blending the ingredients in aqueous solution or slurry and then spray-drying the mixture at elevated temperatures.

It is to be understood, however, that the invention is not concerned with the preparation of detergent compositions and that the particular detergent formulations to which the inhibitors of the invention can be added are not critical. Some surfactants may be subject to attack by the halogen-releasing agents when the compositions are stored. However, those skilled in the art can readily ascertain by simple trial whether the detergent and the halogenating agent are compatible.

In the following examples a test procedure has been developed to facilitate the study of discoloration inhibitors. To accelerate discoloration, the manganese ion concentration employed in these tests is considerably higher than the concentrations normally present in the water used by the housewife. The concentrations of detergent and chlorinating agents correspond to those normally used in conventional commercial formulas.

In the test procedure the sample to be tested was weighed into a marked 250 ml. Pyrex beaker, a platinum strip approximately 15 mm. x 15 mm. x 0.003 inch was suspended therein and about 200 ml. of water containing manganese ion preheated to 145° F. was added. The beaker containing the test solution and the platinum strip was then put into a water bath maintained at a temperaure of about 143° F. After vigorous initial stirring to dissolve the sample, the test solution was agitated at frequent intervals. Several samples and a control were tested simultaneously and test solutions and platinum strips were observed closely for discoloration and other changes. Fifteen minutes after the addition of the water containing manganese ion, the platinum strips were removed from the solutions and examined. The strips were compared and graded against a control and were reintroduced into the solutions for an additional fifteen minute period. After a total exposure period of about thirty minutes, the platinum strips were again removed from the solution and examined, compared and graded. In certain cases, this procedure was varied to extend the total exposure period of the strips to more than thirty minutes.

Example I

The following dishwashing formulation of a conventional type was employed in the test described above:

	Percent
Sodium tripolyphosphate (containing some tetrapotassium pyrophosphate)	45.0
Sodium metasilicate (1:1 ratio of Na_2O to SiO_2)	26.0
Dense soda ash	14.0
Sodium bicarbonate	6.5
Sodium alkyldiphenyloxide sulfonate (85% active)	0.6
Chlorinating agent [1] to yield 0.9%–1% available chlorine, basis total formula wt.	----
Sodium sulfate balance to 100.0.	

[1] The following agents were employed: potassium dichlorocyanurate, dischloroisocyanuric acid, dichlorodimethylhydantoin, sodium chlorite, chlorine gas bubbled into solution, N,N-dicholoro-p-toluenesulfonamide, sodium dichlorocyanurate and trichloroisocyanuric acid.

The test solution consisted of 200 ml. of water containing 5 p.p.m. of Mn^{++} (143°–145° F.) and a sufficient amount of the above detergent to form a 0.25% solution. The results are tabulated below:

Percent Sodium Gluconate in solution	Exposure of Platinum Strip	
	15 mins.	30 mins.
None	Heavy discoloration	Heavy discoloration.
0.0125–0.0250	Noticeable reduction of discoloration.	Do.
0.0375	No discoloration	Slight to moderately heavy discoloration
0.050	do	Very slight discoloration.
0.075	do	No discoloration.

The following table shows the results when lower levels of Mn^{++} are used:

Mn^{++} Concentration, p.p.m.	Sodium Gluconate Concentration, percent	Exposure of Pt-Strip	
		15 mins.	30 mins.
5	0.050	No discoloration	Very slight discoloration.
2.5	0.025	Slight trace of discoloration.	Slight discoloration.
1	0.010	No discoloration	Very slight to slight discoloration.
1	0.005	do	Slight discoloration.

As a general guide to determining the requisite amount of gluconate to be used, it has been found that about 0.5–30% sodium gluconate based on the formula weight of the above composition was effective in retarding platinum discoloration.

When the detergent active in the above formula was replaced by sodium lauryl sulfate and lauryl hydroxyether sulfonate, the inhibiting effect of sodium gluconate remained unchanged.

Example II

Combinations of cerium nitrate and sodium gluconate were considerably more effective as inhibitors than either of these components used alone. Thus, while 0.1% cerium nitrate was ineffective as an inhibitor and 5% sodium gluconate was only moderately effective, a combination of both agents at the stated concentrations prevented discoloration completely during a 15-minute contact. The behavior of combinations of these ingredients under the test conditions described in Example I is set forth in the following table.

Percent inhibitor (basis dry formula wt.)	Plat. discoloration after contact period of—	
	15 mins.	30 mins.
0.1 $Ce(NO_3)_3 \cdot 6H_2O$	Moderate/heavy	Heavy.
0.2 $Ce(NO_3)_3 \cdot 6H_2O$	Moderate	Do.
0.5 $Ce(NO_3)_3 \cdot 6H_2O$	Slight/moderate	Do.
1.0 $Ce(NO_3)_3 \cdot 6H_2O$	Slight	Slight/moderate.
2.0 $Ce(NO_3)_3 \cdot 6H_2O$	Practically none	Slight.[1]
5.0 Sodium Gluconate	Moderate/heavy	Heavy.
10.0 Sodium Gluconate	Very slight	Moderate/heavy.
15.0 Sodium Gluconate	None	Slight.[2]
20.0 Sodium Gluconate	do	Practically none.[2]

[1] No appreciable increase in discoloration after 1.5 hr. contact period.
[2] Pronounced discoloration after 1.5 hr. contact period.

cedure described in Example I above. The results are tabulated below:

Percent inhibitor in detergent solution	Discoloration after contact period of—		
	15 mins.	30 mins.	60 mins.
None	Heavy	Heavy	
0.0250 sodium gluconate	Slight	Moderate	
0.0125 sodium gluconate	Moderate	Heavy	
0.0250 sodium gluconate	None	None	(1)
0.0125 sodium perborate			
0.0125 sodium gluconate			(1)
0.0125 sodium perborate			

[1] Does not discolor even after 1 hr. of contact.

Percent inhibitor (basis dry formula wt.)	Plat. discoloration after contact period of—	
	15 mins.	30 mins.
0.1 $Ce(NO_3)_3 \cdot 6H_2O$ + 5.0 Sodium Gluconate	Practically none	Slight.
0.1 $Ce(NO_3)_3 \cdot 6H_2O$ + 10.0 Sodium Gluconate	do	Practically none.
0.2 $Ce(NO_3)_3 \cdot 6H_2O$ + 5.0 Sodium Gluconate	Trace of discoloration on edges of platinum strip.	Slight discoloring but only on edges of platinum strip.[1]
0.2 $Ce(NO_3)_3 \cdot 6H_2O$ + 10.0 Sodium Gluconate	Practically none	Practically none.[2]

[1] No appreciable increase in discoloration after 1.5 hr. contact period.
[2] Slight discoloration after 1.5 hr. contact period.

Generally, the combination of gluconate and cerium salt can be employed within the following range based on the results obtained with water containing 5 p.p.m. manganese ion: about 0.3–10% of cerium nitrate and sodium gluconate based on the total formula weight with the respective ratios varying from about 1:2 to 1:50.

Example III

It has been observed that cerium compounds are ineffective as platinum discoloration inhibitors in the absence of pyrophosphates. The data below shows that such is not the case when a combination of a gluconate and a cerium compound is employed.

Chlorinating agent: 0.00375% potassium dichloroisocyanurate in aqueous solution.
Mn^{++} concentration: 5 p.p.m.

Percent inhibitor (basis dry formula wt.)	Plat. discoloration after contact period of—	
	15 mins.	30 mins.
None	Heavy	Heavy.
0.1 $Ce(NO_3)_3 \cdot 6H_2O$	None	Slight.
5.0 Sodium Gluconate		
0.2 $Ce(NO_3)_3 \cdot 6H_2O$	do	Practically none.
10.0 Sodium Gluconate		
10.0 Sodium tripolyphosphate (TPP) contg. approx. 10% sodium pyrophosphate.	Heavy	Heavy.
10.0 TPP contg. approx. 10% sodium pyrophosphate.	None	Practically none.
0.1 $Ce(NO_3)_3 \cdot 6H_2O$		
5.0 Sodium Gluconate		
10.0 TPP contg. approx. 10% sodium pyrophosphate.	do	Do.
0.2 $Ce(NO_3)_3 \cdot 6H_2O$		
10.0 Sodium Gluconate		

Example IV

The behavior of combinations of gluconates with sodium perborate was tested in accordance with the pro-

A range of proportions of about 0.3–10% based on the total formula weight for the combination of sodium perborate and sodium gluconate has been used with noticeable results. The respective ratios of perborate to gluconate are about 1:2 to 1:10.

Example V

It was discovered that combinations of dipersulfate salts and gluconates were only effective inhibitors when used with non-alkaline materials such as chlorinating agents alone rather than admixed with dishwasher compositions containing alkaline builders. The procedure described above for testing discoloration was varied in the case of dipersulfates by employing a test solution containing only potassium dichloroisocyanurate rather than a conventional detergent formula containing alkaline builders. The results of the tests were:

Percent inhibitor in 0.0075% solution of potassium dichloroisocyanurate	Platinum discoloration after contact period of—	
	15 mins.	30 mins.
None	Heavy	Heavy.
0.0125 sodium gluconate	Slight/moderate	Moderate.
0.0065 sodium gluconate	Moderate	Heavy.
0.0020 ammonium dipersulfate	None	None.
0.0065 sodium gluconate		
0.00375 ammonium dipersulfate	do	Do.
0.01250 sodium gluconate		

For water containing a manganese ion concentration of less than about 1 p.p.m., a combination of 0.0010% ammonium dipersulfate and 0.0025% sodium gluconate reduced the discoloration of platinum contacted with a 0.0075% aqueous solution of potassium dichlorocyanurate. This concentration of chlorinating agent is about twice the amount normally used in conventional dishwashing formulas.

Example VI

The use of inhibitors as additives to dishwashing solutions or chlorinated sterilizing or rinse solutions in the form of mixtures of inhibitor and inert diluent represents an important feature of the present invention. Typical combinations which have been prepared include the following:

(A)

	Percent
Sodium gluconate	25
Sodium sulfate	75

(B)

$Ce(NO_3)_3 \cdot 6H_2O$	0.2
Sodium gluconate	10.0
Sodium sulfate	89.8

(C)

Sodium gluconate	4.0
Sodium perborate	4.0
Sodium sulfate	92.0

(D)

Ammonium dipersulfate	0.8
Sodium gluconate	2.5
Sodium sulfate	96.7

The above combinations when added to an automatic dishwasher at the same level as regular dishwasher detergents (i.e., to yield 0.25% solutions) prevent platinum discoloration in 5 p.p.m. Mn^{++} water. Under practical conditions less concentrated mixtures are feasible.

Composition D would be effective only in the absence of alkaline materials. As explained above, dispersulfates do not inhibit discoloration when alkaline phosphates, silicates, soda ash, etc. are present. However, Composition D would be effective in retarding discoloration in situations where non-alkaline chlorinating solutions were employed to sterilize clean dishes or other surfaces which are normally subject to discoloration under the conditions discussed above.

Example VII

In another test a dishwasher product consisting of 98.9% of the detergent composition shown in Example I plus 1.0% sodium gluconate+0.1% $Ce(NO_3)_3 \cdot 6H_2O$ was employed to wash platinum trimmed dinnerware in an automatic dishwasher. After fifteen washes with this formula, the platinum trimmings showed very slight discoloring. Identical dinnerware washed the same number of times with a control containing no inhibitors discolored heavily after six washes. The glassware spotting tendencies and lipstick removal properties of the formula containing the inhibitor were practically identical to those of the control.

Another product consisting of 99% of the composition shown in Example I plus 1% sodium gluconate was employed to wash platinum trimmed dinnerware. After ten washes in the automatic dishwasher no discoloring occurred. Moderate discoloring of the platinum trimmings became noticeable after twenty-one washes. A control caused severe discoloration after only six washes.

Example VIII

A. A sterling silver knife was exposed for 1 hr. in a 0.25% solution of a chlorinated dishwasher detergent of the type described in Example I above. The solution contained 5 p.p.m. Mn^{++} ion. Within 15 minutes of exposure a yellow coating became noticeable on the knife; after 1 hour of exposure the coating had turned to a deep brownish-orange. An identical knife, exposed for one hour to a corresponding dishwasher solution to which 0.065% sodium gluconate had been added, did not discolor whatsoever.

B. A gold trimmed china plate was immersed for one hour in the dishwasher detergent solution referred to in part A. Manganese ion in 5 p.p.m. concentration was present. A heavy, bronzy discoloration formed on the gold trim and prominent brown patches became noticeable on the glazed china surface. An identical plate, immersed for one hour in a corresponding solution to which 0.065% sodium gluconate had been added, showed only a faint trace of gold discoloration and no brown patches or other discolorations on the china surface.

Example IX

The following data illustrates the effectiveness of gluconates as inhibitors of hypochlorite induced platinum discoloration. Calcium hypochlorite (Pittchlor, 70% available chlorine) and sodium hypochlorite (Clorox, 5.3% available chlorine) were used in the example which was conducted in water containing 5 p.p.m. Mn^{++}. The water temperature was about 143° F.

The calcium hypochlorite was incorporated in the following dishwasher detergent:

	Percent
Sodium tripolyphosphate	45.0
Sodium metasilicate ($Na_2O:SiO_2=1:1$)	26.0
Soda ash	14.0
Sodium bicarbonate	6.5
Sodium alkyldiphenyloxide sulfonate (85%)	0.6
Calcium hypochlorite (Pittchlor)	2.5
Sodium sulfate balance to 100.0.	

This formula contains 1.75% available chlorine.

	Platinum discoloration after exposure of—	
	15 mins.	30 mins.
0.250% [a] Calcium hypochlorite dishwasher detergent.	Slight/moderate golden discoloration.	Moderate/heavy discoloration.
0.250% Calcium hypochlorite dishwasher detergent. 0.050% Sodium gluconate	No discoloration	Practically no discoloration.

[a] Percentage figures shown pertain to percent detergent, inhibitor, etc. in the test solution.

Similar results were obtained when sodium hypochlorite was added to a solution of the following nonchlorinated formula:

	Percent
Sodium tripolyphosphate	45.0
Sodium metasilicate ($Na_2O:SiO_2=1:1$)	26.0
Soda ash	14.0
Sodium bicarbonate	6.5
Sodium alkyldiphenyloxide sulfonate (85%)	0.6
Sodium sulfate	7.9
	100.0

The addition of 0.45 ml. of sodium hypochlorite solution (Clorox) to one liter of a 0.25% solution of the above nonchlorinated formula in water containing Mn^{++} yielded 23 p.p.m. available chlorine. This chlorine level is well within the available chlorine range of conventional dishwasher detergent use solutions.

	Platinum discoloration after exposure of—	
	15 mins.	30 mins.
0.250% Nonchlorinated formula. 0.045% Clorox	Slight/moderate discoloration.	Severe discoloration.
0.250% Nonchlorinated formula. 0.045% Clorox 0.050% Sodium gluconate	No discoloration	Practically no discoloration.

Chlorine gas bubbled through a solution containing Mn^{++} (to pH 3.5) also produced severe discoloration of platinum and the presence of 0.05% sodium gluconate vastly reduced the discoloration. Furthermore, the presence of 0.05%–0.075% sodium gluconate in a Mn^{++}-containing solution prevented the discoloration of platinum induced by 0.0375% Dichloroamine T (58.5% av. Cl).

I claim:

1. A composition consisting essentially of a halogenating agent which normally discolors hard surfaces in the presence of manganese ions, said halogenating agent being selected from the group consisting of chlorinating agents and elemental bromine, and a discoloration inhibiting amount of a material selected from the group consisting of compounds furnishing gluconate ion in aqueous solution, combinations of compounds furnishing said gluconate ion with compounds furnishing cerium ion in aqueous solution and combinations of compounds furnishing said gluconate ion with a material selected from the group consisting of ammonium dipersulfate and sodium perborate, the composition being free of alkaline materials when ammonium dipersulfate is employed.

2. The composition defined in claim 1 in combination with a synthetic non-soap detergent.

3. The composition defined in claim 1 in combination with a condensed inorganic polyphosphate.

4. The composition defined in claim 1 in combination with a synthetic non-soap detergent and a condensed inorganic polyphosphate.

5. A composition according to claim 1 in which the gluconate ion furnishing compound is selected from the group consisting of alkali metal gluconates, ammonium gluconate, gluconic acid, alpha-sodium glucoheptonate dihydrate and glucono-delta-lactone.

6. A composition according to claim 1 in which the cerium compound is selected from the group consisting of cerium nitrate, cerium chloride and cerium sulfate.

7. A composition according to claim 1 in which the inhibiting material is a combination of a compound furnishing gluconate ions in aqueous solution and a cerium compound.

8. A composition according to claim 1 in which the halogenating agent is a chlorine-containing agent selected from the group consisting of potassium dichloroisocyanurate, sodium dichlorocyanurate, dichloroisocyanuric acid, trichloroisocyanuric acid, dichlorodimethylhydantoin, N, N-dichloro-p-toluenesulfonamide, sodium chlorite, chlorine, chlorinated trisodium phosphate and carcium and sodium hypochlorites.

9. A composition according to claim 1 in which the inhibitor is a combination of a compound furnishing gluconate ions in aqueous solution and sodium perborate.

10. A composition according to claim 1 in which the inhibitor is a combination of a compound furnishing gluconate ions in aqueous solution and ammonium dipersulfate.

11. A detergent formulation consisting essentially a condensed inorganic polyphosphate, a synthetic non-soap detergent, an alkaline reacting chlorinating agent which normally discolors hard surfaces in the presence of manganese ions and said polyphosphate, and a discoloration inhibiting amount of a compound selected from a group consisting of compounds furnishing gluconate ion in aqueous solution, combinations of compounds furnishing said gluconate ion with compounds furnishing cerium ion in aqueuos solution and combinations of compounds furnishing said gluconate ion with sodium perborate.

12. A detergent formulation according to claim 11 in which the synthetic detergent is selected from the group consisting of anionic and nonionic synthetic non-soap detergents.

13. A composition consisting essentially of at least one compound which furnishes gluconate ion in aqueous solution and at least one compound which furnishes cerium ion in aqueous solution, said composition being effective in retarding the discoloring of hard surfaces when added to solutions containing manganese ion and a halogenating agent which normally discolors hard surfaces in the presence of manganese ions, said halogenating agent being selected from the group consisting of chlorinating agents and elemental bromine.

14. A composition consisting essentially of a combination of at least one compound which furnishes gluconate ion in aqueous solution and at least one water-soluble salt of a material selected from the group consisting of ammonium dipersulfate and sodium perborate, said combination being effective in retarding the discoloration of hard surfaces when added to solutions containing manganese ion and a halogenating agent which normally discolors hard surfaces in the presence of manganese ions, said halogenating agent being selected from the group consisting of chlorinating agents and elemental bromine, the compositions being free of alkaline materials when ammonium dipersulfate is employed.

15. A method of inhibiting the discoloration of hard surfaces resulting from exposure of the surface to a solution containing manganese ions and a halogenating agent which normally discolors hard surfaces in the presence of manganese ions selected from the group consisting of chlorinating agents and elemental bromine which comprises adding to the solution a discoloration inhibiting amount of a material selected from the group consisting of compounds furnishing gluconate ions in aqueous solutions, combinations of compounds furnishing gluconate ions with componds furnishing cerium ions in aqueous solutions and combinations of compounds furnishing gluconate ions with a material selected from the group consisting of ammonium dipersulfate and sodium perborate, said solution being free of alkaline materials when ammonium dipersulfate is employed.

16. A method of inhibiting discoloration of a metallic surface resulting from exposure of the surface to a solution containing manganese ions and a halogenating agent which normally discolors hard surfaces in the presence of manganese ions selected from the group consisting of chlorinating agents and elemental bromine which comprises adding to the solution a discoloration inhibiting amount of a material selected from the group consisting of compounds furnishing gluconate ions in aqueous solution, combinations of compounds furnishing gluconate ions with compounds furnishing cerium ions in aqueous solution, and combinations of compounds furnishing gluconate ions with a material selected from the group consisting of ammonium dipersulfate and sodium perborate, said solution being free of alkaline materials when ammonium dipersulfate is employed.

17. A method of inhibiting the discoloration of non-metallic hard surfaces resulting from exposure of the

surfaces to a solution containing manganese ions and a halogenating agent which normally discolors hard surfaces in the presence of manganese ions selected from the group consisting of chlorinating agents and elemental bromine which comprises adding to the solution a discoloration inhibiting amount of a material selected from the group consisting of compounds furnishing gluconate ions in aqueous solution, combinations of compounds furnishing cerium ions in aqueous solution, and combinations of compounds furnishing gluconate ions with a material selected from the group consisting of ammonium dipersulfate and sodium perborate, said solution being free of alkaline materials when ammonium dipersulfate is employed.

18. A composition effective in retarding the discoloration of hard surfaces exposed to solutions containing manganese ions and halogenating agents selected from the group consisting of chlorinating agents and elemental bromide which normally discolor hard surfaces in the presence of manganese ions, said composition consisting essentially of an inert filler and a compound selected from the group consisting of compounds furnishing gluconate ion in aqueous solution, combinations of said gluconate with compounds furnishing cerium ion in aqueous solution and combinations of said gluconates with a water-soluble salt of a material selected from the group consisting of ammonium dipersulfate and sodium perborate, the composition being free of alkaline materials when ammonium dipersulfate is employed.

References Cited by the Examiner

UNITED STATES PATENTS

2,689,225	9/1954	Anderson et al. -- 252—135 XR
3,049,495	8/1962	Jenkins et al. ---- 252—186 XR
3,112,274	11/1963	Morgenthaler et al. ---- 252—99

OTHER REFERENCES

Gregory: "Use and Applications of Chemicals and Related Materials," Reinhold Pub. Co., N.Y., vol. 1 (1939), page 163 relied on.

Prescott et al.: "Gluconic Acid and Its Derivatives," Ind. & Eng. Chem., vol. 45, No. 2, February 1953, pp. 338–342.

LEON D. ROSDOL, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

M. WEINBLATT, *Assistant Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,303,104 February 7, 1967

Fred K. Rubin

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, footnote 1, line 2 thereof, for "dischloro-isocyanuric" read -- dichloroisocyanuric --; column 9, line 59, for "carcium" read -- calcium --; line 68, after essentially" insert -- of --; column 11, line 9, after "furnishing" insert -- gluconate ions with compounds furnishing --.

Signed and sealed this 10th day of October 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents