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[54] CLEANING COMPOSITIONS

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[63] Continuation of Ser. No. 41,550, May 28, 1970, abandoned.

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[58] **Field of Search** 252/95, 99, 187; 423/118

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[57] ABSTRACT

A composition capable of inhibiting overglaze attack containing as essential ingredients an aluminum compound selected from the group consisting of aluminum silicate and aluminum chlorhydroxide, and at least one boron compound selected from the group consisting of boric acid, and boron trioxide, wherein the weight ratio of the aluminum compound to the boron compound is within the range from about 0.025 to about 1.

15 Claims, No Drawings

CLEANING COMPOSITIONS

This is a continuation, of application Ser. No. 41,550 filed May 28, 1970, now abandoned.

The present invention relates in general to cleaning compositions and in particular to the provision of cleaning compositions beneficially adapted for use in connection with the cleaning of substrates such as dishwear and the like having a glazed surface.

Many of the cleaning compositions heretofore recommended for use in connection with the cleaning of substrates having a glazed surface have been subject to one or more significant disadvantages. Perhaps the paramount difficulty involved relates to the pronounced tendency of such compositions to attack or otherwise deleteriously affect substrates such as typified by glass, porcelain and the like, thereby leading to impairment of such articles. As will be recognized, aesthetic considerations rather than purely functional criteria are often of overriding importance as regards the suitability of a given cleaning composition and especially when contemplated for use in connection with the cleaning of fine china and the like having an ornamental or decorative surface. The magnitude of the problems encountered can be readily appreciated in view of the significant risk of economic loss entailed. Without intending to be bound by any theory it has nevertheless been hypothesized in explanation of the overglaze attack phenomenon that one or more of the ingredients present in the cleaning composition exhibit a pronounced if not intolerable tendency to attack the flux constituents present in the bonding material utilized in securing the decorative or ornamental pattern to the substrate and especially under the relatively severe alkaline conditions necessary extant in the cleaning solution during actual use.

In an effort to overcome or otherwise ameliorate the foregoing and related difficulties, considerable industrial activity has centered around the research and development of cleaning compositions specifically and advantageously adapted to minimize the overglaze attack problem and yet capable of providing the requisite measure of cleaning activity. Thus, much of the methodology heretofore promulgated involves as an essential expedient the use of one or more additives which purportedly function as inhibitors under the conditions normally encountered in cleaning; thus, the particular cleaning vehicle or composition may be adapted, for example, for use in industrial bottle washing, automatic dishwashing operations and the like. In this regard, a variety of such inhibitor additives has been recommended by the prior art such as aluminum formate, aluminum acetate, alkali metal aluminum orthophosphates, and alkali aluminate, zincate or berylliate. Although providing relatively effective means whereby to enable substantial alleviation of the overglaze attack problem, the overall advantage realized is often marginal in view of concomitant problems having as their genesis the objectionable tendency of the cleaning composition and more particularly, the inhibitor compound, to yield unsightly deposits or precipitates on the surface of the substrate treated, not to mention the contacting surfaces of the washing receptacle. As will be recognized, the fugitive behavior of the inhibitor material may be such as to substantially vitiate any advantage which might otherwise accrue from its use thereby detracting from commercial feasibility.

The insurmountable nature of the foregiong problem is made manifestly clear by reference to the fact that the residue problem is seemingly exacerbated as the relative concentration of the inhibitor in the cleaning composition is increased and particularly when increased to values acknowledged as being mandatory for purposes of achieving truly optimum effects. Thus, it has been ascertained that those quantities of inhibitor invariably found to be necessary for effective negotiation of the overglaze attack problem correspond to those quantities found to be particularly offensive as regards precipitate formation.

The remedial techniques heretofore provided and specifically devised to overcome the aforementioned difficulties and based on the use of emulsifying agents, suspending agents and the like prove largely ineffective by virtue of adverse effects upon overall cleaning composition functionality.

In accordance with the discovery forming the basis of the present invention, it has been ascertained that problems associated with the formation of insoluble precipitates may be successfully negotiated according to relatively simple means without adversely affecting the efficacy of cleaning compositions of diverse types by utilizing a combination of a boron compound selected from the group consisting of boron oxide and boron trioxide, and an aluminum compound selected from aluminum silicate and aluminum chlorhydroxide as the inhibitors of overglaze attack.

Thus, a primary object of the present invention resides in the provision of compositions advantageously adapted for use in connection with the cleaning of glazed substrates wherein the foregiong and related disadvantages are eliminated or at least mitigated to a substantial extent.

Another object of the present invention resides in the provision of cleaning compositions substantially devoid of any tendency to attack the glazed surface of the wide variety of substrates.

A further object of the present invention resides in the provision of cleaning compositions wherein problems associated with precipitate formation during actual cleaning are virtually eliminated whereby to yield a surface having an aesthetically pleasing appearance.

Yet another object of the present invention resides in the provision of cleaning compositions capable of providing superior cleaning activity, e.g., bleaching, washing, etc.

Other objects and advantages of the present invention will become more apparent hereinafter as the description proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which, in its broader aspects, includes the provision of cleaning compositions capable of inhibiting overglaze attack containing as essential ingredients an aluminum compound selected from the group consisting of aluminum silicate and aluminum chlorhydroxide and at least one boron compound selected from the group consisting of boric acid and boron trioxide and wherein the weight ratio of the aluminum compound to the boron compound is within the range of from about 0.025 to about 1.

The aluminum compounds contemplated for use in the practice of the present invention and capable of inhibiting overglaze attack are selected from the group consisting of aluminum silicate and aluminum chlorhydroxide. It has been found that this particular combination of aluminum compound and boron compound affords superior protection against overglaze attack without the concomitant precipitate problem evident with the use of other aluminum compounds heretofore utilized as overglaze attack inhibitors. It should be emphasized at this particular juncture that the specific chemical nature of the aluminum compound is of secondary importance, the salient requirement imposed being that such compound be characterized in exhibiting a substantial capacity to inhibit or otherwise suppress overglaze attack under the conditions contemplated for use. It will be further understood that the aluminum compounds may be employed in admixtures, the advisability of so proceeding depending primarily upon the requirements of the processor. This particular embodiment offers the singular advantage that the beneficial properties characterizing each of the compounds may be combined and thus exploited in a single application. Nothing critical resides, of course, in the relative proportions of the components comprising the aluminum inhibitor mixture. Implicit in the foregoing is, of course, that the aluminum compound be substantially devoid of any tendency to adversely affect or otherwise impair the essential functional characteristics of the parent composition.

The aluminum silicate contemplated for use in the practice of the present invention and capable of inhibiting overglaze attack is a known material. All aluminum silicates irregardless of the method of preparation, function as an effective overglaze protector in an alkaline dishwashing medium. A specific illustrative example comprises the addition of aluminum sulfate to a soluble silicate at about 140°F. The precipitated aluminum silicate has the composition $Al_2O_3 \cdot 7.8\ SiO_2$ and contains 15.6 percent free moisture, 0.83 percent sulfate, and a very small amount of sodium; it has a pH of 7.0, and a density of the packed composition of 0.4g/cc and a density of 0.23g/cc of the loose composition (not tamped). Aluminum silicates having a pH in the range of 5–9 can also be prepared in accordance with the aforedefined procedure by adding a small amount of sodium aluminate to the aluminum sulfate and sodium silicate reaction mixture to obtain an aluminum silicate of the desired pH. Accordingly, it is apparent that conditions of reaction and reactants can be varied to obtain aluminum silicate having specific physical attributes, such as pH, density, degree of hydration, etc.

The aluminum chlorhydroxide preferred in the practice of the present invention and capable of inhibiting overglaze attack is a slightly off-white powder believed to have the formula, $Al_2(OH)_5Cl \cdot 2H_2O$ where the atomic ratio of Al to Cl is 2:1. Its aluminum content as Al_2O_3 is about 47 percent and a 15 percent solution of the solid has a pH of about 4.2. Aluminum chlorhydroxide is soluble in water in all proportions and forms stable solutions in normally used concentrations (up to about 50 percent). Concentrations above 50 percent became extremely viscous and difficult to handle. Solutions thereof exhibit no significant change in pH even after prolonged periods of standing (2 years) with the pH varying within the range of about 4.0 to about 4.5.

A further critical component of the compositions described herein is, of course, the boron compound and more specifically, boric acid, boron trioxide as well as mixtures comprising two or more thereof. As in the case with the aluminum compound, the particular proportions of the various boron compound employed in forming any admixture is nowise a critical factor in the practice of the present invention, the objectives of the formulator comprising the paramount consideration in this regard. Each of the aforedescribed boron compound is found to provide significant advantage when utilized in general with the aluminum inhibitor defined above as evidenced by the substantial if not complete elimination of problems associated with precipitate formation. It has additionally been determined that boron trioxide is particularly beneficial in providing manifold advantage i.e., cleaning compositions prepared therewith display exceptional tolerance to moisture, remain free-flowing over protracted time intervals despite subjecting to relatively severe conditions of temperature and humidity while exhibiting no appreciable tendency to cake or harden on standing in packaged form.

One of the particularly salutary advantages of the present invention evolves from the fact that the use of the boron compounds specified enables significant reduction in the concentration of aluminum compound inhibitor which would otherwise be required to achieve an equivalent measure of overglaze protection while providing concomitant alleviation of the residual precipitate problem. Thus, as will be made manifestly clear in the examples which follow, for equivalent modes of proceeding, manifold reductions in aluminum compound concentration are permitted without in any way detracting from the overglaze protection efficacy of the composition.

As previously mentioned, it is recommended in the practice of the present invention that the relative proportions of aluminum and boron compounds be confined within certain predetermined ranges in order to assure effective negotiation of both the overglaze attack as well as precipitate problems. More particularly, investigation indicates that the weight ratio of aluminum to boron compounds should be maintained within a range from about 0.025 to about 1 with a range of 0.05 to 1 being particularly preferred. Again, it will be recognized that extra-ordinary or unusual requirements may well dictate departures from the aforesaid parameters and will prove highly beneficial. The quantity of aluminum and boron inhibitor selected for use in the composition will be dependent upon the intended use concentration of the product formulated. Thus, the combined quantities of aluminum and boron compound will range from small amounts i.e., on the order of about 5 percent by weight of total cleaning composition up to amounts on the order of about 20 percent; the upper limiting concentration value is significant primarily from an economic standpoint. In addition to the aluminum and boron compounds, further embodiments of the present invention contemplate the preparation of automatic dishwasher compositions containing ingredients customarily employed in the manufacture thereof.

Water soluble organic detergents i.e., surface active components may be employed, such materials being well known in the prior art, the term detergent comprehending species of the anionic, cationic, amphoteric and zwitterionic types.

Thus, suitable anionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and an anionic solubilizing group. Typical examples os anionic solubilizing groups are sulfonate, sulfate, carboxylate, phosphonate and phosphate. Examples of suitable anionic detergents which fall within the scope of the invention include the soaps, such as the water-soluble salts of higher fatty acids or resin acids, such as may be derived from fats, oils, and waxes of animal, vegetable or marine origin, e.g., the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulfated and sulfonated synthetic detergents, particularly those having about 8 to 26, and preferably about 12 to 22 carbon atoms to the molecule.

As examples of suitable synthetic anionic detergents there may be cited the higher alkyl mononuclear aromatic sulfonates such as the higher alkyl benzene sulfonates containing from 10 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g., the sodium salts of decyl, undecyl, dodecyl, (lauryl), tridecyl, tetradecyl, pentadecyl, or hexdecyl benzene sulfonate and the higher alkyl toluene, xylene and phenol sulfonates, alkyl naphthalene sulfonate, ammonium diamyl naphthalene sulfonate, and sodium dinonyl naphthalene sulfonates.

Other anionic detergents are the olefin sulfonates, including long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkenesulfonates and hydroxyalkanosulfonates. These olefin sulfonate detergents may be prepared, in known manner, by the reaction of SO_3 with long chain olefins, (of 8–25, preferably 12–21 carbon atoms) of the formula $RCH{=}CHR_1$, where R is alkyl and R_1 is alkyl or hydrogen, to produce a mixture of sultones and alkenesulfonic acids, which mixture is then treated to convert the sultones to sulfonates. Examples of other sulfate or sulfonate detergents are paraffin sulfonates, such as the reaction products of alpha olefins and bisulfites (e.g., sodium bisulfite), e.g., primary paraffin sulfonates of about 10–20, preferably about 15–20, carbon atoms; sulfates of higher alcohols; salts of α-sulfofatty esters (e.g., of about 10–20 carbon atoms, such as methyl α-sulfomyristate or α-sulfotallowate).

Examples of sulfates of higher alcohols are sodium lauryl sulfate, sodium tallow alcohol sulfate. Turkey Red Oil or other sulfated oils, or sulfates of mono- or diglycerides of fatty acids (e.g. stearic monoglyceride monosulfate), alkyl poly (ethenoxy) ether sulfates such as the sulfates of the condensation products of ethylene oxide and lauryl alcohol (usually having 1 to 5 ethenoxy groups per molecule); lauryl or other higher alkyl glyceryl ethersulfonates; aromatic poly (ethenoxy) other sulfates such as the sulfates of the condensation products of ethylene oxide and nonyl phenol (usually having 1 to 20 oxyethylene groups per molecule preferably 2–12).

The suitable anionic detergents include also the acyl sarcosinates (e.g. sodium lauroylsarcosinate) the acyl esters (e.g. oleic acid ester) or isothionates, and the acyl N-methyl taurides (e.g. potassium N-methyl lauroyl- or oleyl tauride).

The most highly preferred water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di- and triethanolamine), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of the higher alkyl benzene sulfonates, olefin sulfonates, and higher alkyl sulfates, and the higher fatty acid monoglyceride sulfates. The particular salt will be suitably selected depending upon the particular formulation and the proportions therein.

Nonionic surface active agents include those surface active or detergent compounds which contain an organic hydrophobic group and a hydrophilic group which is a reaction product of a solubilizing group such as carboxylate, hydroxyl, amido or amino with ethylene oxide or with the polyhydration product thereof, polyethylene glycol.

As examples of nonionic surface active agents which may be used there may be noted the condensation products of alkyl phenols with ethylene oxide, e.g., the reaction product of isooctyl phenol with about 6 to 30 ethylene oxide units; condensation products of alkyl thiophenols with 10 to 15 ethylene oxide units; condensation products of higher fatty alcohols of monoesters of hexahydric alcohols and inner ethers thereof such as sorbitan monolaurate, sorbitol mono-oleate and mannitan monopalmitate, and the condensation products of polypropylene glycol with ethylene oxide.

Cationic surface active agents may also be employed. Such agents are those surface active detergent compounds which contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

As examples of suitable synthetic cationic detergents there may be noted the diamines such as those of the type $RNC_2H_4NH_2$ wherein R is an alkyl group of about 12 to 22 carbon atoms such as N-2-aminoethyl stearyl amine and N-2-aminoethyl myristyl amino; amido-linked amines such as those of the type $R^1CONHC_2H_4NH_2$ wherein R is an alkyl group of about 9 to 20 carbon atoms, such as N-2-amino ethyl-stearyl amide and N-amino ethyl myristyl amide; quaternary ammonium compounds wherein typically one of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including such 1 to 3 carbon alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate, methosulfate, etc. Typical quaternary ammonium detergents are ethyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, benzyl-dimethyl-stearyl ammonium bromide, trimethyl stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethylethyl dilauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulfates and acetates.

Examples of specific amphoteric detergents are N-alkyl-beta-aminopropionic acid; N-alkyl-beta-iminodipropionic acid, and N-alkyl, N,N-dimethyl glycine; the alkyl group may be, for examples, that derived from coco fatty alcohol, lauryl alcohol, myristyl alcohol, (or a lauryl-myristyl mixture), hydrogenated tallow alcohol, cetyl, stearyl, or blends of such alcohols. The substituted aminopropionic and iminodipropionic acids are often supplied in the sodium or other salt forms, which may likewise be used in the practice of this invention. Examples of other amphoteric detergents are the betaines containing a sulfonic group instead of the carboxylic group; betaines in which the long chain substituent is joined to the carboxylic group without an intervening nitrogen atom, e.g., inner salts of 2-trimethylamino fatty acids such as 2-trimethylaminolauric acid, and compounds of any of the previously mentioned types but in which the nitrogen atom is replaced by phosphorus.

The detergent material is employed in concentrations ranging from about 0.5 percent to about 5 percent by weight of total composition with a range of 1 to 3 percent being particularly preferred.

Thus, a relatively minor amount of nonionic type detergent, that is, about 2–4 percent is especially beneficial inasmuch as it acts as a foam depressant as well as a detersive agent in an automatic dishwashing solution.

Various other materials may be included in the compositions described herein; thus, water soluble builder salts comprise particularly preferred addenda; included in this group are the inorganic and organic; basic and neutral water soluble salts. The builder salt is employed in amounts ranging up to about 95 percent, i.e., 40–95 percent by weight with a range of from about 70 percent to about 90 percent by weight of the composition being preferred. Suitable builders include without necessary limitation,

Trisodium phosphate
Tetrasodium pyrophosphate
Sodium acid pyrophosphate
Sodium tripolyphosphate hexahydrate
Sodium monobasic phosphate
Sodium dibasic phosphate
Sodium hexameta phosphate
Sodium silicates, SiO_2/Na_2O of 1/1 to 3.2/1
Sodium carbonate
Sodium sulfate
Borax etc.

Other organic builders include salts of organic acids and, in particular, the water soluble salts of aminopolycarboxylic acids. The alkali metal salts such as sodium potassium and lithium; ammonium and substituted ammonium salts such as methylammonium, diethanolammonium and triethanolammonium; and amine salts such as mono, di- and triethanolamine methylamine, octylamino diethylenetriamine, triethylenetetramine and ethylenediamine are efficacious. The acid portion of the salt can be derived from acids such as nitroldiacetic; N-(2-hydroxyethyl) nitrilodiacetic acid, nitrilotriacetic acid (NTA), ethylenediamine tetracetic acid, (EDTA); N-(2-hydroxyethyl) ethylene diamine triacetic acid; 2-hydroxyethyl iminodiacetic acid; 1,2-diaminocyclohexanediacetic acid; diethylenetriamine penta-acetic acid and the like. The builder salt is preferably employed in amounts sufficient to yield a pH in water of from 9.5 to 12 preferably from 10 to 11. Particularly preferred compositions contain for example from about 55 to about 75 percent sodium tripolyphosphate hexahydrate and about 15 to about 25 percent sodium metasilicate as alkaline builders.

The cleaning compositions described herein may further be provided with one or more bleaching agents which may in general be defined as encompassing compounds capable of liberating hypochlorite chlorine and/or hypobromite bromine on contact with aqueous media. Particular examples of bleaching agents include the dry, particulate heterocyclic N-bromo and N-chloro imides such as trichloro-cyanuric, tribromocyanuric acid, dibromo, and dichlorocyanuric acid, the salts thereof with water-solubilizing cations such as potassium and sodium. Such bleaching agents may be employed in admixtures comprising two or more, a particularly efficacious bleaching agent in this regard comprising the material commercially available from the Monsanto Chemical Company under the trade name designation "ACI–66," ACL signifying "available chlorine" and the numerical designation "66," indicating the parts per pound of available chlorine. This particular product comprises a mixture of potassium dichloro-isocyanurate (4 parts) and trichloroisocyanuric acids (one part).

Other N-bromo and N-chloro imides may also be used, such as N-brominated and N-chlorinated succinimide, malonimide phthalimide and naphthalimide. Other compounds include the hydantoins, such as 1,3-dibromo and 1,3-dichloro-5,5-dimethylhydantoin; N-monochloro-5,5-dimethylhydantoin, methylene-bis (N-bromo-5,5-dimethylhydantoin); 1,3-dibromo and 1,3-dichloro 5-isobutylhydantoin; 1,3-dichloro 5, methyl-5-ethylhydantoin; 1,3-dibromo and 1,3-dichloro 5,5-diisobutyl-hydantoin; 1,3-dibromo and 1,3-dichloro 5-methyl-5-n-amylhydantoin, and the like. Other useful hypohalite-liberating agents comprise tribromomelamine and trichloromelamine. Dry, particulate, water soluble anhydrous inorganic salts are likewise suitable for use such as lithium hypochlorite and hypobromite. The hypohalite-liberating agent may, if desired, be provided in the form of a stable, solid complex or hydrate, such as sodium p-toluene-sulfo-bromamine-trihydrate, sodium benzene-sulfo-chloramine-dihydrate, calcium hypobromite tetrahydrate, calcium hypochlorite tetrahydrate, etc. Brominated and chlorinated trisodium phosphate formed by the reaction of the corresponding sodium hypohalite solution with trisodium phosphate (and water as necessary) likewise comprise efficacious materials. The present invention contemplates as an additional embodiment the use of bleaching agents capable of liberating hypochlorite as well as hypobromite such as, for example, the N-brominated, N′-chlorinated heterocyclic imides, as for example the N-bromo, N′-chloro-cyanuric acids and salts thereof, e.g., N-monobromo-N, N-dichloro-cyanuric acid, N-monbromo-N-monochlorocyanuric acid, sodium-N-monobromo-N-monochloro-cyanurate, potassium-N-monobromo-N-monochloro-cyanurate; and the N-brominated, N-chlorinated hydantoins, e.g., N-bromo-N-chloro-5,5-dimethylhydantoin and N-bromo-N-chloro-5-ethyl-5-methyl hydantoin.

The hypohalite-liberating compound is employed in an amount of from 0.5 to 5 percent by weight of the composition, and preferably in an amount of from about 0.5 percent to 3 percent by weight thereof. In any event, the hypohalide material should preferably be employed in amounts sufficient to yield from about 0.5–3 percent available chlorine, bromine etc. in order to assure optimum results.

In general, efficacious cleaning compositions may be formulated in accordance with the present invention by the use of the aluminum-boron compound system in amounts of about 5 to 20 percent by weight of total composition and up to about 90 percent, i.e., from 40 to 90 percent by weight of at least one compound selected from the group of water-soluble, organic detergent, water soluble neutral of alkaline builder salt, bleaching agent capable of liberating hypohalite on contact with aqueous media and caustic alkali.

Minor amounts of other additives which do not interfere with the cleaning and overglaze protection properties of instant composition may be added such as pigments, dyes, perfumes, etc. In some instances, it may be commercially feasible to add such ingredients to make them more attractive to the consumer.

The bleaching ingredient is essential to the implementation of those embodiments of the present invention directed to industrial bottle cleaning compositions. In such instances, the following examples are given for purposes of illustration only and are not to be considered as necessarily constituting a limitation on the present invention. All parts and percentages given are by weight unless otherwise indicated. For purposes of ascertaining the capacity of the various compositions exemplified to ameliorate overglaze attack on fine china samples, the method of the Chemical Specialties Manufacturers Association (CSMA) is employed, such method being described in detail in "Soap and Chemical Specialties," 33, (9), 60, 1957. Such test is designed as an accelerated dishwasher exposure method; thus, the comparative removal of overglaze decoration provides direct means for affording an evaluation of the corrosiveness of dishwashing detergent solutions. According to such method, samples of standard plates (Greenwood pattern) Onondaga Pottery Co., Syracuse, New York) are immersed in deionized or distilled water maintained at a temperature of 211° F. and containing the indicated percent concentration of detergent for periods of 2, 4 and 6 hours. The test samples are thereafter removed, hand-rubbed with cloth and compared with the untreated samples of the same standard plate. The treated samples are visually scrutinized to determine the extent of overglaze damage with numerical indicia being assigned to indicate the extent of overglaze damage involved. Thus, the scale of 0, 1, 2, 3 and 4 correspond, in terms of damage, to none, slight, moderate, considerable and complete, respectively.

EXAMPLE I

This example illustrates the applicability of the present invention to the preparation and use of cleaning compositions specifically adapted for use in connection with dishwashing operations.

The following composition is prepared:

%	Ingredient
62.4	Sodium tripolyphosphate hexahydrate
20	Sodium metasilicate
2	Wetting agents
1.6	Potassium dichloroisocyanurate
4	Sodium sulfate

*Long chain linear alcohol with ethylene oxide addition available under the trade name designation RA-35 from the Wyandotte Chemical Company.

To the above composition is added boric acid (8%) and aluminum silicate (2%). Overglaze damage is evaluated according to the CSMA method hereinbefore described utilizing an 0.3% aqueous solution of the above ingredients, having a pH of about 10.5. The following results are obtained:

Fine China Damage		
2 hrs.	4 hrs.	6 hrs.
0	0	0

As the above data makes manifestly clear, no perceptible overglaze damage is detected despite immersion periods of the fine china standard plate samples ranging up to 6 hours. Of equal importance is the fact that such samples are substantially devoid of aluminum precipitate or other undesired material thereby yielding an aesthetically pleasing surface.

EXAMPLE 2

Example 1 is repeated except that the concentrations of boric acid and aluminum silicate employed are 9 and 1 percent by weight respectively. Results similar to those described in Example 1 are obtained.

EXAMPLE 3

Example 1 is repeated except that the concentration of boric acid and aluminum silicate employed are 9.5 and 0.5 percent respectively. Again, the results obtained compare favorably with those described in Example 1.

EXAMPLE 4

Example 1 is repeated except that the aluminum silicate is replaced by 2 percent of aluminum chlorhydroxide while the boric acid is employed in an amount of 8 percent by weight. The results obtained are itemized, as follows:

Fine China Damage		
2 hrs.	4 hrs.	6 hrs.
0	0	0

EXAMPLES 5–8

Examples 1–4 are repeated except that in each instance, the boric acid is replaced in equivalent amounts by boron trioxide. Similar results are obtained, i.e., cleaning compositions formulated therewith exhibit negligible if any tendency to either deposit aluminum precipitates or attack the overglaze of fine china despite protracted immersion periods ranging up to 6 hours and higher. In addition, detergent compositions containing the boron trioxide material display superior stability on standing, e.g., in packaged form as would be made available to the consumer, have a greater tolerance to moisture and remain free-flowing, being devoid of any tendency to cake or become hard when aged under varying temperature-humidity conditions.

EXAMPLES 9–13

Example 1 is repeated except that the boron compound employed comprises the following:

Example	Mole ratio of Boric Acid to Boron Trioxide
9	1:1
10	1:2
11	1:3
12	2:1
13	3:1

In each instance, the aforedescribed boron compound admixtures provide a superior degree of stabilization against overglaze attack while minimizing if not completely eliminating problems associated with aluminum precipitate formation.

In addition, the exemplified procedures make unavoidably clear that the compositions provided in accordance with the present invention are capable of superior cleaning activity, i.e., displaying an outstanding capacity to readily remove stain deposits from a wide variety of glazed dishwear.

A further and significant advantage of the present invention relates to the fact that the boron compound serves to provide an effective measure of bleach stabilization, i.e., the hypohalide-liberating bleaching agent and particularly the hypochlorite-liberating species in the presence of the boron compound are highly stable against the loss of halogen in the relationships provided, thereby enabling more effective and efficient utilization of the parent cleaning composition in practice.

While the detergent composition of the present invention finds most efficacious utilization in connection with the washing of the dishes and the like in automatic dishwashers, naturally, the detergent may be utilized in other fashions as desired. Usually, however, the best mode of use will be in connection with automatic dishwashers which have the ability of dispensing the detergent of the present invention in one or more separate wash cycles. Accordingly, the detergent composition of the present invention is added to the two receptacles, if such are present, in an automatic dishwasher. When the dishwasher is set into operation, after the dishes have been suitably positioned therein, the automatic devices of the dishwasher permit the addition of sufficient water to produce a concentration of the detergent composition of approximately 0.3 percent by weight. The operation of the dishwasher results in treating, that is, washing of the dishes with the aqueous solution of the detergent composition. Usually, the sequence of operation in utilizing an automatic dishwasher results in one or more rinsing steps following the one or more washing cycles. In utilizing the detergent composition of the present invention it will be noted that even after use in considerable number of washings there will be little or no attack on the overglaze of china or little or no tarnishing of silver or silver plate as a result of the use of the detergent composition.

Effective industrial bottle cleaning compositions may be provided in accordance with the present invention by merely admixing the aluminum compound-boron compound system with suitable active ingredients, e.g., caustic alkali whereby to provide a highly alkaline composition preferably having a pH of approximately 12. Such compositions may be readily formulated in accordance with the parameters hereinbefore described.

Results similar to those described in the foregoing examples are obtained when the procedures delineated therein are repeated but employing in lieu of the specific non-ionic detergent identified a variety of materials selected from nonionic, anionic, cationic, amphoteric and zwitterionic types. Moreover, nothing critical resides in the selection of bleaching agent and accordingly, any of the materials hereinbefore recommended for such purposes may be readily employed to advantatage.

It will further be understood that the aluminum compound-boron compound composition may be provided in the form of a separate component, e.g., package; thus, in use, such materials may be introduced into the aqueous washing medium either prior to, subsequent to, or simultaneous with, the addition of the remaining cleaning ingredients. This comprises a particular effective embodiment of the present invention since the user may dispense quantities having reference to the severity of the cleaning problem to be negotiated.

It will be apparent that many changes and modifications of the several features described herein may be made without departing from the spirit and scope of the invention. It is therefore apparent that the foregoing description is by way of illustration of the invention rather than limitation of the invention.

What is claimed is:

1. A composition capable of inhibiting overglaze attack consisting essentially of an aluminum compound selected from the group consisting of aluminum silicate having a pH in the range of 5 to 9 and a water-soluble aluminum chlorhydroxide wherein the atomic ratio of Al to Cl is 2:1 and having a pH in the range of about 4.0 to 4.5 and capable of forming stable water solutions in concentration up to about 50 percent, and at least one boron compound selected from the group consisting of boric acid and boron trioxide, and wherein the weight ratio of the aluminum compound to the boron compound is within the range of from about 0.025 to 1.

2. A composition according to claim **1** wherein said aluminum compound has the composition $Al_2O_3 \cdot 7.8 SiO_2$.

3. A composition according to claim **1** wherein said aluminum chlorhydroxide has the composition $Al_2(OH)_5Cl \cdot 2H_2O$.

4. A composition according to claim **1** further containing from 0.5 to 5 percent by weight of the composition of a bleaching agent capable of liberating hypohalite on contact with aqueous media.

5. A composition according to claim **1** wherein said boron compound is boric acid.

6. A composition according to claim **1** wherein said boron compound is boron trioxide.

7. A composition according to claim **1,** wherein said overglaze attack inhibitors are aluminum silicate and boric acid.

8. A composition according to claim **1,** wherein said inhibitors are aluminum chlorhydroxide and boric acid.

9. A dishwashing composition according to claim **1** further containing from about 40 percent to about 95 percent by weight of total composition of water soluble neutral or alkaline builder salt.

10. A composition according to claim **9** wherein said builder salt is a mixture of about 55–75 percent by weight sodium tripolyphosphate hexahydrate and about 15–25 percent by weight sodium metasilicate.

11. A composition according to claim **9,** wherein the overglaze attack inhibitors constitutes from about 5–20 percent by weight of the total composition.

12. A composition according to claim **9,** including a water soluble organic detergent selected from the group consisting of non-ionic, anionic, cationic and amphoteric detergents in an amount of about 0.5 percent to about 5 percent by weight of the total composition.

13. A composition according to claim **4** wherein said bleaching agent is potassium dichloroisocyanurate.

14. A method for treating glasses, dishes and like glazed surfaces to remove foreign bodies from the surfaces thereof without modifying the substrata comprising treating said substrata with a dilute aqueous solution of a water soluble alkaline detergent composition as defined in claim **9.**

15. A method in accordance with claim **12** which also includes a rinsing step.

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