The Role of Detergent in Automatic Dishwashing Performance[1]

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Abstract

The ability of automatic dishwashing products to perform satisfactorily in mechanical machines is dependent upon a number of factors, including machine design and composition of product. Although most leading dishwashers are highly satisfactory for food-soil removal, the detergent composition and its usage can affect performance characteristics.

In this paper the objectionable tendency of automatic dishwashing detergent compositions to cause glassware spotting or filming, fading of fine china decoration, and silverware discoloration is considered. The means to minimize these deficiencies are presented.

Introduction

AUTOMATIC DISHWASHERS ARE NOW ONE of the fastest selling of all major household appliances. Concurrently with these sales the demand for detergent products to be used in these machines has grown rapidly. Major improvements in machine design and the availability of better detergent products account for the wide acceptance of household dishwashers. About a year ago the performance characteristics of mechanical dishwashers for home use were evaluated (1). These studies indicated considerable differences among dishwashers; the most significant was cycle. Dishwashers with cycles that included two washes, separated by a rinse, were usually found superior.

In a later article by the same workers (2) the three widely distributed detergent products (nonidentified), used in the dishwasher study, were evaluated. Two of the products had a pH of 11.1 at use concentration, the other a pH of 9.8. The lower pH product contained a chlorine compound, chlorinated trisodium phosphate; the others did not. For removal of a laboratory prepared soil (identified as B-19 and consisting mainly of cooked egg, cooked cereal, milk, and margarine) the high pH detergent products were essentially equivalent and significantly better than the lower pH product. The authors pointed out that the relatively low pH detergent may be satisfactory with soils less difficult to remove than B-19 and stated that it would probably cause less damage to the overglaze on dishes than would the compositions having high pH.

Test work on leading brands of dishwasher detergents by Consumers Union revealed no significant differences in cleaning effectiveness. However, contrary to common claims, water-spotting was evident for all detergents and some damage to overglaze china occurred for eight of nine products tested (3). Experience of the present authors is in general agreement with these findings. In addition to glassware spotting and china damage, their opinion is that discoloration of silverware is also of concern to the owner of a dishwasher. Consequently the primary object of the work reported in this paper is to present the means whereby these undesirable actions, attributable in the main to the detergent being used, may be inhibited.

Experimental Section

Detergent Compositions. Phosphate, silicate, and chlorine compound comprise three of the major constituents which may greatly influence performance properties of automatic dishwashing compositions. Other components may serve as foam depressants, wetting agents, fine china-protective agents, pH regulators, coloring agents, perfume, or general fillers. Numerous methods for the processing of phosphate, silicate, and an active chlorine compound in automatic dishwashing compositions are given in the literature, typical examples of which are given below:

Method I. Dry mixing of anhydrous sodium tripolyphosphate and sodium metasilicate with either chlorinated trisodium phosphate (4,5) or with the sodium or potassium salt of dichlorocyanuric acid (6,7).

Method II. Hydration of anhydrous sodium tripolyphosphate with aqueous silicate and incorporating therein either chlorinated trisodium phosphate (8) or potassium dichloro-isocyanurate (9).

Method III. Treatment of sodium trimetaphosphate with sodium hydroxide to give sodium tripolyphosphate hexahydrate. It is possible to utilize other detergent ingredients in the reaction mixture or to admix them in order to obtain various detergent products, including automatic dishwashing compositions (10). A modified procedure wherein sodium silicate instead of sodium hydroxide is used to open the cyclized phosphate has been published recently (11).

In our work dry-mix detergent compositions were processed in a Patterson-Kelly blender under conditions similar to Method I. Preferred compositions contained 55–75% sodium tripolyphosphate hexahydrate, 15–25% sodium metasilicate, 2% potassium dichloroisocyanurate, and 3% of a nonionic foam depressant. Overglazes-attack inhibitor, color, perfume, and inert filler content varied.

Detergent compositions with SiO_2 to Na_2O ratios greater than 2 were processed by Method III (10). Liquid silicate having an SiO_2 to Na_2O ratio of 2.4 was incorporated into the trimetaphosphate-caustic soda reaction mixture. Potassium dichloroisocyanurate, color, and perfume were post-blended. Major differences in composition prepared in this manner to sodium metasilicate dry-blended compositions, described in the immediate paragraph above, are the lower alkalinity of the silicate and the absence of a special overglaze-attack inhibitor.

Spotting and Film Test. The procedure described in Soaps and Chemical Specialties was used (12). Five numbered tumblers are spaced in the top rack of washer. Six dinner plates are spaced in the lower rack. Detergent receptacles of the machine are each filled with 16.0 g of product. Forty grams of a soil (20% Starlac, 80% margarine) are placed at the bottom of the machine. With water at 140° and 90–100 ppm water hardness, the machine is put through its standard cycle. After each cycle the tumblers are removed and rated in adequate light.

[1] Presented at the AOCS Meeting, New Orleans, May 1967.

Fine China-Protection Ability of Detergent. The procedure recommended by the Chemical Specialties Manufacturers Association (CSMA) was used (12). Briefly, standard plates (Greenwood pattern, Onondaga Pottery Company, Syracuse, N.Y.) are immersed in deionized or distilled water containing 0.25% and/or 0.75% concentration of detergent for two, four, six hours as given in the journal article. The test is designed as an accelerated dishwasher exposure method; the comparative removal of overglaze decoration provides an evaluation of the corrosiveness of dishwashing detergent solutions.

Silverware Discoloration Test. Automatic dishwashing detergent and powdered egg as the soil are dissolved in a bath containing six liters of water (100 ppm hardness) at 140F to give a detergent concentration of 0.35% and a soil concentration of 0.1%. At constant temperature and volume the detergent-soil is agitated with pump and ejected through a spray nozzle onto the silverware object. The silverware is supported within a beaker, which is arranged in a position to return solution to bath for recirculation and continual spraying of object. The degree of discoloration or tarnishing of the silverware occurring within one hour is noted.

Results and Discussion

Effect of Ingredients on Spotting and Filming

Although the removal of soil particles from tableware is no longer a serious problem for late-model dishwashers of advanced design, spot or film deposit on glassware continues to be troublesome. Water hardness, soil type, and limitations in the detergent composition are considered to be responsible. Presumably water film on the surface of glassware can contain solids, and these solids remain as unsightly spots or films upon evaporation of the water. At the AOCS meeting in Philadelphia last fall the reason for the build-up of film on glassware was cited to be the use of too little detergent. In hard water the film composition was shown to consist mostly of calcium phosphate or calcium carbonate, depending upon the detergent composition (13).

Of the ingredients basic to a dishwashing composition, phosphate and active chlorine agents are probably the two most critical constituents which affect spotting and filming of glassware. The wetting action of the surfactant also plays a part, but its value in dishwashing compositions, and indeed its choice, will be dependent mainly upon its ability to act as a foam depressant and to maintain satisfactory odor and/or color stability in the presence of an active chlorine compound.

Anhydrous sodium tripolyphosphate is commonly used in dry-blend processing of automatic dishwashing products containing granular sodium metasilicate (Method I); hydrated sodium tripolyphosphate is formed during processing with liquid silicates by either Method II or Method III. The presence of the hydrated phosphate is more desirable than the anhydrous form since it is less likely to offer solubility difficulties in the machine; this factor may have an indirect relationship to spotting. During the first cycle operation in the machine, anhydrous sodium tripolyphosphate, contained in a detergent awaiting discharge from the second cup, is susceptible to hydration. If this occurs, the full benefit of the detergent composition may not be available to the washload. Possibility of spotting and/or filming is enhanced, and a gummy mass may remain for the housewife to remove.

The combination of sodium tripolyphosphate and chlorinated trisodium phosphate (5) or the combination of sodium tripolyphosphate with a salt of dichloro-isocyanuric acid (6) has been shown to minimize spotting and filming considerably. Both of these chlorinated compounds are used in commercial products and are highly effective. Choice is dictated by formulation and, probably more importantly, by the method of processing. Unbound moisture cannot be tolerated to any appreciable extent in a phosphate-silicate composition containing the salts of dichloro-isocyanuric acid. Yet a critical amount of moisture must remain associated with chlorinated trisodium phosphate if the product is to retain an acceptable level of available chlorine stability.

After preliminary experimental work and full consideration of processing and formulation limitations inherent in the methods described in the literature, we concluded that a dry-blend operation involving the use of stable sodium tripolyphosphate hexahydrate, sodium metasilicate, and potassium dichloro-isocyanurate would be more adaptable to the processing equipment. Compositions containing these ingredients were notable for their excellent chlorine stability; and performance relative to the absence of spotting and filming of glassware was exceptionally good. To afford adequate protection against damage to fine china however, a glaze-protective agent must also be present.

Fine China Protection

The presence of sodium silicates in detergent products for their ability to inhibit corrosion of metals and for their ability to help in the saponification and emulsification of fats is well recognized. In automatic dishwashing compositions they admirably fulfill this role, but, in addition, they contribute to the protection of fine china against overglaze damage, particularly when the SiO_2 to Na_2O ratio is 2 or more. Liquid silicates possess this preferred ratio. They are readily available commercially and are especially adaptable for use in the processing of automatic dishwashing compositions by Method II or Method III. These silicates in the dry state are relatively expensive and at present are not available in satisfactory physical form. For an economical, granular silicate with desirable density characteristics and suitability for dry-blend compounding (Method I), sodium metasilicate with an SiO_2 to Na_2O ratio of 1 is usually preferred. However it does not provide the high-level protective action toward overglaze decoration on fine china that low alkaline silicates do when admixed with sodium tripolyphosphate.

A composition consisting essentially of sodium tripolyphosphate hexahydrate, a minor amount of potassium dichloro-isocyanurate, but no sodium metasilicate or other alkaline material, had a damaging effect on fine china when subjected to the CSMA test conditions. By replacing some of the phosphate with sodium metasilicate, an attempt was made to arrive at an acceptable ratio of sodium metasilicate to sodium tripolyphosphate hexahydrate. Some success was indicated in the area of 1:12 ratio of metasilicate to phosphate, but satisfactory CSMA test results, possibly because of poor blending, could not be obtained consistently. In contrast, overglaze damage on fine china was nil with compositions prepared from silicates with an SiO_2 to Na_2O ratio of 2.0 or higher, provided the detergent contained about 10% SiO_2

TABLE I

Effect of Silicate Alkalinity on Fine China[a]

Silicate used	Fine china damage with time[b]		
	2 hr	4 hr	6 hr
$SiO_2/Na_2O = 2.4$	0	0	0
$SiO_2/Na_2O = 2.0$	0	0	0
$SiO_2/Na_2O = 1.0$	1	2	4

[a] Detergent ingredients: sodium tripolyphosphate hexahydrate, potassium dichloro-isocyanurate, sodium silicate ($SiO_2 = 9.5\%$ for detergent composition).
Test conditions: 0.30% detergent, 211F, 6 hr.
[b] 0 none; 1 slight; 2 moderate; 3 considerable; 4 extensive. Syracuse, Greenwood pattern china.

content and was used at a concentration of about 0.3% or more. In Table I the overglaze removal results for compositions containing about the same SiO_2 content but derived from sodium silicates of varying alkalinity are shown. To provide protection for fine china, equivalent to that afforded by low alkaline silicates, an inhibitor was sought for use with sodium metasilicate.

Among other reasons, attack on china patterns by mechanical dishwashing agents has been attributed to high alkalinity or available chlorine, or both (14). The use of sodium zincate, sodium beryllate, and sodium aluminate to prevent caustic soda attack on glass was described in the literature many years ago (15). More recently aluminum acetate (14) and sodium aluminate (16) have been reported to inhibit attack of detergent on china patterns. In specific phosphate and sodium metasilicate systems, we found sodium aluminate to be effective in the prevention of attack of overglazed decoration on fine china. However an undesirable precipitate would sometimes remain in a dishwasher receptacle or adhere to glassware when the product was used in certain homes. According to the literature (16), this problem is not uncommon whenever a soluble silicate and aluminum compounds are present in a dishwashing composition.

In Table II overglaze damage results are shown for a detergent system containing various additives. In all cases the particular additive was added to a sodium tripolyphosphate hexahydrate and potassium dichloro-isocyanurate (KDCC) detergent composition containing 20% sodium metasilicate and minor amounts of other ingredients. The results show sodium aluminate to be highly effective even though its addition did not alter the pH of the detergent solution. Although the addition of sodium bisulfate, sodium bicarbonate, and benzoic acid lowered the pH of the detergent solution to a level common to a similar noncorrosive composition containing a silicate with an SiO_2 to Na_2O ratio of about 2.4, overglaze decoration damage remained a problem. However, boric acid provided good protection for overglaze from a sodium metasilicate-formulated composition.

It appears that detergent compositions containing silicates of proper alkalinity or the use of special

TABLE II

Fine China Overglaze Decoration Damage[a]

Additive (%)	pH (0.3%)	Fine china damage[b]
None (0)	11.1	4
Sodium aluminate (1)	11.0	0+
Sodium aluminate (2)	11.1	0
Sodium bisulfate (10)	10.6	3
Sodium bicarbonate (10)	10.5	3
Benzoic acid (10)	10.4	3
Boric acid (10)	10.5	0+

[a] Main detergent ingredients: sodium tripolyphosphate hexahydrate, sodium metasilicate, potassium dichloro-isocyanurate.
Test conditions: 0.30% detergent, 211F, 6 hr.
[b] 0 none; 1 slight; 2 moderate; 3 considerable; 4 extensive. Syracuse, Greenwood pattern china.

additives with detergent compositions containing sodium metasilicate are necessary to prevent fine china damage. Experience indicates that, when these conditions are properly met, insufficient detergent must be avoided not only to prevent spotting of glassware but also to assure protection to overglaze decoration on dishes. Of the two concentrations of dishwashing agents recommended in the CSMA test procedure, damage to fine china was usually greater at the lower detergent concentration (0.25%) than at the higher detergent concentration (0.75%).

Discoloration of Silverware

In addition to good inhibition toward fine china attack, the use of boric acid is particularly attractive relative to cost, solubility, and general performance attributes. In the course of consumer testing, certain detergent compositions gave unexpectedly good response in silverware cleaning. The discoloration or tarnishing of silverware in a dishwasher with certain soils, particularly those containing sulfur, has been a problem. In addition, this defect has been attributed to base metal exposure (17), to water hardness, and to undissolved detergent containing active chlorine in contact with silverware (5). In order to determine if soil could differentiate the detergent products with respect to their action on silverware, the test method described in the Experimental Section was developed. Under these conditions, strong discoloration of sterling or silverplate was noted for compositions containing sodium metasilicate with or without available chlorine. Compositions containing low alkaline silicate or sodium metasilicate with boric acid and potassium dichloro-isocyanurate did not appreciably discolor silverware.

In summary, phosphate and active chlorine compound are the main ingredients necessary to inhibit the spotting and filming of glassware. Proper alkalinity ratio or use of a special additive with sodium silicate is required to provide protection for fine china and to minimize discoloration of silverware. It should be emphasized that use of insufficient detergent not only causes spotting and filming of glassware but also enhances the probability of overglaze decoration damage to china. Few consumers recognize that too little detergent or hot water alone in their dishwashers is more harmful to their fine china than is a properly formulated product used at an effective level of between 0.25 and 0.75% of concentration.

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