The Cause and Prevention of Glassware Corrosion in Domestic Mechanical Dishwashers

B.J. RUTKOWSKI, Whirlpool Corporation, Research and
Engineering Center, Monte Road, Benton Harbor, Michigan 49022

ABSTRACT

Laboratory scale procedures and practical tests were used to study the problem of glassware corrosion (permanent filming) in domestic mechanical dishwashers. Results of these tests showed glassware corrosion to be caused by alkali attack of the glass structure. It was also found that sequestrants such as sodium tripolyphosphate greatly accelerate the corrosive action of alkali. Silicates, certain metals and metal oxides were found to inhibit glassware corrosion. The basis for this inhibiting effect is believed to be adsorption on the glass surface of reaction products of these materials in an alkaline solution.

INTRODUCTION

Glassware filming due to variations in water quality has been a problem associated with mechanical dishwashing. Filming problems have been associated with both water hardness and lack of hardness (1,2). The two most prevelant are those occurring in hard water (hard water detergent precipitates and hard water mineral deposits). It has been shown that with the use of an adequate amount of detergent these films can be relatively easily prevented or removed (2). A third type of filming, which occurs almost exclusively in soft or softened water, is more serious because it is progressive and nonreversible. This type of filming has been variously called "soft water etching," "permanent filming" or "glassware corrosion." Typically, the glass surface first appears to have a rather uneven iridescent film, then progressively becomes cloudy and finally etched. Work reported previously by Madden has defined the practical conditions under which permanent filming invariably occurs; these are soft or softened water and a high detergent concentration (1). Madden's work also identified an insoluble silicic acid as the principal constituent of the iridescent film formed on glass surfaces under these conditions. The present work was undertaken to determine the cause of glassware corrosion (permanent filming) as it occurs in mechanical dishwashing and on the basis of this knowledge, the means of its prevention.

EXPERIMENTAL PROCEDURES

Materials

Soda-lime-silica (soft soda) glass in the form of microscope slides, beads and tumblers were used in this study. Before use all were rinsed in distilled water and air dried. Chemicals used in the preparation of test solutions were: sodium carbonate, reagent, anhydrous powder; trisodium phosphate (TSP) reagent, anhydrous; tetrasodium pyrophosphate (TSPP) reagent, decahydrate; sodium tripolyphosphate (STPP) purified, anhydrous; sodium silicate, Philadelphia Quartz Company "G", weight ratio SiO_2/Na_2O = 3.22; nitrilotriacetic acid trisodium salt (NTA) monohydrate, purified; and ethylenediaminetetraacetic acid tetrasodium salt (EDTA), purified.

TABLE I

Effect of Dishwasher Detergent
Components on Glassware Corrosion

Solution, 0.33%	pH	Appearance of slides
Sodium silicate	11.0	No visible change
Sodium carbonate	11.1	No visible change
Trisodium phosphate	11.5	Very slight interference film after 144 hr
Tetrasodium pyrophosphate	10.2	Interference film formed in 48 hr
Sodium tripolyphosphate	9.4	Interference film formed in 72 hr

Methods

Three experimental test methods were used to obtain data concerning the chemical and physical reactions occurring on glass surfaces during the wash process.

Microscope Slide Tests. Microscope slides, 75 x 25 mm, were immersed in distilled water solutions of the various materials studied; they were maintained at a temperature of 140 F for periods up to two weeks. The slides were then rinsed in distilled water and air dried. The presence or absence of interference films, the first visible evidence of corrosion, was noted; in most tests change in the weight of the slides was also determined.

Micro-Electrophoresis. The change in the electrical charge of a glass surface on exposure to the various solutions was determined by electrophoretic-velocity (EV) measurements. Glass beads (Glas-Shot, MS-XLS, 5 to 44 μ, Cataphote Corp., Jackson, Miss.) at a 0.1% by weight concentration were suspended in 500 ml of appropriate solution. The EV of the beads was determined immediately on an aliquot of the suspension. The remainder was maintained at 140 F for six days when EV measurements were repeated. The equipment used to measure the EV of the glass beads is called a "Zeta Meter" (Zeta Meter, Inc., New York). A description of this apparatus and its use has been previously reported (3).

Dishwasher Tests. Several series of tests were conducted in a front-loading, portable dishwasher to confirm, under practical conditions, results of certain of the microscope slide tests. In each test series tared glass tumblers were subjected to 20 complete cycles (two washes with detergent and four rinses) in the dishwasher using 0 gpg softened water. The glasses were then air dried for 2 hr and reweighed to determine weight change. Appearance of the tumblers was also noted.

RESULTS AND DISCUSSION

Preliminary microscope slide tests were run to screen the various dishwasher detergent components as to their corrosiveness toward glass. In these tests the slides were immersed in 0.33% solutions of the various materials and maintained at a temperature of 140 F for 144 hr. Results are shown in Table I.

Glass is attacked in alkaline solutions by reaction of hydroxyl ions with the silica network. At sufficiently high pH, glass constituents tend to be equally dissolved, continuously exposing a fresh surface (4,5). This type of corrosion, which is not visibly apparent, may have occurred on those slides immersed in the highly alkaline silicate and carbonate solutions. Glass may also be corroded by a

TABLE II

Effect of Sequestrants on Glassware Corrosion

Solution, 0.33%	Normality	pH	Weight loss (mg/dm^2), mg[a]	Appearance of slides
Na_3PO_4	0.061	11.5	6.0	Very light film after 144 hr
$Na_4P_2O_7$	0.050	10.2	31.8	Film after 48 hr
$Na_5P_3O_{10}$	0.045	9.4	19.8	Film after 72 hr
Na_3NTA	0.039	10.6	36.2	Film after 24 hr
Na_4EDTA	0.035	10.6	46.4	Film after 24 hr

[a] Exposed surface area per slide = 0.25 dm^2.

preferential leaching or dissolving of certain constituents from its surface leaving a porous surface layer (4). This type of corrosion is visible because the porous layer impairs the surface by reducing gloss or by forming an interference film. The interference film on slides immersed in the three phosphate solutions suggested this preferential leaching type of corrosive action. Composition of this film as insoluble silicic acid was confirmed by IR spectral analysis. It is known that lime or other oxides incorporated into simple alkali glasses makes them more resistant to alkaline corrosion (6). The composition of a typical soft soda glass as used in these studies is: 72-75% SiO_2, 13-17% Na_2O, 5-10% CaO and 1-5% MgO. The probable action of pyro- and tripolyphosphate, both good calcium sequestrants, was to remove calcium from the glass surface, thereby rendering it less resistant to attack by alkali in the solution.

The supposition that calcium (and magnesium) sequestrants accelerate alkaline corrosion of glass was confirmed by further experimentation. It appeared that a direct relationship must exist between strength of sequestrant and the degree of corrosion occurring in an alkaline solution of that sequestrant. To demonstrate this, the corrosive action of TSP, STPP, TSPP, NTA and EDTA were compared. The order of increasing effectiveness as sequestrants of these materials is TSP<TSPP<STPP<NTA<EDTA. Degree of corrosion was determined by weight loss of microscope slides. Solution concentration for these microscope slide tests was 0.33% and immersion time at 140 F was 144 hr. Results are shown in Table II.

With the exception of pyrophosphate, corrosive action increased as sequestering strength increased. Pyrophosphate, although a weaker sequestrant than tripolyphosphate, is the more alkaline. This particular concurrence of alkalinity-sequestration of the pyrophosphate solution could account for the higher rate of corrosion. Trisodium phosphate, highly alkaline, but not a sequestrant, was the least corrosive.

One of the characteristics of permanent filming is that it rarely occurs under hard water conditions. One possible reason for this is now evident. It would appear that calcium and magnesium ions removed by detergent components during a wash cycle could be replaced by an ion exchange mechanism during subsequent hard water rinses. In this event the integrity of the glass surface would be restored and corrosion reduced.

In prior studies visible glassware corrosion could not be demonstrated when detergents with a high (27-35%) silicate content were used. This suggested that silicates effectively inhibit glassware corrosion. To investigate this, the effect of various amounts of silicate on the corrosive action of a 0.33% tripolyphosphate solution was determined. For this test series, immersion time of the microscope slides was 14 days, and temperature was 140 F. Results are shown in Table III.

Data of Table III show that tripolyphosphate solutions containing less than 0.066% silicate are quite corrosive. At higher silicate levels corrosion was practically eliminated. Soluble silicates, which readily adsorb on a glass surface (7), appear to inhibit corrosion by forming a protective barrier against the action of alkali and sequestrants.

The mechanism by which silicates adhere to glass and protect its surface can be explained by the tendency of glass to continue its network structure with the atoms of the silicate. Such a theory is used to explain the high adhesion of metal oxide coatings to glass (8). This suggested that perhaps certain metal oxides would also be effective in preventing glassware corrosion. To test this possibility, microscope slides were immersed in 100 ml aliquots of a 0.33%, 10:1 tripolyphosphate-silicate solution, each containing 0.5 g of one of the following: CaO, CdO, BaO, Al_2O_3 and ZnO. (A 10:1 STPP/SiO_2 was used because it was found to produce a readily observable interference film within 24 hr). The solutions were maintained at 140 F. After 24 hr those slides immersed in STPP-SiO_2 solutions containing CaO, BaO or Al_2O_3 had heavy interference films indicating corrosion. However, the slides immersed in STPP-SiO_2 solutions containing CdO or ZnO were still optically clear after 168 hr of immersion. Further tests were conducted using elemental Cd, Zn and Mg in place of the oxides. In these tests cadmium had no effect; probably because of its very low solubility in alkaline solutions, but both magnesium and zinc prevented the formation of interference films.

The ability of CdO, ZnO, Mg and Zn to prevent glassware corrosion is most likely due to adsorption by the glass surface of reaction products of these materials with an alkaline solution. An attempt was made to clarify these events occurring on a glass surface when corrosion is successfully inhibited. This was done through a EV study of the electrical charge at a glass-solution interface under

TABLE III

Inhibiting Effect of Silicates on Glassware Corrosion

Solution		Weight loss (mg/dm^2), mg	Appearance of slides
Polyphosphate	Silicate		
0.33%	0.33%	+2.2	Clear
0.33	0.133	0.6	Clear
0.33	0.066	1.0	Slight film after 14 days
0.33	0.033	15.2	Film after 24 hr
0.33	0	33.6	Film after 72 hr

TABLE IV

Electrophoretic Study of a Glass Surface Under Corrosive and Noncorrosive Conditions

	Original suspension		Six days immersion			Zinc-inhibited six days immersion		
Solution, 0.33%	pH	EV	pH	EV	Corrosion, (mg/dm^2), mg	pH	EV	Corrosion, (mg/dm^2), mg
STPP	9.9	4.99	9.4	2.44	19.8	10.0	4.45	4.4
NTA	10.5	4.69	10.2	2.48	36.2	11.4	4.30	14.8
EDTA	10.6	4.14	9.7	2.42	46.4	10.6	2.90	41.2
STPP/SiO_2 (10:1)	10.4	4.37	9.5	2.44	7.2	10.1	4.14	0
NTA/SiO_2 (10:1)	10.7	4.68	10.2	2.08	51.6	11.4	3.59	11.0
EDTA/SiO_2 (10:1)	10.6	5.06	9.7	2.22	44.8	11.0	2.69	40.4
STPP/SiO_2 (1:1)	10.6	3.89	10.0	4.16	+1.0	10.0	3.54	1.0

corrosive and noncorrosive conditions. In this study, the EV of glass beads was determined after a short (<10 min) exposure and again after a six-day exposure at 140 F to the solutions listed in Table IV. The EV of the glass beads is reported as microns per second per volt per centimeter (μ/s/v/cm) corrected to 25 C. In all cases velocity was toward the anode indicating negatively charged particles. Degree of corrosion of microscopic slides exposed to similar conditions was also determined. These data are reported as weight loss.

Data of Table IV show that an uncorroded glass surface carries a high negative charge; due primarily to ionization of terminal groups of the silicon-oxygen network. ($\text{-Si-O-Si-O}^- + Na^+$) As corrosion proceeds by reaction of hydroxyl ions of the solution with these terminal structures and with the silica network itself, a surface of unionized hydrated silica is formed, thus negative charge is reduced. In addition to a reduction in EV as corrosion proceeded, a lowering in pH of the solutions was also noted. Depletion of hydroxyl ions by reaction with the glass surface would account for this.

In those solutions effectively inhibited by zinc, the EV of the glass beads was not significantly reduced. Also, pH remained approximately constant or in some cases showed a slight increase. These results indicate that the chemical reactions of corrosion were blocked or at least in certain instances diminished by the presence of zinc. A possible explanation, consistant with the EV results, is that formation and adsorption of a soluble zincate gave the glass surface a protective barrier to alkali and sequestrant attack.

Since the corrosion data of the microscope slides and beads were obtained under static conditions, confirmation under the dynamic conditions encountered in mechanical dishwashing was deemed necessary. Table V presents the results of dishwasher tests conducted for this purpose.

The first test, using only sodium tripolyphosphate as the detergent, substantiated the evidence that this dishwasher detergent component plays a major role in glassware corrosion. Succeeding tests utilized a commercially available dishwasher detergent. This detergent, as the data of test 2 in Table V show, readily produced visible evidence of corrosive action. On analysis, the detergent was found to contain 46.2% sodium tripolyphosphate and 11.0% sodium silicate ($SiO_2/Na_2O = 3.25$). Thus, the wash solution in the dishwasher contained only 0.036% silicate; a level previously shown to be insufficient to prevent glassware corrosion. The inhibitory effects of zinc and zinc oxide were demonstrated in tests 3 and 4 respectively. The zinc employed in test 3 was a 95% zinc, 5% aluminum die cast bar with a total surface area of approximately 60 sq. in. The bar was placed in the bottom dish rack of the dishwasher where it was exposed to the full spray action of both the wash and rinse water. Glass tumblers washed 20 times in the presence of this zinc bar showed no evidence of corrosion. The detergent used in test 4 contained 1% zinc oxide and although corrosion was definitely decreased it was not eliminated.

Thus, permanent filming of glassware, or more correctly glassware corrosion, in mechanical dishwashing is caused by alkali attack on the glass structure. Resistance to such attack is enhanced by the presence of calcium and magnesium in a glass composition. Therefore sequestrants such as tripolyphosphate, which have the ability to leach divalent metal ions, greatly accelerate alkali corrosion. Glassware and magnesium ions are restored to the glass surface by ion exchange during hard water rinses. This would restore alkali resistance to the glass surface and thereby reduce corrosion.

Silicates were found to prevent corrosion when a minimum sodium silicate concentration of approximately 0.066% was maintained in the wash solution. Silicate action is apparently that of a protective, physical barrier to sequestrant and alkali attack.

Certain metals (Zn, Mg) and metal oxides (ZnO, CdO) were shown to inhibit glassware corrosion. This finding is substantiated by the teachings of United States patents 2,447,297 and 2,514,304 (9,10) which essentially indicate that caustic soda-soluble zinc compounds effectively act as inhibitors against the corrosive action of alkali.

TABLE V

Glassware Corrosion in Dishwasher Tests

Test No.	Detergent, 0.33%	Weight loss-tumbler after 20 cycles, mg	Cycle in which film first observed
1	STPP	2.4	11th
2	Commercial product	5.4	5th
3	Commercial product + zinc	1.3	No film observed
4	Commercial product + ZnO	3.0	11th

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