Detergent-Hard Water Interactions in Machine Dishwashing[1]

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Abstract

Insufficient detergent concentration has recently been recognized as a major contributor to film formation on glassware in machine dishwashing. The film is shown to consist largely of calcium tripolyphosphate, $Ca_5(P_3O_{10})_2$; evidence is cited for the presence of a silicate, probably calcium metasilicate, as well. Systematic variation of detergent concentration and of water hardness allows construction of a response surface describing conditions of maximum and minimum rates of film formation. The extent of film formation is minimized when the ionic ratio of Ca or Mg or both to tripolyphosphate is 1:1 and maximized when the ratio is 5:2. These ratios correspond to the 1:1 chelate and the uncharged precipitate, $Ca_5(P_3O_{10})_2$, respectively. The implications of this treatment to other detergency processes are also considered.

Introduction

A variety of factors must be considered in the development of an effective detergency system for the home dishwasher. Among the more significant of these, in general terms, are the detergent, the bath medium, the soil and substrate, and the operating conditions selected. This paper is concerned with the usual bath medium, tap water, and its interactions with the detergent.

One of the most important properties of a natural water in dishwashing is the degree to which it promotes filming of glassware. Historically, filming has generally been considered to be caused by the deposition of calcium carbonate upon evaporation of hard water from the glass surface. Recently, Madden (4) reported a "detergent-hard water film," which he claimed occurs much more frequently. This film is caused by use of an insufficient quantity of detergent in hard waters. Domestic dishwasher detergents generally contain 40–60% sodium tripolyphosphate to sequester the calcium and magnesium ions present in most home water supplies. If an excess of tripolyphosphate is present, this solubilizing action largely prevents the deposition of the well-known lime scale (calcium carbonate). The present work was undertaken to define in greater detail the chemical nature of Madden's "detergent-hard water film" and the conditions under which it is formed.

Identification of the Film

Relatively few published investigations have dealt with the chemical identity of these films. Quimby (5), in studying the system $CaCl_2$–$Na_5P_3O_{10}$–H_2O, found that some precipitates corresponded in composition to $Ca_5(P_3O_{10})_2$, but others contained an appreciable and variable amount of sodium in place of calcium. Diamond and Grove (2), using radiometric techniques, found $Ca_5(P_3O_{10})_2$ to be the primary solid product from solutions 2 mM in Ca^{+2} and 0.4 to 1.2 mM in $P_3O_{10}^{-5}$.

In the present study a modification of Job's method of continuous variations (3) was employed. Solutions were prepared, ranging from 12 to 0 mM in $CaCl_2$ and from 0 to 4.8 mM in $Na_5P_3O_{10}$. The transmittance of these samples was read on a Coleman Model 9 Nephocolorimeter. The results (Fig. 1) indicate a maximum turbidity at a Ca/P_3O_{10} ratio of 5:2. This strongly suggests that the precipitate possesses a formula of $Ca_5(P_3O_{10})_2$, agreeing with the results of Diamond and Grove. It was further noted that substantial precipitate was formed on the $P_3O_{10}^{-5}$—deficient side of this stoichiometric point, but on the $P_3O_{10}^{-5}$—rich side the precipitate redissolved with a slight excess of $P_3O_{10}^{-5}$. This observation is significant when the findings are to be translated into operation of a precipitate-free detergent system.

A similar experiment using Mg^{+2} in place of Ca^{+2} produced no precipitate. This is not surprising in view of the known high solubility of most magnesium compounds, compared to their calcium analogs, and of the similarity of the dissociation constants of their tripolyphosphate complexes. Anderegg (1) has reported a pK_{inst} of 7.05 for the 1:1 magnesium complex and 6.31 for the calcium analog.

Since both phosphates and silicates are present in substantial concentration in dishwasher detergents, both must be considered as possible precipitants for unsequestered calcium ions. Van Wazer and Callis (6) indicate that calcium metasilicate is slightly more soluble than calcium carbonate, therefore silicate would not be expected to compete effectively with carbonate as a precipitating anion for calcium. Nevertheless, we have occasionally identified silicates, as well as tripolyphosphates, in film deposits both on glassware washed in the home and on laboratory test slides.

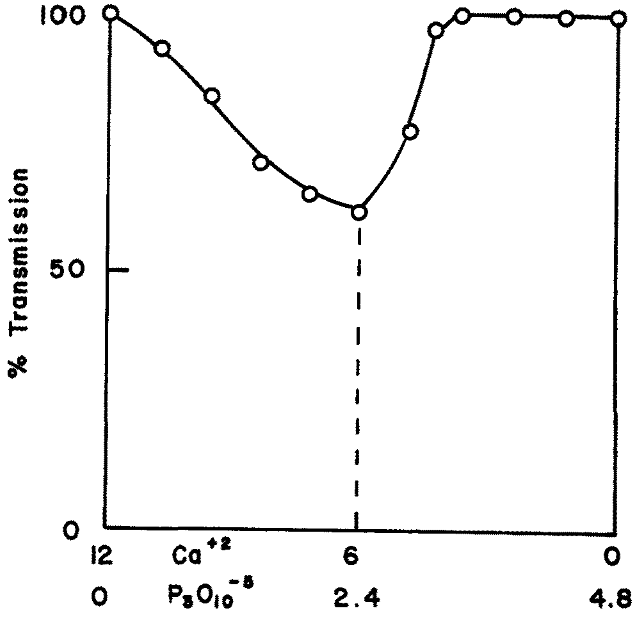

FIG. 1. Identification of calcium phosphate precipitate by Job's method of continuous variations, using turbidity measurement.

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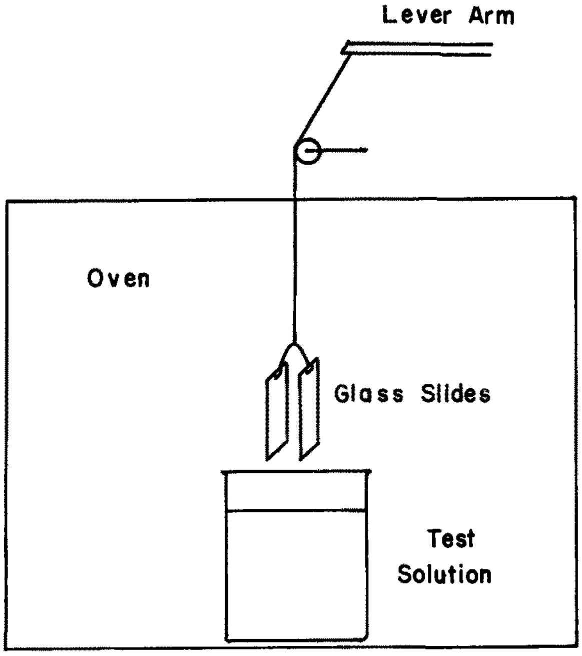

FIG. 2. Apparatus for dipping glass slides.

Rate of Film Formation

In the absence of sufficient tripolyphosphate to complex all of the calcium and magnesium, some of the calcium will be precipitated. In order to avoid in practice the conditions conducive to an undesirable rate of film formation, it is worthwhile to establish the relationship between the detergent concentration and water hardness and the quantity of film actually formed in a practical, easily repeated test.

The test procedure involved repetitive dipping of glass slides into selected concentrations of detergent solution. The detergent chosen was a commercial brand for home dishwashers which contained sufficient tripolyphosphate that a 0.3% solution was capable of softening a water of 241 ppm total hardness. The water was a natural well water having a total hardness of about 325 ppm, of which 61% was due to calcium, the remainder to magnesium. Lower hardnesses were obtained by dilution with distilled water. The glass slides employed were 3¼ × 4 in. Kodak projector slide cover glasses, which had previously been washed in a dishwasher and inspected for cleanliness.

The tared slides were mounted on a harness inside a Freas Model 835-A mechanical convection oven and dipped periodically into beakers of detergent solution by means of an external, automatically timed lever arm (Fig. 2). The dip-and-raise operation required 13 sec and was repeated once a minute. This cycle allowed time for complete drying, except for the drip line at the bottom of the slide. Each experiment consisted of 50 cycles. Oven temperatures were maintained at 158 F. Due to evaporation, the detergent solutions cooled during the run to 136 F. At the conclusion of an experiment, the slides were rinsed by dipping in distilled water and dried at 140 F before reweighing to determine the weight of film formed. Total film weights ranged from 0 to 12 mg.

Systematic variation of both the detergent concentration and the water hardness allowed the construction of a response surface (Fig. 3), upon which contour lines were drawn connecting points of equal weight gain. In the absence of specific interactions one would expect a family of rectilinear hyperbolic curves, due simply to the detergent and the presence of dissolved solids in the water. In fact, however, the curves show two areas of distortion, one indicating more deposit than anticipated, the other less.

The stoichiometry of the sequestering action was shown above to correspond to a 1:1 ratio of calcium or magnesium ions or both to tripolyphosphate ions, as, for example:

$$Ca^{+2} + P_3O_{10}^{-5} \longrightarrow [CaP_3O_{10}]^{-3}$$

The straight line depicting this ratio in Figure 3 corresponds closely to the region of film suppression.

If sufficient tripolyphosphate is not present to complex all of the calcium and magnesium, then some of the uncomplexed divalent ion is readily available for other reaction. The work of Anderegg (1) has indicated that the calcium complex is slightly less stable than its magnesium analog. Also, the present work shows that the calcium tripolyphosphate precipitate is much less soluble than the magnesium analog. Therefore, if the ion product of uncomplexed calcium and tripolyphosphate exceeds the K_{sp} of $Ca_5(P_3O_{10})_2$, as yet undetermined, some

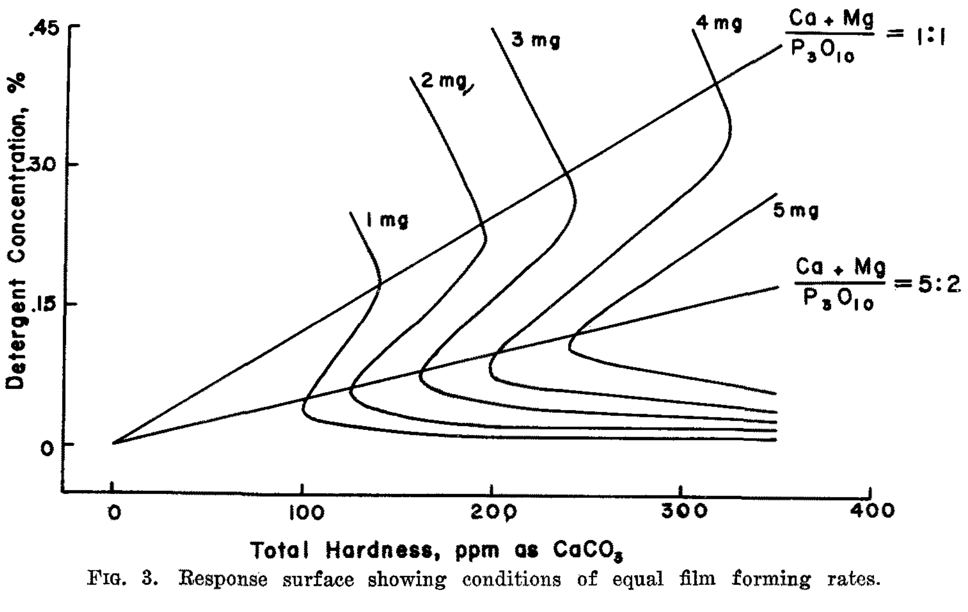

FIG. 3. Response surface showing conditions of equal film forming rates.

precipitation of $Ca_5(P_3O_{10})_2$ will occur. For a given water hardness, the extent of precipitation will reach a maximum at a 5:2 ionic ratio. If the K_{sp} of $CaSiO_3$ is exceeded before that of the tripolyphosphate, then the precipitate will consist of $CaSiO_3$. This is the apparent explanation for the aforementioned silicate films encountered occasionally. The detergent formulation fixes the ratio of tripolyphosphate to silicate, hence, determines whether the K_{sp} of $Ca_5(P_3O_{10})_2$ or that of $CaSiO_3$ is exceeded first. In either case the ion product will reach a maximum at a 5:2 ratio. The competing precipitation reactions are

$$5\,Ca^{+2} + 2P_3O_{10}^{-5} \longrightarrow Ca_5(P_3O_{10})_2$$

$$Ca^{+2} + SiO_3^{-2} \longrightarrow CaSiO_3$$

Indeed, the straight line connecting the points of 5:2 ratio intersects the points of maximum filming. It should be further noted that no measurable film formation occurred in the total absence of detergent, even at high water hardnesses, confirming the observation that detergent interactions are a major cause of glassware filming. In practical situations, of course, if hydrophobic soils survive the wash cycle poor drainage will result and spotting of glassware will occur even in relatively soft waters, due to the presence of dissolved solids in the water.

It is seen, then, that the observed response surface correlates well with the stoichiometry of the expected reactions. By this approach one can predict, for a given detergent formulation, the concentration required to avoid filming in water of any specified total hardness. The results are also of value to many other detergency processes, such as laundering, wall and floor cleaning, bottle washing, and alkaline metal cleaning, since the formation of precipitates is undesirable to these as well.

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