Removal of Fatty Soil from Glass. Electrolyte Detergent-Builder Effect

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COMPOSITIONS DESIGNED for use in mechanical dishwashing machines are characterized by the essentially complete absence of foaming surfactants. The design of the machines generally is such that foam impedes water-droplet impingement on the articles to be cleaned. This negative effect far surpasses the useful potential physico-chemical activity of the surfactant. As a consequence, dishwashing compositions are comprised essentially of electrolyte surfactant builders with only very minor percentages of low-foaming surfactants. Since absence of water spotting and good drainage are adversely affected by water hardness, the materials chosen should soften water, not by precipitation, but by sequestration of Ca and Mg ions. Materials most generally used for this purpose are the polyphosphates, particularly sodium tripolyphosphate ($Na_5P_3O_{10}$). Though other detergent builders, such as the carbonates and silicates, may be added, for this discussion they will be omitted.

A previous paper by the present authors (1) reviewed the characteristics of glass, indicating that primary adsorption sites were present and that tristearin, the radio-tagged fatty soil, was adsorbed at these polar regions. Preliminary work in preparation of the glass slides for the adsorption-cleaning study indicated that once a glass surface had been cleaned with a polyphosphate, the resoiled glass surface then retained the soil much less tenaciously than when a silicate or caustic cleaning agent had been used. This report describes this characteristic property of polyphosphates with glass and suggests its important practical applications.

Experimental

The experimental procedure was essentially that of the previous paper (1) comprising the frosting of microscope slide disks, preparation for soiling, soiling with mono- or multilayers of carbon-14 tagged tristearin, removal in a modified Terg-O-Tometer, and the counting procedure. Deviations from this technique will be indicated.

Preliminary Disk Treatment. Following removal of possible organic contaminants from the frosted disk by immersion in hot nonionic surfactant, after rinsing inorganic contaminants are removed by treatment with hot sodium hydroxide solution. Initially however, since tripolyphosphate is a major constituent of dishwashing compositions, it was natural that this should be used as the glass-pretreating agent. In so doing, it was found that soil subsequently applied was readily removed, so much so that little spread between detergent values could be found. In contrast, when sodium hydroxide was used for pretreatment, the soil was quite tenacious, and good differentiation between detergents (or solvents [1]) could be discerned. This finding led to the development of the data of Table I by pretreating the glass disks after organic contaminant removal as follows.

The initial soil level, as a spotted application, was about 400 cpm. The washing procedure for the replicates of the individual pretreatment materials was a wash for 10 min. at 140°F. in a Hotpoint dishwashing machine. The washed disks were machine-rinsed, again with 140°F. water for 5 min., dried, and counted.

TABLE I
Influence of Glass Pretreatment on Soil Removal

Pretreatment	% Soil removed
Sodium tripolyphosphate	81.8
Glassy sodium phosphate	68.0
Ethylene diamine tetraacetate	85.0
Sodium orthophosphate	20.8
NaOH	18.1
Tetrapotassium ferrocyanide	21.6
Sodium carbonate	28.3

Wash conditions
Hotpoint dishwasher.
0.25% Sodium metasilicate.
10 Min.—140°F.
Initial soil level—400 cpm—spotted soil.

It is quite apparent from Table I that sequestering materials are the effective types, that the precipitating type of water-softening builders are ineffective, and that multivalency of the anion is not the controlling factor. This surprising ability of tripolyphosphate (as representative of the class) to reduce the ability of soil to adhere was further investigated in an attempt to elucidate the mechanism of action.

Soil Removal by Builders. Having verified the pretreatment effect of tripoly, all subsequent disks were prepared with sodium hydroxide solution for pretreatment before soiling.

A series of builders, all at 0.25% concentration (anhydrous basis), were tested for removing spotted soil. The data of Table II, prepared by the now standardized Terg-O-Tometer procedure, verified the preliminary data of Table I. These show that even though the disks were not prepared (or pretreated) with tripoly, this class of compound nevertheless had high effectiveness in soil removal. The lower effectiveness of the glassy phosphate may probably be attributed to a pH effect since the anion is at least as effective a sequestering group as the tripoly ion.

TABLE II
Soil Removal by Builders
0.25% Solutions (anhydrous basis).
Terg-O-Tometer, 75°C., distilled water.
Soil—tristearin (spotted—4,400 cpm).
Time—20 min.

Builder	% Detergency
Sodium tripolyphosphate	82.0
Tetrasodium pyrophosphate	82.0
Glassy sodium phosphate	46.5
Sodium metasilicate	37.0
Na_2CO_3	26.9
NaOH	18.0

Tripolyphosphate (STP) Evaluation.

a) *Wash Time/Concentration.* The data of Figure 1 are a plot of detergency against STP concentration

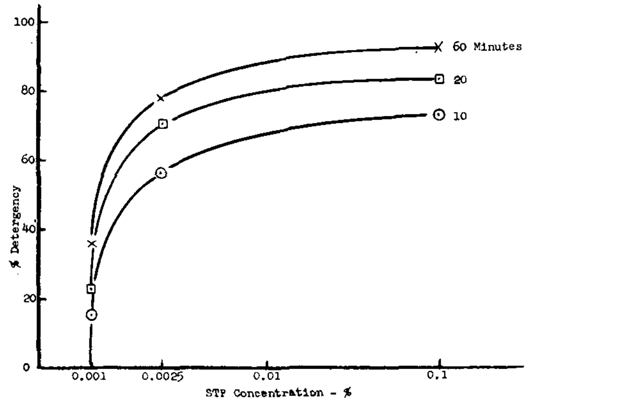

FIG. 1. Soil removal as a function of time. Spotted soil—wash temp. 75°C.

(log scale) for three different wash periods. These data show that an optimum wash time exists and that STP concentration has an important bearing upon the degree of soil removal. Though the curves are indicated as reaching zero detergency at 0.001% concentration, it is likely that actual measurement at lower concentrations would incline the curves toward the origin. The loss of effectiveness at this concentration may possibly be attributed at least in part to hydrolytic reversion to the orthophosphate. It is important however that the 0.001% level seems to be a limiting concentration. Here the maximum variation occurs as the reproducibility shows. Reproducibility (95% confidence level) for from 10 to 13 replicate disks for the several STP concentration levels were 0.001%–±9.8; 0.0025%–±4.8; 0.01%–±2.2; 0.1%–±1.5 (Figure 3, spotted soil curve).

The relative effect of STP concentration is more apparent in Figure 1 while detergency improvement with wash time is shown in Figure 2.

b) *Soil Film.* The data of Figure 3 show the differences in soil removal with an increase in the amount and type of soil application. The more continuous the film of soil, the greater the difficulty and the less complete the soil removal, and the greater the STP concentration required.

c) *Quartz as a Substrate.* Quartz slides were prepared as for glass, and a spotted soil was applied. The curve shown in Figure 3 indicates that the soil removal characteristics for the quartz substrate are similar to glass and that the soil is somewhat more difficult to remove at the lower concentration level.

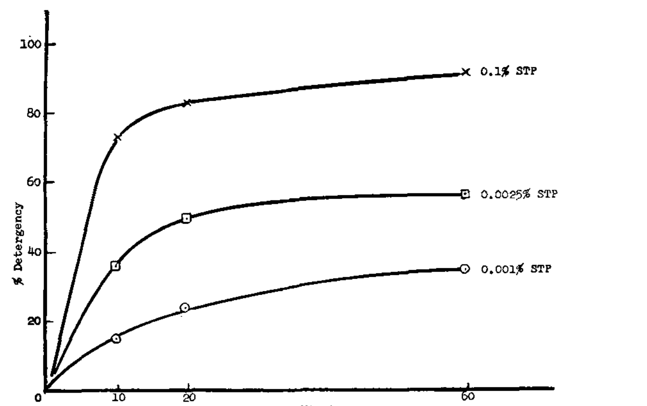

FIG. 2. Soil removal as a function of concentration. Spotted soil—wash temp. 75°C.

Discussion

STP Effect. The surprising ability of STP to prevent the strong adherence of tristearin soil as a result of pretreatment of the glass substrate was not anticipated. The few literature references concerning glass and builders are concerned with the adsorption of sodium (4) or of sodium orthophosphate (3). The latter was said not to be adsorbed in appreciable amount though other investigators who treated glass surfaces with sodium hydroxide found that orthophosphate was adsorbed. This was believed to be a good indication of alkali attack (2). The data of Table I suggest no greater adsorption of orthophosphate than for sodium carbonate or NaOH (or that adsorbed orthophosphate had no effect on resoiling) whereas the adsorption of the sequestrant type of anions had appreciable effect and was considerably greater than for less complex compounds.

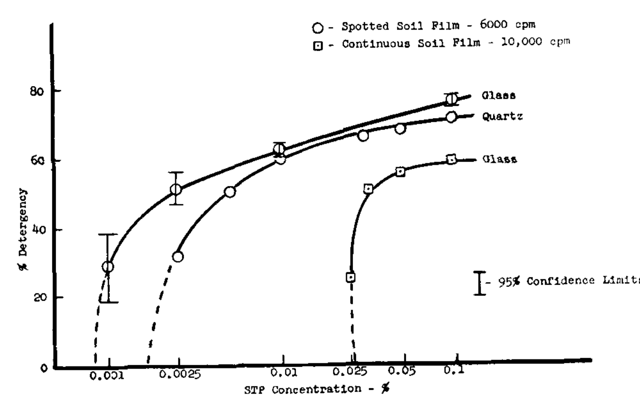

FIG. 3. Spotted *vs.* continuous soil film removal.

The detergent effect of the polyphosphates, and to a much lesser degree, of metasilicate, is evident from Table II, in which the sequestrant type of compounds is the more effective soil remover (from caustic pretreated glass).

Figures 1 and 2 show that soil removal is a function of time and concentration for the temperature studied and that once a 10-min. wash period is attained, soil removal increases less markedly with concentration increase.

Mechanism. Two mechanisms are actually involved: the STP effect (sequestrant anion) and the mechanism of soil removal.

Several hypotheses for the STP effect may be advanced: adsorption at primary sites with a hydration effect, competition for polar adsorption sites *per se,* and base exchange with Mg and Ca ion sites. That a hydration effect (surface-adsorbed moisture) was not involved was shown by baking the soil in a normal manner; the soil remained relatively easy to remove with STP-treated disks. Normally a layer of moisture must probably be present for soil removal is much greater with regularly prepared disks when not "aged." Base exchange is probably not involved since quartz should be essentially free of exchange sites, such as those present in glass; yet, as shown in Figure 3, STP continues to have excellent soil-removal effect. Others (3) have shown that sodium is adsorbed on both glass and quartz though the extent for the latter substrate is less by about 75%. Such a degree of lowering with STP was not found, suggesting either that the same adsorption sites which adsorbed sodium were not involved or that others are active with STP and this soil. This leaves only a competition for polar adsorption sites between STP and the tristearin, and whichever was adsorbed first would have considerable influence on the ease of replacement by the other. The fact that oily soil is more readily removed from a STP-treated substrate and that STP can almost completely remove tristearin from the fat-treated substrate suggests the greater polarity of the STP system, as might be expected.

The mechanism of soil removal for solvent system removal of tristearin (1) from glass consists either of dissolution of coherent soil or a "stripping" or preferential displacement process for removal of adherent (adsorbed monolayer) soil. Since STP is neither a solvent nor a surfactant, neither dissolution nor micelle solubilization is involved for this system in coherent soil removal. Instead it appears that the upper soil layer may be removed in part by emulsification, but more likely that both coherent and adherent soil are removed nearly simultaneously by the "stripping" or preferential displacement mechanism. The lower layer is desorbed and, along with it, coherent soil. In support of this hypothesis is the fact that the continuous soil film of Figure 3 is removed with much more difficulty (time and concentration increase) than the spotted soil application. For the latter type of soil application, the potential area for penetration and contact is obviously much greater.

Implications. Use of STP in dishwashing compositions has generally been based upon its effectiveness as a sequestrant type of water softener. While it certainly has these characteristics, these data show its much broader utility. Sequestrant type of softeners are the only ones found to pretreat glass surfaces so that subsequent soiling is less retentive. Soiling prevention occurs through pretreatment, but, more important, once a soiled glass (not pretreated) has been cleaned with a composition containing appreciable amounts of STP, the effect upon subsequent soiling is that of a soil-preventive pretreatment. STP not only softens water without precipitation, it is an effective detergent for an oily soil and, when used for washing, imparts a soil-resistant surface to the glass.

Additional Factors Requiring Investigation. This report is the first of several, for factors which must be investigated are: effect of other builders, builder combinations, builder-surfactant combinations, adsorption-desorption isotherms, other soils, and other substrates.

Summary

The mechanism of radio-tagged tristearin removal from a glass substrate by sodium tripolyphosphate is primarily one of preferential displacement. Tristearin removal by STP appears to be a competition for primary polar adsorption sites: being the more polar, STP displaces the soil. Continuous soil films are more slowly removed than spotty soil films because initially fewer accessible adsorption sites are available for displacement attack by STP. It is believed that emulsification of these heavy films occurs initially by the "stripping" or preferential displacement by STP of the adsorbed monolayer at a site, followed by a rolling up of coherent soil along with the desorbed monolayer, resulting in a degree of emulsification.

In addition to its sequestrant water-softening action, previously considered its main function, and its detersive effectiveness, another very important feature has been discovered. Tripolyphosphate (and sequestrant type of anion) adsorbs on a glass surface and reduces the tenacity of subsequent fatty resoiling. This may account to a considerable degree for the demonstratedly high practical cleansing effectiveness of the compound.

Adsorption of STP is not by a base exchange mechanism for quartz also displays the same effect as glass. It seems apparent that the same type of adsorption sites exists on both glass and quartz surfaces though those on quartz suggest either a stronger adsorption of a higher energy level or a larger number of adsorption sites.

These data demonstrate the relatively high detersive efficiency of the polyphosphates for this soil/substrate system. Sodium metasilicate and sodium carbonate fall considerably lower in soil-removal value.

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Direct Extraction of Jojoba Seed[1]

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JOJOBA SEED contains about 50% of a liquid wax, the composition of which is unique in that it is one of the few agricultural products known to have such high proportions of C_{20} and C_{22} acids and alcohols combined as esters. This liquid wax is generally referred to as an "oil" because of its liquid state at room temperature. In several reviews and technical publications (1, 8, 10, 11) it has been shown that both the oil and the products derived from the oil have

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