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Soil Redeposition

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AN EFFICIENT detergent composition not only removes soil from substrate but also prevents redeposition. Detergents and soaps formulated with inorganic builders are highly efficient for removing soil; however, without the use of whiteness retention aid, these systems permit soil redeposition and the clean fabric areas soon show loss in whiteness. The redeposition problem first received attention when efficient synthetic detergents useful in hard as well as in soft water became available at attractive costs. Hindered originally by the whiteness retention problem, use of synthetic detergents advanced rapidly after the discovery in Germany (1) that sodium carboxymethylcellulose (CMC) is an effective antiredeposition aid.

Investigations of the antiredeposition mechanisms have emphasized the importance of polymer adsorption on fabric and/or soil with a resulting increase in repulsion force between the two. Adsorption of CMC on cotton has been demonstrated and the exceptional efficiency of this polyelectrolyte has been related to the polymer-fabric interaction.

Laboratory, home, and commercial laundry evaluations illustrate the high level of whiteness retention achieved by use of 0.5–2.0% polymer additive in representative built soap and synthetic detergent compositions.

The extensive literature on this subject, which was ably reviewed in 1959 by Harris (2), attests to the importance of formulating detergents to prevent soiling in the washing cycle.

Because of the commercial importance of antiredeposition, a large number of water-soluble polymers differing widely in composition and functionality have been evaluated. However, despite the variety of polymers tested, only a few offer the high level of efficiency required to make them commercially attractive.

Laboratory Evaluation Procedures

A number of reliable and rapid laboratory procedures have been developed for determining the whiteness retention properties of detergent systems and for studying the interactions of detergents, builders, fabrics, and antiredeposition additives. Unless otherwise indicated, the work reviewed in this paper is based on use of cotton, commonly selected for its commercial importance as a washable fabric. Soil redeposition is usually measured by decrease in apparent reflectance when clean, white fabric is washed either 1) in a washload containing standard soiled fabric, or 2) in a detergent solution to which a controlled amount of soil has been added. The first method has the apparent advantage of similarity to end-use conditions in that clean fabric areas are washed in the presence of heavily soiled ones and the soil load is developed during the washing cycle. One criticism is that the soil load under which the antiredeposition aid must function is variable and dependent on the deterging efficiency of the surfactant. However, many investigators (3,4,5,6) have used this method successfully. Advantages cited (2) for the soil addition method include control of concentration, particle size, and state of aggregation of soil. As will be discussed later, results correlate well with end-use tests.

A variety of materials have been evaluated in the search for representative soils that can be used under controlled conditions. For the soiled fabric method, oily carbon (5,6), synthetic soils based on the analysis of street sweepings (8), and blends of the two (3,4) have been used extensively. Commercially available soiled cotton fabrics can be used for redeposition testing and are described by Harris (9).

Amorphous (10,11) and crystalline (12,13) forms of carbon black have been used as soil additives. Other synthetic soils used include raw and burnt

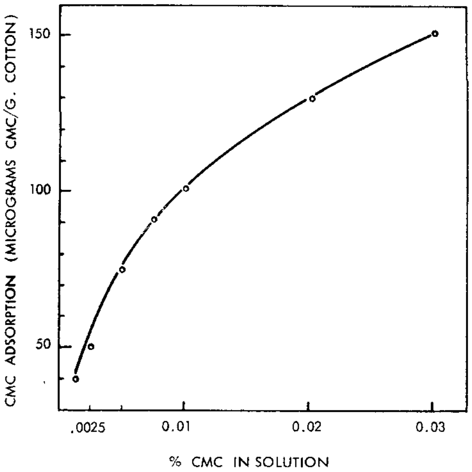

FIG. 1. CMC adsorption on cotton (28).

Test conditions: 10-min exposure of cotton disc at 140F in detergent solution containing 0.1% Na alkylarylsulfonate and 0.15% Na_2SO_4.

umber (10), ilmenite (14), and ferric oxide (15). In the search for realistic systems, vacuum cleaner dust (16,17), clay (18), and simulated street sweepings (8) have been used successfully.

Nearly all reports of redeposition studies are based on the use of reflectance measurements to determine the amount of soil on a substrate. Small differences in reflectance are readily detectable. Several successful applications of the Kubelka and Munk equation (19,20,21) for relating reflectance to quantity of soil on fabric indicate that reflectance values can be used as measures of the quantity of soil at the low levels encountered in redeposition studies.

The amount of redeposited soil has been determined directly by Utermohlen and Wallace (15), who worked with iron oxide pigment as a soil component. Harris and coworkers (21) employed graphite, which was determined turbidometrically after the fabric had been dissolved. Martin and Davis (18) used a gravimetric determination of clay to correlate reflectance values with quantity of soil on fabric. Radioactive carbon prepared by reducing carbon-14 dioxide affords excellent precision for research studies (22).

The validity of laboratory test data obtained with carbon black dispersions and with clay has been demonstrated by comparing results with whiteness retention values obtained in multicyle washing of naturally soiled garments in both commercial laundries and home-type washing machines. Vaughn and Suter (10), found that three detergents—a soap, a built soap, and a built synthetic anionic containing CMC—gave the same ratings when compared in laboratory single-cycle test and in multicycle commercial laundry evaluation. Kramer (23,24) noted the improved whiteness retention obtained by adding CMC to a built soap and to a built alkylarylsulfonate in laboratory single-cycle washings with Aquablak B* and confirmed this effect in commercial laundry trials. In a study of the effect of CMC, Vitale (13) confirmed laboratory test results based on use of a graphite dispersion (Aquadag**) with whiteness retention differences observed in a home washer test, in which towels soiled both in home and plant use were laundered with a built anionic detergent. In work with three detergents—an unbuilt soap and an alkaline-built alkylarylsulfonate used with and without CMC—Martin and Davis (18) obtained the same whiteness retention rankings when comparisons were based on test swatches washed in a Terg-O-Tometer in the presence of clay soil and on five-cycle washing tests in which naturally soiled garments were laundered in a home-type washer.

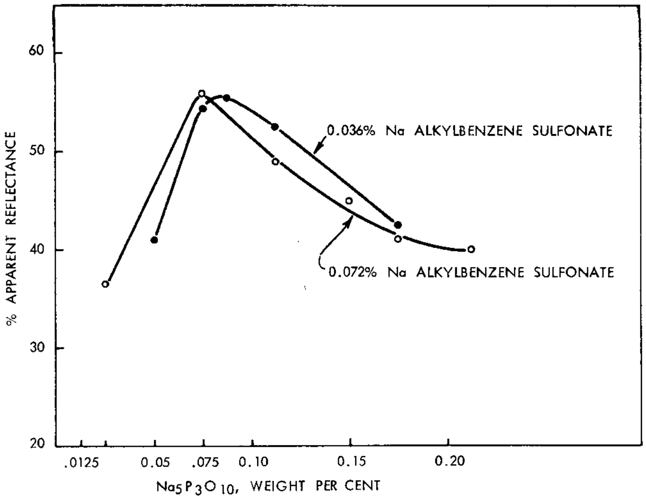

FIG. 2. Effect of sodium tripolyphosphate on the whiteness retention of an alkylarylsulfonate in hard water (38).

Test conditions: temperature—120F; water hardness—360 ppm (as $CaCO_3$); and soil—0.03% "as is" Aquadag.

Mechanisms Proposed to Explain the Soil Redeposition Process and the Function of Antiredeposition Polymer Additives

The large number of variables and possible interactions in aqueous systems containing surfactant, inorganic builders, particulate soils varying widely in chemical and physical properties, fabrics made from a variety of fibers, and ionic or nonionic antiredeposition polymer additives contribute to the problems of experimental work on the redeposition process. The complexity of these systems readily accounts for differences observed in experimental work on the antiredeposition process. Undoubtedly the mode of action of a polymer additive is not limited to a single mechanism, and differs as use conditions vary.

Application of colloid stability theory to the results of studies of adsorption and electrophoretic mobility defines some of the forces that must be effective in preventing redeposition, and also indicates additional processes that may be at work. These studies show that CMC, a polyelectrolyte, is specifically adsorbed on cellulose fibers and increases the effective repulsive force between fabric and soil. Reduced deposition of carbon soil in the presence of nonionic polymers, e.g. PVP* or PVA*, has been related to polymer configuration and resultant steric effects due to polymer adsorption on soil particles.

The deposition and retention of soil on fabric is related to mechanical, chemical, and electrical forces (25). The first includes macro-occlusion, related to inter- and intra-yarn entrapment, and retention due to irregularities of fiber surface described as micro-occlusion (26,27). Ionic effects and coordinate bonding (25), particularly hydrogen bonding, account for important chemical forces. Stains are formed when these forces are strong.

In an aqueous system, fabrics and soil particles

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* Binney and Smith Co., New York, N.Y.

** Acheson Colloids Corp., Port Huron, Mich.

* Polyvinylpyrrolidone and poly(vinyl alcohol).

TABLE I

Examples of Polymers Tested as Antiredeposition Aids

		Reference
A—Ionic Water-Soluble Polymers		
Cellulose Ethers	CMC, Carboxymethyl hydroxyethyl cellulose	2,48
	Hydroxyethyl cellulose	
	Sulfoethyl cellulose	
	Sulfoethyl hydroxyethyl cellulose	
	Sulfomethyl celluose	
Starch Ethers		49
Sodium Polyacrylate		37
Sodium salt of the copolymer of styrene and maleic anhydride		37
Sodium salts of copolymers of acrylic or methacrylic acid with vinyl sulfonic acid		50
Sodium cellulose sulfate		51
Proteins (gliadin, gelatin, and casein)		37
B—Nonionic Water-Soluble Polymers		
Poly(vinyl alcohol), partially acetylated		52
Polyvinylpyrrolidone		53
Poly(ethylene glycol)		37
Cellulose ethers (hydroxyethyl cellulose and methyl cellulose)		44
N-methylacrylamide/vinyl alcohol copolymer		54
Poly(vinyl ether of diethylene glycol)		55
Cyanoalkylated polysaccharide		56

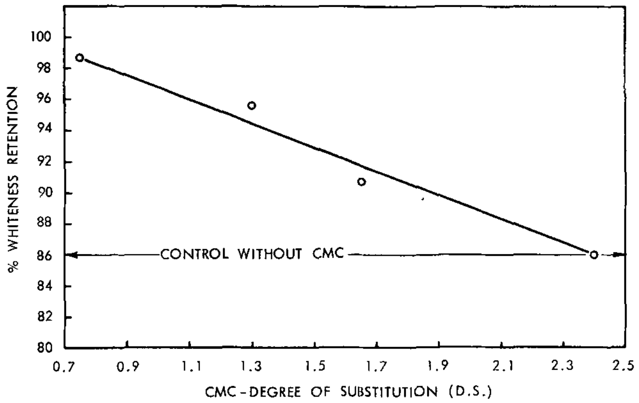

Fig. 3. Effect of degree of substitution on the antiredeposition properties of CMC (32).

Composition of heavy-duty liquid detergent used:

18% Triethanolamine alkylarylsulfonate
4.3% Sodium xylene sulfonate
5% Lauric acid/alkanolamine condensate
15% $K_4P_2O_7$
10% Potassium silicate (29% solids) solution
3% KOH
1.0% CMC, and balance water

usually have negative charges. Magnitude of the repulsion force between particles, which can help to reduce mechanical entrapment, is affected by van der Waals' attractions or dispersion forces effective at molecular distances and by electrokinetic forces due to charges on the particles and the diffuse double layer of ions at the particle-liquid boundary.

The antiredeposition efficiency of CMC for cotton has been related to its adsorption on cellulose fibers, which has been measured by a number of workers (3,28,29,30,31,32,33,34). Radiotracer techniques have been especially useful in these studies. Using carbon-14-labeled CMC, Hensley and Inks (28) as well as Stawitz, Klaus, Höpfner (29) found adsorption was low on cotton from water containing only CMC; however, addition of inorganic electrolytes representing those commonly used in built soaps and detergents gave a pronounced increase in adsorption of CMC. Figure 1 shows the amount of adsorption on cotton at 60C. after a 10-min exposure to an 0.25% solution of a commercial alkylarylsulfonate detergent (40% organic, 60% Na_2SO_4) containing practical use levels of CMC, ½ to 1% of the built detergent.

The development of increased electrokinetic repulsion forces has been related to ionic polymer adsorption on cotton. Stillo and Kolat (12) used Wiley-milled cotton fibers to determine the effect of antiredeposition aids on the electrophoretic mobility of fibers. From these measurements they calculated the change in zeta potential due to adsorption of the antiredeposition aid and concluded that anionic CMC in the viscosity and substitution range of detergent grade polymer increases the negative potential at the fiber—liquid boundary and has little or no direct electrical effect on carbon soil. Using polymers substituted at the 0.7 and 1.2 levels, they found that the lower substitution gave nearly equal negative zeta potentials on fiber and soil thus increasing the repulsion force. The difference in whiteness retention efficiencies of these two polymers was found to be in the agreement with effects on zeta potential.

The efficiency of nonionic additives in improving the whiteness retention of synthetic fiber fabrics suggests that other processes not directly dependent on electrical effects must be considered. Fong and Ward (35) found that a nonionic polymer, PVP, showed no adsorption on fibers but was adsorbed on carbon and could, therefore, reduce the van der Waals' attractions between soil and fiber. Stillo and Kolat (12) note the importance of steric hindrance in preventing soil redeposition and suggest that an increase in the minimum permitted approach of soil and fabric effectively decreases the nonelectrical attraction forces.

In a study of flocculation and soil deposition, Reich (36) noted that, as would be predicted, deflocculation is often accompanied by decreased deposition. However, he also noted many exceptions and concluded that deflocculation is "neither necessary nor sufficient" for preventing deposition.

Although these studies have not as yet led to the development of new additives, they are useful guides for improving the efficiency of polymers known to be active.

Effect of Inorganic Electrolytes

Use of inorganic electrolytes offers important detergency advantages but can cause an increase in soil redeposition (13,14,37,38). However, this effect is not serious, and can readily be corrected by use of an antiredeposition aid. Redeposition increases with increasing cation concentration and valence. The effect can be minimized by choice of anion and by use of monovalent metal salts. Vitale (13) compared the redeposition effects of the sulfate, carbonate, phosphate, and metasilicate salts of sodium in a carbon dispersion redeposition test. Using 0.1% sulfated coconut monoglyceride detergent and an 0.18% inorganic electrolyte concentration, he obtained the least soil deposition with metasilicate and pyrophosphate salts. His work demonstrates the importance of cation valence; a concentration of only 0.0125% of a bivalent metal sulfate caused as much deposition as the sodium salt at 0.2%. Importance of electrolyte cation valence is further illustrated in the work of Ross, Vitale, and Schwartz (38) who used an Aquadag dispersion test and related soil deposition to the flocculating effects of cation concentration and valence as defined by the Schulze-Hardy rule.

In hard water, inorganic phosphate builders reduce soil redeposition by suppressing the concentration of bivalent cations. Figure 2 shows the stoichiometric relationship between bivalent cation concentration in hard water and the amount of tripolyphosphate ion required to give maximum whiteness retention as

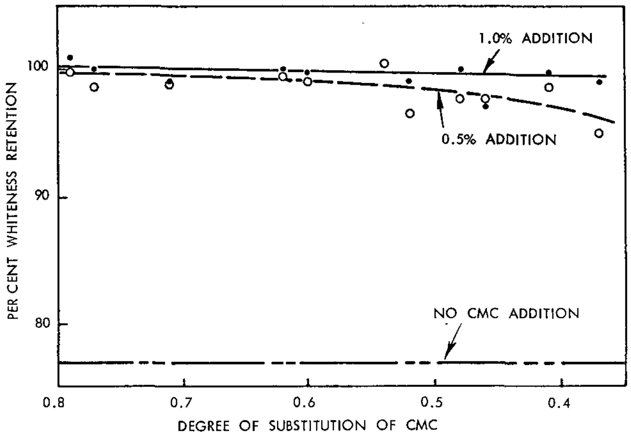

FIG. 4. CMC: Degree of substitution vs. per cent whiteness retention.

Conditions:

Three washing cycles with fresh soiled cloth and detergent solution being added in each cycle.

Detergent formulation: 30% Sodium alkylarylsulfonate, 20% Sodium sulfate, 50% Sodium tripolyphosphate.

Detergent conc.: 0.2% in hard (300 ppm $CaCO_3$) water.

demonstrated by Ross, Vitale, and Schwartz, who used an Aquadag dispersion whiteness retention test. The peaks for the 0.036% and 0.072% alkylbenzenesulfonate curves are at approximately the same sodium tripolyphosphate concentration, that which is required to sequester the calcium ion of 360 ppm hardness (39). Reduced whiteness retention at higher concentrations further illustrates the effect of inorganic electrolytes.

Effect of Molecular Weight and Degree of Substitution on Efficiency of Polymer Additives

Table 1 lists representative polymers for which antiredeposition properties have been reported. The list includes a wide range of water-soluble synthetic and naturally occurring, anionic and nonionic polymers. The wide range of testing conditions used to evaluate these polymers and the evaluation of many of them at high concentrations make it difficult to draw generalizations about the effects of composition on antiredeposition efficiency. However, by working with one polymer type, the effects of molecular weight and degree of substitution (D.S.*) can be studied.

Nieuwenhuis (3), who studied the effect of D.S. of CMC on whiteness retention, suggests the optimum level should be high enough to minimize polymer aggregation in solution, and that values above the optimum reduce adsorption on fiber because of increased negative charge. Investigators working independently in several laboratories have shown that optimum D.S. is in the range of 0.6–0.8. The data in Figure 3 show decrease in antiredeposition efficiency as D.S. is increased to levels above 1.3. Figure 4 shows the effect of D.S. for values of 0.4–0.8 for polymer used with an alkaline-built alkylarylsulfonate detergent at two levels, 0.5 and 1.0% of the weight of detergent. The data show maximum efficiency in the 0.6–0.8 range. Smola and Skoda (4) report that an optimum CMC polymer has a D.S. of 0.6–0.8, freedom from gelled material, and a degree of polymerization (D.P.) of 200–500. The detergent grades of CMC commonly used are in this range.

TABLE II

Effect of Molecular Weight on the Antiredeposition Properties of Nonionic Additives (37)

P V P		P V A (99% Hydrolyzed)	
Design	%, Reflectance	Design	%, Reflectance
K87* – 750,000 MW	29	Elvanol** 72-51, High Visc.	48
K62* – 250,000 MW	33	Elvanol** 71-24, Med. Visc.	53
K44* – 100,000 MW	38	Elvanol** 70-05, Low Visc.	55
K29* – 40,000 MW	53		
K21* – 15,000 MW	55		

Test conditions: White cotton fabric was exposed to an alkaline-built alkylarylsulfonate detergent solution containing 0.1% carbon black and 0.005% of the respective antiredeposition additives.
* General Aniline and Film Corp.
** E. I. du Pont de Nemours and Co.

Several investigators have used nonionic polymers to study composition and molecular weight effects. Work of Fong and Lundgren (37) on the influence of molecular weight of PVP and PVA on efficiency is shown in Table 2. They concluded that the decrease in efficiency at the higher molecular weight range used in the study may be related to the tendency of the larger molecules to coil and react with themselves at a loss in adsorption on soil or fabric. The relationship between molecular weight and efficiency of PVP shown in Table 2 is confirmed in work published by Azorlosa (40) who compared the antiredeposition properties of polymers with a 10,000 mol wt (PVP-K-15**) and 40,000 (PVP-K-30**). The comparison was made in an Aquablak B test in which an alkaline-built anionic containing 1% PVP was used as detergent at a concentration of 0.2%. In a study of the effect of composition, Fong and Lundgren (7) found that 77%- and 88%-hydrolyzed grades of PVA show advantages over the 99%-hydrolyzed grade and concluded that partial "acetylation" also reduces the

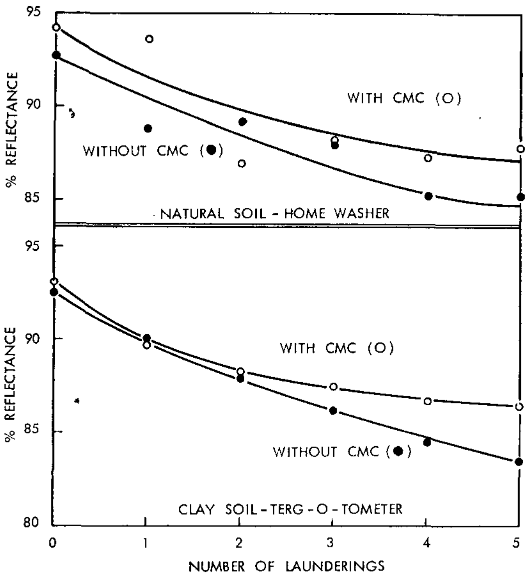

FIG. 5. Effect of CMC on the whiteness retention of a built synthetic anionic detergent (18).

Composition of test detergent:

20%	Sodium alkylarylsulfonate
2.2%	Lauric diethanolamide
10.8%	Sodium sulfate
41.8%	Tetrasodium pyrophosphate
14.0%	Sodium tripolyphosphate
11.2%	Sodium metasilicate

Test conditions:

Detergent conc.—0.25%
Temperature—120F
Water hardness—137 ppm as $CaCO_3$
Fabric—cotton

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* Number of carboxymethyl groups per anhydroglucose unit.

** General Aniline and Film Corporation.

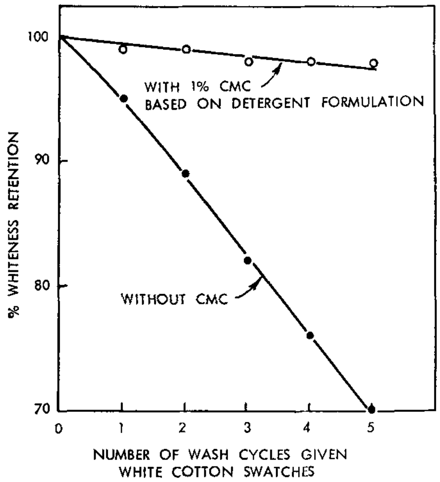

FIG. 6. Effect of CMC on the whiteness retention of a built nonionic detergent.

Test conditions:

Detergent conc.—0.25% of a formulation containing: 22.5% of a 1/1 blend of an ether- and ester-type nonionic, 2.5% sodium alkylarylsulfonate, 50% sodium tripolyphosphate, and 25% sodium sulfonate.
Temperature—110F
Water hardness—340 ppm as $CaCO_3$
Washing device—Terg-O-Tometer

tendency for self-interaction and curling.

Polymeric antiredeposition aids have proved to be commercially important for built anionic, nonionic, and soap systems. The following examples illustrate their use in representative detergent systems for cotton and for synthetic fiber fabrics.

Detergent Formulations for Improved Whiteness Retention of Cotton Fabrics

Alkaline-Built Synthetic Anionic Powders

An investigation by Martin and Davis (18) of the correlation of laboratory test data with whiteness values of fabrics laundered in a home-type washing machine illustrates the use of polymer additive in an alkaline-built, synthetic anionic-type detergent, frequently described as the "work horse" of the household laundry market. Composition of the detergent and the improvement in whiteness retention obtained by use of the whiteness retention additive in both the clay soil test and in the washing of naturally soiled garments are shown in Figure 5.

TABLE III

Antiredeposition Aids for Noncellulosic Fibers
Blend of CMC with PVA (43)

Formulation	%, Reflectance of Nylon after Washing
Ivory Snow*, 0.5%	26
Ivory Snow, 0.5% + CMC-70M, 0.0125% + Elvanol 51-05, 0.0125%	42
Arctic Syntex T**, 0.5%	17
Syntex T, 0.5% + CMC-70M, 0.0125% + Elvanol 51-05, 0.0125%	63

P V P (47)

Fabric	Reflectance Loss	
	Without Antiredeposition Additive	with PVP K-15
Dacron	33.8	4.8
Nylon	63.0	26.1
Orlon	41.1	10.3
Dynel	50.6	37.0

Detergent: 21% active alkylarylsulfonate, 40% $Na_5P_3O_{10}$, 32% Na_2SO_4, 6% metasilicate at a total concentration of 0.20%.
* Commercial fatty acid soap manufactured by Procter and Gamble.
** $C_{17}H_{33}CON(CH_3)C_2H_4SO_3Na$, Colgate-Palmolive Company.

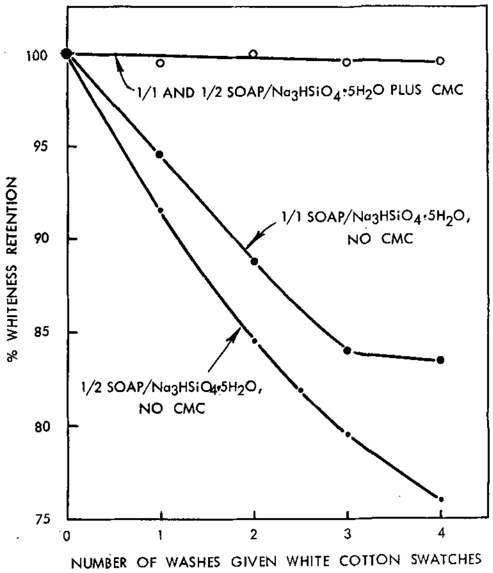

FIG. 7. Effect of CMC on the whiteness retention of a sodium sesqui-silicate built soap.

Test conditions:

Built soap conc.—0.2%
Temperature—140F
Water hardness—50 ppm as $CaCO_3$
Washing device—Terg-O-Tometer
CMC conc.—1.5% based on weight of built soap

Nonionic Synthetic Detergent Powders

Household use of nonionic surfactants in 1962 in a variety of applications has been estimated (41) at 110 million lb. Uses include detergent powders, especially those formulated for low or controlled sudsing. Figure 6 gives a comparison of whiteness retention values for two detergents of this type, one containing CMC at the 1% level, the other used as a control. Differences in reflectance illustrate the advantage of adding a polymer to prevent redeposition.

Alkaline-Built Soap

Alkaline builders are used extensively with soap. However, addition of builders is accompanied by a loss in antiredeposition efficiency, which can be corrected by use of polymer additive as demonstrated by a number of investigators (3,5,34,42,43,44,45,46). Nieuwenhuis (3,46) has summarized the results of extensive laboratory and laundry tests showing improved whiteness retention when an additive is used with built soaps.

Figure 7 shows the ffect of CMC added to a silicate-built soap and compares whiteness values for two ratios of soap to builder. Polymer additive was found to be equally effective at the two soap/builder ratios.

Antiredeposition Aids for Noncellulosic Fibers

Review of the literature on antiredeposition aids shows that most of the work reported has been directed toward improved detergent systems for cotton. In contrast with this emphasis on antiredeposition aids for cotton, to be expected in view of its importance as a washable fabric, the use of additives for washing synthetics has received little attention.

Compton and Hart (43) studied the use of PVA in blends with CMC to obtain antiredeposition properties with nylon. Effectiveness of these blends as additives for either a synthetic detergent or a fatty acid soap is summarized in Table 3. Aquablak B was used as the soil.

Azorlosa and Martinelli (40,47), who worked with cellulosic and noncellulosic fibers, suggest that CMC and PVP might be blended to advantage when whiteness retention of cotton—synthetic fiber blends is the objective. Table 3 summarizes data on the efficiency of PVP for protecting nylon, Dacron*, Orlon*, and Dynel** when washed with an alkaline-built anionic in the presence of a heavy soil load, Aquablak B.

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Correlation of Detergency with Physicochemical Factors

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In 1949, Foster D. Snell suggested that eventually it would be possible to calculate the soil-removing efficiency of surfactants for specific, soil-substrate, detergent applications by a formula whose parameters were selected physiocochemical factors of the detergency mechanism (1). He visualized a hypothetical function (1) like this:

$$\text{Detergency} = 0.14\,X + 0.61\,Y + 0.21\,Z + 0.32\,W$$

In which, X = wetting power
Y = dispersing power
Z = micellar solubilization
W = contact angle

The units of these variables were not defined. This prediction, still unfulfilled, emphasized the complexity of detergency and implied the difficulty of its correlation with a single factor or action. Both points are demonstrated by the changing regard for Preston's well-known relationship (2) that the detergency of an ionic surfactant is *proportional to its long-chain* ion concentration. The relationship is probably more recognizable in its corollary form that maximum detergency occurs at or very near the critical micelle concentration (CMC). The unqualified validity of this concept, which was developed in a study of laundry detergency, has been seriously questioned of late. It has been shown that in hard surface detergency, maximum soil removal is attained at concentrations considerably greater than the CMC (3,4,5). Preston's experiments were influenced by the cotton fabric substrate he used. In addition it is reasonable to assume that his launderometer data, while simulating practical laundering, was dependent to an appreciable degree on mechanical action, another variable of the detergency mechanism. It seems probable, therefore, that the higher surfactant concentrations necessary for attaining maximum hard surface detergency are due in part to the absence of such vigorous mechanical agitation.

Excellent reviews of the extensive field of detergency correlation are available, from the surveys of the older work by McBain (6) and by Fall (7) which include references to the almost forgotten factors of gold number, carbon number and dye number, to the recent treatise of Schwartz and his co-workers (8). It is safe to say that in common with Preston's relationship the principal characteristics of the proposed correlations is their limited applicability.

I hope the preceding remarks concerning some of the problems of detergency correlation will serve as a background for the description of the scope and status of its investigation at the U. S. Army Coating and Chemical Laboratory.

Our work on this subject has been in the fields of both applied and basic research. In applied research we have indicated the presence of detergency correlation in commercial soak alkaline cleaners of improved