

Antiredeposition Additives Face New Opportunities

G.K. GRENINGER, JR., Designed Products Department, 2040 Bldg., Dow Center,
A.S. TEOT, Central Research, 1712 Bldg., and N. SARKAR, Designed
Polymers & Chemicals Res. Lab., 1604 Bldg., Dow Chemical Company, Midland, Michigan, USA

ABSTRACT

Recent trends in fabric composition, choice of raw materials, and government regulations are placing new demands on the use and utility of antiredeposition additives.

INTRODUCTION

The practical problem of preventing redeposition of soil removed during the laundering of fabrics is critical in the design of a detergent formulation. The chemical and physical interactions are very complex, and variables such as fabric composition, the nature of the "builders," the physical nature and composition of the soil, the chemical structure of the surfactants, the product form, and laundering procedures, all can effect the choice and performance of the antiredeposition agent.

The laundering process is an equilibrium situation requiring knowledge of colloidal effects such as adsorption, electrolyte interaction, protective colloid action, and wetting. Much current know-how has been acquired by practical end-use testing in both the laboratory and marketplace. There are still many opportunities and a need to develop newer theoretical bases for better prediction of the activity of antiredeposition additives.

This paper will review some current trends and will focus attention on some unsolved problems facing the chemist when he attempts to improve the performance of antiredeposition agents in a detergent formulation.

EFFECT OF FABRIC COMPOSITION

In recent years, there has been a tremendous growth in the use of synthetic fibers. According to Dr. Brian Smith, chairman of ICI Fibres, this growth should continue, and he expects synthetic fibers to capture 45% of the world market by 1985 (1).

This increasing use of synthetic fibers (having differing affinities for particulate and liquid soils) requires the development of new information on optimum means of removing such soils. The ease with which polyester fabrics adsorb oily soils is a typical problem.

One approach has been the development of permanent-type finishes to be applied at the textile mill or by subsequent treatments in dry cleaning shops. Considering the variety of garments in the average family wash, there is also a place for an additive to be applied during home laundering to provide some degree of antisoiling protection. Such an additive should ideally be effective on both cotton and synthetics, and against both particulate and oily soils. An ideal research target would be development of a universal antiredeposition agent able to satisfy the requirements of various laundering procedures and the various fabric and fiber types.

EFFECT OF LAUNDERING PROCEDURES

There are major differences in home laundering practices and equipment used in Europe and in the U.S. For example, European home washing machines are generally

front-loading; while those in the U.S. are mostly top-loading. This can affect the choice of surfactants and consequently the interaction with the antiredeposition agent. Washing temperatures in Europe were traditionally at the boiling point of water. Those in the U.S. were about 55 C. As energy costs increase and as the use of synthetic fabrics (requiring washing at cooler temperatures) increases, the trend in the U.S. is toward 38 C with a testing range of 32-43 C becoming common.

To date, the impact of the fabric label directions on synthetic fabrics has had a greater effect on the shift to cooler washing temperatures than has the energy crisis. These factors also will affect the laundering practices in Europe although wash temperatures in Europe will probably still remain higher than those in the U.S. Another major difference in laundering practices is the ratio of water to fabric. This ratio in Europe is lower than that in the U.S. European practices differ also in the recycling of the wash water which requires more detergent and increases the demand on the antiredeposition agent.

Major changes will continue to occur in the use of builders in detergent formulations as increased governmental pressures work to reduce the impact of phosphates on the environment. Carbonate, zeolite, and unbuilt surfactant products have appeared in the marketplace. There are many new builders in development stage in the U.S. In Canada and Sweden, sodium nitrilotriacetate (NTA) is being used. All of these changes can influence the performance and choice of the antiredeposition agent.

The possible interaction of the surfactant and the antiredeposition additive introduces still another variable. As the industry has moved from branched type to biodegradable alkylbenzene sulfonate type surfactants, and nonionic type of surfactants, there is a need to understand and predict these interactions. These effects are discussed later.

The shift to cooler washing temperatures makes the use of nonionic thermal gelling cellulose ethers more effective. The increased surface tension reduction provided by the nonionic cellulose ethers (vs. the polyelectrolyte cellulose derivatives) can provide increased soil removal activity and emulsifying action for more severe laundering conditions. Thus, there has been substantial growth in the use of nonionic cellulose ethers in the detergent market in the U.S. A better recognition of the nonionic cellulose ethers as polymeric surfactants can open doors to new types of functionality in both powder and liquid detergents.

RECENT TRENDS IN ADDITIVE STRUCTURE

Cellulose Derivatives

The discovery of the antiredeposition properties of sodium carboxymethylcellulose (CMC) in Germany in 1935 overcame a major deficiency of synthetic detergents and has led to the wide-scale use of CMC as an additive to laundry detergents. CMC is a member of a class of compounds known as cellulose ethers. These products are derived from cellulose, a naturally occurring linear, carbohydrate polymer that provides structure and shape to plants and trees. An idealized structure of a cellulose ether is

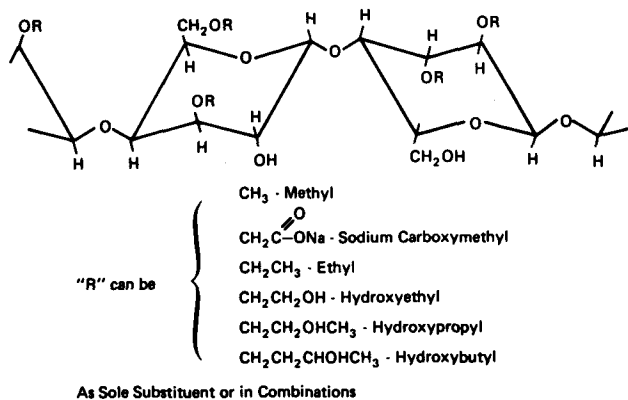


FIG. 1. Idealized structure of a cellulose ether.

TABLE I

Effects of Substitution on Properties of Cellulose Ethers

Substituent group	Surface tension 25 C, Dynes/cm.	Interfacial tension vs. mineral oil, Dynes/cm
$\text{-OCH}_2\text{C}(=\text{O})\text{ONa}$	71	---
$\text{-OCH}_2\text{CH}_2\text{OH}$	~67	23.7-25.5
-OCH_3	47-53	19-23
$\text{-OCH}_3 + \text{-OCH}_2\text{CHOHCH}_3$	44-50	18-19

shown in Figure 1.

The repeating monomer unit is the anhydroglucose ring joined at the one and four positions with a beta conformation. Substitution of modifying groups can occur at any of the three hydroxyls on the ring. A disubstituted polymer is illustrated. Commercial cellulose ethers contain the groups listed under Figure 1 taken either singly or in combination. Of these groups, only sodium carboxymethyl substitution is ionic, all the rest are nonionic in structure.

The type, quantity, and uniformity of the substituent groups have a substantial impact upon the functionality of a specific cellulose ether in a detergent system. Adsorption, surfactancy, cloud point, and compatibility with salts and detergents are affected. For example, hydrophilic CMC, which is a polyelectrolyte, adsorbs onto cotton by hydrogen bonding and repels soil by electrostatic repulsion. However, hydrophilic CMC performs poorly on the hydrophobic synthetic fabrics, and the increasing usage of synthetic fibers in clothing has generated a search for cellulose derivatives with a broader range of activity.

The shift away from the high phosphate builders to carbonate and other types of phosphate-free formulations has resulted in a need for additives able to provide the antiredeposition performance of the phosphate-CMC products. The nonionic cellulose ether which can function as polymeric surfactants provide an additional property not obtained with CMC. The effect of substitution on surface and interfacial tension is shown in Table I.

The many variables affecting the performance of antiredeposition additives make general comparisons difficult; however, the variety of chemical structures appearing in current literature illustrates the present trends for designing specific properties into cellulose derivatives.

A recent study at the University of Tennessee (2) compared the performance of CMC, carboxymethyl hydroxyethylcellulose (CMHEC), and hydroxyethylcellulose (HEC) in anionic and mixed anionic/nonionic detergent formulas. The detergents formulated were ranked by their ability to prevent an oily soil from depositing onto clean fabric swatches. These studies showed that the ability to inhibit

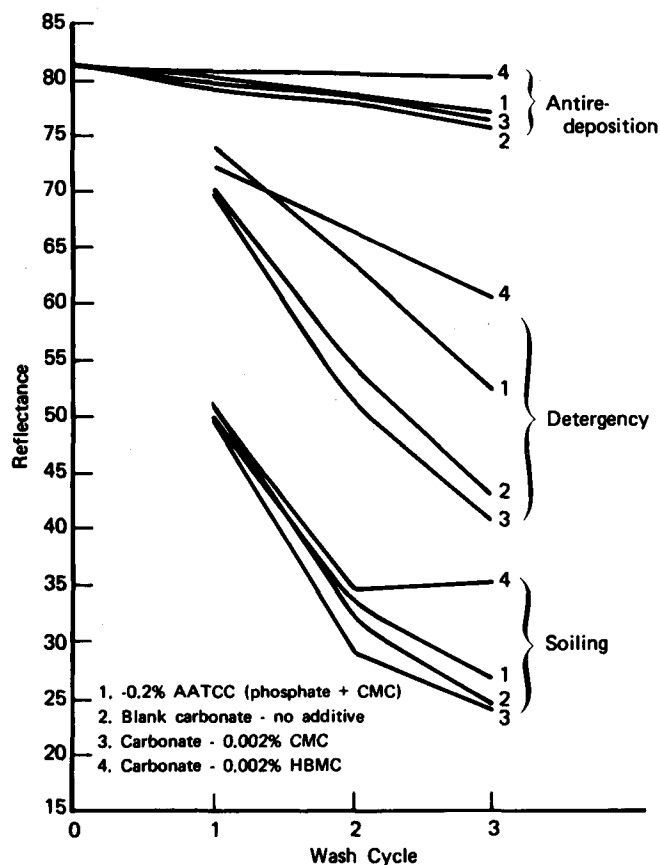


FIG. 2. Detergency and antiredeposition of HBMC. Carbonate formulation - polyester doubleknit.

deposition of oily soil onto blends containing cotton and polyester fiber increased as nonionic hydroxyethyl substitution was added to CMC. The best performance in this series was observed with HEC which contained no carboxymethyl substitution. Two possible effects that may be contributing to the improvement are (a) the introduction of less polar hydroxyethyl substitution on the CMC derivative and (b) the progressive reduction in surface tension as the hydroxyethyl substitution is increased and the carboxymethyl substitution is eliminated.

As shown in Table I, modification of cellulose with methyl and alkylene oxide substitution increases the difference between the hydrophilic and hydrophobic portions of the cellulose derivative resulting in lower surface and interfacial tension and increased emulsification properties for oily materials.

The recent patent literature contains examples of the use of such cellulose derivatives as additives to detergents. A Netherlands patent (3) teaches the use of a nonionic alkyl hydroxylalkylcellulose as an antiredeposition agent with reduced fabric staining by the blue dyes used as whiteners in detergents. The claims cover alkyl groups of 1 to 4 carbons and hydroxyalkyl groups of 2 to 4 carbons. A German patent (4) describes the use of ethyl hydroxyethylcellulose as an antiredeposition agent. Combinations of ionic and nonionic cellulose ethers such as CMC and hydroxypropylcellulose are disclosed in a U.S. patent (5).

If increasing the hydrophobe substitution on a cellulose derivative increases adsorption on a synthetic fiber, there should be an antisoiling effect. This antisoiling effect can be demonstrated by using a laboratory scale soil accumulation detergency test (SAD). Figure 2 (6) shows the results obtained with this type of test.

Polyester doubleknit swatches were used since this type of fabric is tenaciously stained by oily materials. The detergent was a simplified carbonate formula (see appendix for

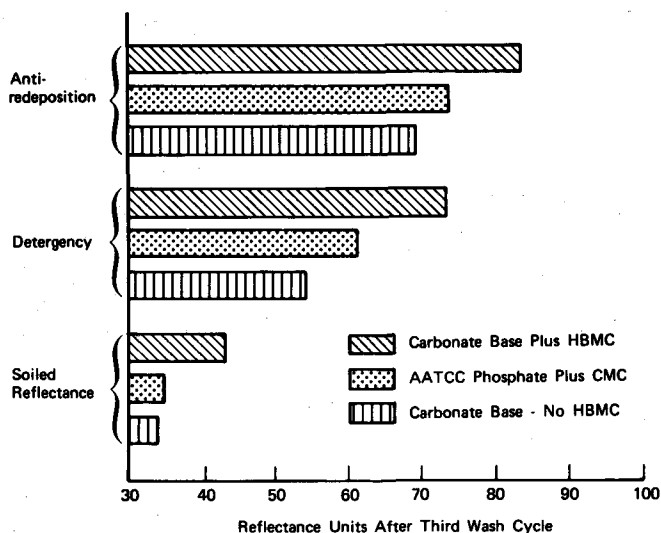


FIG. 3. Effect of prewashing prior to soiling - Dacron 54 spun polyester.

recipe). The effect of the nonionic hydroxybutyl methylcellulose (HBMC) additive was compared against a polyelectrolyte additive, carboxymethylcellulose (CMC). The soil consisted of vacuum cleaner dirt and an artificial sebum of lanolin and oleic acid. The clean and soiled swatches were washed together so this was a redeposition type of test. The soiled swatches were resoiled after each washing. Reflectance measurements were made on the clean swatches to determine graying and on the soiled swatches before and after washing to measure soil shielding and soil removal. A standard AATCC phosphate CMC control was included with each run. Details of these procedures will be found in the appendix.

The top set of curves shows the antiredeposition effect upon the clean swatches. The effectiveness of HBMC, Curve 4, is due in part to the antisoiling effect shown in Curve 4 in the lowermost set of curves which measures the blackening of the soiled swatches upon resoiling. Curve 4 in the latter set plateaus after the second laundering. Multicycle washing shows that the soil shielding effect equilibrates at five cycles. The swatches in this case are presoiled so the adsorption effect requires several laundings to show results. The effect of hydrophobic substitution on improving the antiredeposition and antisoiling properties of the cellulose ether additive is substantial.

Since laundering the fabric with the detergent containing the antiredeposition additive prior to soiling would provide opportunity for the antiredeposition additive to adsorb more effectively onto the fabric, the SAD test was modified by adding a prewash step for all the swatches used in the test. The rest of the procedure remained the same as previously described, and detailed in the appendix.

Reflectance data after the third wash cycle are plotted

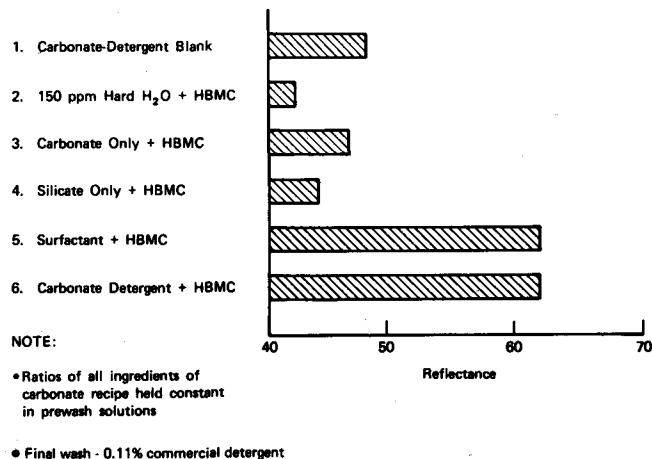


FIG. 4. Interaction of antiredeposition additive with detergent ingredients - used motor oil test.

in Figure 3. The fabric in this case was Dacron 54 spun polyester. Comparison is again made between polyelectrolyte CMC and nonionic HBMC. The improvement in performance obtained by shifting to hydrophobic substitution on the cellulose ether is again apparent.

The used motor oil antisoiling test (UMOAT) is very useful in screening additives and for indicating directions for synthesis of specific structures. This test, which is also detailed in the appendix, consists of a prewash in the detergent solution, drying, staining with several drops of used motor oil, allowing the oil to wick for 2 hours, and a final wash in a commercial detergent followed by measurement of the reflectance of the stain. Any redeposition of oil on the swatch is also readily observed.

This test was used to show the effect of varying the type of substitution on the cellulose ether in Table II. The reflectance of a carbonate detergent system was used as a base line for comparison, and the values are differences from this base. A series of five fabrics was used, and three nonionic cellulose ethers with varying levels of hydrophobic substitution were compared vs. two formulations containing ionic CMC. The data for the CMC-phosphate commercial detergent show decreasing antisoil effectiveness going from 100% cotton to 100% polyester. The phosphate-CMC formulation was better on cotton than the carbonate-CMC formulation. As the level of hydrophobic substitution on the nonionic cellulose derivatives increased, the effectiveness on polyester also increased substantially. The degree of improvement on nylon was substantial compared to CMC, but changing the type of substitution did not result in further improvement in performance. These tests, as mentioned previously, are useful in screening additives and for indicating directions for synthesis of specific structures. Performance in a particular formulation will always require substantiation by other types of testing.

The effect of adding hydroxypropyl methylcellulose to

TABLE II

	Used Motor Oil Test—Fabrics Treated Prior to Soiling Δ from Carbonate Blank-Reflectance Units				
	Commercial phosphate CMC	CMC carbonate	HPMC ^a carbonate	MC ^b carbonate	HBMC carbonate
Cotton	+4.3	-0.6	+1.4	+2.5	-0.4
65/35 Dacron cotton PP	+2.6	+0.1	+8.6	+8.6	+16.9
Dacron 56 doubleknit	+0.4	-0.1	+5.3	+12.2	+32.0
Spun Dacron 54	0.0	+0.9	+9.5	+12.2	+25.2
Spun nylon 6.6	+1.0	+3.0	+8.3	+8.7	+8.9

^aHydroxypropyl methylcellulose.

^bMethylcellulose.

the laundry bath — prior to the start of the laundering cycle to prevent wet soil deposition and to improve stain release — is taught in a British patent (7).

Combinations of methylcellulose and hydroxybutyl methylcellulose, with specific cationic fabric softeners to achieve combined fabric softening and soil release properties, have been disclosed in U.S. patents (8,9). The use of alkyl hydroxyalkylcellulose ethers as soil release agents with water-soluble alkylsulfate surfactants of specific carbon chain lengths is taught in a U.S. patent (10). The patents mentioned point to a trend of using nonionic cellulose ethers containing increased levels of hydrophobic substitution to achieve both improved antiredeposition and soil release on synthetic fibers such as polyester.

Noncellulosic Additives

The noncellulosic antiredeposition additives in commercial use include polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP). The continuing search for better functionality has resulted in modification of these polymers, as with the cellulose derivative. A nondurable antisoiling composition was described (11) as containing copolymers of methylvinyl ether with maleic anhydride and polyacrylic acid, copolymers of acrylic acid with maleic anhydride or *n*-butylacrylate or allyl alcohol, and methacrylic acid-ethylacrylate copolymers. Modification of PVA by copolymerization of vinylacetate with allyl compounds, unsaturated carboxylic acids, and propylene is described in a Japanese publication (12). Combinations of PVA and PVP with borax and either sodium or potassium hydroxide are claimed to be particularly useful for laundering fabrics containing polyester fiber (13). Graft copolymers of vinyl monomers and water-soluble or dispersible polymeric materials are still another route to modification of polymers to achieve antiredeposition properties. A U.S. patent provides examples of the modification of starches with acrylic and methacrylic monomers (14). The trend is again modification of commercial products to achieve better performance in the laundering of fabrics containing synthetic fibers.

Impact of Growth in Liquid Detergents Use

Liquid laundry detergents are expected to have 20% of the U.S. detergent market by 1980, for an average annual rate of growth of 17% (15). The early products were "built" liquids (16). Recently, "unbuilt" products have entered the marketplace. Formulation of liquid detergents can create additional problems for the chemist. The antiredeposition agent must possess compatibility with both inorganic salts and with the surfactants in systems containing builders. In the high surfactant unbuilt systems nonionic cellulose ethers can be salted out by the surfactant.

A recent Soviet publication (17) lists the quantity of substitution necessary to provide compatibility with combinations of sodium and potassium phosphate salts in liquid detergent formulations. The cellulose derivatives cited were hydroxyethylcellulose, carboxymethyl methylcellulose, hydroxypropyl methylcellulose, methylcellulose, and cellulose sulfate. There still is a need for an additive for aqueous liquid detergents that is effective on both cotton and synthetic fabrics, and which also is soluble in the presence of builders and/or high concentrations of surfactants.

One way to avoid solubility problems inherent in aqueous liquid detergents is through formulation of a non-aqueous system. An East German patent (18) discloses the use of a polyethylene glycol mono (carboxymethyl) mono (nonylphenol) ether; sodium salt in such a product.

EFFECT OF SURFACTANT INTERACTION

As the present trend of changing from the hydrophilic polyelectrolyte carboxymethylcellulose to nonionic hydrophobic cellulose ethers takes place, the interactions of sur-

factants with the antiredeposition agent are increasingly important. Effect of this interaction on the detergency, antiredeposition, and antisoiling properties of the laundry cleaning formulation has not been studied. A proper knowledge of these interactions will play an important role in designing proper combinations of surfactant and antiredeposition agent. The used motor oil test can be useful in studying these interactions. Figure 4 shows the effect of pairing the ingredients of a simplified carbonate detergent formulation upon antisoiling properties. In this particular example, the interaction between the surfactant and the hydroxybutyl methylcellulose was the critical factor in achieving antisoiling on polyester fabric (6).

Interactions between polymers and surfactants in aqueous media have been demonstrated by several authors (19-22). The study by Lewis and Robinson (22) is of particular interest since it deals with the interaction between sodium dodecyl sulfate (SDS) and methylcellulose. It is shown that at or near the CMC, a strong binding of SDS onto methylcellulose molecules occurs via hydrophobic bonding. Depending on the mode of interaction, molecular weight of methylcellulose, the concentration of methylcellulose, surfactant, and temperature, the interaction may result in an increase or decrease in viscosity of the solution. Although no studies have been reported on the interaction between nonionic surfactant and nonionic cellulose ethers, similar conclusions are believed to be true in general for any surfactant-cellulose ether systems. The interaction between nonionic surfactant and nonionic cellulose ethers is interesting because individually both behave as nonionic surfactants, show a cloud point, and undergo micellar aggregation. In combination, therefore, they can form mixed micelles. Effect of these mixed micelles on the detergency and antiredeposition character of cleaning formulation is not yet understood, and should be a topic of future research.

Effect of Builders

The choice and type of builder also must be considered for effects on the activity of the antiredeposition agent. The presence of salts with relatively high ionic charge can suppress the cloud point of the nonionic cellulose ethers containing hydrophobic substitution. This can change surface active properties of these polymers. The structure of a builder also can affect the interaction between the surfactant and the antiredeposition additive. This is another area requiring further research. The total system must be considered when formulating a detergent.

DESIGN OF ANTIREDEPOSITION AGENTS FOR THE FUTURE

Because of the ready availability and low order toxicological problems, the cellulosic polymers should be a preferred choice for antiredeposition agents compared to petroleum-based synthetic polymers. As the oil price may increase, the price of synthetic fabric is expected to rise. By the 21st century, cotton, with antisoiling, wash-and-wear, and permanent press properties, could again dominate the clothing market. Depending on the chemical treatment, the need for an antiredeposition agent again will have to be modified. However, in the next decades, synthetic fabrics will remain significant as will demand for a hydrophobic antiredeposition agent.

The design of the antiredeposition agent will be based on a critical balance of hydrophilic and lipophilic properties. Since there are several ways this can be achieved, the emergence of the one with proper HLB to function in presence of both cotton and synthetic fabric is possible. It is not inconceivable that the future antiredeposition agent also will have built-in detergency properties in the molecule.

ACKNOWLEDGMENTS

The detergent test data were obtained by J. Hamlin; O. Neiditch of Lever Brothers Company provided background information. A.B. Savage provided the synthesis support.

REFERENCES

1. Chem. Eng. News, p.15 (May 30, 1977).
2. Noel, C.J., E.C. Easter, and M.E. Carter, *Text. Chem. Color.* 5:93 (1975).
3. Neth. Pat. 7,110,635 to Unilever N.V. (Feb. 8, 1972).
4. W. Ger. Pat. 2,632,218, Dahlgren, K.G., F.A. Koloski, and J.K. Sundberg, to Berol AG (Jan. 27, 1977).
5. U.S. Pat. 3,523,088 to Procter & Gamble Co. (Dec. 13, 1966).
6. Unpublished data from The Dow Chemical Company (1976).
7. Brit. Pat. 1,314,897 to Celanese Corp. (Apr. 26, 1973).
8. U.S. Pat. 3,920,561 to Procter & Gamble Co. (Nov. 18, 1975).
9. U.S. Pat. 3,928,213 to Procter & Gamble Co. (Dec. 23, 1975).
10. U.S. Pat. 4,000,093 to Procter & Gamble Co. (Dec. 28, 1976).
11. U.S. Pat. 4,007,305 to BASF Wyandotte Corp. (Dec. 23, 1974).
12. Jap. Pat. 49,119,902 to Nippon Synthetic Chemicals KK (Mar. 22, 1973).
13. U.S. Pat. 3,927,970 to BASF Wyandotte Corp. (Nov. 12, 1973).
14. U.S. Pat. 3,558,499 to Atlas Chemical Industries, Inc.
15. Galante, D.C., and E.T. Clayton, "Liquid Laundry Detergents on the Line," Paper presented at the October 8, 1976, Workshop of Chemicals and Specialty Manufacturers Association in Chicago, IL.
16. U.S. Pat. 2,994,6635 to Lever Brothers Company (Aug. 1, 1961).
17. Getmanskii, I.K., A.A. Naimushina, N.I. Lyzhina, I.M. Timokhiu, and N.I. Silantiva, "Specifications for New Types of Cellulose Ethers and Polyphosphate Salts Suitable for Improving the Quality of Synthetic Liquid Detergents," *Sb Statei Po Perspektivam Razvitiya I. Soversh. Proiz-Va Sintetich. Zhirn. Kislot, Spirtov I. Razlichn. Produktov Na Ikh. Osnove*, 1973, pp. 305-11.
18. East Ger. Pat. 120,050 (May 20, 1976).
19. Saito, S., *Kolloid-Z.* 137:98 (1954); *Ibid.* 168:128 (1960); *Ibid.* 215:16 (1967); *Ibid.* 226:10 (1968).
20. Nakagaki, M., and Y. Ninomiya, *Bull. Chem. Soc. Japan* 37:817 (1964).
21. Isemura, T., and A. Imanishi, *J. Polym. Sci.* 33:337 (1958).
22. Lewis, K.E., and C.P. Robinson, *J. Colloid Interface Sci.* 32(3):539 (1970).

APPENDIX: Test Methods Used for the Dow Chemical Company Data (Ref. 6)

SOIL ACCUMULATION DETERGENCY TEST (SAD)

The principal test used was the Soil Accumulation Detergency (SAD) test. The test fabric was soiled with sieved vacuum cleaner dirt from the Dow Center carpets. A 2% artificial sebum soil in perchloroethylene was then applied, and the fabrics were laundered in the test detergents. This was repeated for three cycles and the change in reflectance, due to soil accumulation, was measured on a Hunter reflectometer.

A. Soiling Procedure

1. Place three 5 in. x 5 in. cotton, three 65/35 Dacron 54/cotton blend with permappress finish (blend), and one Dacron type 56 doubleknit swatches for each of eight beakers (56 swatches total) in a 1-gal bottle containing 3 liters of deionized condensate water and 25 g of <100 mesh sieved vacuum cleaner soil.
2. Place the bottle on a mechanical shaker for 1 hr at ~200 cycles/min. Pour the swatches from the bottle and squeeze out excess water. Dip each swatch individually twice into warm tap water to remove loose soil. Squeeze out excess water and dry the swatches on chicken-wire racks in an air circulating oven at <55 C.
3. Soil the dry soiled swatches in a 2% artificial sebum (80/20 lanolin/oleic acid) perchloroethylene solution as follows: immerse the cotton swatches as a group, remove, squeeze out, and lay on paper towels in a hood to devolatilize the hazardous chlorinated solvent to the outside atmosphere. Repeat with the blend fabric swatches. Immerse the doubleknit polyester swatches individually, drain off excess by suspending the swatches in air momentarily, then lay on ~6 layers of paper

towels in the hood to devolatilize. Complete the drying in a circulating air oven at <55 C for ca. ½ hr.

B. Laundering

1. Wash the above-soiled swatches in the experimental detergent formulation along with two cotton, two blend, and one polyester swatch that have not been soiled (the unsoiled swatches evaluate antiredeposition activity). Launder for 10 min in 150 ppm (as CaCO₃) synthetic hard water¹ employing a Tergotometer at 49 C using 100 cycles/min (cpm) agitation.
2. Remove the swatches from the detergent solution and squeeze. Rinse under a stream of deionized water by flooding and squeezing out twice. Return the swatches to the Tergotometer, add 1 liter of 150 ppm synthetic hard water, and rinse for 5 min at 100 cpm. Remove the swatches, squeeze and dry in a miniature, portable, tumble clothes dryer for ~½ hr at <55 C.
3. Determine the reflectance of all the swatches on a Hunterlab D40 Reflectometer using the green filter, exclude the optical brightener effect and use the small area test option.

C. Evaluation

Evaluate the effect of the experimental additives by comparing the test swatches with a set of swatches (included in every eight beaker run) laundered in the base detergent formulation without cellulosic additive. Also wash one set of swatches in a standard AATCC (American Association of Textile Chemists and Colorists), high phosphate laundry detergent to establish a performance relationship with a standard detergent formulation widely recognized in the industry.

MODIFIED SOIL ACCUMULATION DETERGENCY TEST (MSAD)

During the research it was discovered that an antisoiling property was being indirectly measured by reading the reflectance of the detergency swatches. A variation on the SAD test was initiated to facilitate better measurement of this property.

Procedure

1. Wash all test swatches destined for both detergency and antiredeposition purposes in the experimental detergent formulations prior to the first application of soil. The balance of the procedure is the same as in the SAD test.

This modified procedure allows the antisoiling property to be imparted to the fabric prior to the first soiling exposure, and hence, the degree of antisoiling caused by the test additive is achieved much sooner.

USED MOTOR OIL ANTISOILING TEST

The test evaluates antisoil properties exclusively by pretreating the fabric with the experimental antisoiling agent, soiling with used motor oil, then washing in a commercial laundry detergent.

Procedure

1. Wash the test fabric in 1 liter of detergent formulation containing the antisoil agent for 10 min at 49 C in the Tergotometer using 90 ppm synthetic hard water (SHW). (Dilute the 150 ppm water [Footnote 1] to 90 ppm).
2. Squeeze out the fabric and rinse for 5 min in 1 liter of 90 ppm SHW in the Tergotometer.
3. Squeeze tightly and dry in a miniature rotary clothes dryer at <55 C.
4. Place the fabric over a 7-cm bottle cap topside down forming a free air space under the fabric and fasten with a rubber band.
5. Add three drops of used motor oil (e.g., 10W30 HD Sears oil after ~4000 miles in a 1969 Pontiac V8) to the fabric and allow to wick for 2 hr. Determine the reflectance.
6. Wash the soiled swatch in a Tergotometer for 20 min at 40 C with 100 cpm agitation using 90 ppm synthetic hard water containing 0.11% Tide (8.7% as phosphorous) laundry detergent.
7. Remove the swatches from the detergent solution, squeeze out, then rinse for 5 min in 1 liter of 90 ppm synthetic water.
8. Dry in a rotary clothes dryer at <55 C and determine the reflectance of each swatch.

¹ 1300 ml of an aqueous solution containing 24.01 g of CaCl₂·2H₂O and 16.6 g of MgCl₂·6H₂O per liter in deionized H₂O diluted with 48 liters of deionized water.

FABRICS

A. Fabrics evaluated in the SAD test were as follows:

1. Cotton (Test Fabrics Inc., Middlesex, NJ) - S/400 bleached 80 x 80 cotton print cloth.
2. Dacron 54W/cotton blend (Test Fabrics Inc., Middlesex, NJ) 65/35 shirting (contains built-in brightener in the Dacron) soil test cloth with durable press finish.
3. Dacron S/720 type 56 (Test Fabrics Inc., Middlesex, NJ) texturized doubleknit jersey polyester.

B. Fabrics evaluated in the used motor oil tests were:

1. The fabrics listed above in the SAD test.
2. Polyester - Dacron type 54, 100% spun fabric (Test Fabrics Inc., Middlesex, NJ).
3. Nylon 6.6 - S/358 spun fabric (Test Fabrics Inc., Middlesex, NJ) type 200.

DETERGENT RECIPES

AATCC -Standard Reference High Phosphate Detergent:

- | | |
|-------|--|
| 14.0% | Linear alkylate sulfonate - Na salts (LAS) |
| 2.3% | Alcohol ethoxylate |
| 2.5% | Soap - high molecular weight |
| 48.0% | Sodium tripolyphosphate (STPP) |
| 9.7% | Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 2.0$) |
| 15.4% | Sodium sulfate |
| 0.25% | Carboxymethylcellulose (CMC) |
| 7.85% | Moisture and miscellaneous (no optical brightener) |

Carbonate Formulation:

- | | |
|-------|---|
| 20.0% | Tergitol 15-S-9 (Union Carbide Corp.) |
| 26.5% | Sodium bicarbonate |
| 33.5% | Sodium carbonate |
| 10.0% | Sodium silicate HSC-24 ($\text{SiO}_2/\text{Na}_2\text{O} = 2.4$) |
| 9.0% | Sodium sulfate |
| 1.0% | Experimental cellulosic polymer |