ZEOLITES AS LAUNDRY DETERGENT BUILDERS

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We hereby recommend that the dissertation prepared under our supervision by Jacquelene Marie Robeck entitled Zeolites As Laundry Detergent Builders

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CHAPTER I

INTRODUCTION

Legislative action spurred by consumer awareness groups has resulted in a phosphate ban in specific geographical areas of the United States. Prior to the late sixties phosphate products were a key ingredient in laundry detergent compositions. Environmentalists convinced local governments that a high level of phosphate concentration, when emitted into waste water, induced accelerated cultural eutrophication.

Laundry detergents account for approximately one quarter of the phosphates discharged into bodies of water (36). Alleviation or a reduction of the phosphates would contribute to the betterment of our natural lakes and streams.

Research groups and individuals, at both industrial and university levels, have sought alternatives to replace the use of phosphates in detergents. The need to supply an environmentally safe product in the phosphate restricted areas of Chicago, Illinois; Dade County, Florida; states of Indiana and New York became necessary by regional law in the 1970s. The detergent industry immediately responded to the bans by substituting other chemical components such as sodium carbonate, sodium citrate, or sodium nitrilotriacetate for phosphate in the detergent compositions. Problems arose with each substitution: doubtful safety for human use, calcium buildup on cloth and washer parts, expensive manufacturing costs, and the ultimate fact that none of these replacements cleaned clothes as efficiently as the former phosphate detergents.

Sodium aluminosilicates, more commonly known as zeolites, are predicted by some experts in the detergency field to become major phosphate replacements in the 1980 decade. Since 1976 patents have been issued to Procter and Gamble for home laundry detergent formulations containing zeolites (34).

Zeolites are environmentally and humanly safe (5, 10, 11). They leave no residual deposit on cloth or on washer parts. The raw material cost of the synthetic chemical and the manufacturing cost is competitive with the low cost of phosphate production.

The consumer of this decade is greatly concerned with obtaining an effective product to wash clothes efficiently and in maintaining an ecological balance. Manufacturers are aware of the consumer's needs in the changing marketplace and are making definite strides to meet these needs.

General Statement of the Problem

This study was designed to investigate the cleaning effectiveness of laundry detergents containing zeolites. Zeolite detergents were compared with a current high phosphate and a carbonate detergent.

CHAPTER II

REVIEW OF LITERATURE

The literature reviewed was divided into six areas as follows: (a) the composition and function of home laundry detergents; (b) partial and total phosphate replacements; (c) structure and functions of zeolites as builders; (d) effects of zeolite formulations on fabrics and environments; (e) zeolite usage in laundry detergents; and (f) future trends in the development of detergent builder trends.

The Composition and Function of Home Laundry Detergents

The two major ingredients of a home laundry detergent are surfactants and builders. Each of these is dependent upon the other to make an effective detergent.

The surfactant solubilizes and suspends soil. The surfactant comprises 10-25 percent of the detergent (Table 1). The four most commonly recognized and used types of synthetic surfactants in the world today are: (a) linear alkylbenzene sulfonates (LAS); (b) alcohol sulfates (AS); (c) alcohol ether sulfates (AES); and (d) nonionics (NI) (22).

Synthetic alkylbenzene sulfonates were developed d[illegible] to shortages of animal fats and vegetable oils during

TABLE 1.--Percentage of Components in Laundry Detergents

Percent	Component	Trade Names	Function
10-25	Surfactant	LAS AS AES NI	Wetting agent Soil suspender
20-50	Builder	STPP Na_2CO_3 Zeolites	Water conditioner Softener
5-10	Corrosion Inhibitor	Sodium Silicate	Corrosion inhibitor Alkalinity Buffering
1-2	Antiredeposition Agent	CMC	Prevent soil redeposition
1-2	Perfume, Dye		Product characteristics Color
0-2	Foam Modifier		Suds control agent
10-60	Processing Aid		Filler Miscellaneous

SOURCE: K.L. Mittal, ed., Solution Chemistry of Surfactants, Vol. 1 (Plenum Publishing Corp., 1979), p. 215.

War II. In 1960 the use of these surfactants were discontinued since some were not biodegradable; they caused foaming of natural waters and were detrimental to aquatic life. Chemists modified the non-biodegradable LAS surfactants by changing the branched chain alkyl groups to straight chains; hence, the name "linear" alkylbenzene sulfonate (LAS). LAS is currently used and is an excellent surfactant, emulsifier and foamer.

The second largest volume of synthetic surfactants used in laundry detergents are the nonionics (NI). These surfactants are commonly found in liquid laundry products and are known to be excellent degreasers. Nonionics remove sebum oil (body oil), mineral oil, and dirty motor oil exceptionally well (37). Nonionics are poor foamers, but are less sensitive to water hardness than other surfactants. The nonionics are being used now in phosphate ban areas as well as in non-ban areas.

Alcohol sulfates (AS) are good surfactants with high foaming properties. Their primary use is in foaming products such as shampoos and dishwashing liquids. Alone, AS as a surfactant, is very sensitive to water hardness. Chemically modified by ether sulfates (ES), the resulting alcohol sulfates are less sensitive to water hardness.

The modified surfactant, alcohol ether sulfate (AES), combines the good foaming features of AS with the low water hardness sensitivity of ES. AES is often used in non-phosphate detergents.

The second major ingredient in powdered laundry detergents is the builder, contributing 20-50 percent of the total detergent formulation. The term builder resulted from the use of alkaline ingredients that were added to soap in the early 1900s to boost or "build up" washing performance. The development of the builder concept for the washing process with soap was based primarily on economics. The combination of soap and less expensive alkaline ingredients was shown to be more effective than soap alone (19).

Builders control water hardness by limiting the action of polyvalent metal ions, particularly calcium and magnesium, which can reduce the effectiveness of a surfactant. In addition to softening water, builders also may perform the following functions:

1. Enhance the wetting effect and cleaning efficiency of a detergent
2. Act as an emulsifier of oily, greasy dirt by dispersing the substance and freeing it from the surface
3. Suspend loosened dirt and prevent it from resettling on fabric surfaces

4. Disperse and suspend inorganic clay type oils
5. Provide safe and effective alkalinity in the water by adjusting water pH to 9-11 for best cleaning results
6. Buffers and/or maintains a safe level of alkalinity to insure good cleaning
7. Prevents deposition of water hardness ions on fabric and machine parts.

Components, other than surfactants and builders, may comprise detergent formulations and aid in detergent functioning. Sodium silicate is a component used in detergents as a corrosion inhibitor for machine parts and aids in buffering and controlling the alkalinity of the water. The amount of sodium silicate in a detergent is 5-10 percent.

Carboxymethylcellulose, known as CMC, is an anti-redepostion agent (1-2 percent). Perfumes and dyes are used (1-2 percent) to enhance product characteristics and to give both pleasing odor and color to the formulation.

A foam modifier, or suds control agent, may be present in a very small quantity (0-2 percent). A filler or a processing aid comprises the remainder of the laundry product (10-60 percent) and keeps the product free flowing and in a desirable condition for use (22).

Partial and Total Phosphate Replacements

In the mid 1940s sodium tripolyphosphate (STPP) became commercially important as a builder in laundry detergents and was used almost exclusively until 1970. STPP worked well with biodegradable surfactants. STPP has superior sequestering ability which prevents calcium and magnesium soap scums from discoloring fabrics. Paralleling the increased usage of STPP in laundry detergents was the decline of soap usage for laundering purposes. Sodium tripolyphosphate was synonymous with the term synthetic detergent builder because of its unique performance, economy, and safety when compared to various builder alternatives (5).

In the latter half of the 1960s, a growing societal awareness of and concern for the quality of the environment and the state of our natural waters began to focus on eutrophication (19). The visibility of acute algae, particularly in older bodies of water (e.g., The Great Lakes) began to generate public concern for controlling this algal growth. Of the 20 chemical elements essential to the growth of algae, phosphorus was found to be the key element. The control of phosphorus levels offered a possible approach to the control of algal growth (27).

As a result of the public's awareness of induced cultural eutrophication, bans were placed on phosphates at the following times and in the following places: (a) Dade County, Florida (1972); (b) Erie County, New York (1972); (c) Indiana (1972); (d) New York State (1973); (e) Chicago, Illinois (1962). The ban in Chicago was rescinded in 1973 and reissued again in 1975.

People in the laundry detergent industry responded to the bans and to consumers by launching extensive research relative to phosphate substitutes. The first step was to drastically reduce the amounts of STPP in product formulations. Prior to the bans, STPP comprised approximately 50 percent of most detergent formulations. STPP was reduced to about 25 percent in formulations after the bans were enacted. STPP was widely recognized as the ideal builder but its substitution proved to be a difficult task.

In 1967 trisodium nitrilotriacetate monohydrate (NTA) was introduced in the United States. NTA was used as a partial and sometimes as a complete phosphate replacement. With continued pressure to eliminate phosphates in detergents nationwide, NTA increased in use as a builder and appeared to be an equal of STPP. In December of 1970 the use of NTA was suddenly halted. The U.S. Surgeon General deemed it unsafe for human exposure due to its high toxicity level. Today, laboratory testing continues in an effort to adequately evaluate the safety of NTA for detergent products. Currently NTA is used in Canada as a non-phosphate detergent builder.

Sodium citrate was evaluated as a detergent builder and was used extensively in 1970-1971. Sodium citrate was popular as a builder because it was humanly safe. Taraborelli and Upton (38) tested trisodium citrate as a builder in liquid detergent formulations. Results revealed considerable promise for this builder as a substitute for phosphates due to its adequate building power and rapid biodegradability. The performance of trisodium citrate as a hardness ion sequestrant is quite poor when compared to STPP, but it is nevertheless the basis for some non-phosphate detergents. Another major drawback of sodium citrate is the high cost of manufacture and use, when compared to other builders on a cost-performance basis (8).

Sodium carbonate is used as a builder, but exhibits slow kinetics in controlling calcium hardness through precipitation. Calcium ions are not reduced to a sufficiently low level quickly enough for good cleaning performance (29).

Sodium silicates and sodium sulfates are used to replace phosphates in detergent compositions as builders or fillers. These chemical compounds do not necessarily contribute to cleaning efficiency (11). Research and development investigators at both the Lever Brothers Company and the Ethyl Corporation have researched sodium carboxymethyloxysuccinate (CMOS) and carboxymethyltartronate (CMT), a constituent of Monsanto's product called "Builder M." Both compounds are moderate sequestrants for calcium and magnesium and rank higher in laboratory tests than sodium citrate, but are less desirable than STPP. Both builders are acceptable from an environmental standpoint. These products are not viewed as total replacements for phosphates, but as compromises between safety and efficiency. However, projected cost-performances place these builder products in a range costlier than STPP.

To date,a suitable replacement for a phosphate builder has not been found. Safety, health, film buildup, manufacturing costs, and poor cleaning performance all are reasons why the detergent industry continues research in an effort to seek alternatives. The best alternative appears to be a compromise: a lowered phosphate content which would exert a minimal negative effect on the environment and the addition of a co-builder.

Structure and Function of Zeolites as Builders

The single, most important property of a builder is the ability to soften water or to sequester calcium and magnesium ions present in water. Unsequestered, these ions are detrimental to the efficiency of the laundering process. Zeolites have been examined for the specific purpose of softening water and the ability to increase detergent efficiency.

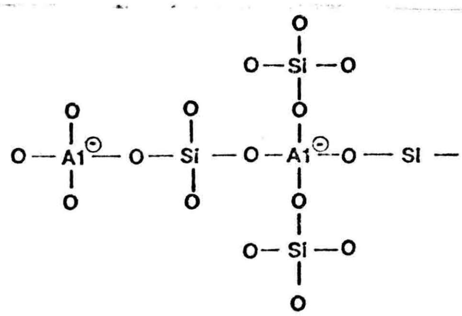
Zeolites, also referred to as molecular sieves, ion exchangers, or sodium aluminosilicates, have received attention for industrial use since 1756. In 1913 Philadelphia Quartz Company patented a water softening product that contained sodium aluminosilicate. In 1950, Union Carbide developed a firm understanding of the crystalline, inorganic structure of sodium aluminosilicates. In 1976, Procter and Gamble first introduced zeolites as inorganic builders (partial phosphate replacements) in a powdered laundry detergent.

Zeolites demonstrate some unique properties. They are sponge-like or cage-like in microscopic appearance and have an extremely large specific surface area (600 M^2/g). They can absorb 22 percent of their weight in water, creating a strong affinity for water. Zeolites selectively adsorb molecules by molecular size and can preferentially adsorb gas or liquid molecules by the relative degree of their chemical polarity.

Molecular sieves have the capability of repeatedly cycling adsorption and desorption of molecules. Normal range temperatures do not affect them. The key function of a zeolite is to exchange ions in solution (31). The use of zeolites as ion exchangers have made them popular for water treatment and worthy of investigation as detergent builders.

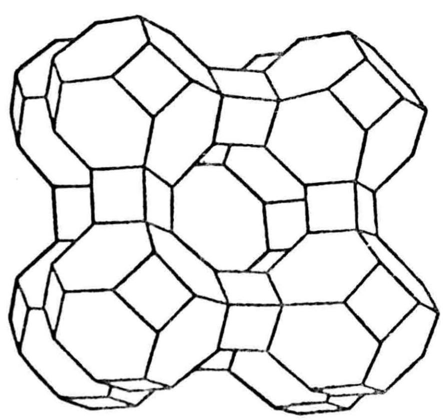
The empirical formula for sodium aluminosilicate is $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$. The aluminum (Al) in the molecule has a negative charge. Calcium and magnesium, water hardness ions, both have positive charges. This electrostatic attraction of the negative aluminum ion, and the positive calcium and magnesium ions, make zeolites natural ion exchangers (Figure 1). The aluminum ion attracts the calcium and/or magnesium into its cage-like structure and releases sodium (Na). Sodium, when released in the laundering process, has no harmful effect on fabric, machine parts, water, or the environment.

The sponge-like structure of zeolites is really a crystalline lattice. Openings to the empty spaces are uniform in size and are accessible only to molecules of a specific size and shape (29).



Al = aluminum si = silicon O = exygen

Two dimensional representation
of an aluminosilicate framework



Cage-like structure of zeolites

Fig. 1. Chemical Structure of Zeolites

SOURCE: Savitsky, Anthony C., "Utilization of Type A Zeolite as a Laundry Detergent Builder," <u>SOAP, Cosmetics, Chemical Specialties</u>, (March 1977), p. 29.

By 1977 there were four commercially produced synthetic zeolites widely used: 3A, 4A, 5A, and 13X. The first three are simple cubic structures and are referred to as Type A zeolites. 13X has a diamond-like structure and is called Type X zeolite.

The most commonly used zeolite in the detergent industry is the 4A zeolite, and will henceforth be referred to as the Type A zeolite. The numbers that precede either A or X zeolites identify the size of the pore openings leading into the framework structure. Type A zeolite (4A) pores are uniformly approximately 4.2 angstroms in diameter. Type X zeolite pores are uniformly about 13 angstroms in diameter.

"Type A zeolites are insoluble in water under normal washing conditions. They soften water by a heterogeneous cation exchange process by reacting with calcium ions. Zeolite X is known to be more effective than zeolite A in removing magnesium ions from solutions (32)." The difference in pore openings allows calcium ions to be exchanged in Type A zeolites; the openings in Type X zeolites are larger and allow magnesium ions to enter the structures and replace sodium ions.

Effects of Zeolite Formulations on Fabrics and Environment

Since the introduction of zeolites in laundry detergents by Procter and Gamble in 1976, other research units have been stimulated to investigate their use as builders. Sittig (34) summarized recent U.S. patents issued to detergent manufacturers and devoted a chapter in his book to zeolite builders. Patents for the manufacture of powdered zeolites have been issued to Rhone-Progil Company (France, 1976), Engelhard Minerals and Chemicals Corporation (U.S., 1977), Procter and Gamble Company (U.S., 1977), J.M. Huber Corporation (U.S., 1978), and Deustche Gold-und Silber-Scheideanstalt and Henkel Kommanditgesellschaft auf Aktein (Germany, 1978). Sittig (34) stated that the use of ion exchange materials as builders is now the "biggest news" in the detergent industry.

If zeolite particles are too large the washing process is impeded. The negative effect is manifested in such a form that the agents, after disseminating into water, remain unwetted for a relatively long time and are kept floating around on the surface of the water (sawdust effect) (34). A complete substitution of phosphate builders by zeolites results in cleaning agents becoming too difficult to wet. Due to the sawdust effect, portions of the zeolites are lost during the washing cycle as they might be deposited on the walls of the machine, or left suspended in air or in wash liquor.

The capacity of zeolites to ionize calcium and magnesium ions in detergent formulations is known. Research is being conducted to improve their wettability by water (to hydrophilize them). During the past three years Procter and Gamble has been issued four separate patents for incorporating zeolites into their detergent powders. Henkel, a German detergent company, has also been issued four patents for detergent formulations containing zeolites. Union Carbide was issued a single patent in 1978 that combined zeolite A and X.

Anthony Savitsky (29), director of research at Procter and Gamble, stated that his company has a continued interest in research concerning the development of new builders, providing hardness control for its laundry detergent products. Savitsky researched Type A zeolites as complete builders and then compared them to STPP, sodium carbonate and NTA. Results of this research were:

1. Type A zeolite is insoluble in water under normal washing conditions; it softens water by heterogeneous cation exchange.

2. When compared to three other builders, in removing free calcium hardness in water, zeolite A worked better than calcium carbonate, but was not as efficient as NTA. STPP was the best product for softening water.

3. In water with a hardness of 7 grains per gallon (medium-hard water) with a ratio of 2 to 1, calcium to magnesium, at room temperature, type A zeolite exchanged calcium ions. No appreciable ion exchange occurs between magnesium and type A zeolites. Any magnesium exchange is slowed down considerably at lower temperatures.

Fast kinetics of water hardness removal contribute significantly to the overall effectiveness of a builder system in the laundry process. Savitsky (29) feels that the first three minutes of the wash cycle are extremely important; during this time the builder, the surfactant and the soil are competing for the mineral hardness. The rapidity of the rate of hardness reduction is most critical.

The kinetics of hardness ion removal are very rapid for both STPP and NTA, both chelating builders. Sodium carbonate, a precipitating builder exhibits noticeably slower kinetics. Zeolite, a heterogeneous ion exchanger, is also relatively slow in hardness removal (Figure 2).

Zeolites, as builders, are slower than chelating builders, but appreciably faster than precipitating builders. Zeolites can remove calcium ions within the first three minutes of laundering. Procter and Gamble has established a minimum acceptable rate for the removal of free hardness ions to be 2 grains per gram of builder, per minute, without affecting cleaning performance (29). Due to the molecular difference in the size of calcium and magnesium ions (magnesium being the larger), the kinetics of calcium removal is much faster than that of magnesium removal. Both STPP and NTA remove calcium and magensium ions within one minute; sodium carbonate does not appreciably remove magnesium ions.

The kinetics of zeolites are known to be dependent on the particle size of the solid zeolite. Procter and Gamble tested zeolite A in laundering black, cotton, test fabrics, and surmised that zeolites larger than 10 microns in size would be trapped on fabric and zeolite deposits might be visible (30).

Environmentally, zeolites are not believed to be harmful and can be removed readily from water at sewage treatment plants (5). If released into untreated waters

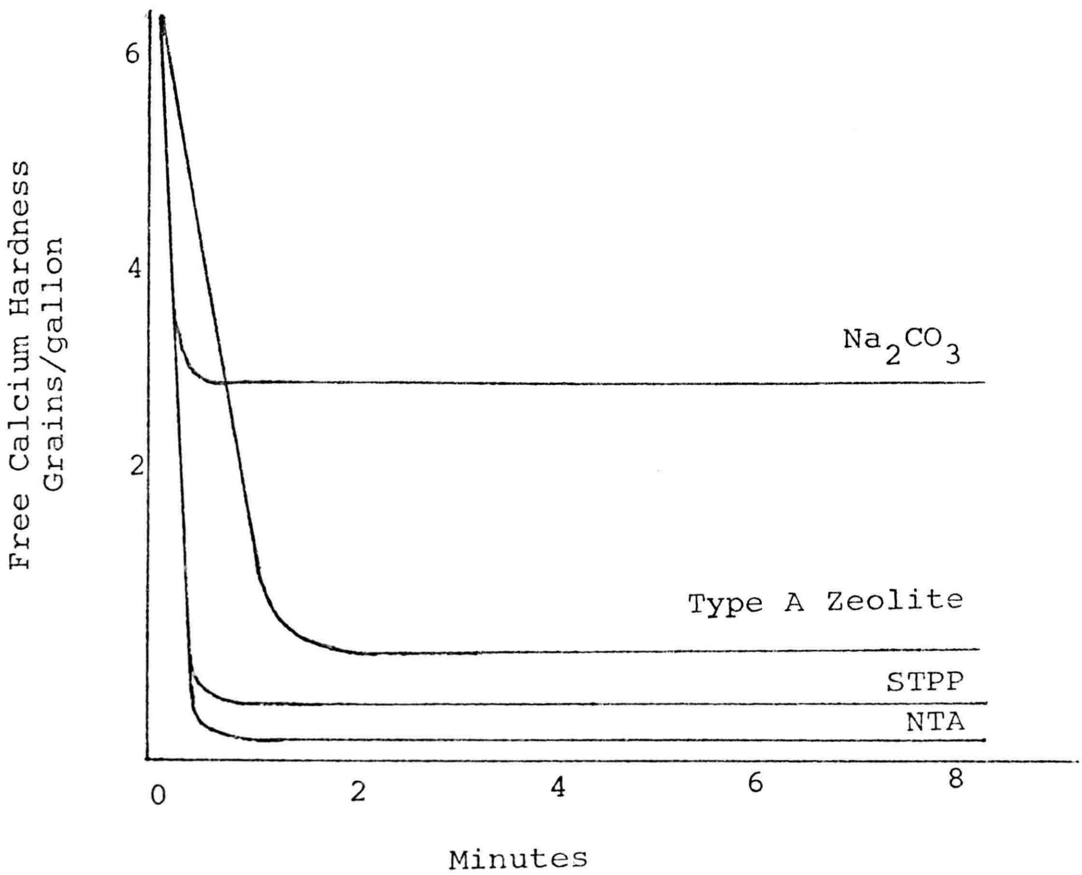


Fig. 2. Kinetics of Calcium Removal by Selected Builders

Source: Savitsky, Anthony C. Household and Personal Products Industry (March 1977), p. 58.

they are nontoxic to aquatic organisms and do not contribute to nutrient input in lakes or streams. Environmentalists believe that zeolite A is thermodynamically unstable in aqueous solutions and will slowly degrade to simple, commonly found components in the environment. Zeolites are nontoxic upon ingestion and are non-irritating to skin and eyes.

Berth,(5) of Henkel Research Laboratories in West Germany,investigated the use of sodium aluminosilicates in inorganic builders and reported that they should be used adjunctly with STPP for best results. A strong interest in inorganic builders for use in detergents was evidenced because inorganic builders are not dependent on petrochemical feedstocks, nor do they interfere with biodegradability.

Inorganic builders can be classified into two groups: (a) water soluble compounds (sodium carbonate, sodium silicate, and sodium phosphate) (b) water insoluble compounds (certain sodium aluminosilicates). Berth (5) believes that water soluble compounds could contribute to the wash properties while insoluble builders could not; contributing properties being alkalization and specific washing action based on interaction with solid surfaces. The combination of a binary builder system of zeolites and phosphates was promoted by Berth. Results of Berth's research revealed that the use of sodium aluminosilicates alone reduced washing performance. Berth stated that ion exchange is not only dependent on ion size, but also on concentration, time, temperature, and pH.

Results of market and panel tests disclosed that the combination of STPP and SASIL (Henkel's acronym of sodium phosphate and zeolite A) was favorably accepted. Test results also revealed that no deposits on fabric or on machine parts were observed.

Results of a one year test (5) at a sewage treatment plant proved that zeolites were eliminated in the process of waste water treatment. Since ion exchange is not limited singly to calcium or magnesium ions, heavy metal ions can be exchanged also, which contribute to the detoxification of waste water.

Researchers at Union Carbide (33) reported on experiments using zeolites. Type A zeolite was used for laundering fabric in glass beakers, terg-o-tometers, and washing machines. Results were the same no matter which laundering device was used. After five hours, type A zeolite did not attain a magnesium equilibrium at any of three different temperatures (hot, warm, cold). A faster ion exchange occurred in hot water than occurred in warm or cold water. Further research led to the development of a product the company labeled ZB300, which is a blended mixture of type A and X zeolites. When zeolite A and X are combined a synergistic effect on water hardness removal is exerted. Separately these zeolites do not remove hardness ions as well kinetically as when used together.

Zeolite Usage in Laundry Detergents

Sherman (33) conducted detergency tests in which zeolite A, X, and a blend of the two were used in laundering a variety of soil cloths. The detergent mixture was comparable to a zero phosphate detergent. Regardless of fiber content or water temperature, the blended zeolite builder performed better than did the separate zeolite A or X builder.

The efficient control of calcium ion water hardness by zeolites has been established. Magnesium ions, however, also need to be controlled for effective cleaning. Schweiker (31) conducted laboratory investigations for Philadelphia Quartz Company to show that sodium silicate controls magnesium ion water hardness. In detergent formulations with zeolite A, favorable results were obtained in laundering cotton and polyester/cotton blend fabrics.

Using the LAS surfactant system, with sodium silicate, zeolite A and X, CMC, sodium sulfate,and STPP as supporting ingredients, Schweiker's test results showed that maximum performance occurred at approximately a 20 percent silicate concentration. When zeolites were deleted from the detergent no significant increase in performance was found beyond the 10 percent level. Schweiker concluded that in a formula containing zeolites and sodium silicate, synergism is demonstrated.

Results also indicated that detergency on polyester/cotton fabrics is improved with the use of zeolites, but no significant improvement in laundering cotton fabrics with zeolites was evidenced. Zeolite A was more effective as a detergent builder than was zeolite X or the blend of zeolites A and X when using a 20 percent level of sodium silicate.

In 1978 Fuchs(14) published the results of a zeolite investigation. Cotton and polyester/cotton clay soiled fabrics were laundered at 100 ppm water hardness in a Terg-o-tometer at $50^{o}C$ ($120^{o}F$) for 10 minutes. Two LAS surfactant detergent formulations were used in laundering the fabrics: (a) 49 percent STPP built detergent, and (b) 16 percent zeolite A and 3 percent Phosphorus built detergent. Results revealed that the STPP detergent performed at a 100 percent level and the zeolite built detergent performed at a 92 percent level. Results were similar for both fabric types.

In 1974 Langguth investigated the effect of a detergent formulation with 18 percent LAS surfactant blended with 33 percent STPP builder on both cotton and blend fabrics. Both fabrics were presoiled by the Spangler method. (Spangler, in 1965, published a method of laboratory soiling of cloth for use in detergent studies (38). The soil is a synthetic/sebum airborne particulate soil.) Langguth found that the harder the water was during laundering, the lower was the cleaning performance of the detergent. Best results were obtained during laundering of fabrics at 100 ppm water hardness (19).

Future Trends in the Development of Detergent Builders

A builder can soften water in two ways. First, a water softening agent can be used to treat the water. This may not be practical nor desirable since hardness ions can be released into the wash water from the soiled cloth. The second alternative is to incorporate a suitable builder into the detergent itself. Market volume projections for the near future indicate substantial growth for sodium aluminosilicates. Suggestions have been made that world production of zeolites will increase more than five times by 1981, due principally to an expected rapid increase in their use in detergent formulations (31).

Based on performance and economics, Henry F. Whalen, Jr. (40), Director of Corporate Development for Philadelphia Quartz Corporation, believes that zeolites will capture a large percentage of the detergent builder business by 1982. Whalen stated that zeolites could save the industry 25-50 million dollars annually and that there are four possible alternatives for builders in the detergent business. One alternative is a total shift to zeolites as complete builders; secondly, a partial shift; thirdly, a shift to carbonate and zeolite builders; and finally, a shift to an all carbonate builder.

In 1975 there was virtually no worldwide commercial production of zeolites for detergent use. In 1977 a total of 27 megatons were produced, while 90 megatons were produced in 1979. By 1981, 225 megatons of zeolites are projected for detergent composition (31).

Zeolites, as builders, have significant advantages. They add superior overall hardness ion control as compared to currently marketed nonphosphate formulas (31). A substantial improvement in cleaning effectiveness is realized. As a co-builder with low phosphates they assure an even better cleaning ability. Based on the conclusions of reported research, zeolites alone cannot be considered complete phosphate builder replacements if existing performance standards are to be maintained.

STPP is the ideal builder in laundry detergents, meeting the requirements of hygiene and cleanliness that are demanded by the consumer. Since phosphates contribute to the eutrophication problem, detergent phosphate limitations and bans are to be expected worldwide. The partial replacement of STPP by sodium aluminosilicates will not solve eutrophication problems, but it will decrease the total amount of phosphates entering waters.

When cost is considered, present acceptable organic builder candidates will encounter difficulty in competing with STPP. The manufacturing cost of zeolites is in the same raw material cost range of STPP; zeolites are also easily accessible. The cost of a laundry detergent containing a low phosphate zeolite based builder would be quite acceptable to the consumer. In spite of the considerable expense incurred in research and development, the use of sodium aluminum silicates in laundry detergents will not create any negative macro-economical consequences (5).

Renewed legislative activity has increased the percentage of the population affected by phosphate bans; this results in a general, nation-wide increase in the use of non-phosphate detergents. Until the bans are repealed, alternatives to the current predicament will be sought.

In July 1980, the Surgeon General retracted his statement that NTA was not considered safe for human use. Results of extensive chemical and laboratory tests could not prove NTA to be harmful to human health. However, the public yet may be afraid to try detergents with NTA compounds.

Alternatives to the use of laundry detergent builders for the future could be viewed in two ways: first, if the phosphate ban is repealed, there will be no need to seek phosphate alternatives. Consumers can revert to the ideal phosphate detergent product they used before 1970. Speculators have voiced their opinion that phosphates really do not contribute significantly to the eutrophication problem, and that laundry detergents contribute even less (36).

The second view is that the current phosphate bans will be upheld, and probably other areas in the United States will be added to the list of ban areas. If the phosphate ban remains in effect, two alternatives need to be investigated: non-detergent and detergent options.

A non-detergent approach places controls on sewage facilities. The addition of tertiary treatment to existing sewage treatment plants will cause additional expenses of about 10 percent of the cost of mechanical and biological sewage treatments (5). This seems likely to occur in populous regions over the long term and has already occurred in some regions. However, waste-water from some residential areas is emitted into natural streams or other bodies of water without any treatment.

Development of new builderless detergent formulations, where the surfactant system is not sensitive to calcium or magnesium ions, could be a detergent alternative. There are some liquids on the market now without any phosphates, and they appear to clean clothes efficiently.

In seeking non-phosphate builder alternatives, a researcher is confronted with the consumer's keen awareness of the energy crisis. In the past five years the shift from hot water to moderately warm and cold wash water by the public is widespread (15). Detergents are manufactured to be used in many areas of the United States; water hardness varies greatly within the country. A researcher is confronted with the problem of developing a detergent that will fulfill many needs. Fabrics are cleaned more efficiently in hot, soft water; less than 50 percent of home launderers wash clothes in hot water and more than half of the United States is supplied with hard water (20).

The most feasible solution to the phosphate water pollution problem appears to be the use of adjunct inorganic builders of zeolites and phosphates. Lowered levels of STPP combined with zeolites as builder systems need further investigation.

CHAPTER III

STATEMENT OF THE PROBLEM

The purpose of this investigation was to determine the cleaning effectiveness of zeolites as detergent builders in laundering cotton and polyester/cotton blend fabrics. Three zeolite formulations were compared to a high phosphate builder and a carbonate builder formulation.

Assumptions

The following assumptions were made for this investigation:

1. Zeolites were considered to be partial phosphate builder replacements.
2. The selected detergent formulations were representative of detergents currently or previously marketed and used in the United States.
3. The two types of fabrics tested were representative of fabrics comprising a typical wash load.
4. Water hardness and water temperature were typical of conditions that exist for home laundering in the United States.

5. Soil removal and whiteness retention were accepted indices of the cleaning efficiency of laundry detergents.
6. Tensile strength was an index for degradative effects of detergents.

Objectives

Specific objectives of the study include the following:

1. To determine the detergent formulation that cleans each fabric type most efficiently.
2. To predict the most effective combination of detergent formulation, water temperature, and water hardness level to optimize soil removal or retain whiteness for the two sample fabrics used.
3. To find the effects of water temperature and water hardness level in laundering the selected fabrics in built detergents.
4. To determine the cleaning efficiency of zeolite built detergents in comparison to phosphate built or carbonate built detergents.
5. To determine the effect of selected detergent formulations on fabric strength.

The main hypothesis of this study was:
There is no significant difference between the cleaning efficiency of the selected detergents in cleaning cotton and cotton/polyester blend fabrics.

Scope and Limitations of the Study

Most of the published research has been performed by detergent companies or raw material manufacturers in an effort to promote or defend a particular product, e.g., zeolites or zeolite builders. This investigation was non-objective as to material brands tested. Popular surfactants and zeolite builders were combined in detergent formulations to investigate cleaning efficiency on specific fabrics. No single raw material manufacturer was favored; chemical ingredients were obtained from primary sources. No comparisons were made between brands of products or companies.

The soiled fabrics tested do not represent a true wash load of the average consumer. Pre-soiled cloth was selected for use in this study. Two different woven fabrics were utilized.

Water temperature and water hardness levels were chosen as representative of possible and popular laundering conditions. A Terg-o-tometer is an accepted laboratory device to simulate a large scale washing machine.

Laboratory methods may vary slightly from actual in-home, consumer use, practices and care.

Four of the five detergents investigated were laboratory blends of various chemicals that are used in actual detergent manufacture. One detergent was purchased from a supplier in a ready to use, spray-dried form of powdered laundry detergent. Detergents that are commercially blended and spray-dried may possess certain performance characteristics not possible to obtain by in-laboratory combination of chemical ingredients (15).

Data obtained from laboratory experiments may vary slightly from that revealed by actual panel or in-the-home consumer use and care. Inferences drawn from statistical results of this investigation may vary in repeated research.

CHAPTER IV

PROCEDURE

The procedure has been divided into the following sections: experimental procedure and statistical treatment of the data.

Experimental Procedure

Laboratory tests were conducted for two purposes: (1) to determine the cleaning efficiency of selected laundry detergent compositions and (2) to find the degradative effects of the selected detergents upon two fabric types.

Fabrics Used

Two different, unfinished fabric types were used for experimental purposes in determining the efficiency of detergents in the first phase of the study.

Type 1. 100 percent cotton broadcloth with an average fabric count of 62 X 71/in (26 X 29/cm) and a weight of 3.47 oz/yd^2 (116 g/m^2)

Type 2. 50/50 percent polyester/cotton broadcloth with an average fabric count of 50 X 57/in

(20 X 23/cm) and weight of 5.28 oz/yd^2 (180 g/m^2)

Each fabric type was obtained in a bleached white cloth and in a pre-soiled cloth. The soiled cloth was obtained from the United States Testing Company, Hoboken, New Jersey. Soil composition included carbon black, mineral oil, and vegetable oil particles, closely representing naturally occurring soil.

Detergents Used

Five detergents were selected for experimental purposes. All detergents were composed of surfactants, builders, alkalinity ingredients, anti-redeposition agents, and fillers, in approximately equal percentages (Table 2). Four of the detergents were chemical blends mixed in a college laboratory. Chemicals were obtained from various sources (Appendix A) and combined in aqueous solution for aliquot usage in laundering. One detergent was purchased in a ready-to-use form from a supplier and dissolved to prepare an aqueous solution.

A high phosphate detergent, used as the control, was commercially produced. This was a spray-dried, built laundry detergent in powder form that was obtained from the American Association of Textile Chemists and Colorists. The compound labeled 124W was a detergent proposed as a

TABLE 2.--Composition of Experimental Detergents

Detergent Type	Surfactant System	Builder System	Alkalinity Control	Anti Redeopisition Agent	Filler
A (NI)	NI - 10%	Zeolite A - 15% Zeolite X - 15% STPP - 25%	Sodium Silicate 10%	CMC - 1%	Sodium Sulfate 24%
B (LAS)	LAS - 20%	Zeolite A - 15% Zeolite X - 15% STPP - 25%	Sodium Silicate 10%	CMC - 1%	Sodium Sulfate 14%
C (AES)	AES - 20%	Zeolite A - 15% Zeolite X - 15% STPP - 25%	Sodium Silicate 10%	CMC - 1%	Sodium Sulfate 14%
D (NACO)	LAS - 20%	Na_2CO_3 - 30%	Sodium Silicate 10%	CMC - 1%	Sodium Sulfate 14%
E (PHOS)	LAS - 14% AE - 2.3% Soap - 2.5%	STPP - 48%	Sodium Silicate 10%	CMC - 0.25%	Sodium Sulfate 16% Moisture and Misc. 7.25%

standard for textile testing that represents a typical high phosphate detergent used by home launderers in the United States prior to 1970 (1). This detergent contained 12 to 14 percent phosphorus, in the form of phosphate, and is referred to as Detergent E, phosphate detergent, or PHOS. PHOS has a LAS surfactant system and a STPP builder system.

Detergent D, referred to as carbonate detergent, or NACO, is a blend of LAS surfactant and a co-builder system of sodium carbonate and STPP. This detergent closely resembles a carbonate built detergent currently marketed for non-phosphate use.

Detergent C, labeled AES in this study has a LAS surfactant. The binary builder is composed of 30 percent zeolite (zeolite A, 15 percent; zeolite X, 15 percent), and 25 percent STPP. AES has a surfactant system that is found in detergents that have limited current use.

Detergent B, referred to as LAS, has a LAS surfactant and a builder system identical to that of detergent C (AES). The LAS detergent has a surfactant system resembling a leading powdered laundry detergent.

Detergent A, a combination of a nonionic surfactant and a zeolite/phosphate binary builder system, identical to that in detergent AES and LAS, is referred to as NI detergent. NI detergent simulates a heavy duty built liquid detergent surfactant system currently used in the United States.

Test Specimens

One hundred eighty 5 x 7 inch specimens were cut from each unsoiled fabric type and each soiled type, making a total of 720 test specimens. Twenty-one 5 x 7 inch specimens were cut from each unsoiled fabric type and each soiled type and reserved for controls. All specimens were serged to eliminate raveling during treatments.

Test specimens were cut from 15 yard lengths, 18 inches wide of each test fabric and soiled type. Control specimens were periodically selected and reserved for measurements. No specimen was cut within 1½ inches of each selvage and within 1 yard of each end of the fabric length.

Treatment of Test Specimens

The test specimens were laundered in accordance with AATCC Test Method 152-1977 and were exposed to one detergent, one water hardness level, and one water temperature condition, chosen from the following:

1. NI built detergent
2. LAS built detergent
3. AES built detergent
4. Na_2CO_3 built detergent

5. Phosphate (PHOS) built detergent
6. Soft water hardness level
7. Medium water hardness level
8. Hard water hardness level
9. Cold water temperature
10. Warm water temperature
11. Hot water temperature

Laundering Procedures

The fabric samples were subjected to a single laundering agitation of 30 minutes, as proposed by AATCC Test Method 152-1977--Soil Redeposition, Resistance to: Terg-o-tometer Method (1979). The laundering was conducted in a U.S. Testing Company, Terg-o-tometer (model 7243) at 100 revolutions per minute.

Two 100 percent unsoiled cotton specimens and two 100 percent soiled cotton specimens were laundered together in each selected wash liquor. Two 50/50 percent polyester/ cotton unsoiled specimens and two 50/50 percent polyester/ cotton soiled specimens were laundered together in the same bin in each selected wash liquor. Soiled and unsoiled specimens were washed together to determine the effectiveness of the detergent upon soil removal and soil suspension. One liter of 0.15 percent concentration of detergent in water was used for each laundry cycle. Following each wash cycle the samples from each bin were rinsed by hand in cold water for 3 minutes and air dried, and reserved for measurements.

Water Hardness

Duplicate specimens were subjected to each of three water hardness levels of laundering. These levels ranged from soft water (0 ppm) to medium water (150 ppm) to hard water (300 ppm) as specified in test procedure AATCC 152-1977. A hard water stock solution was prepared according to ASTM Designation: D3050-75.

Hard Water Stock Solution:

2.940 ± 0.002 g calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$)

plus

2.033 ± 0.002 g magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$)

dissolved in

1 liter of distilled water

This solution contains 3000 ppm hardness (expressed as calcium carbonate), with a calcium to magnesium molar ratio of 2 to 1. An appropriate amount of stock solution was added to distilled water to produce the specified test levels of water hardness.

The following procedure was used to determine water hardness levels:

Fifty milliliters of water were placed in a beaker and buffered by 2 ml of pH10 buffer solution. One drop of Eriochrome Black T indicator was added, and the buffered solution was titrated with an EDTA (Ethylenediamine tetracetic acid) solution (1 ml = 1 mg $CaCO_3$) until a color change from red to blue was noted.

The water hardness was calculated in parts per million calcium carbonate equivalents by using the following formula (35):

$$\text{Parts per million calcium carbonate} = \frac{\text{ml of EDTA (1mg } CaCO_3\text{/ml of EDTA)} \times 100}{\text{sample weight}}$$

Water Temperature

Duplicate specimens were subjected to each of three water temperature levels of laundering. The selected water temperatures were in accordance with AATCC Test Method 135-1978 and ranged as follows:

cold $(85^\circ \pm 5^\circ F/30^\circ \pm 3^\circ C)$
warm $(120^\circ \pm 5^\circ F/50^\circ \pm 50^\circ C)$
hot $(140^\circ \pm 5^\circ F/60^\circ \pm 3^\circ C)$

Soil Removal

The soiled specimens were subjected to light reflectance measurements to determine soil removal. Readings on the front and back of each specimen were made on a Photovolt Reflection Meter 670, using a green tristimulus filter. Readings were made to obtain 45°, 0° luminuous reflectance values.

Soil removal was measured as the numerical difference in light reflectance readings of specimens before and after laundering. The precentage improvement in reflectance values is a direct indication of soil removal on soiled cloth as specified by ASTM Designation: D3050-75 (2). Calculations for improvement in reflectance were made as follows:

Percent improvement in reflectance = (A-B)/(C-B) X 100

where

A = average reflectance of the soiled specimens after washing

B = average reflectance of the soiled specimens before washing

C = average reflectance of the unsoiled specimens before washing

Whiteness Retention

Each unsoiled specimen was subjected to light reflectance measurements to determine the amount of whiteness retained after laundering. Whiteness retention is synonymous with soil redeposition. Soil redeposition is the soiling of clean or relatively clean fabric during the laundering process by soil which has been removed from another fabric (1). Readings were made on a Photovolt Reflection Meter 670, using a green tristimulus filter, on front and back of each specimen. Readings were made to obtain 45°, 0° luminous reflectance values.

Whiteness retention was measured as the difference in light reflectance values before and after laundering. The percentage of whiteness retention was calculated as follows (12):

Percent retention = (A / W) X 100

where A = average reflectance of the unsoiled specimens after washing

where W = average reflectance of the unsoiled specimens before washing

In analyzing laundered fabrics both soil removal and whiteness retention percentages give a better indication of the effectiveness of a detergent. A detergent highly effective in soil removal may be a less effective soil suspender.

Tensile Strength

Identical fabrics were used for the second phase of the study, in which the degradative effect of the selected detergent formulations were assessed relative to fabric strength loss. Fabrics were tested for tensile strength before laundering and after each laundering cycle. All tensile strength samples were conditioned at standard conditions ($70^{\circ} \pm 2^{\circ}$F and 65% ± 2% RH) for a minimum of 8 hours in accordance with ASTM Designation: D 1682-64.

Preparation of the test specimens were in accord with the requirements set forth by ASTM for a grab test (3).

Tensile strength was measured on a Universal Testing Instron machine and recorded in kilograms of force. The percent change in tensile strength was calculated as:

Percent Tensile Strength Loss (or Gain) =

(A - B) / A X 100

where A = recorded tensile strength of unlaundered specimen

where B = recorded tensile strength of laundered specimen

Statistical Treatment of the Data

The experimental design selected was one that involved a factorial treatment arrangement. The factors were:

1. Detergent type
2. Fabric type
3. Soil condition
4. Water temperature
5. Water hardness level

A four-factor analysis of variance was performed on the reflectance values to determine the effects of the individual factors and simultaneously significant interactions between the factors. To examine further factors that exerted the most influence, a three-factor analysis of variance was performed. A Newman-Keuls multiple range test was used to determine a ranked order of the cleaning efficiency of the detergent factor.

The tensile strength data were subjected to a four factor analysis of variance to determine significant degradative effects of the factors investigated upon the selected fabrics. A Newman-Keuls test was used to rank the order of detergent types regarding degradative effects upon tensile strength.

For all analysis of variance tests a probability level of 0.01 was set to render highly significant results and a level of 0.05 was set to render significant results. A probability level of 0.05 was set for all Newman-Keuls tests as significant results.

CHAPTER V

RESULTS

The cleaning ability of the five detergents tested was measured by the degree of soil removed from soiled fabrics and the degree of whiteness retained by unsoiled cloth after launderings. The degradative effect of the detergents was measured by changes in the tensile strength of the fabrics after laundering.

Results are presented under the major headings of: Detergent Efficiency and Tensile Strength. Major emphasis was placed upon measurements of detergent efficiency.

Detergent Efficiency

The ability of a detergent to remove artificially applied soil from fabrics is a guideline for determining detergent efficiency (3). Whiteness retention of a fabric laundered with a detergent is a second criterion for measuring detergent efficiency (4).

A relationship between whiteness retention and soil removal cannot always be made. The soil removal value represents the amount of soil removed from soiled fabrics; whiteness retention values ascertain the amount of soil redeposition on unsoiled fabrics.

A low percentage for whiteness retention may be due to factors such as poor soil suspension (redeposition) or an accumulation of chemical residues in the fabric. If a low whiteness retention value is due to soil redeposition, then a relationship with the amount of soil removed should exist.

For example, when the percentage of soil removal is low and the percentage of whiteness retention is high, one may assume that the detergent is poor in removing soil. Since little soil is being removed from the fabric there is only a small amount of soil available to be redeposited on the unsoiled fabric. If soil removal is high and whiteness retention is low, the effectiveness of the detergent would be questionable, as an efficient detergent, due to a lack of soil suspension ability.

Reflectance measurements were statistically analyzed to determine the efficiency of the selected detergents and the optimum laundering conditions when these detergents were used. Results are presented and discussed under the following subheadings: (1) Effects of Detergent, Water Hardness, and Water Temperature; (2) Zeolite, Carbonate, and Phosphate Detergents; and (3) Cleaning Efficiency of Detergents Upon Cotton and Polyester/Cotton Fabrics.

Effects of Detergent, Water Hardness and Water Temperature on Fabrics

A three-factor analysis of variance was performed for each fabric type and soil condition (cotton, unsoiled; cotton, soiled; polyester/cotton, unsoiled; polyester/cotton, soiled) to determine the effects of factors involved and the optimum laundering conditions. Results revealed significant effects of all factors investigated. (Table 3)

Soil Removal From Cotton Fabric

Results of the three factor analysis of variance for soil removal from the 100 percent cotton fabric are shown in Table 3. The main effects of the individual factors were highly significant. Results also indicated that the combination of detergent and water temperature exerted the greatest effect on soil removal.

Soil removal from cotton fabrics was best attained by the sodium carbonate detergent (NACO), at a hot water temperature and in soft water (Fig. 3). Figure 3 was generated from the mean values of soil removal percentages of 100 percent cotton specimens (Appendix C). The combination of alcohol ether sulfate surfactant and zeolite built detergent (AES) demonstrated the least desirable cleaning ability at all water temperatures and hardness levels. It was least efficient in warm, hard water. The AES surfactant system is not marketed widely in heavy duty laundry detergents (22).

TABLE 3.--Summary of the Analysis of Variance for Percent of Soil Removal From Cotton Specimens

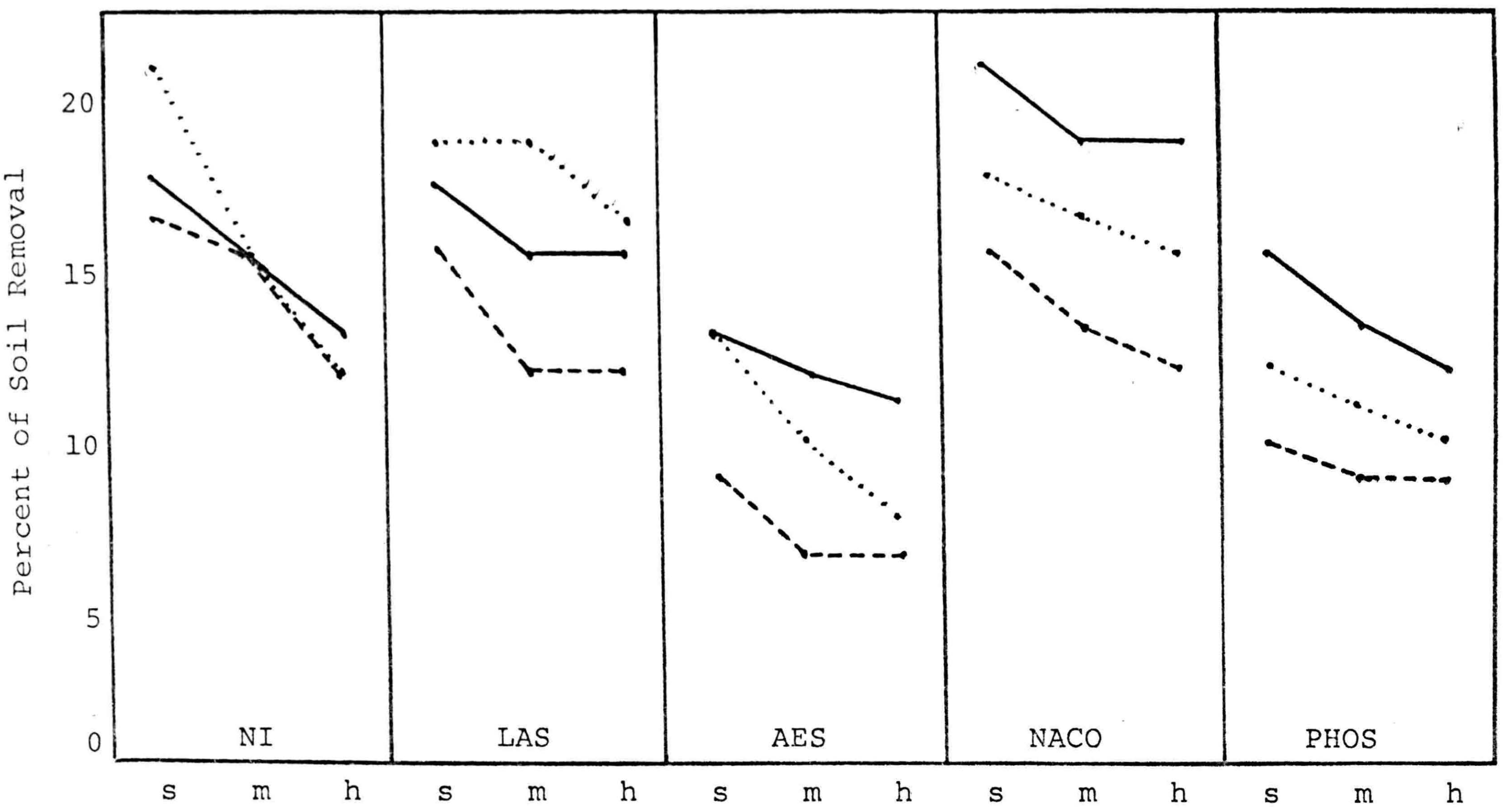
Source of Variation	df	MS †	F Ratio
Main Effects			
Detergent Type (1)	4	264.30	279.30**
Water Hardness (2)	2	135.34	143.02**
Water Temperature (3)	2	165.06	174.42**
Two Way Interactions			
1 X 2	8	8.76	9.25**
1 X 3	8	13.84	14.63**
2 X 3	4	1.72	1.82
Three Way Interactions			
1 X 2 X 3	16	2.60	2.75**
Residual Error	135	0.95	

*Significant at α = 0.05 level of probability

**Significant at α = 0.01 level of probability

df = degrees of freedom

†MS = mean square



Water Hardness Levels: s=soft m=medium h=hard

Water Temperature: ····· =cold ----- =warm ——— =hot

Fig. 3. Percent of Soil Removal From 100 Percent Cotton Specimens for Five Detergents, Three Water Temperature, and Three Water Hardness Levels

AES is used principally for surfactants in light duty detergent products.

The main effect of the detergent factor was significantly high ($\alpha = 0.01$). Figure 4 shows mean values of soil removal percentages from cotton fabrics treated with the five detergents. The mean values reflect the effect of detergent only (water temperature and water hardness were disregarded). The nonionic (NI), the LAS surfactant/zeolite built (LAS), and the sodium carbonate (NACO) detergents were the most efficient detergents for soil removal.

A Newman-Keuls multiple range test was conducted to determine where the significant differences existed among the detergent types. LAS and NACO detergents varied significantly from the other three detergents and were ranked as the two best detergent types for soil removal from cotton fabrics ($\alpha = 0.05$). There was not a significant difference between the LAS and NACO detergents.

Soil Removal From Polyester/Cotton Fabric

A three-factor analysis of variance was performed for soil removal from polyester/cotton specimens (Table 4). All main effects were highly significant.

Figure 5 graphically interprets the mean reflectance values for soil removal from blend fabrics by detergent type with regard to water temperature and water hardness level. Means and standard deviations appear in Appendix C.

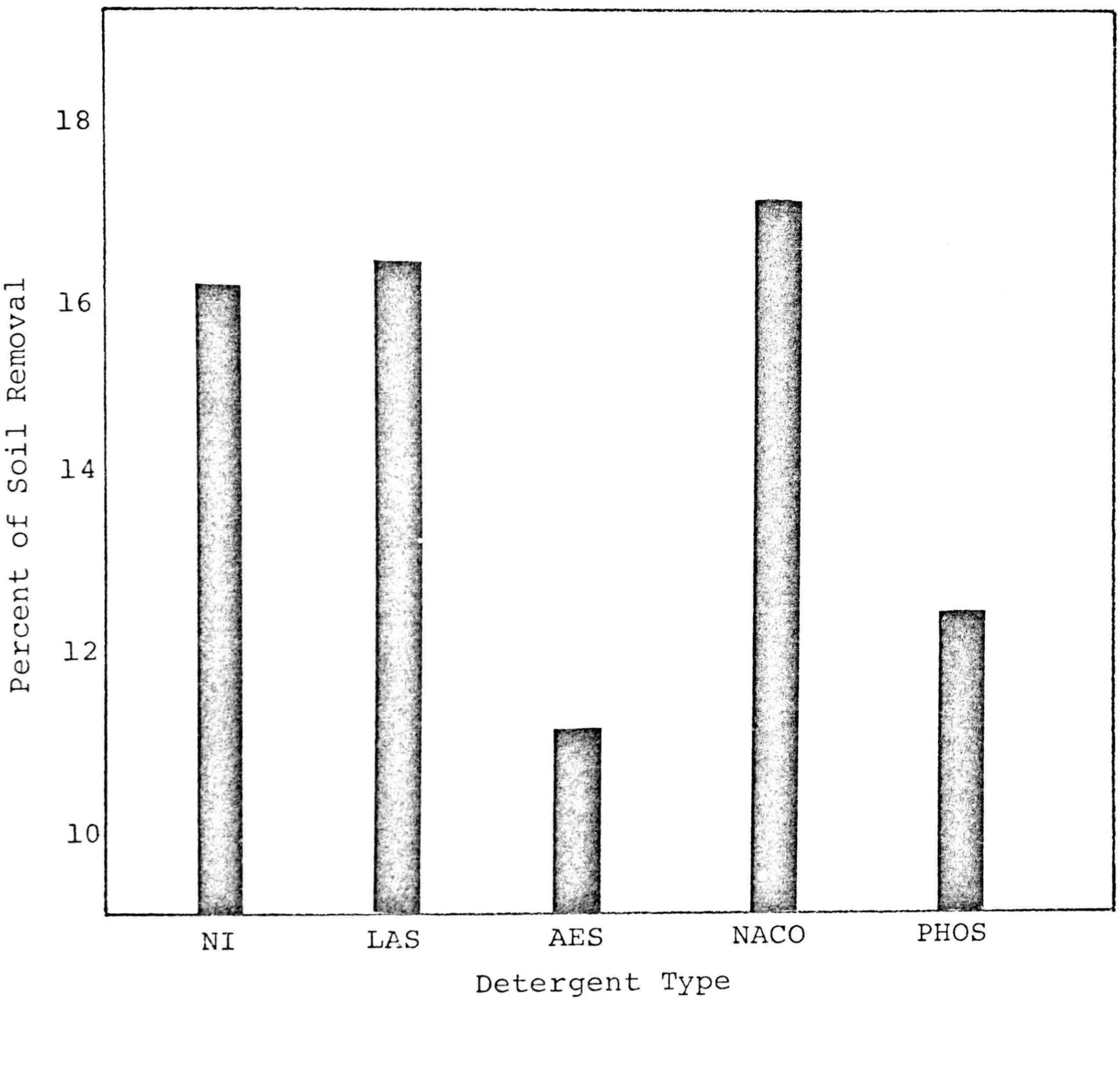


Fig. 4. Percent of Soil Removal from 100 Percent Cotton Specimens for Each of Five Detergents

TABLE 4.--Summary of the Analysis of Variance for Percent of Soil Removal From Polyester/Cotton Specimens

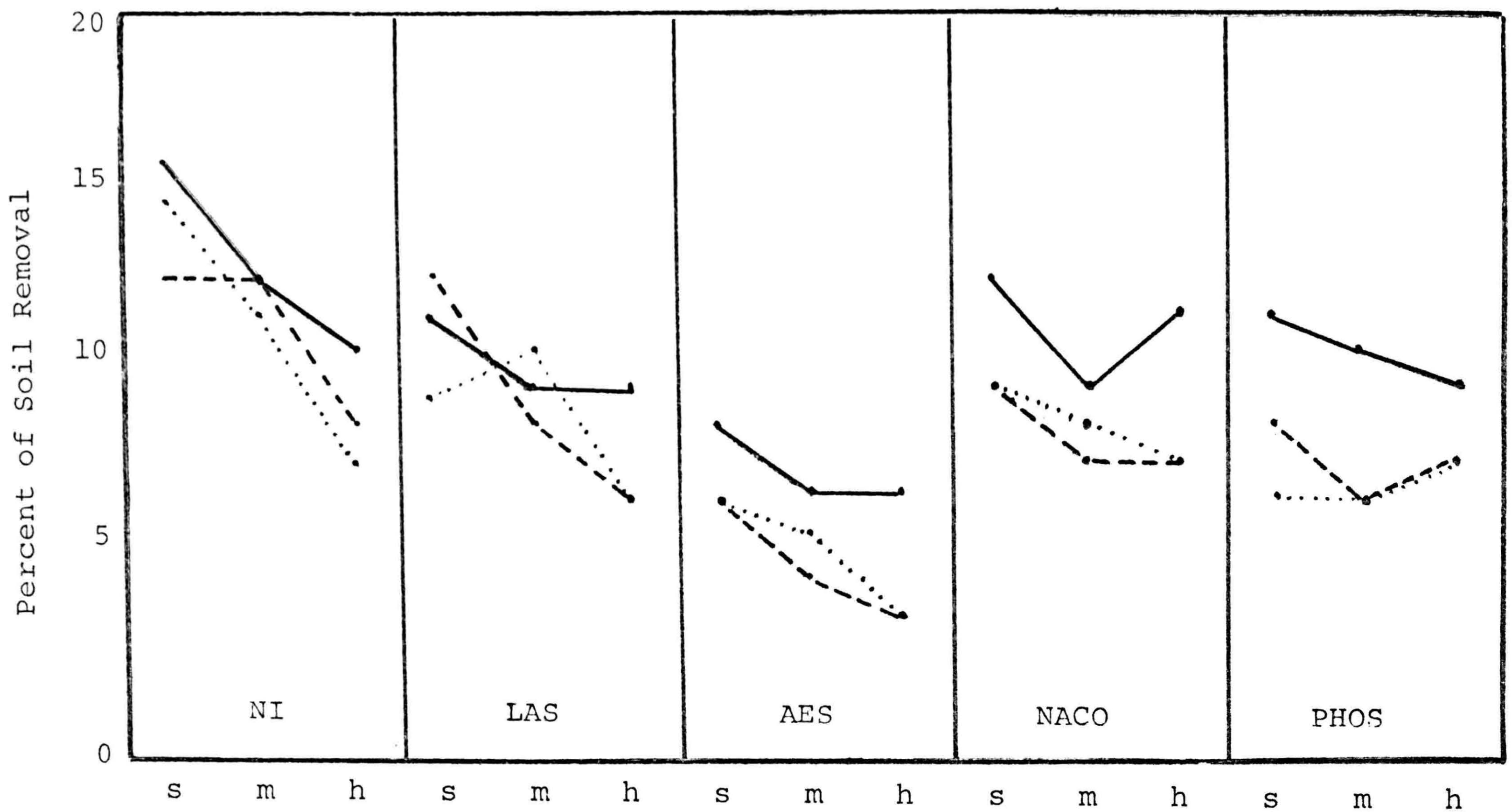
Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	4	169.50	83.86**
Water Hardness (2)	2	125.95	62.31**
Water Temperature (3)	2	87.22	43.15**
Two Way Interactions			
1 X 2	8	11.19	5.54**
1 X 3	8	4.57	2.26*
2 X 3	4	5.83	2.88*
Three Way Interactions			
1 X 2 X 3	16	3.74	1.85*
Residual Error	135	2.02	

*Significant at α = 0.05 level of probability

**Significant at α = 0.01 level of probability

***df = degrees of freedom

†MS = mean square



Water Hardness Levels: s = soft m = medium h = hard

Water Temperatures: ····· = cold ----- = warm _____ = hot

Fig. 5. Percent of Soil Removal from 50/50 Polyester/Cotton Specimens for Five Detergents, Three Water Temperatures, and Three Water Hardness Levels

The NI detergent most efficiently removed soil from blend (polyester/cotton) specimens. Optimum conditions for the NI detergent were hot water and soft hardness level.

The AES detergent demonstrated poor soil removal ability. It performed least efficiently in hard water and at medium and cold temperatures.

Figure 6 depicts the mean values of percent of soil removal from polyester/cotton fabrics, disregarding water temperature and hardness level. The best detergent for soil removal was the NI detergent. The NI detergent varied significantly in a Newman-Keuls ranking test as being the detergent that removed the greatest amount of soil from the blend specimens.

Whiteness Retention of Cotton Fabric

Results of the three-factor analysis of variance for whiteness retention of 100 percent cotton fabrics are shown in Table 5. Main effects, two-way and three-way interactions were all highly significant.

The highest performance level of whiteness retention was achieved by the use of the sodium carbonate built detergent (NACO) in hot water and soft hardness level (Fig. 7). Mean values and standard deviations appear in Appendix C. NACO suspended soil best in hot water and was not as effective at other water temperatures as other detergents were.

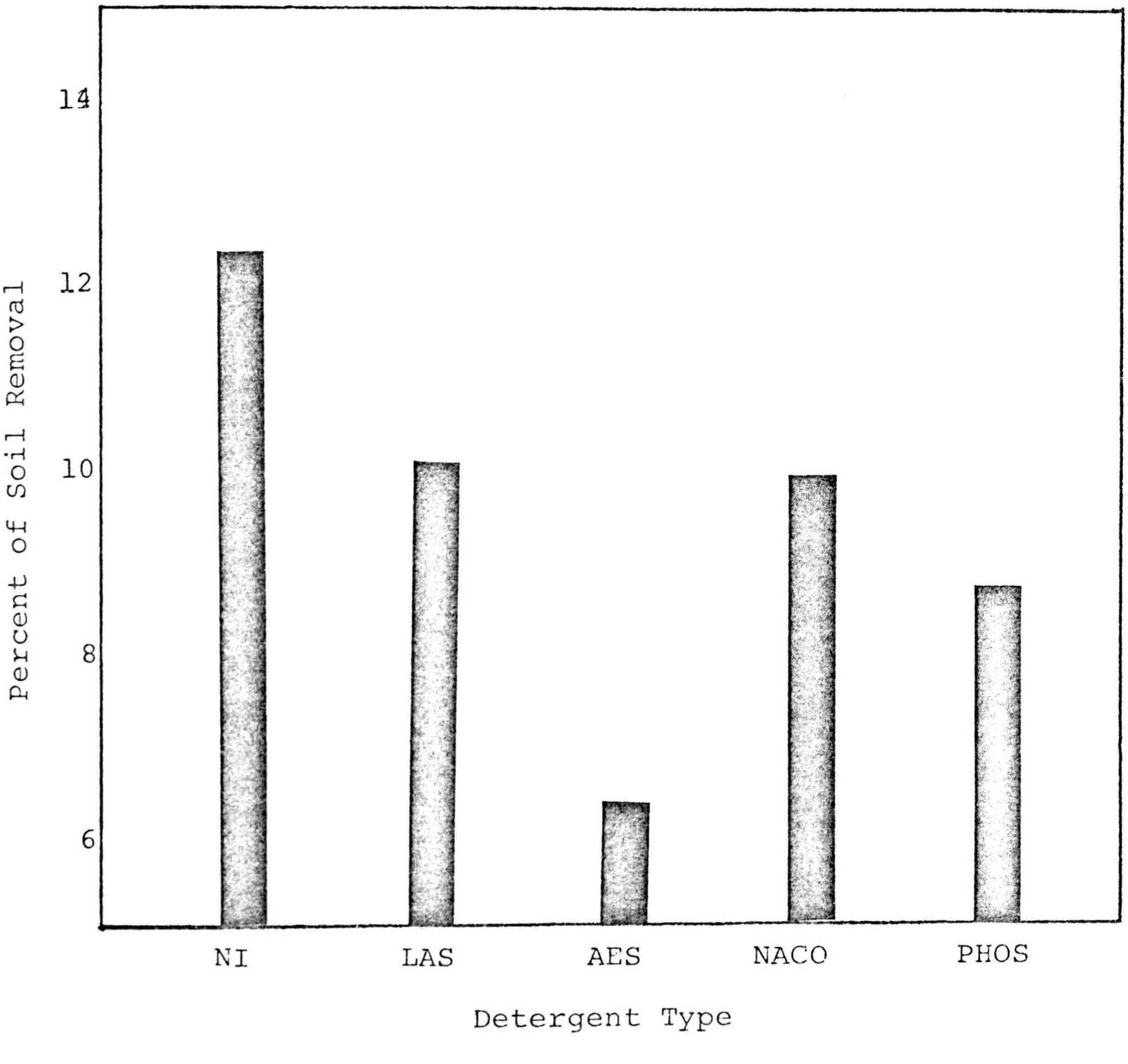


Fig. 6. Percent of Soil Removal from 50/50 Polyester/ Cotton Specimens for Each of Five Detergents

TABLE 5.--Summary of the Analysis of Variance for Percent of Whiteness Retention of Cotton Specimens

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	4	44.24	211.21**
Water Hardness (2)	2	108.21	516.68**
Water Temperature (3)	2	175.65	838.65**
Two Way Interactions			
1 X 2	8	5.37	25.64**
1 X 3	8	16.11	76.93**
2 X 3	4	1.48	7.08**
Three Way Interactions			
1 X 2 X 3	16	1.70	8.10**
Residual Error	135	0.21	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

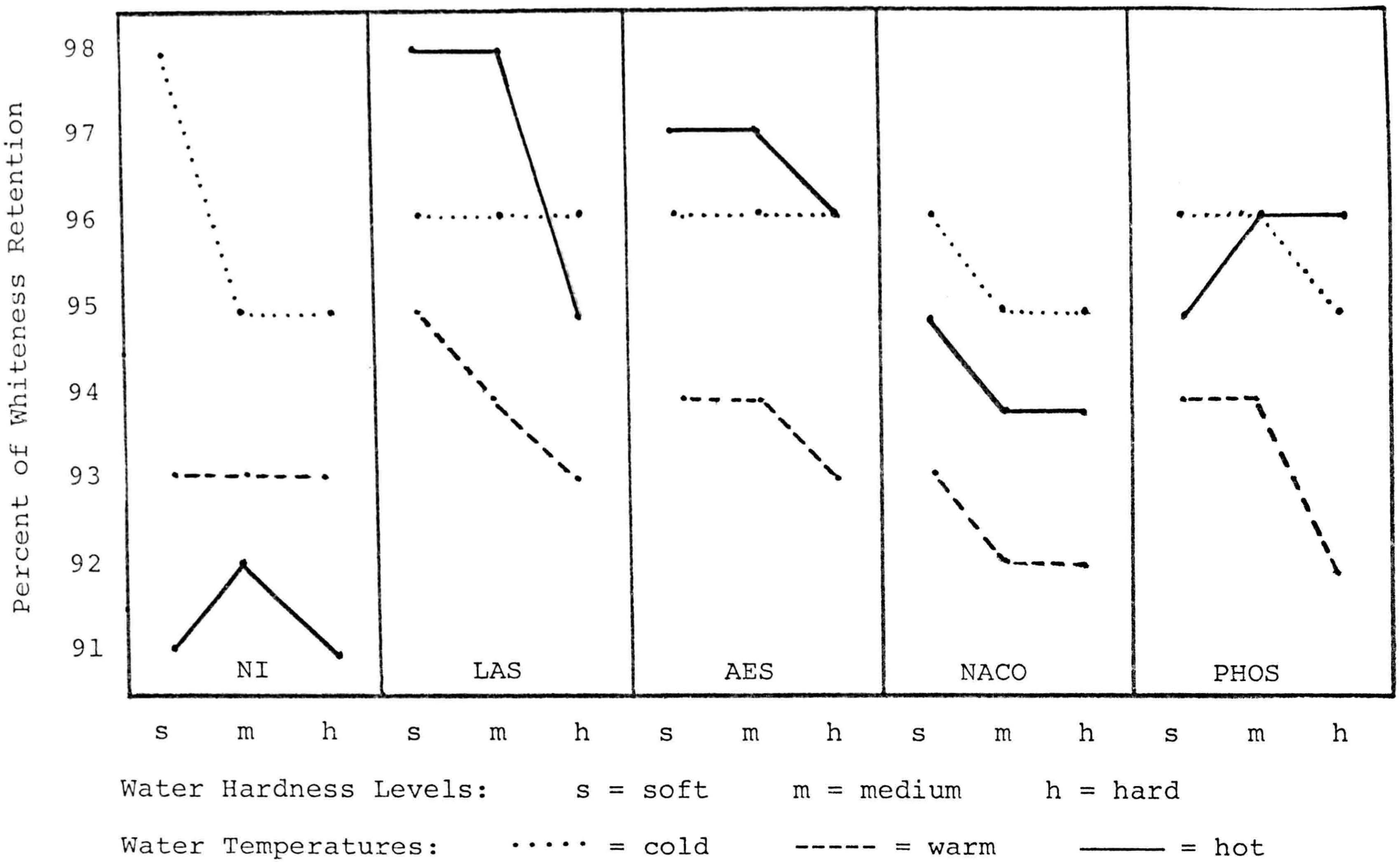


Fig. 7. Percent of Whiteness Retention of 100 Percent Cotton Specimens for Five Detergents, Three Water Temperatures, and Three Water Hardness Levels

The lowest score of whiteness retention was found on fabrics exposed to the phosphate built detergent (PHOS) in cold water temperature and at medium and hard water hardness levels. PHOS appeared to be superior in hot water and decidedly less efficient in warm and cold water temperatures.

Figure 8 is a bar graph representation of the mean values of whiteness retention percentages yielded by the five selected detergents on cotton fabrics. The three zeolite detergents cleaned the cotton fabric most efficiently regarding soil suspension.

A Newman-Keuls test was administered to the single factor detergent. LAS was significantly the highest ranked detergent for suspending soil when laundering cotton fabrics.

Whiteness Retention of Polyester/Cotton Fabric

A three-factor analysis of variance was performed for whiteness retention of polyester/cotton specimens (Table 6). The three main factors were each highly significant. All two-way and three-way interactions were also highly significant.

The use of the nonionic (NI) detergent and the LAS surfactant and zeolite built (LAS) detergent rendered the highest percentages of whiteness retention for blend fabrics in soft hardness level water conditions. The NI detergent performed best in cold water at all hardness levels; least efficiently in hot water, all hardness levels (Fig. 9).

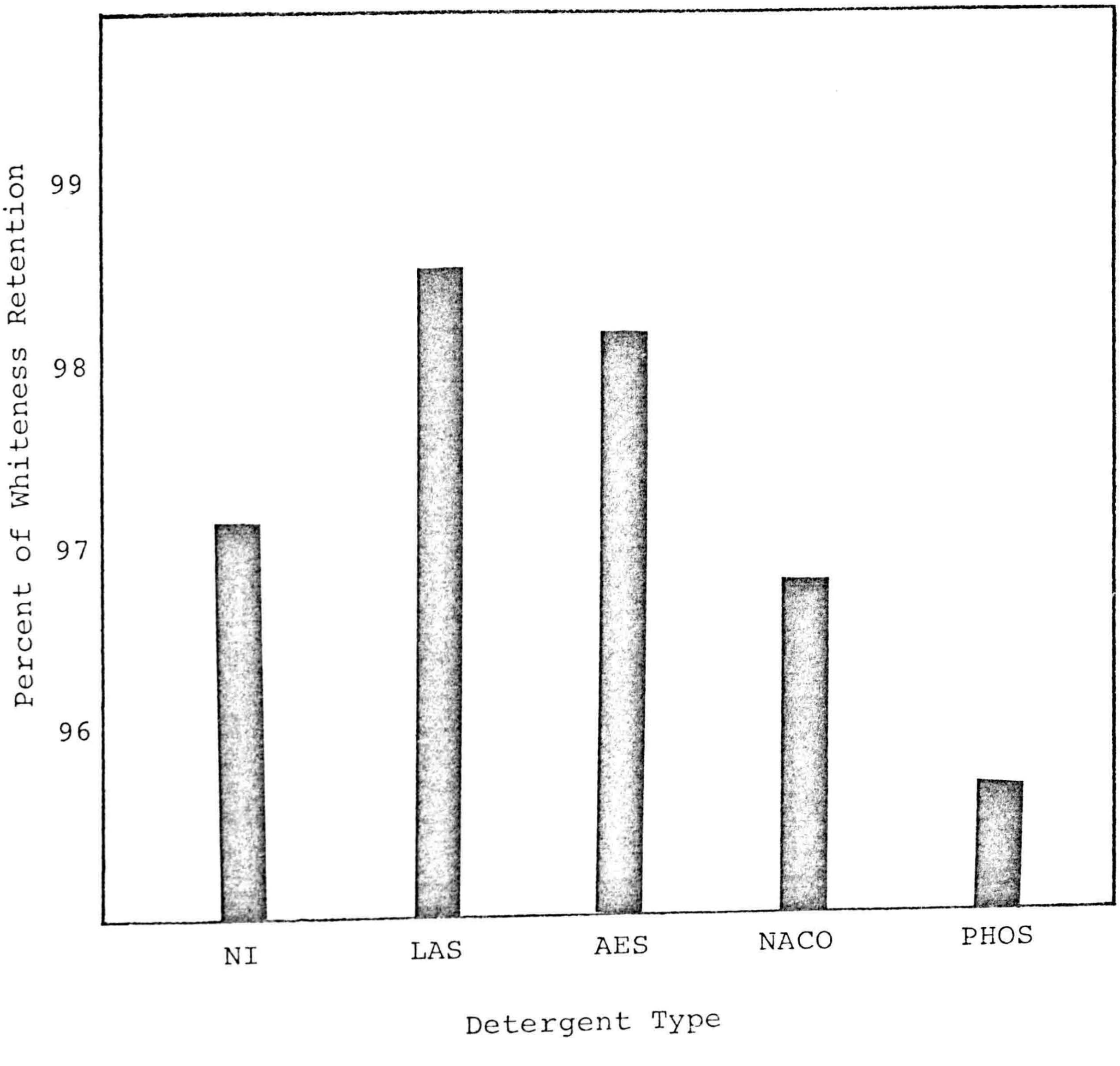


Fig. 8. Percent of Whiteness Retention of 100 Percent Cotton Specimens for Each of Five Detergents

TABLE 6.--Summary of the Analysis of Variance for Percent of Whiteness Retention of Polyester/Cotton Specimens

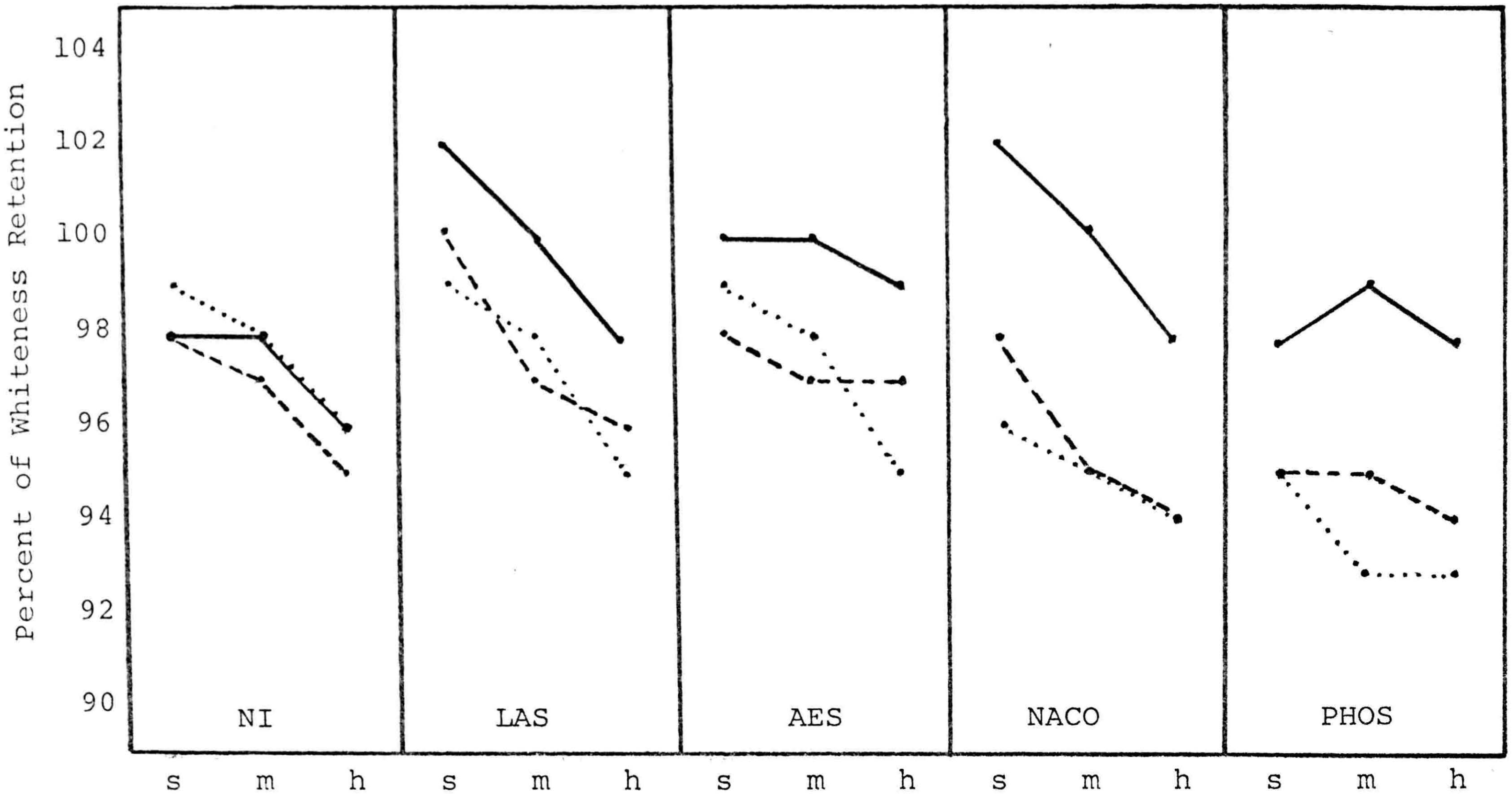
Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	4	29.69	127.80**
Water Hardness (2)	2	13.60	58.55**
Water Temperature (3)	2	109.13	469.76**
Two Way Interactions			
1 X 2	8	1.70	7.34**
1 X 3	8	19.00	81.78**
2 X 3	4	2.24	9.65**
Three Way Interactions			
1 X 2 X 3	16	1.96	8.43**
Residual Error	135	0.23	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square



Water Hardness Levels: s = soft m = medium h = hard

Water Temperatures: ····· = cold ----- = warm ——— = hot

Fig. 9. Percent of Whiteness Retention of 50/50 Polyester/Cotton Specimens for Five Detergents, Three Water Temperatures, and Three Water Hardness Levels

Supporting mean values and standard deviations are in table form in Appendix C.

The LAS detergent maintained whiteness retention best in hot water, soft and medium hardness levels. Higher retention scores were attained on cotton fabrics over blend fabrics.

Figure 10 graphically illustrates the mean values of whiteness retention percentages for polyester/cotton fabrics. The LAS detergent was most efficient in suspending soil.

Mean values for whiteness retention of the single factor detergent were subjected to a Newman-Keuls multiple range test. The LAS detergent ranked significantly highest over four detergents in suspending soil.

Water Temperature

A general trend was noted when water temperature and detergent interactions were analyzed. Hot water, with some exceptions, appeared to be the best temperature condition for each detergent. Cold water was a more favorable condition than warm water.

The significant main effect of water confirmed that all detergents performed best in hot water. The exception was that cold water was the most favorable temperature for whiteness retention of blend fabric (Fig. 11). A Newman-Keuls multiple range test was performed and confirmed that hot water was the best water temperature. The Newman- Keuls

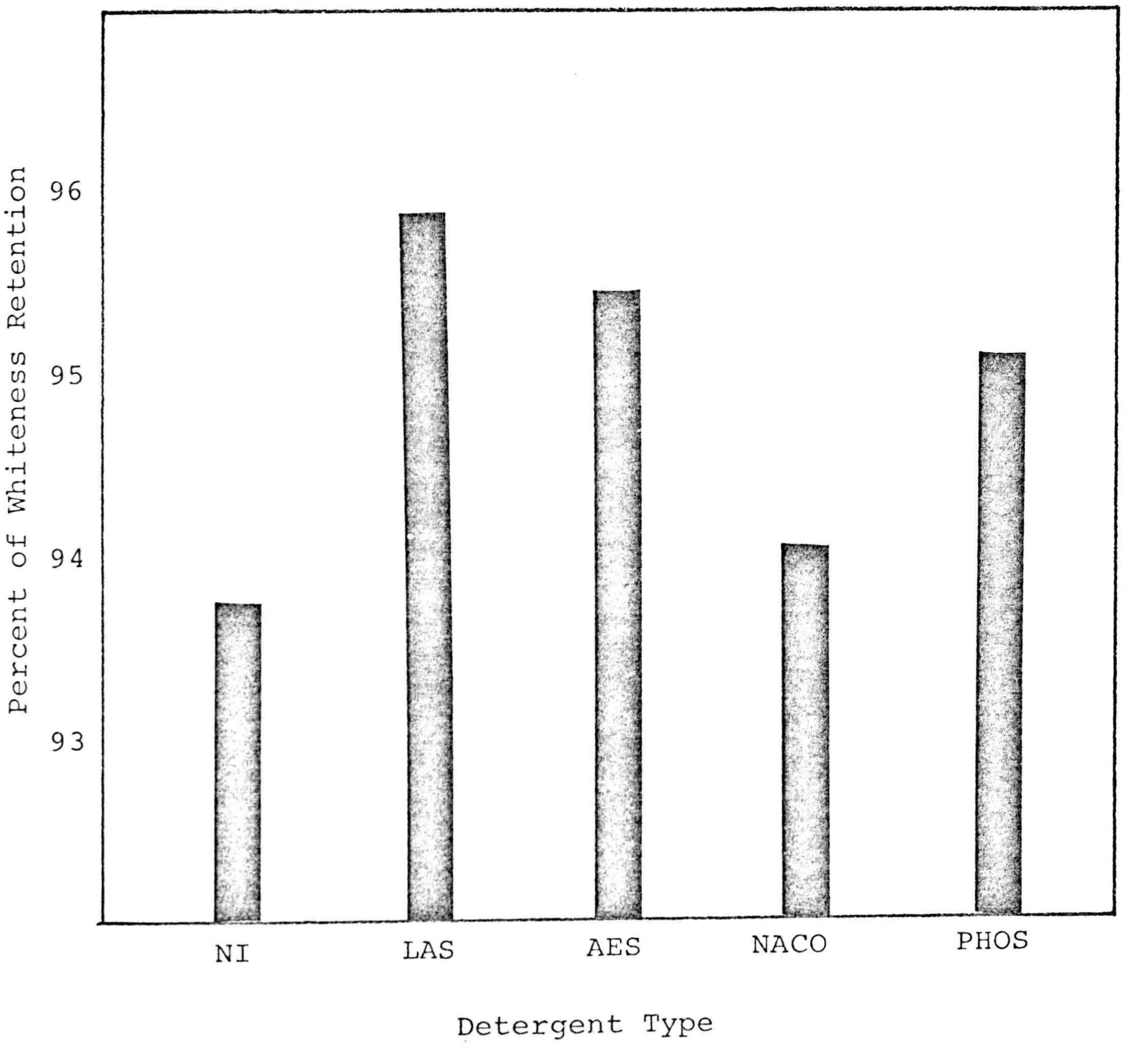


Fig. 10.--Percent of Whiteness Retention of 50/50 Polyester/Cotton Specimens for Each of Five Detergents

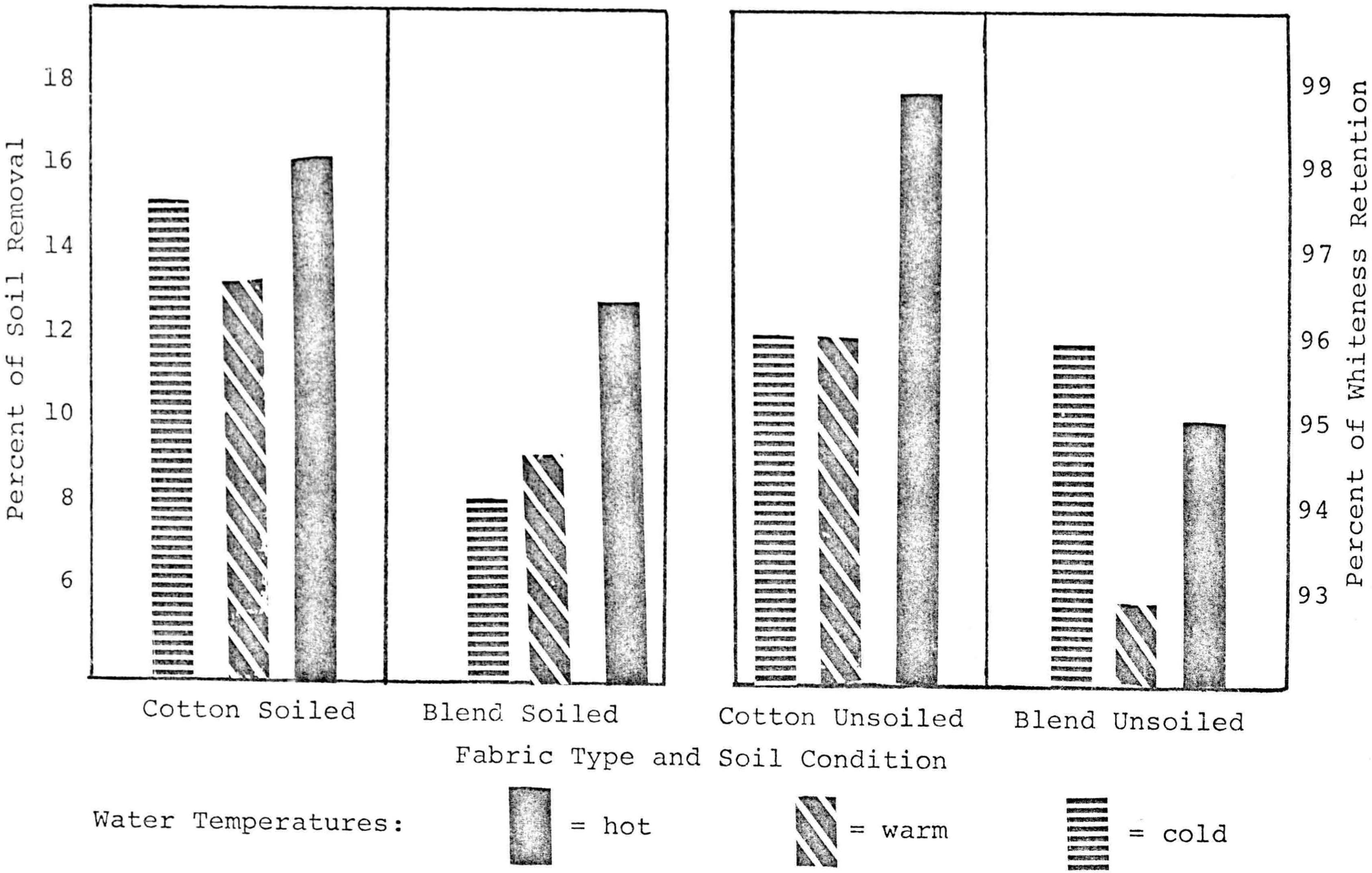


Fig. 11. The Effect of Water Temperature on the Percent of Soil Removal and Whiteness Retention of 100 Percent Cotton and 50/50 Polyester/Cotton Specimens

tested the mean values of water temperature effect; detergent type and water hardness level were disregarded.

Water Hardness

From viewing the graphs previously presented (Figs. 3,5,7,9) soft water appeared to be the best water condition for all detergents, hardness levels, and fabric types. Generally, the harder the water conditions, the lower the performance level of detergents at any water temperature.

Figure 12 illustrates the means of water hardness (disregarding detergent type and water temperature) of each fabric type and soil condition. Soft water was the best condition and was confirmed by a Newman-Keuls multiple range test which ranked soft water highest for laundering temperature.

Zeolite, Carbonate, and Phosphate Detergents

After analyzing data on all five detergents, further statistical tests were performed to determine which of the three zeolite built detergents was the most efficient. An analysis of variance was performed on each fabric type and soil condition (Appendix D). For each fabric and soil type the detergent factor was highly significant. Of the three zeolite-containing formulations the LAS surfactant system had the highest mean values for both soil removal and whiteness retention in the majority of cases.

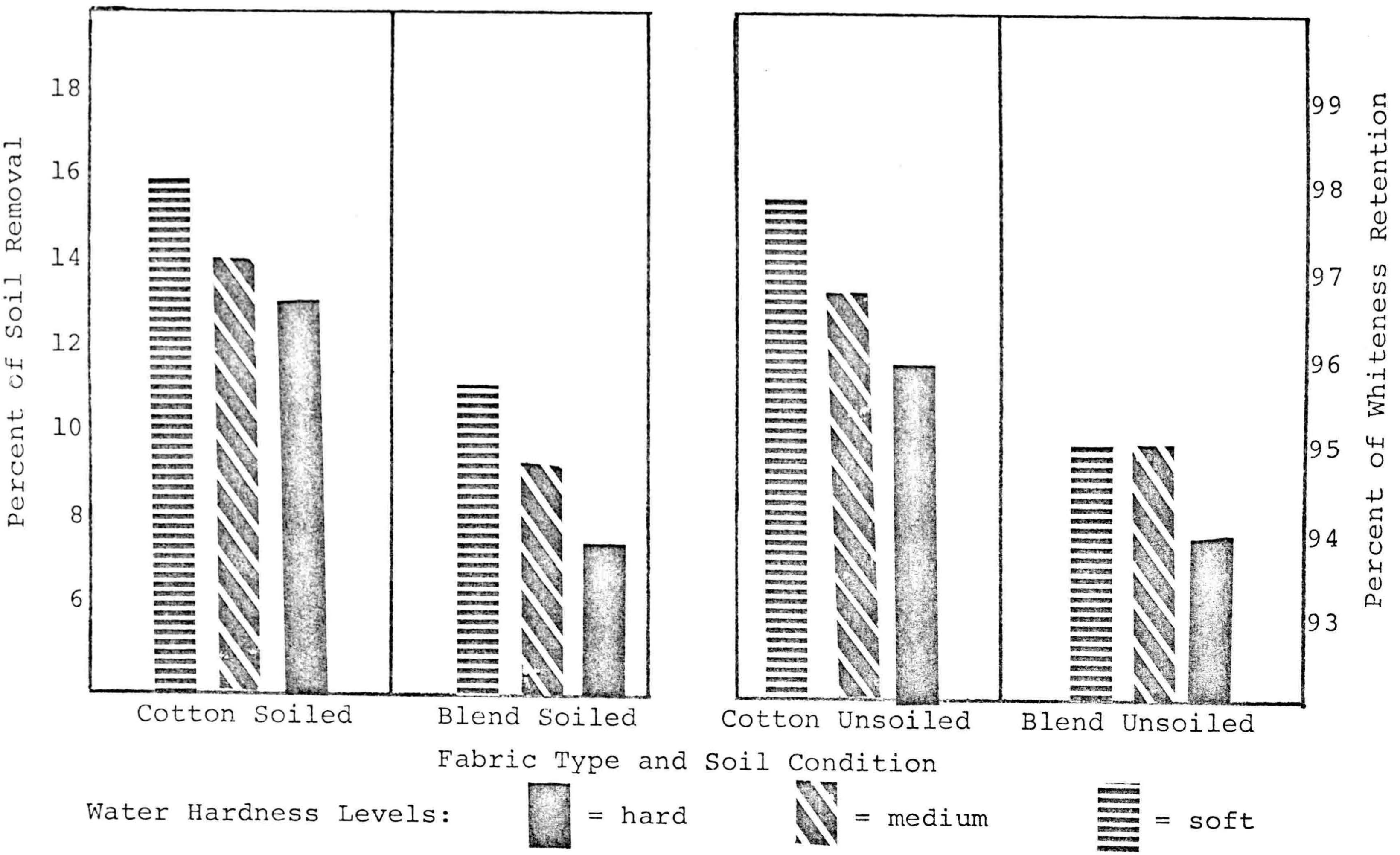


Fig. 12. The Effect of Water Hardness Level on the Percent of Soil Removal and Whiteness Retention of 100 Percent Cotton and 50/50 Polyester/Cotton Specimens

A Newman-Keuls multiple range test was performed to determine significant differences between the three detergents regarding cleaning efficiency (Table 7). The LAS surfactant detergent was significantly better than the AES surfactant detergent for all fabric types and soil conditions.

TABLE 7.-- Newman-Keuls Multiple Range Test Ranking of Detergents for Soil Removal and Whiteness Retention of Cotton and Polyester/Cotton Fabrics

Fabric Type Soil Condition	Mean Values by Detergent Type (%)		
	NI	LAS	AES
Cotton Soiled	<u>16.06</u>	<u>16.45</u>	10.90
Polyester/Cotton Soiled	<u>12.20</u>	9.91	6.22
Cotton Unsoiled	97.14	<u>98.47</u>	98.06
Polyester/Cotton Unsoiled	93.66	<u>95.78</u>	95.45

<u>Underlined Means</u> = highest ranked detergent(s) regarding detergent efficiency

The LAS surfactant system worked well with zeolite builders in maintaining whiteness for both fabric types. The NI surfactant system ranked highest for soil removal from blend fabrics. Both the LAS and NI surfactant systems were good soil removers for cotton fabrics.

Cleaning Efficiency of Detergents Upon Cotton and Polyester/Cotton Fabrics

For purposes of laboratory control, cotton and polyester/cotton fabrics were laundered separately. Results reported thus far were by fabric type and soil condition.

The consumer often washes garments of mixed fabric types in a single wash load. One detergent must be chosen for the washing cycle.

To date, there is no evaluation index that can measure the combined efficiency of a detergent's soil removal and whiteness retention abilities. For this investigation, data were combined in order to determine the most efficient detergent for both fabrics.

A three-factor analysis of variance was performed (Tables 8, 9). Each factor (detergent type, water hardness level, and water temperature) was highly significant in tests for both soil removal and whiteness retention. No single factor exerted more influence than another.

Mean values for soil removal by the five detergents from cotton and polyester/cotton fabrics are shown in Figure 13. In a Newman-Keuls multiple range test the NI, LAS, and carbonate detergents ranked highest, as a group, for soil removal. There was no significant difference between the three detergents regarding soil removal.

Figure 14 illustrates the mean values for whiteness retention by detergent type for both fabric types combined.

TABLE 8.--Summary of the Analysis of Variance for Percent of Soil Removal From Cotton and Polyester/Cotton Specimens

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	4	390.05	39.37**
Water Hardness (2)	2	266.19	26.36**
Water Temperature (3)	2	198.52	20.04**
Two Way Interactions			
1 X 2	8	17.49	1.77
1 X 3	8	14.62	1.48
2 X 3	4	5.30	0.54
Three Way Interactions			
1 X 2 X 3	16	5.61	0.57
Residual Error	315	9.91	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

TABLE 9.--Summary of the Analysis of Variance for Percent of Whiteness Retention of Cotton and Polyester/Cotton Specimens

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	4	53.91	16.03**
Water Hardness (2)	2	99.25	29.52**
Water Temperature (3)	2	163.03	48.49**
Two Way Interactions			
1 X 2	8	5.57	1.66
1 X 3	8	28.65	8.52**
2 X 3	4	2.48	0.74
Three Way Interactions			
1 X 2 X 3	16	2.32	0.69
Residual Error	315	3.36	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

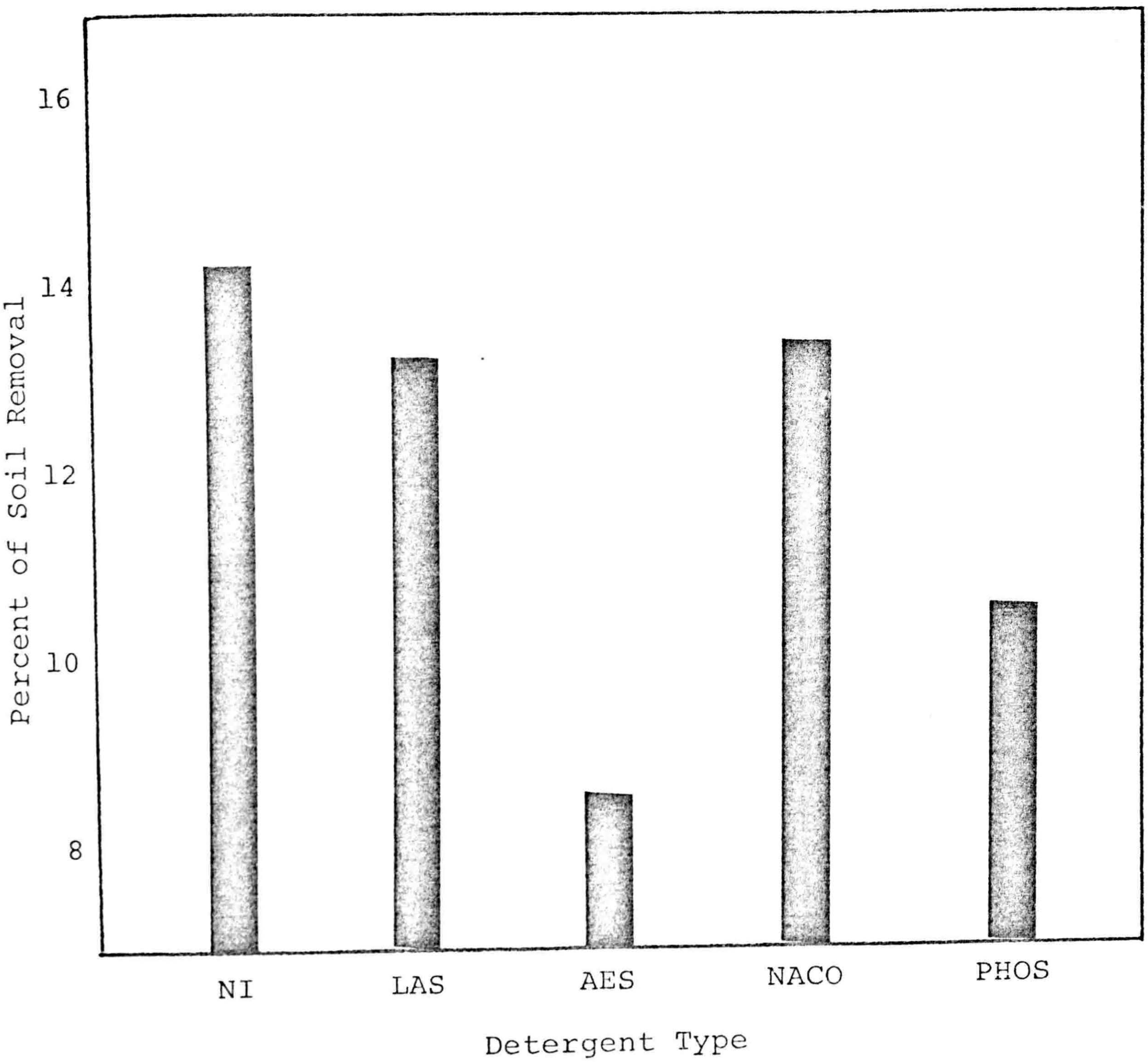


Fig. 13. Percent of Soil Removal from 100 Percent Cotton and 50/50 Polyester/Cotton Specimens for Each of Five Detergents

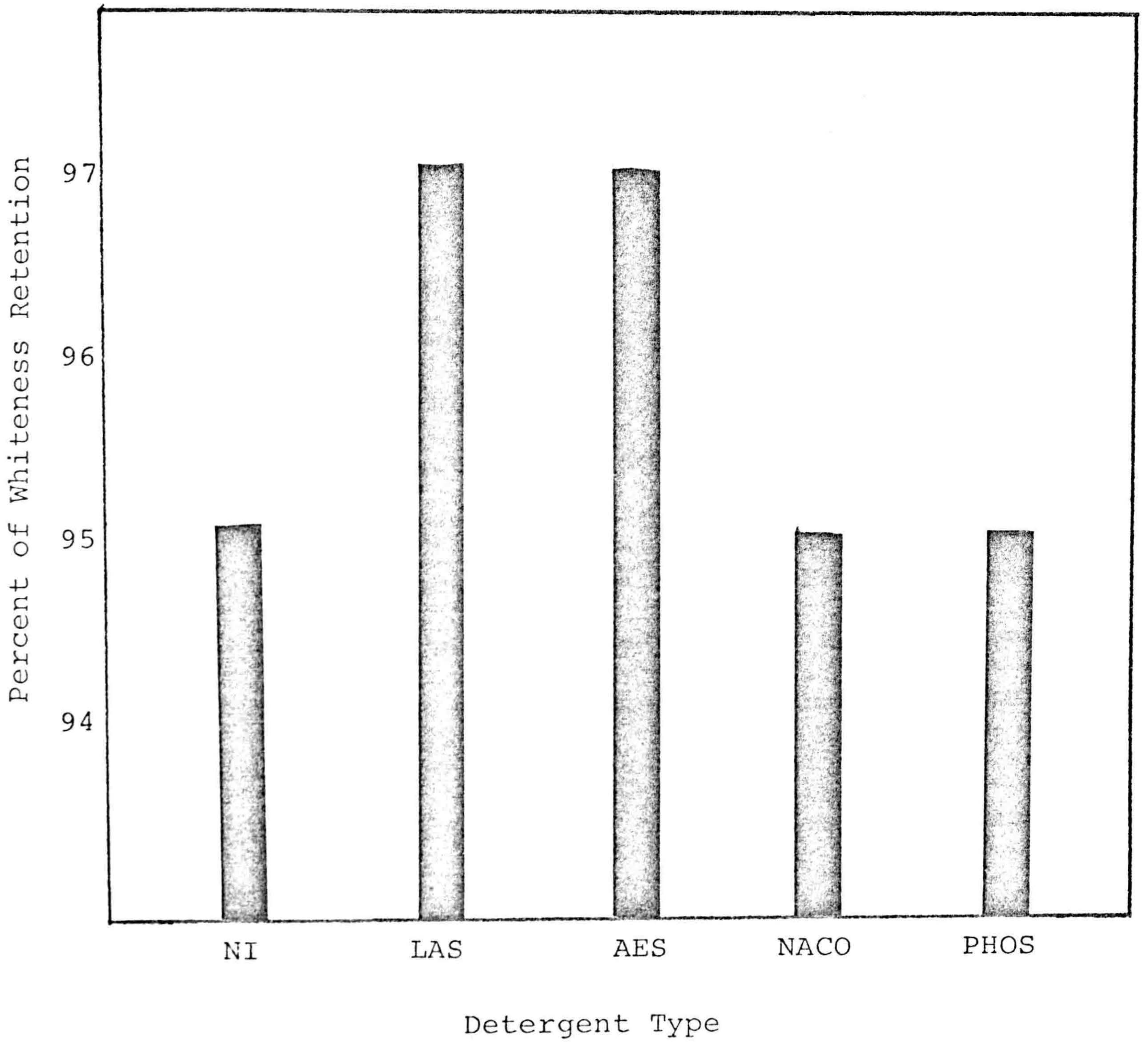


Fig. 14. Percent of Whiteness Retention of 100 Percent Cotton and 50/50 Polyester/Cotton Specimens for Each of Five Detergents

When detergent means were subjected to a Newman-Keuls multiple range test, the LAS and AES detergents were ranked significantly highest. There was not a significant difference between the LAS and AES detergents.

Figures 13 and 14 must be compared to evaluate the cleaning efficiency of the detergents. NI, the best detergent for soil removal, ranked low in whiteness retention. Apparently, the high amount of soil removed was not held in suspension and was redeposited onto the white fabric.

The LAS detergent was efficient in removing soil and in maintaining whiteness. When soil was removed it was held in suspension in the wash liquor during the laundering cycle.

The amount of soil removed by the AES detergent was minimal. What little soil was removed may not have been deposited on the white fabric (therefore, a high whiteness retention score). However, because its soil removal score ranked significantly lowest, its overall evaluation as an efficient detergent is doubtful.

The sodium carbonate detergent removed a high percent of soil, but did not appear to hold it in suspension. The low whiteness retention score makes it a less desirable detergent regarding overall effectiveness.

The phosphate detergent maintained a low position in both soil removal and whiteness retention. It was not as efficient a detergent as the others tested.

The main hypothesis of this research, as stated earlier, is: There is no significant difference between the five detergents tested in cleaning cotton and polyester/cotton fabrics. A three-factor analysis of variance test was performed on the soil removal and whiteness retention values (Tables 8, 9). An additional Newman-Keuls multiple range test was performed to determine significant differences between mean values in ranking detergent types for cleaning efficiency. The hypothesis was accepted at a probability level of 0.05. There was no single detergent that was most efficient in removing soil and in maintaining whiteness.

Tensile Strength

In addition to measurements of detergent efficiency, the degradative effect of the detergents upon fabrics during laundering was determined. Tensile strength was the index selected for measuring the degradative effects.

The specimens were evaluated to indicate a loss (or gain) of tensile strength after laundering. Sometimes a fabric shows a gain in strength after laundering. Fabrics that tend to shrink when washed in hot water (e.g. cotton) may increase in tensile strength due to fiber shrinkage. A majority of fabrics, however, tend to lose strength after laundering. A great loss in tensile strength of a fabric may be associated with a harmful detergent. A detergent may remove and suspend soil well, but if it degrades fabric it is undesirable. A detergent should clean fabric well (high percentage of soil removal and whiteness retention) and not be unduly harmful to that fabric regarding strength loss.

Mean values and standard deviations of tensile strength loss percentages of all specimens are depicted in Table 10. A four-factor analysis of variance was performed on the tensile strength data for all specimens (Table 11). Results revealed all main effects to be significant at the $\alpha = 0.01$ level of probability.

Table 10.--Mean Values and Standard Deviations for Tensile Strength Loss of Cotton and Polyester/Cotton Fabrics

Detergent Type	Mean Values (in percent loss)	Standard Deviations
NI	18.52	7.84
LAS	17.49	7.29
AES	18.55	6.77
NACO	16.81	6.48
PHOS	16.97	7.45

The AES and NI detergents appeared to be most harmful to both fabric types tested. The NACO and PHOS detergents appears to be least damaging to fabrics. Mean values

TABLE 11.--Summary of the Analysis of Variance for Percent of Loss in Tensile Strength of Cotton and Polyester/Cotton Specimens

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	4	99.23	3.86**
Water Hardness (2)	2	318.87	12.39**
Water Temperature (3)	2	102.63	3.99*
Fabric Type (4)	3	4243.17	164.89**
Two Way Interactions			
1 X 2	8	59.12	2.30*
1 X 3	8	222.82	8.66**
1 X 4	12	89.86	3.49**
2 X 3	4	76.43	2.97*
2 X 4	6	40.10	1.56
3 X 4	6	46.49	1.81
Three Way Interactions			
1 X 2 X 3	16	23.00	0.89
1 X 2 X 4	24	31.92	1.24
1 X 3 X 4	24	95.07	3.69**
2 X 3 X 4	12	13.38	0.52
Four Way Interactions			
1 X 2 X 3 X 4	48	35.28	1.37*
Residual Error	540	25.73	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

for tensile strength loss by detergent type are graphed in Figure 15. A Newman-Keuls multiple range test revealed that there were significant differences between groups of detergents. The group of the three zeolite detergents was significantly more detrimental to fabrics than were the PHOS, NACO, and LAS detergents. There was not a significant difference between means of tensile strength loss of fabrics laundered in the zeolite-containing detergents.

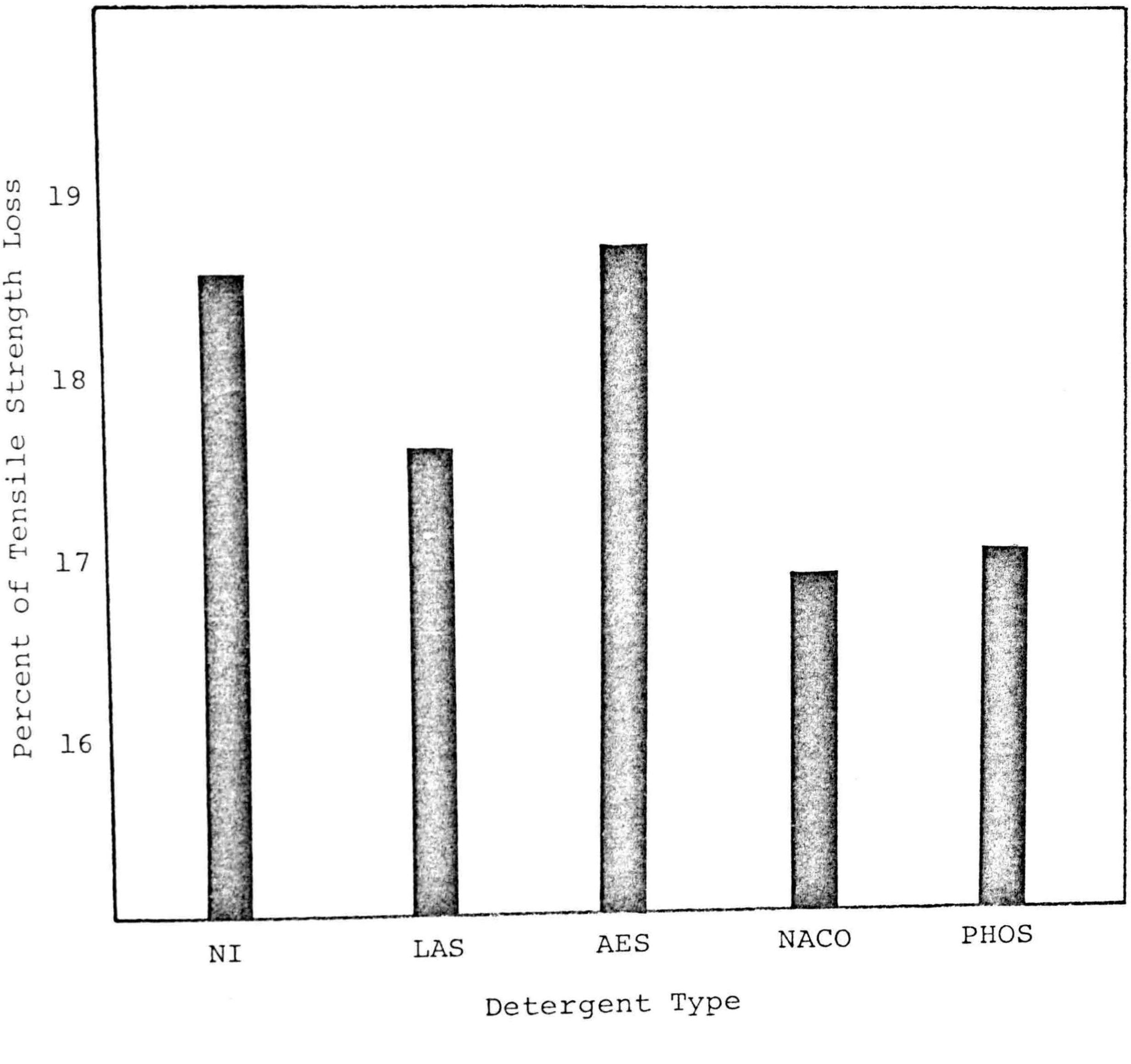


Fig. 15. Percent of Tensile Strength Loss of 100 Percent Cotton and 50/50 Polyester/Cotton Specimens by Detergent Type

CHAPTER VI

DISCUSSION

Results of research obtained in this study are compared to reported findings of research performed by others. Zeolite usage as a laundry detergent builder has been explored only within the past five years, yielding a limited quantity of published articles. Three comparisons are discussed relevant to zeolite detergent laundering: 1) Water Hardness Comparisons, 2) Phosphate Detergents Compared to Zeolite Built Detergents, 3) Effect of Zeolite Built Detergents on Soil Cloth.

Water Hardness Comparison

Results of the interactions of detergent, water temperature and water hardness revealed that the softer the water, the better the cleaning efficiency of any of the five detergents tested.

The LAS surfactant and zeolite built, carbonate, and phosphate detergents tested in this research used a LAS surfactant system. Optimum results were obtained at 0 ppm hardness level (soft).

Results coincide with Langguth's findings (19). When he tested a LAS surfactant/phosphate built detergent he found that soft to medium (100 ppm hardness) water was an optimum laundering condition for the specified detergent formulation.

Phosphate Detergents Compared to Zeolite Built Detergents

Reports of published research reveal that phosphate detergents clean fabric more efficiently than non-phosphate detergents. Fuchs reported that a STPP detergent performed at a higher performance level than a zeolite built detergent (14). Results of this study directly contradicted the results of Fuchs.

Zeolite built detergents were generally better detergent performers as reported in results of this research. Exposed to similar laundering conditions the LAS/zeolite built detergent outperformed the phosphate built detergent (warm water, medium hardness, phosphate built detergent compared to zeolite built detergent, both using a LAS surfactant system). One factor varied in testing conditions between the two research studies and may be the attributal factor: Fuchs used only zeolite A in his laboratory experiments, whereas zeolite A and X were used in this research study.

Effect of Zeolite Built Detergents on Soil Cloth

Results of this study can be compared to research done by Sherman (32). Sherman found that a LAS surfactant and zeolite A and X built detergent cleaned a clay soil, blend fabric best. Sherman tested a variety of fabric types to determine which fabric and soil conditions zeolite detergents were most effective in cleaning.

Results reveal that the LAS surfactant and zeolite built detergent removed the highest percentage of soil in medium hardness, cold water conditions from blend fabrics. The two fabric types (cotton and blend) were not subjected to tests to determine fabric ranking. However, a trend was noted that the LAS detergent appeared to remove a higher percentage of soil in 100 percent cotton cloth over the blend fabric.

CHAPTER VII

SUMMARY AND RECOMMENDATIONS

Consumers face the dilemma of selecting a single laundry detergent that will perform the best when laundering clothes. In some geographical locations in the United States the consumers' choices is limited to only non-phosphate detergents. There is a barrage of products from which to choose. The shopper experiences difficulty in deciding which one will clean best.

Prior to the 1970s the consumer used one basic type of detergent, a phosphate, which seemed to clean clothes quite well. Due to restrictive codes governing the use of phosphates in detergents in certain locations of the United States, new detergent products have appeared on the market. None marketed, thus far, appear to clean as well as the "old" phosphate detergent.

The detergent manufacturer wants to please as many consumers in the United States as possible with a single product. Both the manufacturer and the consumer share a common goal: they want to obtain maximum cleaning performance from a detergent. This goal becomes a difficult task for the manufacturer. Prior to 1970 one detergent would do the job well. A detergent with a high percentage of phosphate would work well on cotton fabrics in any water hardness level, and especially well in hot water temperatures. Now, the present trend of the consumer is to launder mixed fabric loads in cold water. The consumer is more ecologically minded, and whether in a phosphate ban area or not, many consumers seek detergents without phosphates.

The manufacturer meets the consumer's demand by testing and marketing detergents with phosphate builder replacements. Manufacturers want to produce a detergent that removes soil and maintains whiteness in fabrics over a wide range of laundering conditions. Detergent researchers want to find a non-phosphate detergent that will clean clothes as efficiently, and at about the same cost, as a phosphate detergent.

Zeolites are considered by people in the detergency field to be a prime phosphate replacement that will meet the consumers' demands as well as please the manufacturer. Non-phosphate detergents were explored in this research to determine the best surfactant system to compliment zeolite builders. Three zeolite detergents were compared to carbonate and phosphate built formulations. Different water temperatures and hardness levels were tested utilizing two fabric types to determine the best combination of laundering conditions. Fabric, detergent, water hardness level and water temperature were examined.

The efficiency of a detergent is determined by the detergent's ability to remove soil and to maintain whiteness. Laboratory tests were performed to measure soil removal and whiteness retention by the difference in light reflectance readings of fabric before and after laundering.

Results revealed that the two most efficient detergents in cleaning both cotton and polyester/cotton blend fabrics were a nonionic surfactant with a zeolite builder and a LAS surfactant/zeolite built detergent. Of the three zeolite built detergents, the LAS surfactant system appeared to be the most effective in removing and suspending soil in all water conditions. The LAS surfactant/zeolite built detergent also ranked high in cleaning efficiency when compared to carbonate and phosphate built detergents.

Results revealed that water temperature and water hardness levels were significant conditions when washing the two fabric types. Hot, soft water was the best wash water combination. Cold water was better than warm water in laundering 100 percent cotton and blended fabrics with any of the five detergents investigated. When laundering in hard water, a hot temperature was an optimum condition.

When fabric was laundered in soft water, wash liquor temperature was relatively unimportant.

The nonionic detergent formulation cleaned blended fabrics best. The carbonate built detergent cleaned 100 percent cotton fabric best. Soil suspension of both detergent types was relatively high.

The results of this study supported the possibility of zeolites being used as phosphate builder replacements. Zeolites combined with nonionic and LAS surfactant systems consistently performed well in comparison to phosphate built detergents.

Recommendations

Further investigation of zeolite built laundry formulations is indeed probable for the future. Ideas and suggestions for future research have emerged from this study. Following are topical suggestions for further research:

1. Comparison of laboratory blended detergents with spray-dried detergents regarding cleaning efficiency
2. The effects of zeolite built detergents on a wider range of fabric types, more closely resembling a home laundering situation
3. Investigation of different water hardness

levels and wash water temperatures in conjunction with various detergent concentrations

4. Comparison of a variety of soil cloths (pre-soiled versus actual use soil) and performance of detergents regarding soil removal
5. A possible measurement index that could help determine cleaning efficiency of a detergent by both its soil removal and soil suspension abilities

APPENDIX A

GLOSSARY OF TERMS

GLOSSARY

AES - Alcohol ethoxylate sulfate; a high sudsing anionic surfactant that functions well in the presence of water hardness ions

BIODEGRADABILITY - The capability of organic matter to be decomposed by biological processes

BUILDER - A material that upgrades or protects the cleaning efficiency of the surfactant

BUILT DETERGENT - A cleaning product containing surfactant and builder

CMC - Carboxymethylcellulose; a large molecule derived from degraded cellulose; CMC is present in most built laundry detergents to minimize redeposition of soil that has been removed by washing

CHELATING AGENT - A special type of organic sequestering agent that inactivates water hardness and other metallic ions in water

DETERGENT - Technically, any cleaning agent; in popular usage, washing and cleaning agents with a composition other than soap that clean by much the same mechanism as does soap

HEAVY DUTY DETERGENT - A term that describes products designed for doing the total family laundry, including heavily soiled items

LAUNDRY DETERGENT - A product containing a surfactant and other ingredients, formulated to clean and care for the many different fabrics in the family wash

LAS - Linear alkylate sulfonate; readily biodegradable form of alkylbenzene sulfonate surfactant; the workhorse of the detergent industry; anionic and high sudsing

LIGHT DUTY DETERGENT - An unbuilt, or low-level built detergent based washing product designed for light cleaning tasks, especially hand dishwashing

LIQUID DETERGENT - May be formulated as heavy duty laundry detergents, light duty detergents, or hard surface cleaners; liquid detergents that do not contain a high percentage of surfactant

NI - Nonionic; a detergent surfactant that contains neither positively nor negatively charged functional groups; such surfactants have been found to be particularly effective in removing oily soil

pH - An abbreviation expressing the degree of acidity or alkalinity of a solution; scale runs from 0 to 14; numbers increase as alkalinity increases

PHOSPHATES - Salts of the various phosphoric acids; the complex phosphates are a group of sequestering agents widely used in detergent formulations

PRECIPITATING AGENT - A chemical that softens water by converting hardness minerals to an insoluble form; a common agent being sodium carbonate

SOAP - The product formed by the saponification or neutralization of fats, oils, waxes, rosins, or their acids with organic or inorganic bases

SEQUESTERING AGENT - Any compound that, in aqueous solution, combines with a metallic ion to form a water-soluble combination in which the ion is substantially inactive

SODIUM SULFATE - The sodim salt of sulfuric acid; sodium sulfate improves the physical state of detergent granules by aiding pourability and by making the granules crisper; used as a filler, manufacturing aid, or quality control agent

SODIUM SILICATE - A sodium salt of silicic acid, may serve as builders at higher quantity levels in some detergent formulations, provide a source of buffered alkalinity; aids in keeping soil suspended in laundry wash water, and add crispness to detergent granules; also used as a corrosion inhibitor.

STPP - Sodium tripolyphosphate; a complex phosphate

SURFACTANT - Surface active agent; an organic chemical that, when added to a liquid, changes the properties of that liquid at a surface

SYNTHETIC DETERGENT - A term describing washing and cleaning products based on synthetic surfactants rather than traditional soaps

UNBUILT DETERGENT - A detergent without a builder, also known as light duty detergents

WASH LIQUOR - Wash water used in laundering

WATER HARDNESS - Soluble metal salts, principally those of calcium and magnesium, and sometimes iron and manganese, that when present in water in sufficient amounts create cleaning problems; hardness is expressed in grains per gallon (gpg), grains per liter (gpl), or parts per million (ppm). One gpg equals 17.1 ppm. Water essentially free of calcium and magnesium is described as soft; appreciable amounts of either, hard.

WATER SOFTENER - An agent that inactivates or removes water hardness minerals, principally calcium and magnesium

WATER TEMPERATURE - Degree of hotness or coldness of water

ZEOLITE - Sodium aluminosilicate, molecular sieve, ion exchanger; an inorganic material that may be used as a detergent builder

SOURCE: SDA, A Handbook of Industry Terms, 1979.

APPENDIX B

CHEMICALS AND SOURCES

The listed chemicals were obtained from the following sources and blended in the designated proportions in preparing Detergents A, B, C, and D, as discussed in the procedure.

1. Nonionic (NI) surfactant was obtained from Shell Chemical Company, Houston, Texas. Neodol 25-7® is Shell's name for their version of a condensation product of fatty alcohols and ethylene oxide. Shell Company manufactures alcohols by a variation of the hydrofomylation of olefins, also known as the modified OXO process.

2. LAS surfactant was obtained from Monsanto Industrial Chemicals Company, St. Louis, Missouri. The sodium alkylbenzene sulfonate is a laboratory-prepared sample from Monsanto's Alkylate A-230 alkylbenzene, having a typical carbon number of 13.1 , with a corresponding molecular weight of 261. The sodium salt was obtained by sulfonating the alkylbenzene and then neutralizing the reulting sulfonic acid with sodium hydroxide.

3. AES surfactant was obtained from Shell Company as the sulfate salt, NEODOL 25-3S®, differing from the NI surfactant in having three ethoxylate (EO) groups.

4. Zeolite A was provided by Ethyl Chemical Corporation, Baton Rouge, Louisiana.

5. Zeolite X, made only by the Union Carbide Company in the United States, and furnished by them, was labeled as LINDE® Zeolite Detergent Builder ZB-400. This was a sodium form of the type X zeolite structure.

6. Sodium silicate was obtained from Ethyl Corporation, but was manufactured by Philadelphia Quartz Company.

7. CMC was contributed by Ethyl Corporation.

8. Sodium sulfate and sodium carbonate were obtained from a local chemical supplier.

APPENDIX C

MEAN VALUES AND STANDARD DEVIATIONS

broken down by DETERG
by HARD
by TEMP

100 % Cotton Specimens -- Soil Removal Mean Values and Standard Deviations

Variable	Code	Value label	Sum	Mean	Std dev	Variance	N
For entire population			2612.8526	14.5158	3.3552	11.2575	(180)
DETERG	1.	NI	578.0564	16.0571	2.7004	7.2922	(36)
HARD	6.	SOFT	225.8621	18.8218	1.6527	2.7313	(12)
TEMP	9.	COLD	82.6019	20.6505	0.7503	0.5630	(4)
TEMP	10.	WARM	69.2790	17.3197	0.7837	0.6142	(4)
TEMP	11.	HOT	73.9812	18.4953	1.1083	1.2284	(4)
HARD	7.	MEDIUM	196.0815	16.3401	0.8920	0.7956	(12)
TEMP	9.	COLD	66.1442	16.5360	0.4525	0.2047	(4)
TEMP	10.	WARM	63.7931	15.9483	1.3384	1.7914	(4)
TEMP	11.	HOT	66.1442	16.5360	0.7837	0.6142	(4)
HARD	8.	HARD	156.1129	13.0094	1.0567	1.1167	(12)
TEMP	9.	COLD	50.4702	12.6176	1.0118	1.0236	(4)
TEMP	10.	WARM	50.4702	12.6176	1.0118	1.0236	(4)
TEMP	11.	HOT	55.1724	13.7931	0.9049	0.8189	(4)
DETERG	2.	LAS	592.1630	16.4490	2.2658	5.1338	(36)
HARD	6.	SOFT	211.7555	17.6463	2.1256	4.5180	(12)
TEMP	9.	COLD	76.3323	19.0831	0.7503	0.5630	(4)
TEMP	10.	WARM	65.3605	16.3401	3.0268	9.1616	(4)
TEMP	11.	HOT	70.0627	17.5157	1.3384	1.7914	(4)
HARD	7.	MEDIUM	192.9467	16.0789	2.5768	6.6397	(12)
TEMP	9.	COLD	76.3323	19.0831	0.9861	0.9725	(4)
TEMP	10.	WARM	53.6050	13.4013	1.0118	1.0236	(4)
TEMP	11.	HOT	63.0094	15.7524	0.7837	0.6142	(4)
HARD	8.	HARD	187.4608	15.6217	1.6484	2.7173	(12)
TEMP	9.	COLD	67.7116	16.9279	0.6399	0.4095	(4)
TEMP	10.	WARM	54.3887	13.5972	0.7503	0.5630	(4)
TEMP	11.	HOT	65.3605	16.3401	0.7503	0.5630	(4)
DETERG	3.	AES	392.3197	10.8978	2.3159	5.3634	(36)
HARD	6.	SOFT	150.6270	12.5522	1.9616	3.8480	(12)
TEMP	9.	COLD	55.1724	13.7931	0.9049	0.8189	(4)
TEMP	10.	WARM	40.2821	10.0705	0.3918	0.1535	(4)
TEMP	11.	HOT	55.1724	13.7931	0.9049	0.8189	(4)
HARD	7.	MEDIUM	124.7649	10.3971	2.1484	4.6157	(12)
TEMP	9.	COLD	42.6332	10.6583	0.9049	0.8189	(4)
TEMP	10.	WARM	31.6614	7.9154	0.7837	0.6142	(4)
TEMP	11.	HOT	50.4702	12.6176	0.7837	0.6142	(4)
HARD	8.	HARD	116.9279	9.7440	1.9723	3.8898	(12)
TEMP	9.	COLD	37.9310	9.4828	0.7837	0.6142	(4)
TEMP	10.	WARM	30.8777	7.7194	0.7503	0.5630	(4)
TEMP	11.	HOT	48.1191	12.0298	0.7503	0.5630	(4)
DETERG	4.	NACO	606.2696	16.8408	2.3004	5.2917	(36)
HARD	6.	SOFT	217.2414	18.1034	2.3981	5.7510	(12)
TEMP	9.	COLD	71.6301	17.9075	0.9861	0.9725	(4)
TEMP	10.	WARM	63.0094	15.7524	1.5007	2.2520	(4)
TEMP	11.	HOT	82.6019	20.6505	1.3384	1.7914	(4)
HARD	7.	MEDIUM	196.8652	16.4054	1.9002	3.6107	(12)
TEMP	9.	COLD	68.4953	17.1238	0.7503	0.5630	(4)
TEMP	10.	WARM	56.7398	14.1850	1.5007	2.2520	(4)
TEMP	11.	HOT	71.6301	17.9075	0.3918	0.1535	(4)
HARD	8.	HARD	192.1630	16.0136	2.1871	4.7832	(12)
TEMP	9.	COLD	63.7931	15.9483	0.3918	0.1535	(4)
TEMP	10.	WARM	54.3887	13.5972	0.7503	0.5630	(4)
TEMP	11.	HOT	73.9812	18.4953	0.9049	0.8189	(4)
DETERG	5.	PHOS	444.0439	12.3346	2.0705	4.2871	(36)
HARD	6.	SOFT	161.5987	13.4666	2.2531	5.0763	(12)
TEMP	9.	COLD	50.4702	12.6176	0.7837	0.6142	(4)
TEMP	10.	WARM	45.7680	11.4420	0.6399	0.4095	(4)
TEMP	11.	HOT	65.3605	16.3401	0.3918	0.1535	(4)
HARD	7.	MEDIUM	146.7085	12.2257	1.9485	3.7969	(12)
TEMP	9.	COLD	47.3354	11.8339	0.4525	0.2047	(4)
TEMP	10.	WARM	41.0658	10.2665	1.0118	1.0236	(4)
TEMP	11.	HOT	58.3072	14.5768	0.0000	0.0000	(4)
HARD	8.	HARD	135.7367	11.3114	1.4882	2.2148	(12)
TEMP	9.	COLD	45.7680	11.4420	1.1083	1.2284	(4)
TEMP	10.	WARM	38.7147	9.6787	0.3918	0.1535	(4)
TEMP	11.	HOT	51.2539	12.8135	0.3918	0.1535	(4)

Total cases = 180

Broken down by DETERG
by HARD
by TEMP

50/50 Polyester/Cotton Specimens -- Soil Removal Mean Values and Standard Deviations

Variable	Code	Value label	Sum	Mean	Std dev	Variance	N
For entire population			1689.7356	9.3874	2.9771	8.8628	(180)
DETERG	1.	PL	439.1913	12.1998	2.7178	7.3866	(36)
HARD	6.	SOFT	176.2053	14.6838	1.9179	3.6784	(12)
TEMP	9.	COLD	59.2535	14.8134	1.3280	1.7636	(4)
TEMP	10.	WARM	53.0327	13.2582	1.1664	1.3605	(4)
TEMP	11.	HOT	63.9191	15.9798	2.3220	5.3916	(4)
HARD	7.	MEDIUM	150.5443	12.5454	1.3400	1.7957	(12)
TEMP	9.	COLD	46.8118	11.7030	0.7445	0.5543	(4)
TEMP	10.	WARM	50.6998	12.6750	0.7776	0.6047	(4)
TEMP	11.	HOT	53.0327	13.2582	1.3339	1.7792	(4)
HARD	8.	HARD	112.4417	9.3701	1.5596	2.4324	(12)
TEMP	9.	COLD	33.5925	8.3981	0.6349	0.4031	(4)
TEMP	10.	WARM	35.1477	8.7869	1.0039	1.0078	(4)
TEMP	11.	HOT	43.7014	10.9254	1.6031	2.5698	(4)
DETERG	2.	LAS	356.7652	9.9101	2.3287	5.4228	(36)
HARD	6.	SOFT	141.9907	11.8326	1.7996	3.2386	(12)
TEMP	9.	COLD	41.3684	10.3421	2.0573	4.2327	(4)
TEMP	10.	WARM	53.8103	13.4526	0.7776	0.6047	(4)
TEMP	11.	HOT	46.8118	11.7030	0.7445	0.5543	(4)
HARD	7.	MEDIUM	118.6625	9.8885	1.2164	1.4796	(12)
TEMP	9.	COLD	42.9238	10.7309	1.0997	1.2093	(4)
TEMP	10.	WARM	37.4806	9.3701	1.3280	1.7636	(4)
TEMP	11.	HOT	38.2582	9.5645	1.0039	1.0078	(4)
HARD	8.	HARD	96.1120	8.0093	2.1360	4.5625	(12)
TEMP	9.	COLD	28.9269	7.2317	1.4890	2.2171	(4)
TEMP	10.	WARM	28.1493	7.0373	1.9440	3.7792	(4)
TEMP	11.	HOT	39.0358	9.7589	2.1414	4.5854	(4)
DETERG	3.	AES	223.7947	6.2165	2.0262	4.1055	(36)
HARD	6.	SOFT	92.2240	7.6853	1.7688	3.1287	(12)
TEMP	9.	COLD	27.3717	6.8429	1.5552	2.4187	(4)
TEMP	10.	WARM	29.7045	7.4261	2.0451	4.1823	(4)
TEMP	11.	HOT	35.1477	8.7869	1.4890	2.2171	(4)
HARD	7.	MEDIUM	71.2286	5.9357	1.6523	2.7302	(12)
TEMP	9.	COLD	23.4837	5.8709	0.9785	0.9574	(4)
TEMP	10.	WARM	21.1509	5.2877	2.0078	4.0311	(4)
TEMP	11.	HOT	26.5941	6.6485	1.9440	3.7792	(4)
HARD	8.	HARD	60.3421	5.0285	1.7958	3.2249	(12)
TEMP	9.	COLD	14.9300	3.7325	1.0997	1.2093	(4)
TEMP	10.	WARM	17.2628	4.3157	0.3888	0.1512	(4)
TEMP	11.	HOT	28.1493	7.0373	1.4720	2.1667	(4)
DETERG	4.	NACO	354.4324	9.8453	2.3004	5.2918	(36)
HARD	6.	SOFT	134.2146	11.1846	2.3553	5.5474	(12)
TEMP	9.	COLD	41.3686	10.3421	2.2448	5.0389	(4)
TEMP	10.	WARM	39.8134	9.9533	1.4197	2.0156	(4)
TEMP	11.	HOT	53.0327	13.2582	2.1414	4.5854	(4)
HARD	7.	MEDIUM	106.9984	8.9165	1.4579	2.1255	(12)
TEMP	9.	COLD	35.1477	8.7869	1.9569	3.8296	(4)
TEMP	10.	WARM	33.5925	8.3981	1.5552	2.4187	(4)
TEMP	11.	HOT	38.2582	9.5645	0.7776	0.6047	(4)
HARD	8.	HARD	113.2193	9.4349	2.4664	6.0833	(12)
TEMP	9.	COLD	31.2597	7.8149	1.3280	1.7636	(4)
TEMP	10.	WARM	32.8149	8.2037	1.7242	2.9730	(4)
TEMP	11.	HOT	49.1446	12.2862	1.0997	1.2093	(4)
DETERG	5.	PHOS	315.5521	8.7653	1.9361	3.7485	(36)
HARD	6.	SOFT	110.8865	9.2405	2.2842	5.2176	(12)
TEMP	9.	COLD	26.5941	6.6485	0.7445	0.5543	(4)
TEMP	10.	WARM	36.7030	9.1757	0.0000	0.0000	(4)
TEMP	11.	HOT	47.5894	11.8974	0.4490	0.2016	(4)
HARD	7.	MEDIUM	103.8880	8.6573	2.1573	4.6541	(12)
TEMP	9.	COLD	29.7045	7.4261	1.6031	2.5698	(4)
TEMP	10.	WARM	29.7045	7.4261	1.3280	1.7636	(4)
TEMP	11.	HOT	44.4790	11.1198	0.7776	0.6047	(4)
HARD	8.	HARD	100.7776	8.3981	1.2842	1.6491	(12)
TEMP	9.	COLD	30.4821	7.6205	1.2698	1.6125	(4)
TEMP	10.	WARM	31.2597	7.8149	0.3888	0.1512	(4)
TEMP	11.	HOT	39.0358	9.7589	0.7445	0.5543	(4)

Total cases = 180

Criterion Variable [illegible]
broken down by DETERG
by HARD
by TEMP

100% Cotton Specimens -- Mean Values and Standard Deviations for Whiteness Retention

Variable	Code	Value label	Sum	Mean	Std dev	Variance	N
For entire population			17501.1814	97.2288	2.3373	5.4631	(180)
DETERG	1.	NI	3497.0414	97.1400	1.4459	2.0908	(36)
HARD	6.	SOFT	1182.2485	98.5207	0.8176	0.6684	(12)
TEMP	9.	COLD	397.6331	99.4083	0.0000	0.0000	(4)
TEMP	10.	WARM	390.5325	97.6331	0.4831	0.2334	(4)
TEMP	11.	HOT	394.0828	98.5207	0.3416	0.1167	(4)
HARD	7.	MEDIUM	1167.4556	97.2880	0.6891	0.4748	(12)
TEMP	9.	COLD	390.5325	97.6331	0.4831	0.2334	(4)
TEMP	10.	WARM	386.3905	96.5976	0.5665	0.3210	(4)
TEMP	11.	HOT	390.5325	97.6331	0.4831	0.2334	(4)
HARD	8.	HARD	1147.3373	95.6114	0.9256	0.8568	(12)
TEMP	9.	COLD	385.2071	96.3018	1.1201	1.2546	(4)
TEMP	10.	WARM	378.6982	94.6746	0.0000	0.0000	(4)
TEMP	11.	HOT	383.4320	95.8580	0.0000	0.0000	(4)
DETERG	2.	LAS	3544.9704	98.4714	2.2471	5.0493	(36)
HARD	6.	SOFT	1207.1006	100.5917	1.1834	1.4005	(12)
TEMP	9.	COLD	397.6331	99.4083	0.8368	0.7003	(4)
TEMP	10.	WARM	401.7751	100.4438	0.2959	0.0875	(4)
TEMP	11.	HOT	407.6923	101.9231	0.2959	0.0875	(4)
HARD	7.	MEDIUM	1182.8402	98.5700	1.5442	2.3846	(12)
TEMP	9.	COLD	391.1243	97.7811	0.5665	0.3210	(4)
TEMP	10.	WARM	389.3491	97.3373	0.3416	0.1167	(4)
TEMP	11.	HOT	402.3669	100.5917	0.0000	0.0000	(4)
HARD	8.	HARD	1155.0296	96.2525	1.4123	1.9947	(12)
TEMP	9.	COLD	380.4734	95.1183	0.5665	0.3210	(4)
TEMP	10.	WARM	382.2485	95.5621	0.3416	0.1167	(4)
TEMP	11.	HOT	392.3077	98.0769	0.2959	0.0875	(4)
DETERG	3.	AES	3530.1775	98.0605	1.7645	3.1134	(36)
HARD	6.	SOFT	1189.3491	99.1124	1.2489	1.5597	(12)
TEMP	9.	COLD	397.0414	99.2604	0.2959	0.0875	(4)
TEMP	10.	WARM	390.5325	97.6331	0.4831	0.2334	(4)
TEMP	11.	HOT	401.7751	100.4438	0.2959	0.0875	(4)
HARD	7.	MEDIUM	1178.1065	98.1755	1.1957	1.4297	(12)
TEMP	9.	COLD	390.5325	97.6331	0.4831	0.2334	(4)
TEMP	10.	WARM	388.7574	97.1893	0.2959	0.0875	(4)
TEMP	11.	HOT	398.8166	99.7041	0.3416	0.1167	(4)
HARD	8.	HARD	1162.7219	96.8935	2.0517	4.2095	(12)
TEMP	9.	COLD	378.6982	94.6746	0.0000	0.0000	(4)
TEMP	10.	WARM	386.3905	96.5976	0.5665	0.3210	(4)
TEMP	11.	HOT	397.6331	99.4083	0.0000	0.0000	(4)
DETERG	4.	NACO	3485.7988	96.8277	2.6354	6.9456	(36)
HARD	6.	SOFT	1182.2485	98.5207	2.5669	6.5888	(12)
TEMP	9.	COLD	383.4320	95.8580	0.0000	0.0000	(4)
TEMP	10.	WARM	391.7160	97.9290	0.3416	0.1167	(4)
TEMP	11.	HOT	407.1006	101.7751	0.0000	0.0000	(4)
HARD	7.	MEDIUM	1158.5799	96.5483	2.3780	5.6551	(12)
TEMP	9.	COLD	378.6982	94.6746	0.0000	0.0000	(4)
TEMP	10.	WARM	381.0651	95.2663	0.4831	0.2334	(4)
TEMP	11.	HOT	398.8166	99.7041	0.5917	0.3501	(4)
HARD	8.	HARD	1144.9704	95.4142	2.1128	4.4641	(12)
TEMP	9.	COLD	374.5562	93.6391	0.2959	0.0875	(4)
TEMP	10.	WARM	377.5148	94.3787	0.3416	0.1167	(4)
TEMP	11.	HOT	392.8994	98.2249	0.0000	0.0000	(4)
DETERG	5.	PHOS	3443.1953	95.6443	2.3844	5.6851	(36)
HARD	6.	SOFT	1150.8876	95.9073	1.8619	3.4668	(12)
TEMP	9.	COLD	378.6982	94.6746	0.0000	0.0000	(4)
TEMP	10.	WARM	378.6982	94.6746	0.0000	0.0000	(4)
TEMP	11.	HOT	393.4911	98.3728	0.7446	0.5544	(4)
HARD	7.	MEDIUM	1151.4793	95.9566	2.6200	6.8646	(12)
TEMP	9.	COLD	373.3728	93.3432	0.7446	0.5544	(4)
TEMP	10.	WARM	381.0651	95.2663	0.4831	0.2334	(4)
TEMP	11.	HOT	397.0414	99.2604	0.2959	0.0875	(4)
HARD	8.	HARD	1140.8283	95.0690	2.6860	7.2148	(12)
TEMP	9.	COLD	371.0059	92.7515	0.8876	0.7878	(4)
TEMP	10.	WARM	375.7396	93.9349	0.5665	0.3210	(4)
TEMP	11.	HOT	394.0828	98.5207	0.7639	0.5835	(4)

Total cases = 180

BROKEN DOWN BY DETERG BY HARD BY TEMP — 59/00 Polyester/Cotton Specimens -- Mean Values and Standard Deviations for Whiteness Relation

Variable	Code	Value Label	Sum	Mean	Std Dev	Variance	N
For entire population			17059.9548	94.7775	1.8331	3.3604	(180)
DETERG	1.	NI	3371.8063	93.6557	2.1479	4.6136	(36)
HARD	6.	SOFT	1131.2217	94.2685	2.9274	8.5699	(12)
TEMP	9.	COLD	391.9683	97.9921	0.2828	0.0800	(4)
TEMP	10.	WARM	373.4688	93.3672	0.5415	0.2933	(4)
TEMP	11.	HOT	365.3846	91.3462	0.5656	0.3199	(4)
HARD	7.	MEDIUM	1121.0407	93.4201	1.4028	1.9680	(12)
TEMP	9.	COLD	380.0905	95.0226	0.0000	0.0000	(4)
TEMP	10.	WARM	373.3032	93.3258	0.6531	0.4266	(4)
TEMP	11.	HOT	367.6471	91.9118	0.5656	0.3199	(4)
HARD	8.	HARD	1119.3439	93.2787	1.8753	3.5166	(12)
TEMP	9.	COLD	381.2217	95.3054	0.5656	0.3199	(4)
TEMP	10.	WARM	373.8688	93.4672	0.2828	0.0800	(4)
TEMP	11.	HOT	364.2534	91.0633	0.6531	0.4266	(4)
DETERG	2.	LAS	3447.9638	95.7768	1.5883	2.5228	(36)
HARD	6.	SOFT	1150.9367	95.9781	1.1344	1.2869	(12)
TEMP	9.	COLD	385.7466	96.4367	0.5656	0.3199	(4)
TEMP	10.	WARM	381.7873	95.4468	0.5415	0.2933	(4)
TEMP	11.	HOT	391.4027	97.8507	0.4618	0.2133	(4)
HARD	7.	MEDIUM	1149.8869	95.8239	1.6789	2.8187	(12)
TEMP	9.	COLD	384.6153	96.1538	0.0000	0.0000	(4)
TEMP	10.	WARM	375.0000	93.7500	0.2828	0.0800	(4)
TEMP	11.	HOT	390.2715	97.5679	0.5656	0.3199	(4)
HARD	8.	HARD	1139.1403	94.9284	1.5599	2.4333	(12)
TEMP	9.	COLD	385.7466	96.4367	0.5656	0.3199	(4)
TEMP	10.	WARM	372.1719	93.0430	0.5656	0.3199	(4)
TEMP	11.	HOT	381.2217	95.3054	0.5656	0.3199	(4)
DETERG	3.	AES	3436.0860	95.4468	1.5905	2.5296	(36)
HARD	6.	SOFT	1149.3213	95.7768	1.6593	2.7532	(12)
TEMP	9.	COLD	386.3122	96.5781	0.5415	0.2933	(4)
TEMP	10.	WARM	374.4344	93.6086	0.3266	0.1066	(4)
TEMP	11.	HOT	388.5747	97.1437	0.2828	0.0800	(4)
HARD	7.	MEDIUM	1145.9276	95.4940	1.5599	2.4333	(12)
TEMP	9.	COLD	383.4842	95.8710	0.5656	0.3199	(4)
TEMP	10.	WARM	374.4344	93.6086	0.5656	0.3199	(4)
TEMP	11.	HOT	388.0091	97.0023	0.5656	0.3199	(4)
HARD	8.	HARD	1140.8371	95.0698	1.6081	2.5860	(12)
TEMP	9.	COLD	384.6154	96.1538	0.0000	0.0000	(4)
TEMP	10.	WARM	371.6063	92.9016	0.2828	0.0800	(4)
TEMP	11.	HOT	384.6154	96.1538	0.0000	0.0000	(4)
DETERG	4.	NACO	3385.1810	94.0328	1.4397	2.0726	(36)
HARD	6.	SOFT	1135.7466	94.6456	1.2609	1.5899	(12)
TEMP	9.	COLD	382.3529	95.5882	0.6531	0.4266	(4)
TEMP	10.	WARM	372.1719	93.0430	0.3266	0.1066	(4)
TEMP	11.	HOT	381.2217	95.3054	0.3266	0.1066	(4)
HARD	7.	MEDIUM	1123.8688	93.6557	1.3740	1.8880	(12)
TEMP	9.	COLD	379.5249	94.8812	0.2828	0.0800	(4)
TEMP	10.	WARM	367.6471	91.9118	0.3266	0.1066	(4)
TEMP	11.	HOT	376.6968	94.1742	0.5656	0.3199	(4)
HARD	8.	HARD	1125.5656	93.7971	1.5784	2.4915	(12)
TEMP	9.	COLD	380.0905	95.0226	0.0000	0.0000	(4)
TEMP	10.	WARM	367.0814	91.7704	0.2828	0.0800	(4)
TEMP	11.	HOT	378.3937	94.5984	0.8484	0.7198	(4)
DETERG	5.	PHOS	3419.1177	94.9755	1.4133	1.9974	(36)
HARD	6.	SOFT	1139.7059	94.9755	1.3310	1.7717	(12)
TEMP	9.	COLD	386.3122	96.5781	0.5415	0.2933	(4)
TEMP	10.	WARM	374.4344	93.6086	0.3266	0.1066	(4)
TEMP	11.	HOT	378.9593	94.7398	0.3266	0.1066	(4)
HARD	7.	MEDIUM	1146.4932	95.5411	1.2638	1.5972	(12)
TEMP	9.	COLD	383.4842	95.8710	0.3266	0.1066	(4)
TEMP	10.	WARM	376.6968	94.1742	0.3266	0.1066	(4)
TEMP	11.	HOT	386.3122	96.5781	1.2542	1.5729	(4)
HARD	8.	HARD	1132.9186	94.4099	1.5715	2.4697	(12)
TEMP	9.	COLD	380.6561	95.1640	0.2828	0.0800	(4)
TEMP	10.	WARM	369.1437	92.2859	0.2828	0.0800	(4)
TEMP	11.	HOT	382.9186	95.7296	0.2828	0.0800	(4)

Total cases = 180

APPENDIX D

SUMMARY OF ANALYSIS OF VARIANCE

Summary of the Analysis of Variance for Percent of Soil Removal From Cotton Specimens of Three Zeolite Detergents

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	2	345.53	320.35**
Water Hardness (2)	2	114.36	106.02**
Water Temperature (3)	2	78.27	72.57**
Two Way Interactions			
1 X 2	4	13.58	12.59**
1 X 3	4	14.50	13.44**
2 X 3	4	4.38	4.06**
Three Way Interactions			
1 X 2 X 3	8	2.52	2.33*
Residual Error	81	1.08	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

Summary of the Analysis of Variance for Percent of Soil Removal From Polyester/Cotton Specimens of Three Zeolite Detergents

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	2	328.11	151.43**
Water Hardness (2)	2	139.10	64.20**
Water Temperature (3)	2	25.55	11.79**
Two Way Interactions			
1 X 2	4	6.21	2.87*
1 X 3	4	2.19	1.01
2 X 3	4	5.54	2.56*
Three Way Interactions			
1 X 2 X 3	8	3.93	1.82
Residual Error	81	2.17	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

Summary of the Analysis of Variance for Percent of Whiteness Retention of Cotton Specimens of Three Zeolite Detergents

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	2	16.73	83.69**
Water Hardness (2)	2	90.02	450.28**
Water Temperature (3)	2	42.80	214.06**
Two Way Interactions			
1 X 2	4	3.51	17.58**
1 X 3	4	10.09	50.46**
2 X 3	4	1.89	9.45**
Three Way Interactions			
1 X 2 X 3	8	1.88	9.42**
Residual Error	81	0.20	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

Summary of the Analysis of Variance for Percent of Whiteness Retention of Polyester/Cotton Specimens of Three Zeolite Detergents

Source of Variation	df***	MS†	F Ratio
Main Effects			
Detergent Type (1)	2	46.89	212.05**
Water Hardness (2)	2	11.26	50.91**
Water Temperature (3)	2	60.65	274.25**
Two Way Interactions			
1 X 2	4	0.94	4.26**
1 X 3	4	35.86	162.14**
2 X 3	4	2.26	10.23**
Three Way Interactions			
1 X 2 X 3	8	2.54	11.49**
Residual Error	81	0.22	

*Significant at $\alpha = 0.05$ level of probability

**Significant at $\alpha = 0.01$ level of probability

***df = degrees of freedom

†MS = mean square

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