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I am submitting herewith a thesis written by Paula Ann Metcalf entitled "Effects of Temperature and Water Hardness on the Soil-Removal Ability of Detergent Systems Containing Hydroxyethyl Cellulose." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Textiles and Clothing.

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EFFECTS OF TEMPERATURE AND WATER HARDNESS ON THE SOIL-REMOVAL ABILITY OF DETERGENT SYSTEMS CONTAINING HYDROXYETHYL CELLULOSE

A Thesis

Presented for the

Master of Science

Degree

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ABSTRACT

The objective of this research was to evaluate the soil removal ability of low phosphate detergents formulated with hydroxyethyl cellulose as an antiredeposition agent under selected conditions of water hardness and temperature. It was assumed that these conditions more closely resemble actual detergent use.

Only one fabric was used in this evaluation: a presoiled 65% polyester/35% cotton woven fabric with a durable press finish. The soil was basically an oil bound particulate soil.

Detergent efficiency was evaluated by determining the ability of the detergent to both remove soil and suspend soil, thus preventing redeposition. Soil removal and soil redeposition were determined by reflectance measurements taken before and after exposure to the simulated laundering on both the soiled and unsoiled portions of each fabric specimen.

Data analysis was based on the factorial analysis of variance. The independent variables were detergent, water hardness, and temperature. The dependent variables were soil removal and soil redeposition as calculated from reflectance readings.

The optimum conditions for soil removal under selected conditions of water hardness and temperature are a low

phosphate detergent with a mixed surfactant system and a high level of hydroxyethyl cellulose in moderately hard water. Increased levels of water temperature also enhanced these conditions for soil removal. An anomalous interaction between detergent and water hardness over temperature levels was also observed with the high phosphate detergent with a mixed surfactant system and a high level of hydroxyethyl cellulose.

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CHAPTER I

INTRODUCTION

The formulation of synthetic detergents as substitutes for soaps was an important scientific breakthrough. For years, combinations of fat and alkali called soaps had been used to clean clothes, producing less than satisfactory results. The primary problem with soaps is that they combine with minerals naturally present in water to form insoluble precipitates: soft, sticky materials that cling to whatever they contact. This undesirable aspect of soap's performance helped to promote the development of a material that cleaned like soap without any undesirable interaction with water.

In the early 1930's, the first synthetic cleaning agents became commercially available; these consisted almost entirely of surfactant (28). The surfactant or surface active agent is the ingredient most responsible for soil removal. At first, these detergents performed unsatisfactorily. Then, during World War II, the search for a soap substitute was intensified by a shortage of fats for use in soap manufacture. Further research led to the development of the built detergent which appeared on the market shortly after World War II. This detergent was a combination of surfactant and a phosphate or similar builder. The phosphate

builder enabled the surfactant to perform its function of soil removal more efficiently.

These built synthetic detergents continued to grow in both popularity and market share, eventually relegating soap to its present minute share of the market. With the introduction of new textile products such as synthetic fibers and finishes, the synthetic detergents continued to provide high performance. Only one aspect of detergent performance was overlooked: the interaction of detergents and the environment.

The first attack on detergents came in the early 1960's when it was noted that detergents were "persisting, and sometimes sudsing, in the environment" (28). This sudsing was due to the presence of nonbiodegradable surfactants. Detergent manufacturers switched to biodegradable ingredients (those able to be broken down into harmless end products through the action of living microorganisms) and eliminated the problem of sudsing.

However, the recent history of the use of the synthetic built detergent has been marked by debate and indecision. As a result of pressures by both the Federal Government and environmentalists, synthetic detergent manufacturers have been forced to develop new detergent formulations that are ecologically safe, while still adequately performing their function of soil removal.

The major thrust of the attack on synthetic detergents has been directed toward the phosphate builder, which aids the active detergent ingredient (the surfactant) in soil removal. The function of the phosphate builder is threefold:

1. to remove hardness ions so that they do not interfere with the soil removal process,

2. to keep soil from being redeposited on the fabric once it has been removed, and

3. to maintain the alkalinity of the solution thereby aiding the soil removal process (5).

Although the phosphate builder is important in the soil removal process, it has also been cited as a major source of fresh water pollution. Phosphorus, together with compounds of carbon and nitrogen, is believed to be responsible for the acceleration of a natural process called eutrophication (34). Eutrophication occurs when fresh water plants have such an oversupply of nutrients that they proliferate rapidly (32). These plants exhaust the supply of dissolved oxygen in the water, thus making it unavailable to other living things in the same environment. The end result of this accelerated eutrophication is an unbalanced ecological system which cannot naturally renew itself.

Due to hasty thinking by some government officials and environmentalists, detergent phosphates were singled out as the primary offender in the eutrophication process. The

solution seemed simple: eliminate the phosphates from the detergents and the eutrophication will begin to reverse itself. The problem was not quite that simple. Even if detergent phosphates were eliminated, there remained an overabundance of phosphorus from other sources such as human waste and agricultural runoff. Also, there was not, and still is not, an entirely satisfactory phosphate replacement available for use in synthetic detergent formulations.

Both the Federal Government and the detergent manufacturers agree that a satisfactory replacement for detergent phosphates must be found. World supplies of phosphorus are dwindling and must be conserved for a more important use as fertilizers for agricultural applications (28).

Recent detergency research efforts have concentrated on various alternatives to the use of the phosphate builder. One such alternative, nitrilotriacetic acid (NTA), was used briefly as a detergent builder during the height of the phosphate controversy. It was quickly withdrawn when other evidence linked it to both cancer and birth defects (34). Now, commercially available detergents are either low-phosphate, nonphosphate, or nonbuilt formulations. The nonphosphate detergents have either carbonate, silicate, or citrate builders, which could have potentially harmful effects on humans if ingested into the body (8). The

low-phosphate and the nonbuilt formulations rely on either an improved surfactant system or a higher level of an antiredeposition agent to provide adequate soil removal.

This research will evaluate the soil removal ability of low-phosphate detergents formulated with hydroxyethyl cellulose (HEC), as the antiredeposition agent. Commercially available detergents contain small amounts of antiredeposition agents to prevent suspended soils from being redeposited on the fabric; the antiredeposition agent most commonly used is carboxymethyl cellulose (CMC). In research by Easter, hydroxyethyl cellulose was found to be superior to carboxymethyl cellulose in performing the function of antiredeposition (12). Further research by Cobble, Hurley, and Shelton confirmed the effectiveness of HEC as an antiredeposition agent and also as an enhancer of the soil removal ability of a detergent system (6, 17, 31).

The soil removal process is a complex one, not only dependent on detergent type, but also on many other variables. These variables include detergent concentration, soil type, degree of soiling, fiber content, fabric construction, fabric finish, water temperature, water hardness, and mechanical agitation. The detergent consumer has to deal with all these different and sometimes opposing conditions and still maintain an acceptable degree of soil removal.

With the introduction of synthetic fabrics and finishes, the trend has been more toward warm- or cold-water laundering instead of the hot-water laundering that was preferred for all-cotton fabrics. It is estimated that for permanent press and colored fabrics, 23% are laundered in hot water, 37% in warm, and 40% in cold. Even for all-cotton and white fabrics, only 40% are laundered in hot water, while 32% and 28% are laundered in warm and cold, respectively (2). Another factor that has recently contributed to the increase in cold-water laundering is the increased cost of heating water for laundering purposes, due to the energy crisis.

Detergent users must contend with the mineral content of water, sometimes referred to as water hardness. Some level of hardness is always present because a certain amount is brought to the laundering situation by the soiled fabrics. In addition to this amount, different levels of water hardness occur naturally in the various regions of the country. It is estimated that 10% of the population live in an area that has hard water (over 225 ppm*), 40% have moderate to hard water (85 to 225 ppm), and 50% have soft water (under 85 ppm) (2).

Earlier research evaluated the soil removal ability of synthetic detergents containing hydroxyethyl cellulose at a constant temperature and in distilled water. The problem

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*parts per million.

undertaken here is to examine these formulations under conditions that more closely resemble those experienced by the detergent user.

The soil removal ability of detergent systems containing hydroxyethyl cellulose was evaluated by:

1. formulating detergents with constant levels of anionic and nonionic surfactants and hydroxyethyl cellulose but with varying levels of phosphate builder;

2. exposing white fabrics printed with a band of soil to certain combinations of detergent, water hardness, and water temperature in a simulated laundering;

3. determining soil removal and soil redeposition by measuring change in reflectance of the soiled and unsoiled portions of the test fabrics.

Objectives

The objectives of this study were:

1. To determine the effect of water hardness on the soil removal ability of detergent systems containing hydroxyethyl cellulose.

2. To determine the influence of temperature on the soil removal ability of detergent systems containing hydroxyethyl cellulose.

Assumptions

The research was based on the following assumptions:

1. A carbon-black particulate soil dispersed in oil is a valid and acceptable (representative) soil for the purposes of this study.

2. The levels of 100°F, 120°F, and 140°F are representative of cold, warm, and hot water laundering temperatures, respectively.

3. The water hardness levels of 0 ppm, 100 ppm, and 200 ppm are acceptable values for soft, moderate, and hard water, respectively.

4. Fabric reflectance, as measured by the Hunter Color Difference Meter, is a valid measurement of soil removal for the purposes of this research.

Limitations

The research was limited as follows:

1. A 65% polyester/35% cotton fabric with a durable press finish printed with a four-inch strip of a soil consisting of a carbon-black particulate soil dispersed in oil was the only fabric and source of soil used in this study.

2. The number of detergents evaluated was limited to four.

3. Only three levels of water hardness were investigated: 0 ppm, 100 ppm, and 200 ppm.

4. Only three temperature levels were investigated: 100°F, 120°F, and 140°F.

5. All soil removal experiments were carried out in the Tergotometer, a four-position laundry simulator.

Definitions

1. Antiredeposition Agent—an ingredient in synthetic detergents which serves the purpose of holding soil particles in suspension preventing them from washing back onto a fabric substrate (9).

2. Builders—important ingredients in synthetic detergents that aid the surfactant in soil removal by complexing metal ions, maintaining alkalinity, and preventing soil redeposition (9).

3. Detergency—process of removing soil from the surfaces of a solid while immersed in a liquid medium containing a chemical agent that reduces the attractive forces between the soil and the surface (9).

4. Detergent—a chemical formulation consisting primarily of surfactants and builders and smaller amounts of suds-controlling agents, soil suspending agents, whiteners, bleaches, softeners, enzymes, and perfumes (9).

5. Sequestration—process of inactivating metal ions by combining with them to form soluble complexes rather than undesirable precipitates (10).

6. Soil—any undesirable matter that adheres to textile fibers.

7. Soil redeposition—soil precipitated from the washing solution back onto a fabric substrate (9).

8. Surfactant—any substance which, at low concentration, reduces the surface tension of a solvent (1). In detergents, surfactants overcome the natural attraction between fabrics and soil by attaching themselves to both (9).

CHAPTER II

REVIEW OF LITERATURE

Recent literature pertaining to the broad subject of detergency was reviewed under the following headings: Detergency, Surfactants, Builders, Antiredeposition Agents, Soiling, Soil Removal, and Detergent Evaluation.

Detergency

Detergency, or the removal of soil from a fabric surface, is a complex process influenced by the natures of the detergent, the soil, and the fabric substrate. Until about the 1930's, the detergent was a simple soap and the fabric was most likely a woven cotton fabric. Since then, both the detergent and textile industries have undergone radical and revolutionary changes. Soaps are no longer widely used; they have been replaced by synthetic detergents. Along with cotton, we are now faced with synthetic fibers such as polyester, nylon, and acrylic. Further complicating the problem are the chemical finishes that are used to impart various aesthetic and performance characteristics to the fabric such as soil release, crease retention, water repellency, and flame retardancy. All of these factors contribute to the complexity of the laundering process and

also explain why the study of detergency is still going on today.

The detergency process can be broken down into three steps. The first step is the wetting-out of fabric surfaces. In this step, the wash liquor penetrates into the fabric replacing the fiber-air interfaces with fiber-aqueous solution interfaces (9). The second step is the actual removal of the foreign matter or soil. The final step is the stabilization of soil in the wash liquor making it unavailable for resettling onto the fabric surfaces.

Synthetic detergents are formulated chemical products. The active content of these detergents is composed of surfactants, builders, and antiredeposition agents. Other ingredients may be added to the formulation to improve the aesthetic characteristics of fabrics; among these ingredients are fluorescent whitening agents, fabric softeners, and perfumes. Processing aids or fillers are included to promote ease in processing and to standardize the formulation so that the recommended use level will deliver the necessary active ingredients (5). Small amounts of corrosion inhibitors and suds control agents may also be included in a synthetic detergent formulation.

Surfactants

Surfactants, or surface active agents, are a class of chemical substances containing two parts: a hydrophilic or

water soluble group and a hydrophobic or water insoluble long chain hydrocarbon group. It is this bicomponent nature that gives the surfactant its unique chemical ability to "make water wetter." When used in low concentration, a surfactant will reduce the surface tension of water, i.e., reduce the attractive or cohesive forces between the individual water molecules at the surface.

The adsorption of surfactants in water creates a liquid medium that is well suited to the purpose of removing soil from a fabric substrate. A primary requirement of a soil removal or detergent solution is that the solution must be able to wet the fabric effectively. Water, because of its high surface tension, is not a very good wetting agent. Adding surfactant molecules to water causes the individual surfactant molecules to cluster at the surfaces or interfaces with their hydrophilic head groups in the water. The hydrophobic tails are out of the water diminishing the forces parallel to the water surface, allowing the water to spread out and wet more effectively (5).

Surfactants also help to dislodge soil. Oily soils attract the hydrophobic tails of surfactant molecules. These molecules cover the surfaces of an oily soil. Gradually, the oily soil is removed from the fabric substrate by being completely surrounded by surfactant molecules. Soils that are attracted to the hydrophilic head group also are

surrounded by surfactant molecules. In this case, the hydrophobic tails are pointed outward, providing an oily medium for the hydrophobic tails of other surfactant molecules. The soils surrounded by surfactant are now charged so that they repel each other and remain in suspension (5).

Surfactant molecules cluster first at the surfaces of water. In any given body of water, there is only so much surface available for the accumulation of surfactant molecules. When the surface concentration of surfactant is high, any additional surfactant molecules are forced to cluster within the solution; these surfactant molecules form molecular aggregates called micelles and the concentration at which they form is called the critical micelle concentration (1). In micelles, the surfactant molecules are oriented with their hydrophobic tails in the center and the hydrophilic groups in the water. These micelles provide an oily environment for the solubilizing of oily soils.

Surfactants are classified into four groups based on "the charge carried by the surface active ion in an aqueous solution" (1). These four groups are anionic, cationic, nonionic, and amphoteric. The anionic and cationic types yield negative and positive ions in solution, respectively. The amphoteric types may yield either positive or negative ions, or be neutral depending on solution pH. The nonionic

types do not ionize in solution. The anionic and nonionic types are the most widely used in home laundering applications.

The active content of a typical detergent formulation contains some combination of anionic and nonionic surfactants. The anionic surfactants perform well in hot water, while the nonionic surfactants are effective in cold water. Both types are used in temperatures ranging from 60°F to 180°F (7). Both types can also be successfully used in hard water. The nonionics, because they do not dissociate in water, are not available for reaction with the Ca^{++} and Mg^{++} ions present in hard water. Although the anionic types do react with hardness minerals, only soluble complexes are formed; these do not interfere with detergency (7).

Builders

Builders constitute an important part of synthetic detergent formulations. Detergent builders are of two types: those that are detergency promoters and those that are processing aids or fillers (16). The former group will be examined in depth here.

In order for a builder to promote or enhance detergency, it must be capable of:

1. formation of soluble complexes with metal ions;
2. pH buffering and alkalinity;

3. dispersion and peptization of both organic and inorganic soils;

4. electrolytic activity (10).

Other aspects of builder performance are also taken into account when choosing a builder for a specific detergent formulation. The builder should be:

1. compatible with other detergent ingredients and any laundry additives;

2. nondamaging to the environment;

3. nontoxic;

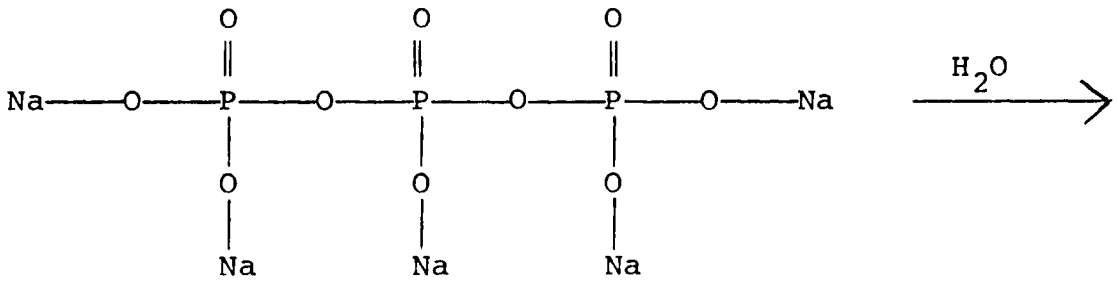
4. easily processed;

5. economically feasible (competitive) when compared to possible alternatives (10).

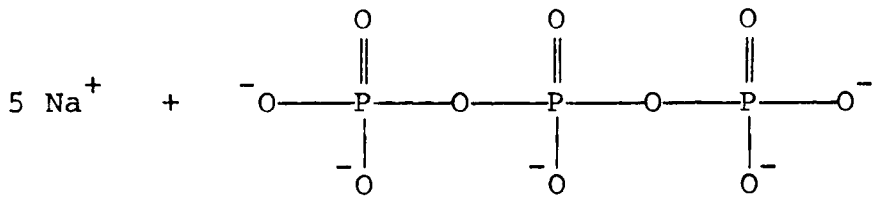
The builders used in today's synthetic detergent formulations are sodium tripolyphosphate, sodium silicate, sodium citrate, and sodium carbonate. Sodium tripolyphosphate (STPP) is the most widely used synthetic detergent builder.

When STPP is in solution, it ionizes to yield positively charged sodium ions and negatively charged tripolyphosphate ions as illustrated in Figure 1.

The tripolyphosphate ion with its negative charges promotes detergency in several ways. First, it maintains a high solution pH, which favors soil removal. Secondly, the negative charges on the large tripolyphosphate ion keep negatively charged soils suspended. Finally and most



Sodium tripolyphosphate



Sodium ions tripolyphosphate ion

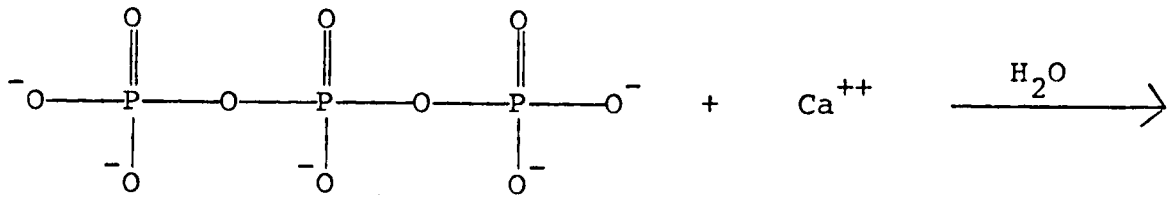
Figure 1. Ionization of Sodium Tripolyphosphate.

importantly, the tripolyphosphate ion is effective in complexing hardness minerals present in water (11). This process is called sequestration and is illustrated in Figure 2 (33). Enough negative charges are left after the Ca^{++} ion has been complexed so that the calcium tripolyphosphate entity is still soluble.

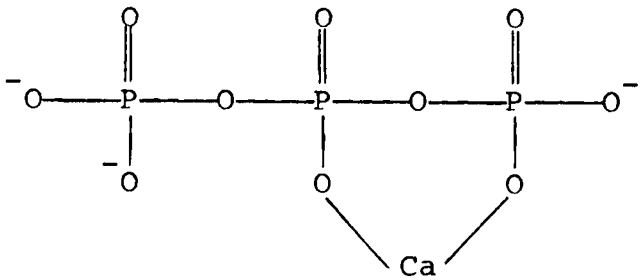
Ninety percent of all the sodium tripolyphosphate produced in the United States is used in synthetic detergents (11). The concentration of phosphates in these detergents is generally expressed as percent STPP or percent elemental phosphorus (P). The percent STPP is approximately four times the percent elemental phosphorus (P). Before the detergent controversy in 1970, the average home laundry detergent contained about 44% STPP (11% P). After legislation limiting the amount of phosphates in laundry detergents was passed, this level dropped to 35% STPP (8.7% P) (11). Current levels range from 24% to 35% STPP (6.0 to 8.7% P) (20).

Antiredeposition Agents

In addition to the initial removal of soil, a detergent must also have the ability to suspend that soil thereby preventing its redeposition onto the fabric substrate. Small quantities of antiredeposition agents are included in synthetic detergent formulations for this purpose.



tripolyphosphate ion Calcium ion



Calcium tripolyphosphate complex

Figure 2. Sequestration of Calcium.

Antiredeposition agents are generally present at concentrations between 1 and 2% (9, 25). Several cellulose-derived polymers have the ability to suspend soil; however, only sodium carboxymethyl cellulose (CMC) has gained wide acceptance as an antiredeposition agent in synthetic detergents (35).

Antiredeposition agents are believed to suspend soil by adsorbing on both the fabric and the soil, creating repulsive forces between them (9). CMC is capable of creating this repulsion by virtue of its many negative charges in solution (5).

In research by Easter, the antiredeposition ability of CMC was compared to that of hydroxyethyl cellulose (HEC) and carboxymethyl hydroxyethyl cellulose (CMHEC). Like CMC, both HEC and CMHEC are cellulose derivatives. Levels of the three antiredeposition agents were incorporated with mixed surfactant systems and phosphate builders into detergent formulations. An analysis of the oily soil deposition experiments revealed that HEC was the most effective of the three antiredeposition agents (23).

A study by Cobble examined the effectiveness of HEC at relatively high levels—5.0% and 7.5%. In this series of soil redeposition experiments, HEC was effective at both levels but more so at the higher level. This research also revealed the importance of the surfactant content; the best

results were obtained with a 2:3 ratio of nonionic to anionic surfactant (22).

Since the effectiveness of hydroxyethyl cellulose as an antiredeposition agent was confirmed, further investigations were directed to other factors involved in the soil removal systems; these factors were surfactant type and content. Hurley's research evaluated the antiredeposition ability of detergent formulations containing constant levels of phosphate builder and HEC with surfactant systems of variable type and content (17). The results were not conclusive; however, they seemed to indicate that a combination of 16% anionic/8% nonionic was effective on cotton fabrics and 12% anionic/8% nonionic was effective for polyester/cotton blends. There was no clear preference for a specific anionic or nonionic surfactant.

A soil removal study by Shelton, again using detergent formulations with a constant level of HEC, found the best surfactant system to be sodium p-tridecylbenzene sulfonate (anionic) and ethoxylated fatty alcohol (nonionic) (24). She also found that significantly lower phosphate levels (3 or 4% phosphorus as opposed to the current commercial level of 6.3% phosphorus) were effective.

Soiling

Soil may be loosely defined as any undesirable matter that adheres to textile fibers. The actual components of

soil vary according to environmental factors and individual use conditions. Basically, soil is considered to be one of three types: fluid or oily, solid or particulate, or a combination of both. The latter soil type is the most prevalent soil on fibers and fabrics.

The cleaning of fabrics was not considered a major problem until the mid-1960's when advances in textile technology began to change the nature of the fabric substrates to which the soil became attached. The changes which had the most impact on soiling were the increased usage of polyester staple in blends with cotton and the addition of durable press finishes (13). Polyester, being oleophilic in nature, has a strong affinity for oily, or oleophilic soils; a polyester/cotton fabric picks up and retains oily soil more readily than an all-cotton fabric. The addition of a crosslinking durable press finish also increases soiling and difficulty in removal due to a change in the electrostatic properties of the fabric; the fabric also becomes more oleophilic (27).

Oily soils found on fabrics consist of organic soils, greases, and tars; by weight the major soil present is sebum, an oily skin secretion consisting primarily of triglycerides (9). Sebum presents a major problem to soil removal systems because it serves as a matrix to entrap and hold particulate soils both before and during laundering, thereby increasing redeposition.

Particulate soils consist of finely divided particles including topsoil fragments, skin cells, and incomplete combustion products from homes, different forms of transportation, and industry (9). Particulate soils account for much of the dingy grey appearance of soiled fabrics (15). These particles range in size from 1000 to 50 microns (visible) and 50 to 0.01 microns (microscopic) (14). As particle size decreases, apparent darkness and difficulty in removal increase; smaller particles therefore present the greatest problems for soil removal systems.

The soiling process can be broken down into two phases: contact and retention (29). There are three mechanisms by which soil comes into contact with fabric; these are direct contact, contact with air-borne soil, and contact with liquid-borne soil (14). Direct contact soiling will transfer soil onto a fabric by means of mechanical forces, e.g., a fabric rubbed against a soiled surface. Soil may be transferred to fabric through the air by means of chance collision, settling due to gravity, or by means of electrostatic attraction. The third contact mechanism is contact with a liquid-borne soil or redeposition. Redeposition generally occurs during the laundering process when the detergent fails to keep the soil suspended and it settles back onto the fabric.

Redeposition, the gradual decrease in whiteness due to soil settling back onto the fabric from the wash liquor, is

a soil removal problem that has received much attention recently. This transfer of soil in washing is a two-phase process; first, the soil must be removed from one fabric and suspended in the wash liquor, then the soil must be redeposited from the wash liquor onto the same or an accompanying fabric (4). There is an important relationship between the ability of a detergent formulation to suspend soil and the amount of redeposition that actually occurs; if there is more soil present than can be suspended by the detergent system, that soil will redeposit onto the fabric substrate.

Once the soil has come in contact with the fabric, it is retained on the fabric surface by four mechanisms:

1. macro-occlusion—trapping of soil particles between yarns or between fibers in a yarn;

2. micro-occlusion—trapping of soil particles in fiber surface irregularities;

3. adhesion of soil particles by van der Waals or coulombic forces; and

4. hydrophobicity and oleophilicity, i.e., hydrophobic fibers such as polyester will retain oily soils (14).

Both macro- and micro-occlusion depend on mechanical factors, i.e., the geometry of soil particles, fibers, yarns, and fabrics. Theoretically, considering only geometric factors, "the fiber having the minimum surface area per unit

of volume will have the maximum resistance to mechanical soil entrapment" (14). In other words, a fiber of large diameter, circular cross-section, and smooth surface will soil less than a fiber of small diameter, serrated cross-section, and irregular surface. This interaction between soiling and fiber geometry is by no means absolute; many other factors influence the soiling of fibers.

Factors of yarn and fabric geometry also influence fabric-soil interactions. Fibers that protrude from low-twist yarns have been observed to soil preferentially. The existence of these fibers increases the surface area available to soiling and therefore, increases the soiling of the fabric (26). Places where yarns cross in woven structures also provide soiling sites; these sites occur when pressure is applied to spread the yarns as in direct contact soiling.

Soil retention can also result from forces other than mechanical; these forces are interfacial or electrostatic. Interfacial attraction due to van der Waals or similar forces serves to bind soil to a fabric surface (9). Soiling is also affected by the oleophilic natures of the fiber and the soil; an oleophilic fiber such as polyester will retain an oily soil (3).

Soil Removal

The mechanism of soil removal depends largely on the nature of the soil, i.e., whether it is an oily soil or a particulate soil. Oily soil sometimes acts as a binder for particulate soil; in this case, the process for soil removal would involve mechanisms of both oily soil and particulate soil.

The wetting of the fabric substrate is the first step in the soil removal process, regardless of the soil type. The surfactant lowers the surface tension of water so that it can effectively wet-out the fabric by replacing the fiber-air interfaces with fiber-aqueous solution interfaces (9). Wetting-out does not cause any serious problems in detergency because the surfactant lowers the surface tension of water to a level sufficiently below the critical surface tensions for spreading of the polymers used for textile fibers (9).

There are four soil removal mechanisms for oily soil; these are rolling-up, solubilization, mesomorphic phase formation, and the breaking up of polycrystalline aggregates.

Rolling-up is generally accepted as the primary oily soil removal mechanism (18). Surfactant molecules are adsorbed on both the fabric and the oily soil; those adsorbed on the fiber surface gradually displace the soil because they are more strongly attracted to the fiber. This gradual displacement causes the contact angle between the

oily soil and the fabric surface to increase as the oily soil "rolls up" into droplets; further agitation removes these oil droplets completely and enables them to be suspended in the wash liquor (18).

Solubilization refers to the solubilizing of oily soils in surfactant micelles; therefore, solubilization can only be considered as a soil removal mechanism at surfactant concentrations well above the critical micelle concentration. Solubilization has been found to be an important soil removal mechanism only at higher concentrations of nonionic surfactant (9).

Mesomorphic phase formation and the breaking up of polycrystalline aggregates are less significant soil removal mechanisms because they are primarily concerned with very specific soil types. Mesomorphic phase formation has been observed to be a soil removal mechanism for the polar constituents of oily soils (9). The breaking up of polycrystalline aggregates concerns the removal of sebum in cold water where it is a pasty solid rather than an oily liquid soil (9).

Particulate soils may be bound to fabric surfaces by van der Waals or similar forces. Surfactant molecules overcome these forces by attaching themselves in a thin layer to both soil and fabric. After the soil has been removed, this layer of surrounding surfactant molecules breaks it up into

colloidal particles which can be stabilized in the wash liquor (9).

Both the rate and the effectiveness of soil removal are dependent upon many factors: detergent type and content, fiber content, fabric structure, nature of soil, water temperature, water hardness, and mechanical agitation. All of these factors must be evaluated in studying soil removal.

Detergent Evaluation

Detergent evaluation is based on a variety of criteria; the most important single criterion being the ability to remove soil. Actual soil removal and soil redeposition can be determined by optical and gravimetric analysis, and through the use of radiotracer soils (19). Optical assessments of soil removal are either subjective or objective; the objective methods using either a color difference meter or reflectometer are more reliable than subjective visual evaluations. Objective optical assessments involve comparisons of readings taken on the fabric before and after its exposure to the laundering conditions (30). Gravimetric analysis includes all methods of determining soil removal by determining the actual weight of the soil (9). For this analysis, some type of extraction is necessary to separate the soil from the fabrics. This extraction creates a problem because some soils cannot be removed without

destroying the fabric substrate. Radiolabeled soils may also be used; these soils can be "counted" by Geiger counters both before and after laundering.

The first step in the evaluation of a detergent formulation is laboratory evaluation through the use of a standard soil cloth and the Tergotometer or similar laundry simulator (30). This procedure enables the evaluator to choose from a wide variety of testing conditions and to determine soil removal and soil redeposition properties of a particular formulation. Following this preliminary investigation, the evaluator may want to choose a more complex set of conditions based on any specific end use for the detergent.

The next major step in detergent evaluation would be full-scale laboratory testing of garments actually worn by a specified group of individuals (30). After this test, detergent formulations may be distributed to consumers for evaluation in home-use situations (30).

Once the soil removal ability of a detergent has been established, any further evaluation would be concerned with aesthetic, safety, use, and environmental factors (21). Aesthetic factors would include the aesthetics of the detergent product itself—form, color, odor, and packaging. These should be pleasing in order to promote acceptability of the detergent by the consumer. The detergent should be safe for the consumer to use; i.e., it should not damage washing

machines through corrosion or build-up, and it should not damage fabrics or counteract the effect of specific finishes such as durable press or flame retardant finishes. The detergent should also have no adverse effects on the environment.

CHAPTER III

PROCEDURE

The purpose of this study was to evaluate the soil removal ability of certain low phosphate detergent formulations under selected conditions of water temperature and hardness. It was assumed that these conditions more closely resembled those experienced by the detergent consumer.

The study was conducted as follows:

1. Low phosphate detergents were formulated with a mixed (anionic-nonionic) surfactant system. Hydroxyethyl cellulose was used as the antiredeposition agent. Commercially purchased Tide (Proctor and Gamble) was used as a control.

2. The effectiveness of each detergent in removing soil was determined by measuring the change in reflectance of the soiled and unsoiled portions of the fabrics after exposure to the laundering systems.

Fabric

Based on the results of previous research, only one fabric was used in this study. This fabric was a plain weave, presoiled, shirting fabric purchased from Testfabrics, Inc., P. O. Box 53, 200 Blackford Avenue, Middlesex, N. J. 08846. The fabric was a blend of 65% dacron 54W polyester/

35% cotton with a durable press finish. The dacron 54W polyester contained a built-in brightener. The durable press finish, Rigmel, was a glyoxal-based finish produced by the Bradford Dye Association.

The fabric was available in 8 1/2 inch wide rolls printed with an oil bound particulate soil. The exact composition of this soil is given in the Appendix. Each individual fabric specimen was cut to measure 4 1/4 by 8 1/2 inches. Two swatches were used for each set of experimental conditions; these were differentiated by cutting off a corner of one swatch in each pair. A 3 3/4 inch wide soil strip was printed on the fabric allowing a 3 3/4 inch wide unsoiled strip on one side and a 1 inch unsoiled strip on the other side. The equal areas of soiled and unsoiled fabric allowed for comparative whiteness measurements. The small unsoiled portion was utilized for coding purposes. Each swatch was conded according to replication, detergent, water hardness, and temperature. Each fabric specimen was zig-zagged with a polyester/cotton corespun thread to prevent raveling.

Detergent Ingredients

The following materials were used to formulate the detergents evaluated in this research:

1. Anionic Surfactant

   CONOCO C-650 (sodium p-tridecylbenzene sulfonate)

   Conoco Chemicals, Continental Oil Company

   Ponca City, Oklahoma

2. Nonionic Surfactant

   ALFONIC 1412-60 (ethoxylated linear fatty alcohol)

   Conoco Chemicals, Continental Oil Company

   Ponca City, Oklahoma

3. Antiredeposition Agent

   NATROSOL 250-LR (hydroxyethyl cellulose—HEC)

   Hercules, Inc.

   Wilmington, Delaware

4. Phosphate Builder

   (sodium tripolyphosphate—STPP)

   Monsanto Company

   St. Louis, Missouri

5. Inert Filler

   (sodium sulfate, anhydrous, technical grade—Na_2SO_4)

   Sargent-Welch Scientific Co.

   Skokie, Illinois

Three detergents were formulated using the above ingredients. The control detergent, Tide, was used as purchased. The exact detergent formulations are given in Table I.

TABLE I

DETERGENT FORMULATIONS

Detergent	Percent of formulation				
	Anionic	Nonionic	HEC	STPP	Na_2SO_4
1	16	8	5	12	59
2	16	8	5	18	53
3	16	8	5	24	47
4	NA*	NA	NA	25	NA

*Not available.

Detergent Formulation

The detergent concentration in each experiment was 0.15% of the total wash liquor; this concentration is approximately equal to that recommended for home laundry. The amounts of anionic surfactant, nonionic surfactant, and antiredeposition agent were held constant. The builder systems were varied in order to determine their effectiveness in aiding the soil removal ability of the detergent solution when combined with the minerals in hard water.

A total of 12 grams of each detergent was prepared for each replication. Each ingredient was weighed on a Mettler analytical balance and then dissolved in hot distilled water. After cooling, each ingredient was transferred volumetrically to a 1 liter volumetric flask. The detergent ingredients were then diluted to 1 liter total volume. One hundred milliliters of detergent solution was used for each experiment.

Addition of Hardness Minerals

In order to insure an even dispersion of hardness minerals in the wash liquor, a superconcentrated stock solution of hard water was prepared. Appropriate amounts of calcium chloride and magnesium chloride hexahydrate (Allied Chemical Co.—General Chemical Division, Morristown, N. J.) were dissolved in distilled water so that a small amount of

this stock would produce the desired hardness when added to the wash liquor. For the purposes of this research, 133.2 grams of calcium chloride and 164.2 grams of magnesium chloride hexahydrate were dissolved in one liter of distilled water. With the addition of five milliliters of this stock solution to the total wash liquor volume of 800 milliliters, the water hardness of the solution was 100 ppm with calcium and magnesium ions present in a 3/2 ratio, respectively.

Experimental Design

A full factorial design (4 × 3 × 3) was carried out with four detergents, three water temperatures, and three levels of water hardness giving a total of thirty-six treatment combinations; each treatment combination was replicated three times. Complete randomization of the order of treatment combinations was impossible due to the water temperature maintenance system of the Tergotometer; i.e., all four buckets are immersed in a single hot water bath, making individual temperature adjustments impossible.

The independent variables were detergent, water temperature, and water hardness; dependent variables were soil removal and soil redeposition.

Laundering Procedure

All experiments were carried out in the Tergotometer with a constant agitation of 100 rpm. For each experiment, the following procedure was used:

1. Seven hundred milliliters of distilled water were placed in each bucket and agitated to insure uniform temperature.

2. The water hardness was introduced by adding 0, 5, or 10 milliliters of the stock hardness solution to the appropriate bucket by pipette.

3. One hundred milliliters of a detergent solution were then added by pipette to the correct bucket.

4. After the water temperature had stabilized in all four buckets, two dry swatches were added and laundered for ten minutes.

5. The fabric specimens were removed, hand-squeezed, and returned to their respective buckets for rinsing.

6. Each rinse solution consisted of 800 milliliters of distilled water with either 0, 5, or 10 milliliters of the stock water hardness solution.

7. Rinsing was carried out at 100 rpm for five minutes.

8. The fabrics were removed from the rinse and blotted between paper towels to remove excess water. The use of the paper towel also served to prevent any transfer of soil between the individual fabric specimens.

9. The fabric samples were tumble dried alone in a home dryer at a moderate setting for ten minutes.

Whiteness Evaluation

Reflectance readings were taken on both the soiled and unsoiled portions of each fabric specimen using the Hunter Color Difference Metter—Model D25D2. Initial readings were taken to determine whiteness and/or greyness before laundering. After laundering, readings were taken on the unsoiled portion to determine if any redeposition had occurred, and on the soiled portion to determine the increase in whiteness.

For each reading, the white porcelain plate and seven pieces of white filter paper were placed behind a matched pair of experimental fabric specimens. The Y value (total light reflectance) was used as a measure of fabric whiteness. All readings were taken to the nearest 0.1 unit.

A total of four readings were taken on each fabric specimen. These readings were referred to as follows:

R_o - initial reflectance on the unsoiled portion

R_s - initial reflectance on the soiled portion

R_r - reflectance after laundering on the unsoiled portion

R_l - reflectance after laundering on the soiled portion

The percent soil removal (%SR) and percent soil redeposition (%SD) were calculated using the following equations:

$$\%SR = \frac{R_l - R_s}{R_o - R_s} \times 100$$

$$\%SD = \frac{R_o - R_r}{R_o} \times 100$$

Analysis of Data

The IBM 360 Computer at the University of Tennessee Computing Center was used for the data analysis. A three-way analysis of variance was used to evaluate the data derived from reflectance readings. The independent variables in this analysis were detergent (phosphate level), temperature, and water hardness. The dependent variables were percent soil removal and percent soil redeposition.

Following this initial analysis, a sorted analysis of variance was performed. The data was sorted by replication and a separate analysis of variance was done for each of the three replications.

For all data analyses, F values were considered significant at probability levels less than 0.05 ($p < 0.05$).

CHAPTER IV

RESULTS AND DISCUSSION

A full factorial experimental design was carried out using four detergents, three levels of water hardness and three levels of water temperature. Specific levels of each of the three variables were:

Variable	Levels
Detergent (% STPP)	12, 18, 24, 25
Water Hardness (ppm)	0, 100, 200
Water Temperature (°F)	100, 120, 140

The three experimental detergents all contained a mixed anionic-nonionic surfactant system and a high level of antiredeposition agent. These were held constant at the levels of 16% sodium p-tridecylbenzene sulfonate (anionic), 8% ethoxylated fatty alcohol (nonionic), and 5% hydroxyethyl cellulose (antiredeposition agent). Each detergent contained a low level (12%, 18%, or 24%) of sodium tripolyphosphate as a builder. A high level (5%) of hydroxyethyl cellulose was included in the three experimental detergents to compensate for the reduced phosphate levels. The control detergent, commercial Tide, contained a higher level (25%) of sodium tripolyphosphate; the rest of the formulation was unknown. The exact formulations of all the detergents are given in Table I, page 34. The water hardness of each detergent

solution was adjusted to either 0 ppm, 100 ppm, or 200 ppm according to the design. A presoiled 65% polyester/35% cotton plain woven fabric with a durable press (Rigmel) finish was the only fabric used in this research. The soil was basically an oil bound particulate soil. The entire 4 × 3 × 3 factorial experiment was replicated three times in twenty-seven blocks of four treatment combinations, based on water temperature.

The dependent variables in this investigation were percent soil removal and percent soil redeposition. These measurements were calculated from reflectance readings taken on the soiled and unsoiled portions of the fabric before and after exposure to the soil removal systems. Percent soil removal and percent soil redeposition for each treatment combination of detergent, water hardness, and temperature are given in Table II and Table III, respectively. A separate Three-Way Analysis of Variance was performed for both the soil removal and the soil redeposition data using the programs of the Statistical Analysis System and the University of Tennessee IBM 360 computer system. The results of the ANOVAs are given in Table IV for soil removal and in Table V for soil redeposition.

The analysis of variance for soil removal shows that the three main effects of detergent, water hardness, and temperature are all very highly significant ($p = 0.0001$).

TABLE II

PERCENT SOIL REMOVAL FOR TREATMENT COMBINATIONS

Detergent Composition** Percent				Hardness	Temperature	Percent Soil Removal*
A	N	HEC	STPP	(ppm)	(°F)	
16	8	5	12	0	100	52.24
16	8	5	12	100	100	64.34
16	8	5	12	200	100	60.71
16	8	5	12	0	120	59.17
16	8	5	12	100	120	65.97
16	8	5	12	200	120	63.63
16	8	5	12	0	140	59.08
16	8	5	12	100	140	66.91
16	8	5	12	200	140	63.82
16	8	5	18	0	100	53.49
16	8	5	18	100	100	61.23
16	8	5	18	200	100	61.16
16	8	5	18	0	120	59.83
16	8	5	18	100	120	65.57
16	8	5	18	200	120	64.60
16	8	5	18	0	140	61.14
16	8	5	18	100	140	66.64
16	8	5	18	200	140	64.05
16	8	5	24	0	100	51.89
16	8	5	24	100	100	55.62
16	8	5	24	200	100	62.96
16	8	5	24	0	120	61.25
16	8	5	24	100	120	55.46
16	8	5	24	200	120	63.98
16	8	5	24	0	140	60.99
16	8	5	24	100	140	59.85
16	8	5	24	200	140	65.61
--	-	-	25	0	100	55.01
--	-	-	25	100	100	44.04
--	-	-	25	200	100	42.43
--	-	-	25	0	120	60.37
--	-	-	25	100	120	50.12
--	-	-	25	200	120	49.14
--	-	-	25	0	140	60.83
--	-	-	25	100	140	50.89
--	-	-	25	200	140	51.82

** A = Anionic; N = Nonionic.

* This figure represents the mean percent soil removal for three replications.

TABLE III

PERCENT SOIL REDEPOSITION FOR TREATMENT COMBINATIONS

Detergent Composition** Percent				Hardness	Temperature	Percent Soil Redep.*
A	N	HEC	STPP	(ppm)	(°F)	
16	8	5	12	0	100	-1.197
16	8	5	12	100	100	-1.418
16	8	5	12	200	100	-0.820
16	8	5	12	0	120	-0.480
16	8	5	12	100	120	-0.660
16	8	5	12	200	120	-0.283
16	8	5	12	0	140	-0.940
16	8	5	12	100	140	-0.002
16	8	5	12	200	140	-0.140
16	8	5	18	0	100	-1.342
16	8	5	18	100	100	-1.238
16	8	5	18	200	100	-0.860
16	8	5	18	0	120	-0.955
16	8	5	18	100	120	-0.620
16	8	5	18	200	120	-0.402
16	8	5	18	0	140	-0.787
16	8	5	18	100	140	-0.500
16	8	5	18	200	140	-0.040
16	8	5	24	0	100	-1.515
16	8	5	24	100	100	-0.980
16	8	5	24	200	100	-1.296
16	8	5	24	0	120	-0.755
16	8	5	24	100	120	-0.520
16	8	5	24	200	120	-0.600
16	8	5	24	0	140	-0.777
16	8	5	24	100	140	-0.103
16	8	5	24	200	140	-0.163
--	-	-	25	0	100	-1.378
--	-	-	25	100	100	-1.453
--	-	-	25	200	100	-1.438
--	-	-	25	0	120	-0.833
--	-	-	25	100	120	-0.793
--	-	-	25	200	120	-1.040
--	-	-	25	0	140	-1.277
--	-	-	25	100	140	-0.380
--	-	-	25	200	140	-0.780

** A = Anionic; N = Nonionic.

* This figure represents the mean percent soil redeposition for the three replications.

TABLE IV

THREE WAY ANOVA FOR PERCENT SOIL REMOVAL

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	3840.84	1280.28	640.22	0.0001***
Water Hardness	2	88.01	44.01	22.01	0.0001***
Water Temperature	2	1248.56	624.28	312.18	0.0001***
Detergent × Hardness	6	2969.48	494.91	247.49	0.0001***
Detergent × Temperature	6	65.13	10.86	5.43	0.0001***
Hardness × Temperature	4	123.99	31.00	15.50	0.0001***
Detergent × Hardness × Temperature	12	160.87	13.41	6.70	0.0001***
Replication	2	25.90	12.95	6.48	0.0023**

*** Very highly significant.

** Highly significant.

TABLE V

THREE WAY ANOVA FOR PERCENT SOIL REDEPOSITION

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	4.506	1.502	10.114	0.0001***
Water Hardness	2	5.413	2.707	18.225	0.0001***
Water Temperature	2	22.503	11.252	75.759	0.0001***
Detergent × Hardness	6	2.687	0.448	3.020	0.0080**
Detergent × Temperature	6	0.587	0.098	0.659	0.6854
Hardness × Temperature	4	3.206	0.802	5.397	0.0006***
Detergent × Hardness × Temperature	12	2.060	0.172	1.156	0.3182
Replication	2	52.360	26.180	176.300	0.0001***

*** Very highly significant.

** Highly significant.

Table VI reveals that the commercial detergent, Tide, had the lowest overall values for soil removal and that the three experimental detergents had only slight differences in overall performance. Table VII and Table VIII show that the mean percent soil removal increased with both water hardness and temperature, respectively.

This main effect analysis is also supported by the analysis of variance for soil redeposition in Table IV, showing significance for detergent, water hardness, and temperature ($p = 0.0001$). Tables VI, VII, and VIII show mean percent soil redeposition as a function of detergent, water hardness, and temperature, respectively. Negative values for soil redeposition indicate that redeposition did not occur; the unsoiled portion of the fabric had higher reflectance after washing than before washing.

Definite conclusions cannot be drawn from the analysis of main effects because the ANOVA for soil removal also shows high significance for the three two-way interactions: detergent by water hardness, detergent by temperature, and water hardness by temperature, and the three-way interaction of detergent by water hardness by temperature.

The detergent by water hardness level interaction was highly significant at $p=0.0001$. Figure 3 shows that all the detergents performed similarly at a level of 0 ppm water hardness; detergent 4 (commercial Tide) performing best.

TABLE VI

MEAN PERCENT SOIL REMOVAL AND SOIL REDEPOSITION AS A FUNCTION OF DETERGENT TYPE

Detergent	% STPP	Mean % SR**	Mean % SD*
1	12	61.76	-0.660
2	18	61.97	-0.749
3	24	59.74	-0.746
4***	25	51.63	-1.041

***Tide.

**This figure represents the mean percent soil removal for all combinations of water hardness and temperature for the three replications.

*This figure represents the mean percent soil redeposition for all combinations of water hardness and temperature for the three replications.

TABLE VII

MEAN PERCENT SOIL REMOVAL AND SOIL REDEPOSITION AS A FUNCTION OF WATER HARDNESS

Water Hardness (ppm)	Mean % SR**	Mean % SD*
0	57.94	-1.020
100	58.89	-0.722
200	59.49	-0.655

**This figure represents the mean percent soil removal for all combinations of detergent and temperature for the three replications.

*This figure represents the mean percent soil redeposition for all combinations of detergent and temperature for the three replications.

TABLE VIII

MEAN PERCENT SOIL REMOVAL AND SOIL REDEPOSITION AS A FUNCTION OF WATER TEMPERATURE

Water Temperature (°F)	Mean % SR**	Mean % SD*
100	55.43	-1.245
120	59.92	-0.662
140	60.97	-0.491

**This figure represents the mean percent soil removal for all combinations of detergent and water hardness for the three replications.

*This figure represents the mean percent soil redeposition for all combinations of detergent and water hardness for the three replications.

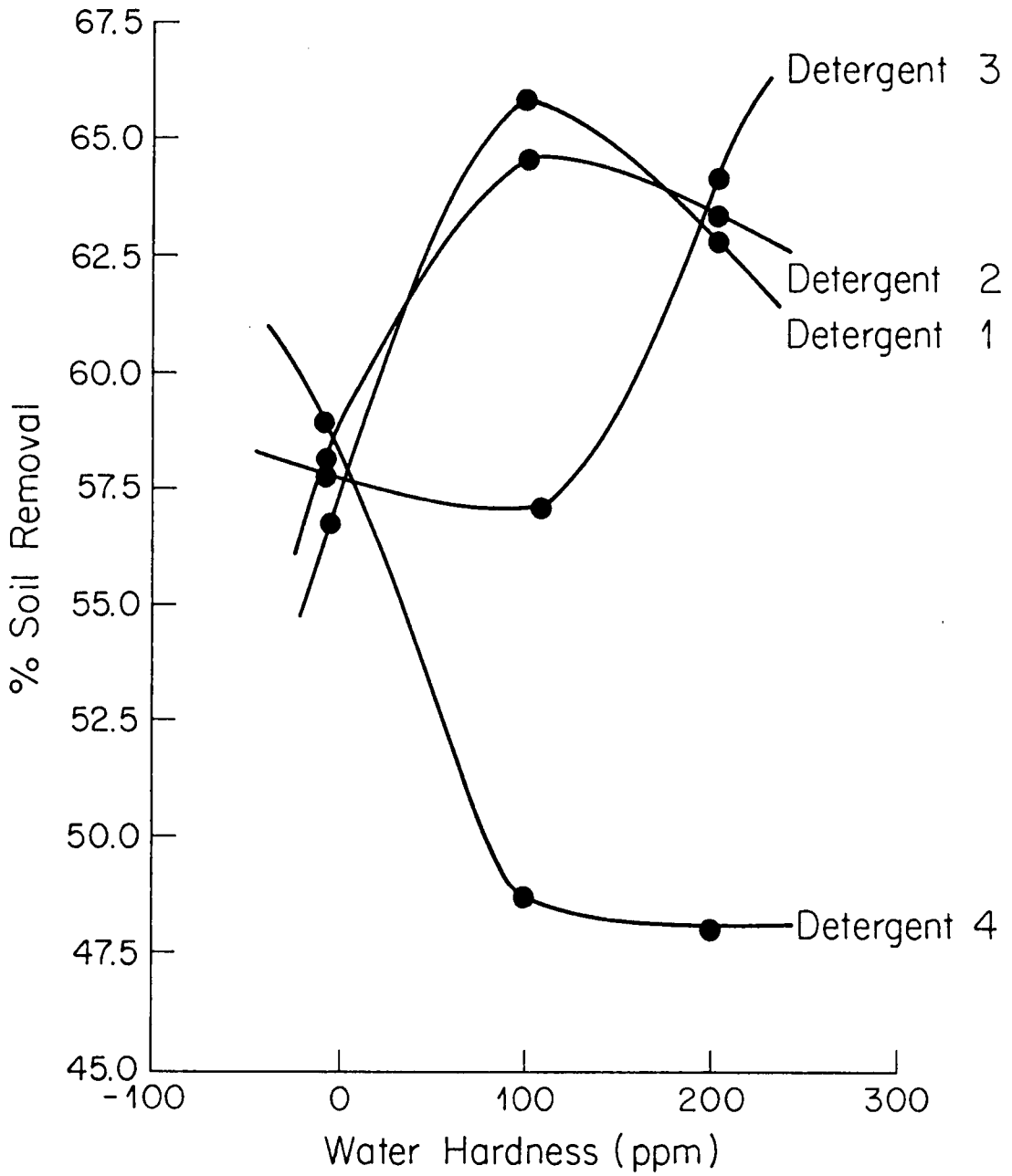


Figure 3. Mean values of soil removal for water hardness levels and detergents.

However, at a hardness of 100 ppm, Tide's performance dropped off significantly and continued to drop slightly at 200 ppm hardness. Of the three experimental detergents, detergents 1 and 2 performed similarly over the three levels of water hardness, with the highest soil removal at 100 ppm. Detergent 3 performed best at a water hardness level of 200 ppm. The optimum conditions for soil removal were a low-phosphate detergent (detergent 1—12% STPP) and a water hardness of 100 ppm.

The detergent by temperature level interaction shown in Figure 4 was also highly significant at $p = 0.0001$. The soil removal ability of all four detergents increased with temperature. Detergent 4 (commercial Tide) performed much less satisfactorily than the three experimental detergents. Best soil removal occurred at 140°F with detergent 2 (18% STPP).

The interaction of water hardness and water temperature shown in Figure 5 was highly significant at $p = 0.0001$. The best levels for soil removal were a water hardness of 200 ppm and a temperature of 140°F. At the temperature levels of 100°F and 140°F, soil removal increased as the level of water hardness increased. However, at a temperature of 120°F, soil removal was better at a water hardness of either 0 ppm or 200 ppm than at the moderate level of water hardness, 100 ppm.

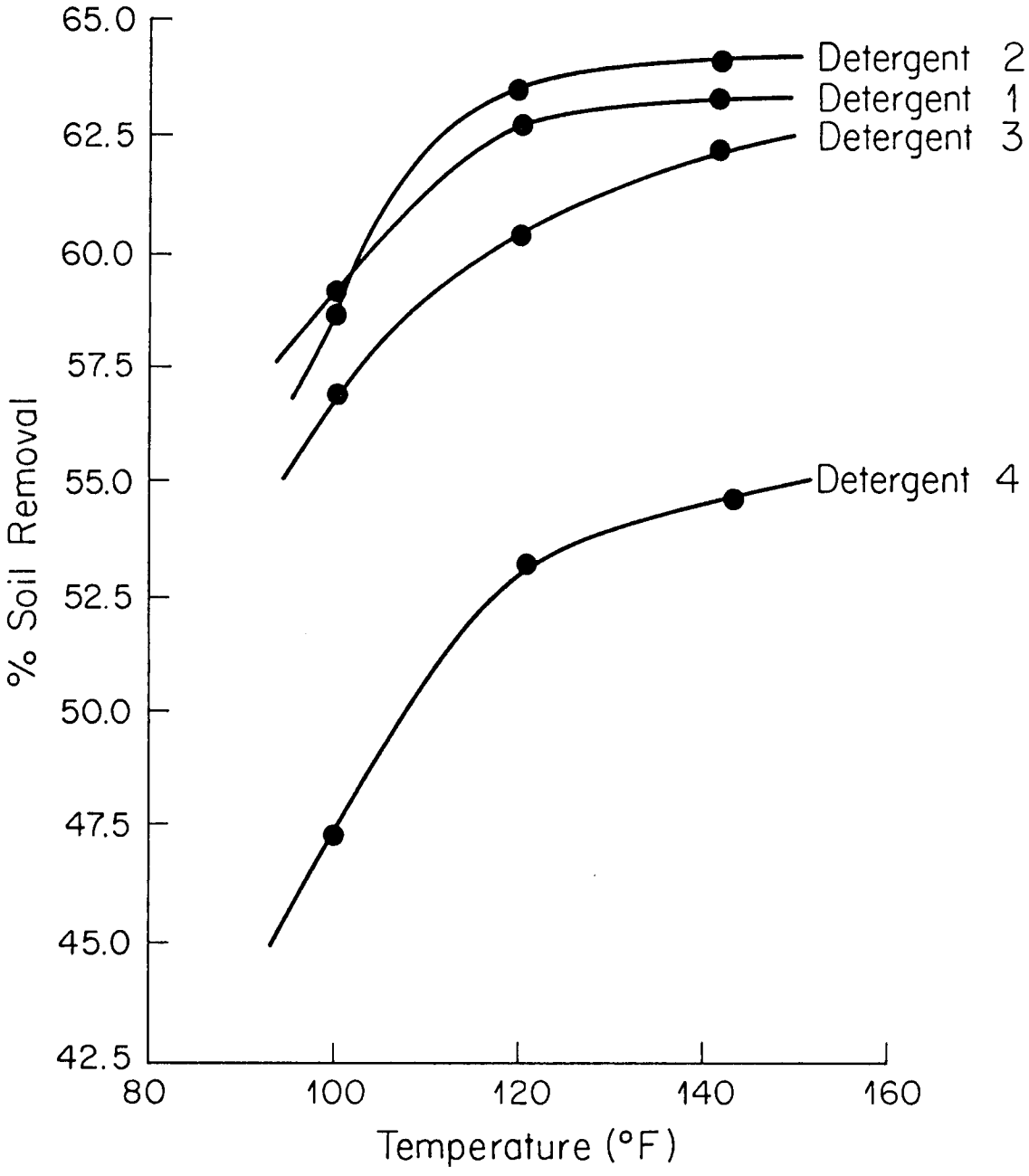


Figure 4. Mean values of soil removal for temperature levels and detergents.

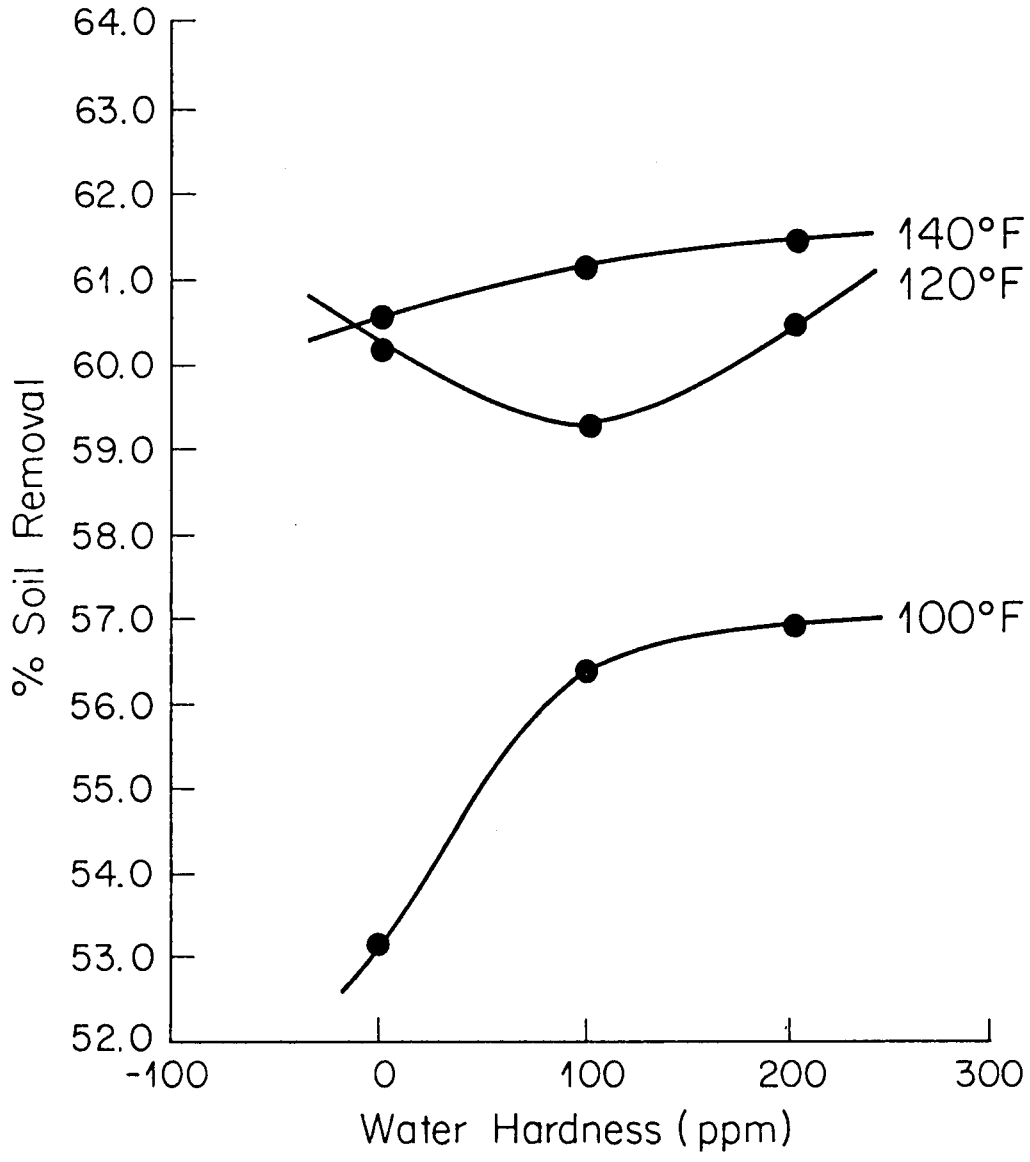


Figure 5. Mean values of soil removal for levels of water hardness and temperature.

Figure 6 shows the three way interaction of detergent by water hardness by water temperature. This interaction was also significant at $p = 0.0001$ as indicated by the dissimilar patterns formed by the three simple interactions. Figure 6 indicates that the conditions best suited to soil removal in cold (100°F), warm (120°F), or hot (140°F) water are a low phosphate detergent (detergent 1—12% STPP) and a moderate level of water hardness (100 ppm). Both low phosphate detergents 1 and 2 performed similarly over the levels of water hardness and temperature. As seen in Figure 6 (a), the soil removal ability of detergent 3 (24% STPP) increased with water hardness in cold water (100°F). In warm (120°F) and hot (140°F) water, the soil removal of detergent 3 was best in hard water (200 ppm) and worst in moderately hard water (100 ppm). The high phosphate detergent 4 (commercial Tide) removed less soil at low temperature levels and high water hardness levels, except for one case as shown in Figure 6(c). Figure 6(c) reveals that, in hot (140°F) water, detergent 4 (commercial Tide) performed best in distilled water (0 ppm); then Tide's performance dropped significantly in moderately hard water (100 ppm), but improved slightly in hard water (200 ppm).

Detergent 3, the high phosphate experimental detergent, was the only detergent to exhibit anomalous behavior over the levels of water hardness and temperature. The soil

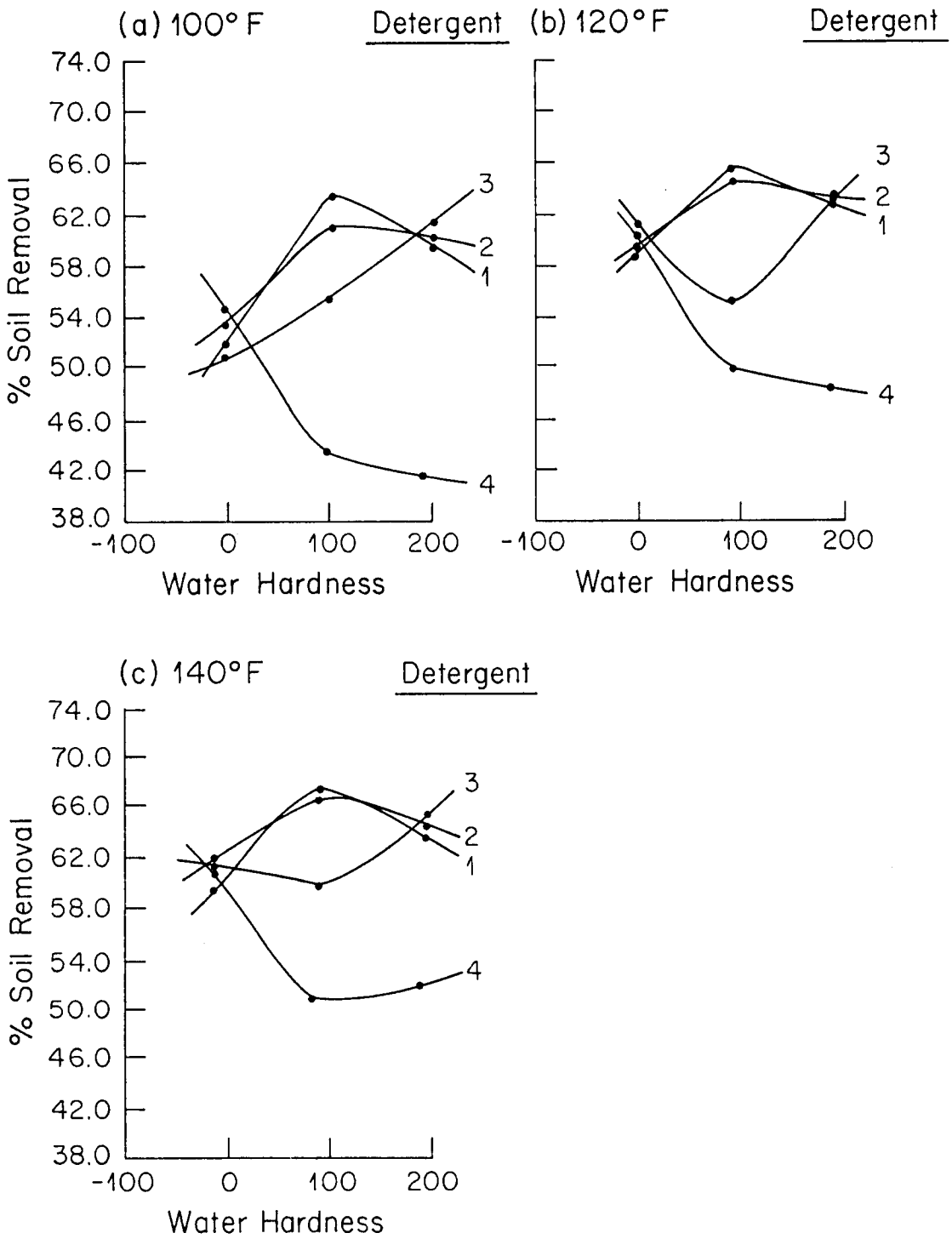


Figure 6. Mean values of soil removal for temperature, water hardness, and detergent interaction.

removal ability of the low phosphate experimental detergents 1 and 2 seemed to be enhanced by a moderate level of water hardness (100 ppm) in all temperature levels. The performance of detergent 4, commercial Tide, was definitely decreased by the presence of hardness minerals at all temperature levels.

The analysis of significant interactions for soil removal is not entirely supported by the soil redeposition data. Table V, page 45, indicates that only two interactions are significant for soil re eposition: detergent by water hardness and water hardness by temperature.

Both the ANOVA for soil removal (Table IV, page 44) and the ANOVA for soil redeposition (Table V, page 45) indicate a significant difference in the three replications. Because of this difference, the data was sorted by replication and six separate analyses of variance were done for soil removal and soil redeposition for each of the three replications. The three way ANOVAs for soil removal appear in Tables IX, X, and XI for replications #1, #2, and #3, respectively. These analyses support the original unsorted analysis of variance for soil removal; all main effects, all two-way interactions, and the three-way interaction are very highly significant ($p=0.0001$). The three way ANOVAs for soil redeposition appear in Tables XII, XIII, and XIV. In these analyses, all sources of error were very highly significant

TABLE IX

THREE WAY ANOVA FOR SOIL REMOVAL—
REPLICATION #1

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	1299.13	433.04	1029.68	0.0001***
Hardness	2	46.22	23.11	54.95	0.0001***
Temperature	2	543.64	271.82	646.32	0.0001***
Det. × Water Hardness	6	1039.12	173.19	411.80	0.0001***
Det. × Water Temperature	6	19.62	3.27	7.78	0.0001***
Water Hardness × Water Temp.	4	62.03	15.51	36.87	0.0001***
Det. × Water Hardness × Water Temp.	12	96.42	8.03	19.10	0.0001***

*** Very highly significant.

TABLE X

THREE WAY ANOVA FOR SOIL REMOVAL—
REPLICATION #2

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	1130.04	376.68	909.81	0.0001***
Water Hardness	2	13.94	6.97	16.84	0.0001***
Water Temp.	2	320.70	160.35	387.30	0.0001***
Det. × Water Hardness	6	1058.20	176.37	425.98	0.0001***
Det. × Water Temperature	6	73.74	12.29	29.68	0.0001***
Water Hardness × Water Temp.	4	36.30	9.08	21.92	0.0001***
Det. × Water Hardness × Water Temp.	12	79.91	6.63	16.02	0.0001***

*** Very highly significant.

TABLE XI

THREE WAY ANOVA FOR SOIL REMOVAL—
REPLICATION #3

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	1429.03	476.34	1045.31	0.0001***
Water Hardness	2	49.41	24.70	54.21	0.0001***
Water Temp.	2	433.19	216.60	475.31	0.0001***
Det. × Water Hardness	6	908.19	151.37	332.17	0.0001***
Det. × Water Temperature	6	19.50	3.25	7.13	0.0001***
Water Hardness × Water Temp.	4	56.65	14.16	31.08	0.0001***
Det. × Water Hardness × Water Temp.	12	91.71	7.64	16.77	0.0001***

*** Very highly significant.

TABLE XII

THREE WAY ANOVA FOR SOIL REDEPOSITION—
REPLICATION #1

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	2.973	0.991	47.456	0.0001***
Hardness	2	4.135	2.067	99.003	0.0001***
Temperature	2	1.916	0.958	45.866	0.0001***
Det. × Water Hardness	6	2.828	0.471	22.573	0.0001***
Det. × Water Temperature	6	19.622	3.270	7.776	0.0001***
Water Hardness × Water Temp.	4	62.026	15.507	36.870	0.0001***
Det. × Water Hardness × Water Temp.	12	96.417	8.035	19.104	0.0001***

*** Very highly significant.

TABLE XIII

THREE WAY ANOVA FOR SOIL REDEPOSITION—
REPLICATION #2

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	3.862	1.287	60.642	0.0001***
Hardness	2	1.511	0.755	35.583	0.0001***
Temperature	2	8.095	4.048	190.678	0.0001***
Det. × Water Hardness	6	1.398	0.233	10.975	0.0001***
Det. × Water Temperature	6	1.008	0.168	7.912	0.0001***
Water Hardness × Water Temp.	4	2.374	0.593	27.593	0.0001***
Det. × Water Hardness × Water Temp.	12	1.198	0.100	4.703	0.0001***

*** Very highly significant.

TABLE XIV

THREE WAY ANOVA FOR SOIL REDEPOSITION—
REPLICATION #3

Source	DF	Sum of Squares	Mean Square	F	Prob.
Detergent	3	0.053	0.018	0.909	0.5514
Water Hardness	2	0.721	0.360	18.636	0.0001***
Water Temp.	2	19.181	0.187	9.649	0.0001***
Det. × Water Hardness	6	1.133	0.189	495.927	0.0001***
Det. × Water Temperature	6	1.112	0.187	9.649	0.0001***
Water Hardness × Water Temp.	4	0.438	0.109	5.660	0.0015**
Det. × Water Hardness × Water Temp.	12	2.232	0.186	9.617	0.0001***

*** Very highly significant.

** Highly significant.

except for two cases, shown in Table XIV. Detergent was not significant for soil redeposition in replication #3. The interaction water hardness by temperature was less significant for soil redeposition than the other sources in replication #3.

CHAPTER V

SUMMARY AND CONCLUSIONS

The purpose of this study was to evaluate the soil removal ability of experimentally formulated detergents containing hydroxyethyl cellulose as an antiredeposition agent under selected conditions of water hardness and water temperature. Previous study of detergents containing hydroxyethyl cellulose was carried out in distilled water at a constant temperature; it was assumed that the levels of water hardness and temperature in this study more closely resemble the conditions of actual detergent use.

Three experimental detergents were formulated with constant levels of anionic surfactant (16% sodium p-tridecyl-benzene sulfonate), nonionic surfactant (8% ethoxylated fatty alcohol), and antiredeposition agent (5% hydroxyethyl cellulose). Each of these detergents had a variable level of phosphate builder (12, 18, or 24% sodium tripolyphosphate); each formulation was brought to 100% with the inert filler, sodium sulfate. Commercial Tide (Proctor and Gamble) with 25% sodium tripolyphosphate was used as a control.

Only one fabric was used in this research: a presoiled 65% polyester/35% cotton woven fabric with a durable press finish. Levels of water hardness (0, 100, or 200 ppm) and

water temperature (100, 120, or 140°F) were adjusted according to the experimental design.

Each detergent was evaluated by both soil removal and soil redeposition experiments. The soil removal experiments evaluated the ability of each detergent to remove the oil bound particulate soil from the presoiled fabric. The soil redeposition experiments evaluated the ability of each detergent to suspend soil thereby preventing redeposition onto the clean fabric. Both soil removal and soil redeposition were measured by comparative reflectance readings taken on the soiled and clean portions of the fabric before and after exposure to a selected treatment combination of detergent, water hardness, and water temperature. All experiments were carried out in the Tergotometer.

The soil removal and soil redeposition data were analyzed by factorial analyses of variance. All sources of error were very highly significant for soil removal. For soil redeposition, the three main effects of detergent, water hardness, and temperature, and the interaction of water hardness and temperature were very highly significant; also less significant was the interaction between detergent and water hardness.

Overall, the three experimental detergents containing hydroxyethyl cellulose performed better as soil removal systems than the commercial detergent, Tide. As expected,

overall detergent efficiency increased with increasing water temperature. Detergent efficiency was expected to decrease with increasing water hardness; this was true only with the commercial detergent, Tide. The soil removal ability of the three experimental detergents was enhanced by water hardness.

The two-way interactions of detergent by water hardness, detergent by water temperature, and water hardness by water temperature were also significant for soil removal. The three way interaction of detergent by water hardness by temperature was very highly significant at $p = 0.0001$.

The three-way interaction revealed that experimental detergents 1 and 2 (12% and 18% STPP, respectively) performed similarly over all levels of water hardness and temperature, with the highest soil removal at a moderate level of water hardness (100 ppm). Detergent 3, the high phosphate experimental detergent, did not perform consistently over the treatment combinations of water hardness and temperature. In cold (100°F) water, the soil removal ability of detergent 3 increased with water hardness. In warm (120°F) and hot (140°F) water, the soil removal ability of detergent 3 was highest in hard (200 ppm) water, but dropped significantly in moderately hard (100 ppm) water. The soil removal ability of detergent 4, commercial Tide, decreased significantly with the addition of hardness minerals. Tide performed best in hot distilled water, a condition that is virtually nonexistent in actual detergent use.

Based on the above, the optimum conditions for soil removal appear to be a low phosphate (12% or 18% STPP) detergent in moderately hard (100 ppm) water. Increasing the water temperature also enhances these conditions for soil removal.

This investigation of detergent efficiency under conditions of water hardness and temperature is primarily a preliminary investigation. Further research is necessary to evaluate the anomalous behavior of the high phosphate (24% STPP) detergent in hard water. Beyond that evaluation, future research should include an evaluation of these formulations under actual use conditions.

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APPENDIX

COMPOSITION OF SOIL APPLIED TO FABRICS

1.0 part	ethyl cellulose showing a viscosity of from 8 to 12 centipoises at 25°C. when 5 parts are dissolved in a mixture of 57 parts of toluene (ACS) and 38 parts of ethyl alcohol (ACS)
14.0 parts	naptha
0.5 parts	butanol
2.0 parts	lampblack, conforming to the requirements of Fed. Spec. TT-L-70
2.5 parts	hydrogenated vegetable oil conforming to the requirements of Fed. Spec. EE-S-321
20.0 parts	mineral oil (U.S.P.) medicinal grade
0.8 parts	purified sodium alginate
57.1 parts	cold water
1.3 parts	cornstarch
0.5 parts	oleic acid (U.S.P.)
0.3 parts	morpholine solvent

COMPOSITION OF CONTROL DETERGENT, COMMERCIAL TIDE

The commercial detergent Tide was purchased in Knoxville, Tennessee, during the fall of 1976. The following information pertinent to detergent composition appeared on the package:

> Ingredients: Tide contains ingredients to lift dirt from clothes (anionic surfactants) and soften water (complex sodium phosphates). There are also agents to protect washer parts (sodium silicate) and improve processing (sodium sulfate), plus small quantities of agents to prevent deposition, fabric whiteners and perfume.
>
> Phosphorus Content—This Tide formula averages 6.1% phosphorus, in the form of phosphates, which is equivalent to 5.9 grams per 1 1/4 cup use level.

VITA

Paula Ann Metcalf, the daughter of Mr. and Mrs. Walter J. Metcalf, was born in Coatesville, Pennsylvania, on November 8, 1953. She graduated from Coatesville Area Senior High School in 1971. In September, 1971, she entered the University of Delaware, Newark, Delaware. She received her Bachelor of Science degree in home economics with a major in textiles and clothing in June 1975.

She entered the graduate program at the University of Tennessee, Knoxville, in September 1975 and received a research assistantship from the U.S.D.A., A.R.S., Textiles and Clothing Laboratory. While attending the University of Tennessee, she became a member of the Student Chapter of the American Association of Textile Chemists and Colorists, and was elected to membership in the Omicron Nu and Phi Kappa Phi honorary societies. In March 1977, she received her Master of Science degree in textiles and clothing.