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   DETERMINATION OF SURFACTANT BUILD-UP
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   The University of North Carolina at
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DETERMINATION OF SURFACTANT BUILD-UP

AND ITS EFFECTS ON RESIN

TREATED COTTON FABRICS

by

Uchenna Ogbogu

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APPROVAL PAGE

This dissertation has been approved by the following

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ii

OGBOGU, UCHENNA. Determination of Surfactant Build-Up and
Its Effects on Resin-Treated Cotton Fabrics. (1976)
Directed by: Dr. Victor Salvin. Pp. 141.

This study investigated the build-up of anionic and

nonionic surfactants on untreated and resin-treated cotton

fabrics and the effects of this build-up on the tensile

strength, abrasion resistance and wrinkle recovery of the

fabrics.

A laboratory experiment was employed for data col-

lection, using a four-factor experimental design with two

levels of each factor. The factors were fabric finish,

surfactant type, laundering temperature and laundering

cycle. A sample size of three was assigned to each level

of the factors and three unlaundered samples of each fab-

ric served as the control. The samples were washed for 10

minutes and rinsed for 6 minutes in an automatic home

washer. Drying was carried out in an automatic home dryer

for 30 minutes at a high temperature setting. Swatches of

the laundered samples were extracted for three hours in

distilled water and tested for residual surfactant, using

the methylene blue indicator method for the anionic and the

phosphomolybdic acid method for the nonionic surfactant.

AATCC and ASTM standard test methods were used to test the

tensile strength, wrinkle recovery and abrasion resistance

of each sample. To determine the significance of the

observed changes, the data were subjected to a multivariate

analysis of covariance with the surfactant content, warp

and filling wrinkle recovery and the abrasion resistance of

the control samples serving as the covariates and the warp

and filling tensile strength, warp and filling wrinkle

recovery, abrasion resistance and surfactant content of the

laundered samples as the dependent variables. Multiple com-

parisons were made, using the Newman Keul's method, to

identify the different means where the univariate analysis

of covariance indicated a significant effect. A .05 level

of significance was chosen for the test of hypotheses.

Twelve of the 15 multivariate effects were signi-

ficant at the .05 level or less. The canonical correlations

showed that surfactant content and abrasion resistance were

responsible for most of the significance. The univariate

analysis for surfactant content yielded 12 significant

effects. Multiple comparisons of the means showed that the

untreated fabric retained a significantly larger quantity

of surfactant than the resin-finished fabric and that the

build-up of the anionic surfactant was significantly higher

than that of the nonionic surfactant. It was found that

increases in temperature and laundering cycle resulted in

increased build-up, but while temperature was important in

the build-up of the anionic surfactant, laundering cycle was

more important for the nonionic surfactant. No significant
relationship was found between surfactant content and the
other fabric properties. It was concluded that cotton,
untreated and finished, did not retain large quantities of
surfactant.

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Special appreciation is extended to Dr. Pauline Keeney, professor and chairman of the Clothing and Textile area, and Dr. William Tullar, professor in Business and Economics, for their helpful criticisms and suggestions. To the other members of the dissertation committee, Dr. Eunice Deemer, professor in Home Economics, and Dr. Mildred Johnson, professor in Home Economics, the author expresses her gratitude for their support and guidance all through the graduate program.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Textile fabrics become readily soiled in use. The

process of soil removal by an aqueous solution of surface

active agent is of considerable interest to both the manu-

facturer who is concerned with the removal of waxes and other

natural impurities from textile fibers and the consumer for

whom soil removal is a means of restoring the fabric to a

serviceable state. Early investigations of the effectiveness

of soaps in detergency included extensive research into the

mode of action of surfactants.[1] Meader and Fries described

this in their well-known equation:

Fabric.Dirt + Soap = Fabric.Soap + Dirt.Soap[2]
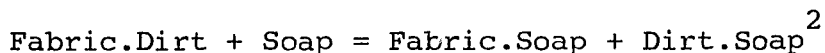
What happens to the "fabric.soap" portion of the equation

---

[1]F. H. Rhodes and S. W. Brainard, "The Detergent
Action of Soap," Industrial and Engineering Chemistry, 21
(January, 1921), 60-68 and N. K. Adam, "Detergent Action and
Its Relation to Wetting and Emulsification," Journal of the
Society of Dyers and Colourists, 53 (April, 1937), 121-129.

[2]Arthur L. Meader and Bernard R. Fries, "Adsorption
in the Detergent Process," Industrial and Engineering
Chemistry, 44 (July, 1952), 1632-1638.

when the "dirt.soap" is flushed away in the wash water is still subject to some controversy and is the subject of this investigation.

Surfactants are characterized by the fact that they are unbalanced. A surfactant molecule consists of an oil-soluble portion (hydrophobe) and a water-soluble portion (hydrophile). This dual characteristic causes instability in water solutions which is overcome in two ways: (1) the formation of micelles and (2) orientation at the interface. The latter characteristic, known as adsorption, is responsible for detergency. The process of adsorption is further aided by fabric characteristics such as electrophoteric charge and the presence of chemically reactive substances on the fiber. Most of the surfactant is removed in the rinsing process but some is left behind and the possibility of a build-up exists.[3] Such foreign matter, if present in large enough quantities, could affect several fabric performance properties.

This study was designed to explore the build-up of anionic and nonionic surfactants on resin-treated and

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[3]Walter L. Maple, "Evaluation of the Rinsing Process," in W. C. Cutler and R. C. Davis, Detergency-Theory and Test Methods, Vol. 5 (New York: Marcel Derker, Inc., 1975), p. 505.

untreated cotton, and to determine the effects of such a
build-up on the tensile strength, abrasion resistance, and
wrinkle recovery of the fabrics. The experimental conditions
were those which take place in machine washing, using sur-
factants at concentrations normally used and with the regular
cycle of laundering.

The adsorption of surfactant by cotton has been
studied. This study, however, deals specifically with the
build-up of surfactant after rinsing. During the washing
cycle, there is an equilibrium between the fiber and the wash
bath. This equilibrium changes with the introduction of
fresh water in the rinse. This study differs from other
work on adsorption in that previous research methods dealt
with the distribution of the surfactant and did not consider
that rinsing, as in the wash cycle, sets up a new equilibrium
and reduces the adsorbed surfactant.

Although studies have pointed out the fact that
desorption is not complete and that surfactant build-up
could occur, few studies have undertaken to determine the
extent of these phenomena. More specifically, no investi-
gation has been undertaken into the conditions under which
it occurs or the effect of such a build-up on fabric prop-
erties. Researchers have recognized that adsorbed surfactant

affects fabric properties. The practice of not using
cationic surfactants in the processing of cotton, since this
class of surfactants is strongly chemisorbed on cotton,
demonstrates explicit recognition of this problem.[4] Another
serious handicap with the few available studies on the build-
up of surfactants is the lack of statistical analysis of the
data. This casts some doubts on the conclusions reached.
In the absence of statistical tests, it becomes difficult to
determine any real significance of the observed build-up.

Incomplete as surfactant build-up studies on cotton
are, more research exists on untreated cotton than there is
on resin-treated cotton. A thorough search of the literature
failed to yield any studies on the desorption of surfactants
by resin-treated cotton in spite of the commercial importance
of this group of fabrics, and the fact that they behave dif-
ferently from cotton in laundering.

Some researchers have pointed the characteristics
of textile fibers which could affect adsorption. These
include:

1. the presence of chemically reactive groups.

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[4]Harry T. Zika, "Using Nonionic Surfactants," *Textile Chemists and Colorists*, 15 (July, 1969), 26-31.

2. electrophoteric charge,

3. the presence of chemically reactive substances resulting from chemical action or deposition by intent, and

4. free energy forces and Van Der Waal forces and hydrogen bonding.

The durable press process on cotton involves an alteration of the chemical nature of the fiber by an introduction of chemically reactive crosslinking compounds as well as the introduction of softeners to counteract the stiffening of the fibers that result from the crosslinking.[5] The high temperature under which curing is carried out and the presence of acidic catalysts invariably result in some degradation of the fiber. Degraded cotton differs from native cotton in its reactivity to chemical compounds. This would tend to suggest that cotton treated for durable press should adsorb and desorb surfactant differently from native cotton.

An attempt is made in this study to provide information that is lacking on the build-up of surfactant on cotton under varied conditions found in laundering as well

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[5] J. T. Marsh, _Introduction to Textile Finishing_ (London: Chapman and Hill Ltd., 1966), p. 257.

as comparative information on resin-treated cotton. Untreated cotton fabrics form the bulk of the production of Nigerian cotton mills and so is of prime importance to this researcher. Although very limited quantities of cotton treated with resin to give durable press fabrics are marketed, it is of importance to establish the behavior of resin-treated fiber as a component of the polyester-cotton blend.

OBJECTIVES

The objectives of the study were: (1) to determine surfactant build-up on untreated and resin-treated cotton, (2) to determine the effects of such a build-up on the tensile strength, wrinkle recovery and abrasion resistance of the fabrics.

HYPOTHESES

The hypotheses developed for the study were:

1. There is no significant surfactant build-up attributable to the durable press finish.

2. There is no significant surfactant build-up attributable to surfactant type.

3. There is no significant surfactant build-up attributable to laundering temperature.

4. There is no significant surfactant build-up attributable to any combination of fabric finish, laundering temperature, and surfactant type.

5. There is no significant difference in fabric properties attributable to surfactant build-up.

ASSUMPTIONS

It was assumed that changes in fabric properties are detectable after three and eight laundering cycles.

LIMITATIONS

1. Some wear is expected as a result of the mechanical action of the washing machine. This should be borne in mind when interpreting the data.

2. The surfactant could be trapped between yarns because of the inefficiency of rinsing. Therefore the results of the study are applicable only to fabrics of similar construction.

3. The results of the study are limited to a pH of 5 which was the pH obtained using tap water which was delivered at an acidic pH of 5.

4. The study does not include the effect of builders which not only raise the pH but give a different system.

DEFINITION OF TERMS

Critical Micelle Concentration. A concentration at which surfactant molecules form micelles. It is in the micellar form that detergent action is postulated by some investigators as taking place.

Durable Press Fabric. A fabric that has been treated with resin to retain its smooth appearance, shape, and creases. This term is used interchangeably with permanent press fabric and resin treated fabric in this paper.

Detergency. The term refers to the process of cleaning a solid material by means of an aqueous solution of a surface active compound.

Soil. All foreign matter which is not deposited by intent on textile fabrics. Such soils generally consist of oil and finely divided solids or one of these.

Adsorption. The attraction of gases, liquids, or solids to the surface areas of textile fibers, yarns, fabrics, or any other material resulting in deposition.

Degradation. The loss of desirable physical properties by a textile material as a result of some process or some physical/chemical phenomenon.

CHAPTER II

REVIEW OF LITERATURE

The adsorption of surfactants (both soap and syn-
thetic) on natural fibers has been studied extensively. Few
of the reported studies, however, were concerned with the
desorption of surfactant from cotton: rather, more emphasis
has been given to this phenomenon in wool. Though the
mechanism of adsorption of surfactants on cotton and wool
differ, the studies on wool provided some valuable insights
into possible problems in cotton and were included in this
review of literature.

Studies on adsorption were reviewed only as a back-
ground to desorption. As a result, only those studies that
most directly related to the problem were included.

The first part of this chapter provides a general
background of detergency studies. This is followed by a
review of the structure of surfactants and their role in the
process of detergency. The studies related to the adsorption
of surfactant are also reviewed. The chapter concludes with
a review of the studies on the desorption of surfactants

from cotton fabrics. Particular attention is given to the

phenomenon of build-up which represents the affinity of

the surfactant for the fabric with recognition of the impor-

tance of desorption of surfactant in the rinsing cycle.

GENERAL BACKGROUND OF DETERGENCY STUDIES

It has long been recognized that detergent action

is to a large extent, surface action. As early as 1907

Spring suggested that:

> . . . . not only dispersion and emulsification, but
> also detergent action depend on the alteration of the
> hydrophobic surface of the solid being dispersed, the
> liquid being emulsified, or the grease or black being
> washed off the fibre, into a more hydrophylic or water-
> attracting surface.[6]

This occurred through the adsorption of the surfactant on

the hydrophobic surface. He described the useful properties

of the paraffin chains that made them ideally suited for

this purpose.

The process of detergency is however, more complex

than the conversion of a hydrophobic surface to a hydro-

phylic surface. Pickering pointed out the useful properties

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[6]Spring, in N. K. Adam, "Detergent Action and its
Relation to Wetting and Emulsification," Journal of the
Society of Dyers and Colourists, 53 (April, 1937), 121.

of suds in the suspension of soils in the wash liquor to prevent redeposition.[7] Adam, using more complex equipment, came to the conclusion that the essential part of detergent action was the displacement of soil from the solid surface by an aqueous detergent solution. To this end, the contact angle formed by the detergent solution and the oil was more crucial than the lowering of interfacial tension or surface tension alone.[8]

Though most of these early studies related what took place rather than why they occurred, they formed the background for more complex investigations. The studies also laid the foundation for the methods used in studying detergency. They established that the process of detergency consists of wetting, emulsification of liquids, lubrication, and deflocculation of soils. These processes were recognized as a result of the adsorption of surfactant molecules on hydrophobic surfaces. The ability of surfactants to do this is a result of their structure.

Since these early works, more complete explanations have been provided for the process of detergency and work

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[7]Spencer U. Pickering, "Detergent Action of Soap," Journal of London Chemical Society, 111 (March, 1917), 86-101.

[8]Adam, op. cit, p. 125.

is still in progress to explore all the areas of this com-

plex subject.

STRUCTURE OF SURFACTANTS

Chemical analysis of the structure of surfactants

reveals that a surfactant molecule contains a hydrophobic

portion and a hydrophylic portion. This combination of a

water-soluble system with an oil-soluble system is responsi-

ble for the special properties of these compounds.[9]

Surfactants are classified into anionic, cationic,

amphoteric, and nonionic surfactants, depending on the

charge on the surface ion in an aqueous solution. The

structure of surfactants varies with the group. Some of

these groups are of less commercial importance than others

so while mention will be made of these, the discussion will

be centered on anionic and nonionic surfactants.

Cationic Surfactants

These compounds dissociate in water to give posi-

tively charged ions. They form less than five percent of

the surfactants produced. Cationic surfactants may have

[9]"Surfactants," Ciba-Geigy Review, 1971/72, p. 3

special uses in manufacturing processes, but are not used

in household detergents. Their positively charged ions are

adsorbed on the fiber and bind the negatively charged dirt

particles closely to the fiber.[9]

Amphoteric Surfactants

The molecules of amphoteric surfactants dissociate

into positively or negatively charged particles, depending

on the pH of the solution. They, therefore, behave essen-

tially like anionic or cationic surfactants.

Anionic Surfactants

Anionic surfactants form the most numerous category

of all surfactants. They contain groups that impart a neg-

ative charge to the surface active ions. These compounds

differ from one another in the composition of their solu-

bilizing groups. The basic pattern for anionic surfactants

can be seen in the alkali salt of fatty acids (alkali soap)

as shown in Figure 1.

Anionic surfactants were the first surfactants in

use. Their detergent power is dependent on the length of

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[9]Sidney M. Edelstein, "Detergents--A Dilemma,"
American Dyestuff Reporter, 40 (August, 1951), 519-539.

the hydrocarbon chain. Good soaps contain fatty acids with twelve to eighteen carbon atoms. The hydrophylic carboxyl group is found at the end of the hydrophobic hydrocarbon chain. Soap, however, suffered the handicap of being precipitated by water containing magnesium and calcium. It has been gradually replaced by synthetic surfactants.[10]

$$C_{17}H_3COO-Na+$$

Figure 1

Sodium Stearate

Synthetic surfactants substitute the carboxylic acid with mineral acids. They are found as sulfuric acid esters, sulfonic acid derivatives, and as esters of phosphoric acid. Sulfonic acid derivatives are the most important class of anionic surfactants. A member of this group, alkyl benzene sulfonate, is the most widely used surfactant for household detergents.[11]

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[10]Ciba-Geigy Review, op. cit., p. 3.

[11]W. J. Schwarz, A. R. Martin, and R. C. Davis, "Influence of Calcium on the Adsorption of Sodiumdodecyl-benzene Sulfonate on Cotton," Untergruppe, D/1 Nr 4 (1960), 37.

Sulfonic acid derivatives have ten to fourteen car-
bon atoms on a hydrophobic alkyl residue. They have the
structure shown in Figure 2.

$$CH_3(CH_2)_{11} - \text{benzene ring} - SO_3Na$$
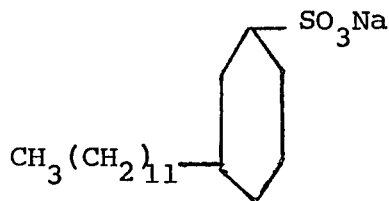
Figure 2

Sodium Dodecylbenzene Sulfonate

Anionic surfactants were found to be effective
detergents for cotton when suitably built. The formulation
for detergents includes not only surfactants but also builders
of diverse nature such as sodium phosphates and sodium sili-
cates. These raise the alkalinity of the system and act as
sequestering agents for calcium and magnesium and they are
postulated to have auxiliary action in neutralizing attrac-
tive forces between the soil and the fiber. This fact,
coupled with the availability and relatively low cost of
the starting materials, (n-paraffin and benzene), has made
anionic surfactants commercially important. They form sixty
percent of the world's surfactant consumption.[12]

_____

[12] A. Davidsohn and B. M. Milwidsky, <u>Synthetic Detergent</u>,
(London: Leonard Hill, 1967), p. 11.

Nonionic Surfactants

Nonionic surfactants are the second largest group

of surfactants used. They are gaining increasing importance

for both domestic and industrial uses.[13] The hydrophilic

component of this group is made up of a hydroxyl group and

a chain of ethoxy groups. The most important starting

materials are alkyl phenol and ethylene oxide. It has the

chemical structure shown in Figure 3.

$$OCH_2-CH_2O-(CH_2-CH_2O)_8-CH_2-CH_2OH$$

R
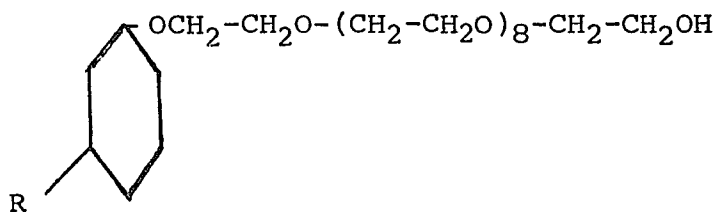
Figure 3

A Nonionic Agent

The water solubility of this group is dependent on the

ability of the oxygen in either to form a loose bond with

water through hydrogen bonding links. Figure 4 explains

the hydrophilic action.

In summary, surfactants are capable of wetting out,

emulsifying oils, and deflocculating aggregate solids because

---

[13]Davidsohn and Milwidsky, loc. cit.

they contain a water-compatible portion and an oil-compatible

portion in the same molecule. The oil-soluble portion,

usually located at the end of the hydrocarbon chain for

maximum detergency in an anionic surfactant, is an acid

group. Nonionic surfactants lack this solubilizing group.

They depend on the water-bonding ability of their oxygen

atoms for their solubility. The function of the surfactants

is to convert the large soil aggregates into smaller parti-

cles which are then surrounded by surfactant molecules in

micellar form. This loosens the soil from the fabric and

suspends it in the wash water and prevents re-aggregation

and redeposition. In the case of oils and waxes, the sur-

factant breaks up the continuous film into small droplets

which are in an emulsified form being surrounded by micelles

as in the case of the solid particles.

$$R - O-C_2H_4 - O\ldots\ldots\ldots\ldots O - C_2H_4- OH$$

..	..	..	..
H	H	H	H
.	.	.	.
O	O	O	O
.	.	.	.
H	H	H	H
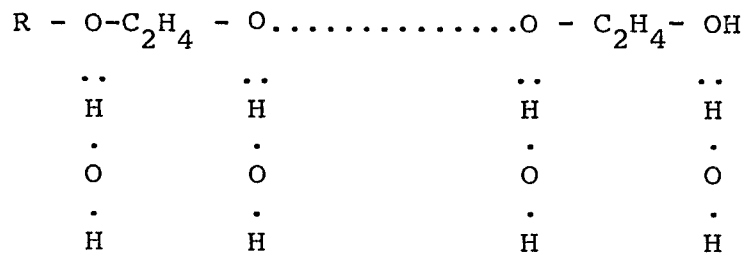
Figure 4

Solubilization of Nonionic Agent[14]

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[14]Ciba-Geigy Review, op. cit., p. 9.

SURFACTANTS IN THE PROCESS OF DETERGENCY

Detergency involves the wetting out of the substrate,
adsorption at solid interfaces, emulsification, removal of
soil and its dispersion in the wash solution.[15] This process
involves a complicated reaction between the fiber, soil and
surfactant in aqueous solution.

Soil on clothes is composed of sand, grit, and food
particles, covered by oily substances secreted by the skin.[16]
The oily coating presents a problem in laundering since
laundering takes place in an aqueous medium and oil and
water are incompatible. Surfactants alter this incompati-
bility at the contact surface. This is made possible by the
tendency for the hydrophobic portion to seek an escape from
water. This causes surfactant molecules to aggregate at
interfaces, with the oil-compatible end outward toward the
soil and the water-compatible portion in the water. This
bridges the gap.

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[15]W. W. Morgan-Thaler, "Sequestering Agents," in
W. G. Cutler and R. C. Davis, Detergency: _Theory and Test_
Methods, Vol. 5 (New York: Marcel Derker, Inc., 1975), 454-
504, and Irving Reich and Forster Dee Snell, "Preferential
Wetting of Cotton Fabrics," _Industrial and Engineering_
Chemistry, 41 (December, 1949), 2797-2800.

[16]W. C. Powe and W. L. Maple, "Fatty Acid Composition
of Soil," _Journal of the American Oil Chemists' Society_, 37
(April, 1960), 136-137.

Once the fabric is wetted out, it becomes necessary
to break the bond between the soil and the fabric. This is
the function of the anions. The surfactant molecules which
are adsorbed on the fabric and the soil give both materials
negative charges. This causes them to repel each other.
The soil is thus gradually removed from the fabric. Enough
surfactant is left in the wash liquor to maintain the equi-
librium. During the rinse cycle, a new equilibrium is
established.[17] This implies that some surfactant is always
left on the fabric.

Nonionic surfactant molecules do not dissociate into
charged particles. They do, however, acquire the charge
necessary for soil removal by their ability to form micelles.
Such micelles possess a weak but effective negative charge.
No useful work is attained until this tendency to form
micelles is satisfied.[18] The concentration at which this
occurs (critical micelle concentration), is considerably
lower for nonionic than for anionic surfactants. A number

[17]R. C. Aiken, "The Adsorption of Sodium Alkyl
Sulphates by Wool and Other Fibres," Journal of the Society
of Dyers and Colourists, 60 (March, 1944), 60-64.

[18]Harry T. Zika, "Using Nonionic Surfactants,"
Textile Chemists and Colorists, 1 (July, 1969), 26-31.

of factors may result in a lowering of this concentration for this group of surfactants.[19]

ADSORPTION OF SURFACTANTS BY TEXTILE FIBERS

Effect of Substrate on Adsorption

It has been fairly well established that the adsorption of surfactants on fabrics occurs in two main forms. The first is the formation of a chemical bond. Such a reaction is irreversible. This occurs in wool and other amine-containing fibers. The second is of a physical nature. Such surfactant is removed more easily from the fabric. This characterizes the adsorption of surfactant on native cellulose.

Cellulose is a polymer containing anhydrous glucose molecules in a linear chain of high molecular weight. Unlike wool or nylon, it does not contain polar groups capable of forming ionic bonds. However, cellulose has an oriented structure in which the polymer molecules exert free energy forces from Van Der Waals forces and hydrogen bonding. These free energy forces are also available for holding other chemical compounds. The importance of these forces

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[19]Aiken, op. cit., p. 60.

is more readily seen in dyeing. Thus direct dyes are sub-
stantive to cotton. Their affinity and resistance to loss
in washing is due to the attractive forces of the cellulose
molecules for the free energy forces of the benzene rings
and the hydroxy and amino groups of the dye molecule. This
affinity is sufficient to cause exhaustion of the dye from
the dye bath. However, on subsequent washing, new equili-
brium is obtained so that the dye is lost to the wash
water.[20]

Surfactants contain benzene rings and, at least in
the case of the nonionics, the opportunity for hydrogen
bonding exists. The attractive forces may not be as strong
as that of dyes but could still be strong enough to account
for adsorption and some degree of build-up.

Aiken conducted a study on the adsorption of sodium
alkyl sulphate on wool and other fibers. Adsorption was
measured by determining the amount of surfactant in a 100
ml surfactant solution before 2 gms of fabric sample was
added and 24 hours after sample immersion. It was found
that wool adsorbed more surfactant than cotton or nylon.

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[20]Thomas Vickerstaff, The Physical Chemistry of
Dyeing, (London: Oliver and Boyd, 1950), p. 165.

To determine the mode of adsorption, another series of experiments using wool, silk, nylon and cotton was conducted. The first three fibers were polyamides. A decrease in adsorption with decreasing numbers of amino groups was reported. To verify the role of amino groups, the adsorption on wool in the presence of hydrochloric acid was measured. This broke up the salt linkages with the formation of carboxy groups and an ionized ammonium type radical associated with the chlorine ion. The ammonium ion can be readily displaced by the alkyl sulphate ion. Aiken reported an increase in adsorption.[21]

Aiken's study showed rather conclusively that adsorption on polyamides was of a chemical nature. It was, however, not so detailed on the mechanism of adsorption on cotton. It was merely pointed out that the adsorption mechanism was of a different nature. The weakness of this study was the number of samples used. One has the impression that the conclusions were reached on the basis of a single sample. Studies by other workers, however, seem to support his findings.

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[21]Aiken, loc. cit.

Lambert, using more sophisticated techniques, pro-
duced data which confirmed the idea that characteristics of
the substrate affect adsorption. Though the investigation
was primarily concerned with developing the radio tracer
technique as a means of studying detergency, the results
produced are of interest in the present study.

The study used radio-active calcium as an indirect
means of measuring surfactant adsorption by used and unused
cotton fabrics. It was found that used cotton adsorbed more
surfactant than new cotton. He attributed this to the
chemical changes in the fiber which resulted in an increase
in the number of the carboxyl groups as well as in the
amorphous areas of the fiber.[22] A lengthy discussion of
the results was not presented since this was not his con-
cern. This technique has since proved a useful means of
studying detergency.

Meader and Fries, using the radio tracer technique
conducted a comprehensive study of the adsorption of alkyl
benzene sulphonate by wool and cotton fabrics. The alkyl
benzene sulphonate was prepared with radioactive sulphur.

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[22]Joseph M. Lambert, "Cationic Adsorption and Exchange
as shown by Radiocalcium Tracer Studies," Industrial and
Engineering Chemistry, 42 (October, 1950), 1394-1398.

Fabric swatches were soaked in surfactant solutions of pre-
determined radioactivity, for 24 hours (the length of time
was greater for wool). The radioactivity of the blotted
samples was measured.

They observed, among other things, that the rate of
adsorption was greatest in the first ten minutes. The
adsorption isotherm for cotton showed an almost vertical
climb in the first ten minutes and then levelled off. The
isotherm for wool was different. It showed the initial
rapid climb as was obtained for cotton, then the curve
became more gradual, lasting over a much longer period. The
initial rapid rate represented the physical adsorption in
both fibers. The more gradual adsorption rate in wool repre-
sented a chemical reaction.[23] Their results confirmed
Aiken's findings.

The foregoing studies showed that the substrate was
an important consideration in adsorption and that adsorption
on cotton was of a physical nature. These authors did not
go into the details of the mechanism involved.

The nature of surfactant adsorption on cotton was
studied by Schwarz et al., using radio-active dodecyl

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[23]Meader and Fries, op. cit., p. 1648.

benzene sulphonate. A 0.5 percent surfactant solution was

heated to 51 C, and a count of the specific activity was

taken. Cotton swatches that had undergone the following

treatments were used:

1. commercially bleached and finished cotton,

2. commercially bleached and finished cotton,

treated to remove metallic ions,

3. commercially bleached and finished cotton,

treated to remove metallic ions and further treated with

sodium chloride.

The washing lasted for ten minutes in a terg-o-to-

meter. Rinsing, when it was employed, was carried out in

the same equipment for the same length of time. The samples

were wrung dry and a count of their specific activity was

taken.[24] From their observations, the authors postulated

that polyvalent cations were responsible for the adsorption

of anionic surfactants on cotton.

In a second article, the authors established the

role of calcium in adsorption on cotton. A 0.5 percent

surfactant solution was prepared from artificially hardened

[24]W. L. Schwarz, A. R. Martin, B. J. Ruthowski, and
R. C. Davis, "The Adsorption of Sodium Dodecylbenzene
Sulphonate on Cotton," Untergruppe, D/1 Nr4 (1960), 37-42.

water. The fabric swatches were washed in the solution and
wrung dry. Another set of swatches was washed in water
which had been hardened with radiocalcium. The surfactant
bound calcium was determined by subtracting the quantity
of calcium adsorbed in the absence of surfactant from that
adsorbed in the presence of surfactant. The study also
investigated the build-up of surfactant on cotton. It was
concluded that surfactant adsorption was in the form of
calcium dodecylbenzene suphonate salt.[25]

This study is of special merit because the washings
were carried out under conditions that were close to house-
hold laundering conditions. Secondly, the precision of the
radio tracer technique and the number of replications involved
leave no doubt as to the validity of conclusions.

Other studies have also shown that impurities in
cotton could affect the adsorption of surfactant. Ginn and
co-workers, using dewaxed and natural cotton showed that
surfactant was adsorbed on the wax. This study employed an
indirect method in determining the amount of surfactant

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[25]W. J. Schwarz, R. A. Martin and R. C. Davis,
"Influence of Calcium on the Adsorption of Sodium Dodecyl-
benzene Sulphonate on Cotton," Textile Research Journal, 32
(January, 1962), 1-8.

adsorbed. Conditioned samples were introduced into a sur-
factant solution and stirred for ten minutes. The liquid
was decanted and the quantity of surfactant left in the
solution was determined. The two-phase method was used for
the anionic surfactant and the methylene blue extraction
method was used for the cations. The adsorbed surfactant
was calculated using the formula:

mg sorbed/gm cotton = $\frac{\text{\% conc. x flask sol. vol x 1000}}{\text{gm cotton x cotton \% solids}}$ [26]

It was shown that wax-containing samples adsorbed
more surfactant than the dewaxed samples. Adsorption on
the latter was negligible. It was concluded that the hydro-
phobic surface of the wax was responsible for adsorption.
At critical micelle concentration the wax solubilized,
leaving a wax-free surface which resulted in a decline in
adsorption.[27]

This is a plausible explanation and still does not
dispute the fact that hardness minerals in water affect
adsorption. Instead, it supports the view that adsorption

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[26]M. E. Ginn, F. B. Kinney, and J. C. Harris, "Effect
of Cotton Substrate Characteristics Upon Surfactant Adsorp-
tion," Journal of the American Oil Chemists' Society, 39
(March, 1961), 138-142.

[27]Ibid.

of surfactant on fabrics is a complex process which is

affected by many things. Among these are soil, natural

impurities and polyvalent cations.

The absence of statistical analysis was clearly

evident in these studies. However, Ginn and others attempted

to correlate adsorption with fiber swelling. The data were

so variable that no conclusions could be reached.[28] This

raises the question of whether these kinds of data lend

themselves to statistical analysis. This shortcoming may

weaken individual cases, but there is such a consistency in

the reported findings that one may safely conclude that

characteristics of the substrate are an important factor in

adsorption.

These studies and others also pointed out other

factors that could affect adsorption. These include the

concentration of the surfactant, the laundering temperature,

the class of the surfactant, and the pH of the wash liquor.

Effect of Surfactant Concentration
on Adsorption

Researchers seem to agree that adsorption increases

with surfactant concentration to a point that corresponds

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[28]Ginn, Kinney, and Harris, op. cit., p. 138.

to critical micelle concentration. Beyond this point, there is no agreement on the effect of surfactant concentration.

Aiken, in the study discussed in the previous section, showed that adsorption increased with surfactant concentration up to a point that corresponds with critical micelle concentration, then declined. After a temporary minimum, another climb was started and maintained. The slope of the second increase was, however, more gradual than that of the initial increase. This pattern was attributed to a fluctuation of the single ions. Single ions were involved in adsorption. At critical micelle concentration their number was reduced. As more of these ions were removed from the solution after critical micelle concentration, the equilibrium between the micelles and the single ions was upset and more of these were released to restore the equilibrium. This increase in the number of the single ions led to another increase in adsorption.

Rose and others, using carbon black as a substrate, showed that adsorption increased with increasing surfactant concentration, up to critical micelle concentration. They, however, failed to observe the cubic trend reported by Aiken. They reported a levelling of adsorption at critical micelle

concentration.[29] These differences could probably be attributed to the differences in the substrates used. Carbon black, being chemically inert, would probably react differently from wool or cotton. The use of different substrates has been blamed for many of the inconsistencies found in detergency studies.[30]

Weatherburn and Bailey also reported studies on cotton in which the decline at critical micelle concentration was absent. They found that for the anionic and nonionic surfactants, adsorption increased up to critical micelle concentration and then levelled off. Adsorption of the cationic surfactants, however, continued to increase even after the other had levelled off. They attributed the levelling off of the anionic and nonionic surfactants to the formation of micelles. Micelles have no hydrophobic-hydrophilic properties so are not involved in adsorption.

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[29]G. R. R. Rose, A. S. Weatherburn, and C. H. Bailey, "The Sorption of Synthetic Surface Active Compounds by Carbon Black," Textile Research Journal, 21 (June, 1951), 427-432.

[30]J. C. Harris, "Adsorption of Surface Active Agents by Fibers," Textile Research Journal, 18 (November, 1948), 669-678.

Cationic micelles possess a positive charge and so have electrostatic attraction.[31]

The explanation of the behavior of cationic compounds is not entirely in agreement with the views of other researchers. Zika stated that nonionic micelles possess a weak but effective negative charge.[32] In such a case the nonionic surfactant would be expected to behave in a similar manner to the cationic surfactant used in the study.

Meader and Fries observed peaks in their adsorption isotherms. They, however, stated that the point at which the peaks occurred was greater than critical micelle concentration in all cases.[33]

Flett and Walter reported sharp increases in adsorption with small increases in concentration up to .2 percent. At this point, small increases in concentration caused a sharp drop in adsorption till a minimum was reached at a

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[31]A. S. Weatherburn and C. H. Bailey, "The Adsorption of Synthetic Surface Active Agents by Textile Fibers," Textile Research Journal, 22 (December, 1952), 797-804.

[32]Harry T. Zika, "Using Nonionic Surfactants," Textile Chemists and Colorists, 15 (July, 1969), 26-31.

[33]Meader and Fries, op. cit., p. 1368.

concentration of .4 percent. Another increase started after this and exceeded the first maximum.[34]

It was not possible to compare this study with the other studies reported since no indication was given of the critical micelle concentration of the surfactants used. No explanation for the observed maxima was provided and, on the whole, the details of the study were not clear.

Ginn et al. observed drops in adsorption at around critical micelle concentration. It was attributed to a decrease in the single ion concentration. The drops were evident in both the built and unbuilt surfactants. While the built surfactant showed a rise after a temporary minimum, as observed by other investigators, the unbuilt surfactant levelled off at the minimum.[35]

In summary, there is agreement on the fact that adsorption is affected by concentration. There is, however, no consensus on the details of this effect. The available evidence has established that initial increases in

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[34]L. H. Flett and J. Walter, "Quantitative Data on the Adsorption of Detergents by Cotton Sheeting Under Textile Processing Conditions," American Dyestuff Reporter, 41 (March, 1952), 139-143.

[35]Ginn, Kinney, and Harris, op. cit., p. 138.

concentration result in increased adsorption. At concentrations around critical micelle concentration, a change occurs in the adsorption isotherm. There is no agreement on the direction of this change. The studies suggesting a drop and then a rise after a temporary minimum seem to have employed more rigid controls and used more valid techniques.

Effect of Temperature on Adsorption

The temperature of the wash bath has been shown to be an important factor in adsorption. As with concentration, there is no agreement on the exact effect of this factor.

Aiken showed that increases in temperature resulted in slight increases in adsorption. It also resulted in a decrease in the concentration at which the change in the adsorption isotherm occurred.[36]

This information appears contradictory to his explanation of the break in the isotherm. If the break was a result of micelle formation and temperature lowered the concentration at which the break occurred, then, in essence, the critical micelle concentration was being lowered.

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[36]Aiken, op. cit., p. 64.

Rose and others reported findings which contradict Aiken's findings. They found that adsorption increased with temperature within the range of 30 C to 70 C. Above 70 C, adsorption decreased with increase in temperature. The concentration at which the break in the curve occurred increased slightly with increasing temperature, within the temperature range given above.[37]

Flett and others produced data in support of this. They showed increased adsorption between the temperature of 80 F and 180 F. Beyond this point, adsorption dropped substantially.[38]

Meader and others found that increases in temperature affected the adsorption of surfactant only when certain builders were present. Temperature had no effect on surfactant alone.[39]

There appears to be quite a bit of contradictory evidence regarding the effect of temperature. One can safely conclude that temperature affects adsorption. It is impossible to state the manner of this effect from the available literature.

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[37]Rose, Weatherburn, and Bailey, loc. cit.

[38]Flett and Walter, op. cit., pp. 139-143.

[39]Meader and Fries, op. cit., pp. 1636-1648.

Effect of Surfactant Class
    on Adsorption

Few studies were found which reported the adsorption
of different classes of surfactant on cotton. Those found
presented contradictory views.

Weatherburn and Bailey investigated the adsorption
of anionic, cationic and nonionic surfactants on a group of
fibers. It was found that nonionic surfactants were
absorbed the least while the cationic surfactants had the
highest adsorption. Cotton absorbed more nonionic surfactant
than it adsorbed the other categories.[40] This result is
contrary to what is known of the behavior of cationic sur-
factants on cotton. It cannot, however, be blamed on
experimental conditions since these were rigidly controlled.

Ginn et al. employed the same classes of surfactant
in their study. Their data showed that wax-containing
cotton adsorbed more anionic surfactant than the other two
classes of surfactant. The dewaxed cotton on the other
hand, absorbed more of the cationic surfactant.[41]

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[40]Weatherburn and Bailey, op. cit., p. 797.

[41]Ginn, Kinney, and Harris, op. cit., p. 138.

Summary

Though opinion is still divided on various aspects of adsorption of surfactant on textile fibers, there is agreement on at least four points:

1. Adsorption of surfactants on textile fibers is of both chemical and physical nature.

2. Adsorption of surfactants on native cotton is due in part to polyvalent cations which bind the surfactant molecule to the fiber.

3. The quantity of surfactant adsorbed by cotton increases with increases in concentration up to critical micelle concentration when a change occurs in the adsorption isotherm.

4. Temperature has a yet undetermined effect on adsorption.

The points on which more information is required can be summarized as:

1. the effect of temperature on the adsorption of surfactants by cotton,

2. the direction of change in the adsorption isotherms for the effect of concentration,

3. the class of surfactants most adsorbed by cotton.

These studies were not concerned with the desorption of the adsorbed surfactant from the fabric. A few studies have suggested that some relationship may exist between these two aspects of detergency.

BUILD-UP OF SURFACTANT ON COTTON FABRICS

Few studies have been concerned with the build-up of surfactant on cotton. Each of the few available studies was concerned with a different aspect of surfactant build-up so the conclusions reached by individual researchers have not been verified by the works of others.

Schwarz et al. investigated the build-up of surfactant on fabric as part of the study reviewed. The study was conducted using:

1. commercially bleached and finished cotton;

2. commercially bleached and finished cotton, treated to remove metallic ions;

3. commercially bleached and finished cotton, treated to remove metallic ions and further treated with sodium chloride.

A build-up of surfactant which reached a maximum on the third laundering for the commercially bleached and finished

cotton was reported.[42] After further investigations, it was noted that adsorption took place as a calcium dodecyl-benzene sulphonate salt.[43] It was also shown that at the same time as the anionic exchange, cation exchange was occurring between the bath and the cotton. Some of the calcium was being replaced by sodium. This sodium salt of cotton carboxylic acid, being monovalent, was incapable of binding the surfactant to cellulose. This accounted for the maximum.

Meader and Fries observed that all the surfactant adsorbed on the fabric was not washed off. After two hours of rinsing, cotton swatches that had been soaked in surfactant solution for twenty-four hours still retained ten percent of the adsorbed surfactant. After forty-eight hours of rinsing, two percent of the surfactant was still left on the fabric. It was also found that distilled water removed more surfactant than hard water.[44] This shows that equilibrium exists but that rinsing reduces the quantity of surfactant adsorbed. It also shows that the surfactant is not held very strongly.

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[42]Schwarz, Martin, Ruthowski, and Davis, op. cit., p. 37.

[43]Schwarz, Martin, and Davis, op. cit., p. 1.

[44]Meader and Fries, op. cit., p. 1636.

This result also lends strength to the argument that hardness minerals account for some of the bound surfactant. In addition, the authors reported that the initial concentration did not affect the rate of adsorption.

Maple investigated the build-up of surfactant on laundered cotton fabrics. He was primarily concerned with the effectiveness of the rinse cycle of the automatic household washer. In a preliminary experiment, cotton swatches were soaked in a one-percent solution of linear alkyl benzene sulfonate. It was found that twenty-five percent of the surfactant remained on the fabric after rinsing. In a follow-up experiment simulating household conditions, he found that after forty laundering cycles in a household washer, .05 mg of the surfactant was retained per gram of fabric. Maple also reported that less surfactant was retained as the temperature increased from 60 F to 100 F.[45]

In summary, the few available studies on the build-up of surfactant on cotton agree that:

1. The surfactant used in laundering is not completely rinsed off and a build-up occurs over several launderings.

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[45]Maple, op. cit., p. 505.

2. This build-up is caused by polyvalent cations which are chemisorbed on the cotton fabric. These cations bind the surfactant molecules to the fiber.

There are, however, areas where more information is required. The reported studies have not clearly specified the effect of temperature on the build-up of surfactant, and the effect of surfactant concentration still needs to be explored.

CHAPTER III

PROCEDURE

The purpose of this study was to investigate the
build-up of anionic and nonionic surfactants on untreated
and resin-treated cotton fabrics and to determine the
effects of such a build-up on the tensile strength, wrinkle
recovery and abrasion resistance of the fabrics. Analytical
methods were used to determine residual surfactant after
repeated launderings. The experiment was conducted in the
laboratory under conditions obtained in the regular cycle
of machine washing and surfactants were used in normal
concentrations.

Eighty yards of cotton twill with a thread count of
120 x 44 were obtained from the fabric manufacturer. Forty
yards of this fabric had been scoured, bleached and mer-
cerized and the remaining forty yards had been further
treated with glyoxal, a resin used for durable press per-
formance, and cured. Tests were conducted to confirm the
fiber content and to determine: (1) the extent of cross-
linkage and curing, (2) fabric weight and (3) percent resin

on the fabric. The fabric was cut into smaller widths and laundered in an automatic home washer and dryer using unbuilt anionic and nonionic surfactants. After three and eight laundering cycles the fabrics were analyzed for surfactant content by accepted chemical procedures. The tensile strength, wrinkle recovery and abrasion resistance of the fabrics were also tested using standard ASTM test methods. Multivariate analysis of variance was used to determine the significance of the observed changes.

PRELIMINARY TESTS

Tests were made to confirm the fiber content of the fabrics obtained from the manufacturer, to determine the extent of crosslinking and curing, the weight and resin content of the fabric.

Fiber Identification

The fiber content of the fabrics was determined using the AATCC test method 20-1973. Microscopical examinations and solubility tests were performed as stated in the test method.[46]

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[46] "Fibers in Textile Identification," Technical Manual of the American Association of Textile Chemists and Colorists, (Raleigh, N. C.: Research Triangle Park, 1975), p. 50.

Determination of the Extent of
  Crosslinkage and Curing

The extent of crosslinkage and curing was determined
using the Cone Microscopic method. In this procedure, the
yarn is untwisted and the fibers feathered out by using a
pick needle. The fibers are spread out on a dry slide and
covered with a cover glass. The microscope is focused on
the dry longitudinal mount at a 150 X magnification. A few
drops of cupriethylene diamine (cuen) are applied to the
edge of the cover glass and allowed to flow into the mount.
Observed changes are recorded immediately and after fifteen
minutes in cuen. The observations are interpreted as follows:

1. Immediate degradation indicates the absence of
a crosslinking resin.
2. A. Rapid initial swelling and slight degradation
after 15 minutes indicates a resin either with low
crosslinking properties or one that has been dried but
not cured.
    B. Cure a new sample and retest. If fibers
show no initial reaction to the solvent this confirms a
good finish capable of being post cured and crosslinked.
If results are the same as in A, the resin has little
crosslinking properties.
3. A. Slow initial swelling and fiber deconvula-
tions and no degradation after 15 minutes indicate a
resin with some crosslinking and part curing.
    B. Cure a new sample and retest. If fibers
show no initial reaction to the solvent it confirms
an incompletely cured fabric. If results are the same
as in A, the resin has only moderate crosslinking
properties.

4. No initial swelling and only moderate irregular swelling after 15 minutes indicate a well cured and good crosslinking finish.[47]

Percent Resin on the Fabric

The method recommended by Mitzner was used to determine the amount of resin on the fabric. A preweighed oven dry sample is heated for the specified time in .1N hydrochloric acid at a temperature of 65 C. This results in an acid hydrolysis of the resin. The resin-free sample is washed and reweighed. The resin content is calculated as a percent of the dry weight of the extracted sample using the formula:

% resin (material removed by hydrolysis) = $100 \frac{Wm}{Mw} - 1$

Where M = weight of the moisture sample

m = weight of moisture sample after oven drying

W = weight of original fabric before hydrolysis

w = weight of original fabric after hydrol-ysis[48]

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[47] "Qualitative Analysis for Crosslinkage and Curing of Resin Treated Cellulosic Fibers," Cone Mills R & D Laboratory Microscopic Methods, 1966.

[48] Stanley Mitzner, "Determination of Textile Finishes, Acid Extractable Resins," Analytical Methods for Textile Laboratory, (Raleigh, N. C.: American Association of Textile Chemists and Colorists, 1968), p. 119.

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Fabric Count

The ASTM test method D 1910-64, (reapproved 1970), was used to determine the fabric count. The test method involves the counting of the number of warp yarns (ends) and filling yarns (picks) per inch of fabric.[49] An Alfred Suter yarn counter was used. Since the fabric was a closely woven twill, the samples were ravelled down for one inch before the fabric count was made for greater accuracy.

Fabric Weight

The determination of the fabric weight was made as specified in the ASTM test method D 1910-64, (reapproved 1970). The sections applicable to narrow fabrics, sections 40 and 41 were used.[50] No allowance was made in the calculations for the selvedge. The results of these tests are shown in Table 1.

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[49]"Standard Method of Test for Construction Characteristics of Woven Fabrics," 1974 Annual Book of ASTM Standards (Philadelphia: American Association for Testing and Materials, 1974), p. 357.

[50]1974 Annual Book of ASTM Standards, op. cit. p. 357.

Table 1

Results of Preliminary Tests

Fabric Weight	7 oz/sq yd
Percent Resin	6%
Extent of Crosslinkage and Curing	Fully Crosslinked and Cured

LAUNDERING OF SAMPLES

Samples of unfinished and resin treated cotton fabrics were laundered at temperatures of 105 F and 130 F, using anionic and nonionic surfactants. Half of the samples within each temperature and surfactant groups were laundered three times while the other half were laundered eight times. Three unlaundered samples from each class of fabrics served as the control.

Preparation of Laundering Samples

The untreated and resin-treated fabrics were cut into 36 x 45 inch widths. A code was inserted in the selvedge of each sample with a laundry marker. The selvedge was not included in any of the chemical or physical tests. The samples from the resin-treated fabric were sorted into four different loads to be washed with different surfactants and

at different temperatures. Each load contained six samples,
three of which were laundered three times and the other
three laundered eight times. The loads were as follows:

1. anionic surfactant group washed at 105 F

2. anionic surfactant group washed at 135 F

3. nonionic surfactant group washed at 105 F

4. nonionic surfactant group washed at 135 F.

The untreated fabric samples were sorted into corresponding
loads. Each load weighed 4½ lbs. A table of random numbers
was used to assign the order of washing of the loads within
each laundering cycle.

Laundering Procedure

Since the experiment was designed to simulate
service conditions as closely as possible, the fabric was
not prewashed to remove excess finish. The fabric would
therefore contain, at the start, adsorbed surfactant residual
from the scouring process. The resin treated fabric will
contain some nonionic surfactant as a constituent of the
resin system, catalyst, and polyethylene softeners. Regular
tap water of medium hardness, 38 parts per million, was
used. The temperatures of 105 F and 135 F chosen for the
study represent temperatures used for hand wash and hot wash

in the home setting. Unbuilt anionic surfactants were used.

The anionic surfactant was a dodecylbenzene sulphonic acid

of the structure widely used in household detergents. It

contains small quantities of sodium sulphate but is close

to 100 percent active. It has the formula given in Figure

5.
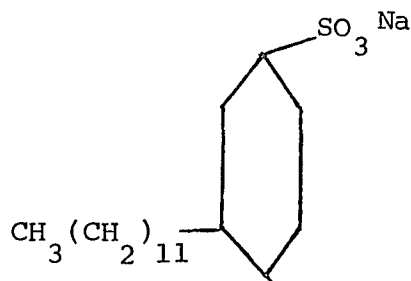
Figure 5

Sodium Dodecyl Benzene Sulphonate

The nonionic surfactant was Triton X 100 (Rohm and Haas).

This is an ethylene oxide condensation product with

t-octylphenol. It is essentially 100 percent active and

has the formula shown in Figure 6.

The household detergent formulation contains flores-

cent whiteners, sequestering agents, phosphates and anti-

redeposition compounds. Since the objective of this

research was to examine the behavior of the surfactants,

the presence of these additional materials would not

necessarily interfere with adsorption but could introduce

interferences in analytical procedures.

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \langle\ \rangle - (OCH_2\ CH_2)_9\ OH$$
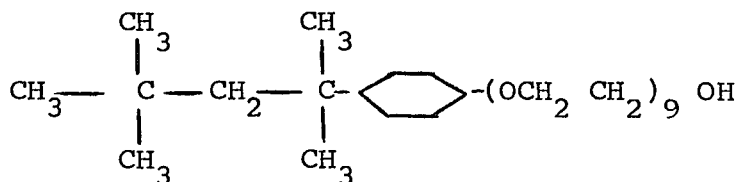
Figure 6

Alkyl Phenoxy Polyethoxy Ethanol[51]

The washing machine was set to deliver 13 gallons

of water. The water was adjusted to the desired temperature.

Fifty grams of surfactant were added to the wash water, to

give a surfactant concentration of 0.08%. The pH of the

wash bath as taken with a pH paper was 5. The washer was

set for a washing time of ten minutes and a rinsing time of

six minutes. The samples were added and the washer was

allowed to procede to the final spin. The fabrics were

removed immediately and tumble dried for 30 minutes at a

high temperature setting. After three laundering cycles half

of the total number of samples from each of the eight loads

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[51]"Triton X-100," Textile Chemical Technical Bulletin (Philadelphia: Textile and Paper Chemicals Department, Rohm and Haas Company), p. 2.

was withdrawn for testing. The other half was laundered

eight times before testing. Analytical methods for deter-

minations of surfactant was carried out on each of the

laundered sample as well as the unwashed samples which

served as the control. The samples were also subjected to

standard tests for abrasion resistance, wrinkle recovery

and tensile strength.

ANALYSIS OF SURFACTANT CONTENT

The laundered samples were extracted with distilled

water and analyzed for surfactant content. Each sample was

analyzed for the particular class of surfactant in which it

was laundered. The control samples were analyzed for both

the anionic and nonionic surfactants.

Extraction

Anionic surfactant. A nine-inch square sample of

approximately 11.12 gm was cut from each laundered sample

and dried to constant weight. The samples were allowed to

cool in a dessicator before being weighed on an analytical

balance. The samples were prepared and extracted in a

soxhlet extraction equipment as recommended by Maple, using

200 cc of distilled water. Each sample was extracted for

three hours.[52] A sintered glass crucible rather than the
Buchner funnel was used to filter the hot extract. The
methylene blue indicator method was used for quantitative
determinations.

Titration of Extract

Two solutions were prepared for the titration of the
extract and the known concentration of surfactant used as a
control.

1. Methylene Blue Indicator Solution. A one-tenth
gram methylene blue was dissolved in 100 ml of distilled
water. Thirty milliliters of this was transferred to a
1-liter volumetric flask. Five milliliters of distilled
water, 6.8 ml of concentrated sulphuric acid and 50 gms of
sodium biphosphate, were added. The solution was diluted to
one liter and mixed thoroughly.

2. CTAB Solution. Cetyltrimethylammonium bromide,
1.8 gms was transferred to a 1-liter volumetric flask and
made up to one liter with distilled water.

A 50 ml aliquot of the extract was pipetted into a
100 ml graduated cylinder. Twenty-five milliliters of

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[52]Maple, op. cit., p. 505.

methylene blue indicator solution and 15 ml of chloroform were added. The solution was titrated with CTAB solution to the correct end point. The correct end point was taken at the point where there was a change from a reddish-blue chloroform layer, greenish-blue water to a reddish-blue water, greenish-blue chloroform.

A solution containing a known amount of surfactant was titrated in the same manner as the extract. This established the ratio of CTAB solution to surfactant.[53]

The quantity of surfactant retained per gram of fabric was calculated using the formula:

mg surfactant/gm fabric = $\dfrac{\%\text{conc. x flask sol. vol. x 1000}}{\text{gm cotton x cotton \% solids}}$[54]

Determination of Nonionic Surfactant

The extraction of the samples was carried out as described for the anionic surfactant, using distilled water. The dissolved surfactant was precipitated by the phosphomolybdic acid method described by Oliver and Preston. Three solutions were prepared for the precipitation.

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[53] W. Garner, "Methylene Blue Method for Determining Anionic Surfactant," Textile Laboratory Manual (London: Heywood Books Publishing Co., Inc., 1960), pp. 52-53.

[54] Ginn, Kinney and Harris, op. cit., p. 139.

1. Hydrochloric Acid Solution. One volume of con-
centrated hydrochloric acid was diluted to four volumes with
distilled water.

2. Barium Chloride Solution. Ten grams of barium
chloride was dissolved in 100 ml of distilled water.

3. Physphomolybdic Acid Solution. Ten grams of
phosphomolybdic acid was dissolved in 100 ml of distilled
water.

One hundred milliliters of the extract were pipetted
into a 250 volumetric flask to which was added in the fol-
lowing order: 5 ml each of hydrochloric acid, barium
chloride, and phosphomolybdic acid solutions. The content
of the flask was made up to 150 ml with distilled water.
The yellowish-green precipitate was flocculated by raising
the mixture to the boil. The flask was covered and allowed
to stand for 18 hours. The precipitate was filtered through
a tarred no. 4 sintered glass crucible, previously heated
at 100 F for 15 minutes and cooled to room temperature in a
dessicator. The precipitate was washed in a minimum of
100 mls of distilled water and dried to a constant weight.

A solution containing a known amount of surfactant
was precipitated in the same manner as the extract. This

established the ratio of weight of complex to the weight of
detergent.[55]

The amount of surfactant retained per gram of fabric
was calculated as in the anionic surfactant.

PHYSICAL TESTS

Abrasion Resistance

The samples were tested for abrasion resistance
using the ASTM test method D 1175, Rotary Platform Double
Head method. The Taber Abraser was used along with car-
borundum wheels with a pressure of 500 gms.

This method measures the abrasion resistance of the
fabric by subjecting the fabric sample to a rotary rubbing
action under controlled conditions of pressure and abrasive
action.[56] The abraded portion was not large enough to
permit the measuring of the braking strength so the number
of cycles at the appearance of the first hole was reported.
Although the reporting of the number of cycles at the
appearance of the first hole is not a precise method, it is

[55]J. Oliver and C. Preston, "Estimation of Nonionic
Detergents," Nature, 164 (August 6, 1949), 241-242.

[56]1974 Book of ASTM Standards, op. cit., p. 136.

the most highly recommended of the four methods suggested

for research purposes.[57]

The wheels were resurfaced after every five samples

by abrading a carborundum-coated paper of medium coarseness

for ten cycles. The resurfacing disk was discarded after

every six resurfacings.

Tensile Properties

The tensile strength of the samples was tested as

specified in the ASTM test method D 1682, (reapproved 1970),

Ravel Strip method. The Scott Tester Model J was used.

This pendulum-type strength tester operates on the constant

rate of elongation (CRE).

The test method measures the breaking load and

elongation of textile fabrics by continually increasing the

load applied in the longitudinal direction until the sample

ruptures.[58] It is recommended that when possible, samples

that differ in only one respect should be used for comparison

since this method measures the minimum rather than the

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[57]John H. Skinkle, Textile Testing, 2nd ed. (New York: Chemical Publishing Co., Inc., 1949), p. 136.

[58]1974 Book of ASTM Standards, op. cit., p. 306.

average strength of the samples. Under these conditions the
test method gives precise results.[59]

Wrinkle Recovery

The wrinkle recovery of the samples was determined

as stated in the AATCC test method 66-1972. The test

involves the creasing of the fabric sample under controlled

conditions of time and load. The creased sample is suspended

from the instrument for a five-minute recovery period after

which the recovery angle is measured.[60]

The data obtained from the tests were subjected to

a multivariate analysis of covariance to determine the sig-

nificance of the changes in fabric properties. The sur-

factant content, warp and filling wrinkle recovery, and

abrasion resistance of the control samples were used as

covariates.

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[59]Skinkle, loc. cit.

[60]"Wrinkle Recovery of Fabrics, Recovery Angle
Method," Technical Manual of the American Association of
Textile Chemists and Colorists (Raleigh, N. C.: Research
Triangle Park, 1975), p. 249.

STATISTICAL PROCEDURE

A factorial experimental design was employed for

the analysis of the data. The levels of the four factors

involved were:

Surfactant – Anionic and Nonionic

Finish – Untreated and Resin Treated

Temperature – 105 F and 135 F

Laundering Cycle – 3 and 8 Cycles.

A sample size of three samples per cell was used. Unlaun-

dered untreated, and resin-treated fabrics were used as

control. The data thus collected was subjected to a multi-

variate analysis of covariance with surfactant content,

warp and filling tensile strength, warp and filling wrinkle

recovery, and abrasion resistance as the dependent variables.

The warp and filling wrinkle recovery, abrasion resistance

and surfactant content of the control samples served as the

covariates. The Roy's Maximum Root Criteria obtained were

tested for significance using the table of Greatest Charac-

teristic Root Distribution provided by Harris.[61] Where the

univariate analysis of covariance indicated a significant

---

[61] Richard J. Harris, _A Primer of Multivariate
Statistics_ (New York: Academic Press, Inc., 1975), p. 300.

effect, multiple comparisons were made to determine which

of the means differed using Newman Keul's method.

CHAPTER IV

PRESENTATION OF DATA

The objectives of the study were to determine the build-up of anionic and nonionic surfactants on untreated and resin-treated cotton fabrics and to ascertain the effects of this build-up on the tensile strength, wrinkle recovery, and abrasion resistance of the fabrics. To this end, data were collected in a laboratory experiment, using a factorial experimental design. The four factors and the levels involved were:

1. fabric finish - untreated and resin treated

2. temperature - 105 F and 135 F

3. surfactant - anionic and nonionic

4. laundering cycle - three and eight.

Unlaundered fabric samples served as the control. The dependent variables were surfactant content, warp and filling tensile strength, warp and filling wrinkle recovery, and abrasion resistance.

Multivariate analysis of covariance was used to determine the significance of the observed differences. A

5% level of significance was chosen for the test of hypotheses. Where the univariate analysis of covariance showed a significant effect a multiple comparison was made, using Newman Keul's method, to determine which of the means differed.

These data are presented in the following order:

1. multivariate analysis of covariance

2. univariate analysis of covariance

3. correlation between surfactant content and the other dependent variables.

MULTIVARIATE ANALYSIS OF COVARIANCE

Multivariate analysis of covariance was performed on the six dependent variables, surfactant content, warp and filling tensile strength, warp and filling wrinkle recovery, and abrasion resistance. The surfactant content, warp and filling wrinkle recovery, and abrasion resistance of the control samples were used as covariates. The result of the analysis are shown in Table 2.

All but two of the multivariate effects were significant at the .05 level. The canonical weights revealed that mainly surfactant content accounted for the significance of the analyses for surfactant and finish. Abrasion

Table 2

Multivariate Analysis of Covariance
Summary Table

Source	Roy's Max. Root Criterion	Deg. of Freedom Num.	Den.	F
Covariates				
Surfactant Content	0.26	1	28	1.0
Warp Wrinkle Recovery	.23	1	28	.9
Filling Wrinkle Recovery	.18	1	28	.8
Abrasion Resistance	.38	1	28	1.4
Surfactant	1.07	6	23	4.1*
Finish	.98	6	23	3.7*
Temperature	3.55	6	23	13.3**
Laundering Cycle	17.57	6	23	67.3*
Surfactant x Finish	.57	6	23	2.1
Surfactant x Temperature	1.14	6	23	4.4*
Surfactant x Laundering Cycle	6.82	6	23	26.1**
Finish x Temperature	.88	6	23	3.4*

Table 2 (continued)

Source	Roy's Max. Root Criterion	Deg. of Freedom Num.	Den.	F
Finish x Laundering Cycle	3.35	6	23	12.19**
Temperature x Laundering Cycle	3.20	6	23	12.3
Surfactant x Finish x Temperature	.94	6	23	3.6*
Surfactant x Finish x Laundering Cycle	1.4	6	23	5.6*
Surfactant x Temperature x Laundering Cycle	2.70	6	23	10.3**
Finish x Temperature x Laundering Cycle	.99	6	23	3.8*
Surfactant x Finish x Temperature x Laundering Cycle	.61	6	23	2.4

*p = .02

**p = .01

Num.= Numerator

Den.= Denominator

resistance also received average weights. Of the thirteen

significant multivariate effects, the dependent variables,

surfactant content and abrasion resistance accounted for

most of the significance, with surfactant content receiving

the heavier weight. The exception was the interaction

between finish and temperature where equal weights were

assigned to surfactant content, filling tensile strength,

and warp and filling wrinkle recovery. The canonical corre-

lations are shown in Appendix A.

The multivariate analyses were used to examine the

composite effects of the dependent variables. The results

of the univariate analyses will now be examined for the

interpretation of the individual dependent variables. Where

a univariate significance was obtained, the adjusted means

are given in the body of the text. Corresponding original

means can be found in Appendix B.

UNIVARIATE ANALYSIS OF COVARIANCE

Surfactant Content

The univariate analysis of covariance for the vari-

able surfactant content, yielded significant results for 13

of the 15 effects. Where more than two means were involved,

as in the case of the interactions, multiple comparisons

were made to determine which of the means differed. The
results of the analysis are shown in Table 3.

A significant surfactant effect was obtained. The
means are shown in Table 4. An examination of the means
revealed that the anionic surfactant had a greater affinity
for the fabrics than the nonionic surfactants.

The effect for finish was also significant at p=.02
level of significance. The means in Table 5 indicate that
the untreated fabric had a higher mean surfactant content
than the resin-treated cotton fabrics.

The laundering temperature was found to be an impor-
tant factor in the quantity of surfactant retained by the
fabric. The quantity of surfactant left on the fabric
increased as the temperature was raised from 105 F to 135 F.
The means are given in Table 6. More surfactant was also
deposited on the fabric as the number of times the fabric
was laundered increased from three to eight times. Table 7
shows these means.

The interaction between surfactant and finish was
significant and a multiple comparison was made to determine
which of the means differed. It was found that the untreated
and resin-treated fabric differed appreciably in the amount
of anionic and nonionic surfactant they contained. The

Table 3

Analysis of Covariance Summary Table
For Surfactant Content

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Covariates				
Surfactant Content	36.59	1	36.59	666.4
Warp Wrinkle Recovery	9.11	1	9.11	160.9
Filling Wrinkle Recovery	1.45	1	1.45	25.6
Abrasion Resistance	.15	1	.15	2.7
Surfactant	.98	1	.98	17.5**
Finish	.31	1	.31	5.5*
Temperature	4.74	1	4.74	83.8**
Laundering Cycle	17.14	1	17.14	302.8**
Surfactant x Finish	.78	1	.78	13.8**
Surfactant x Temperature	.59	1	.59	10.4*
Surfactant x Laundering Cycle	9.59	1	9.59	169.4**
Finish x Temperature	.15	1	.15	2.6

Table 3 (continued)

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Finish x Laundering Cycle	.13	1	.13	.3
Temperature x Laundering Cycle	0.02	1	0.02	.3
Surfactant x Finish x Temperature	.33	1	.33	5.8*
Surfactant x Finish x Laundering Cycle	2.35	1	2.35	41.5**
Finish x Temperature x Laundering Cycle	.74	1	.74	13.0**
Surfactant x Finish x Temperature x Laundering Cycle	.36	1	.36	6.4*
Error	1.58	28	.08	
Total	88.18	47		

*p = .02

**p = .001

Table 4

Adjusted Mean Surfactant Content
For Surfactant Type
(mg/gm fabric)

Surfactant	No. of Samples	Mean Surfactant Content
Anionic	24	3.28
Nonionic	24	.87

Table 5

Adjusted Mean Surfactant
Content for Finish
(mg/gm fabric)

Finish	No. of Samples	Mean Surfactant Content
Untreated Cotton	24	2.28
Resin Treated Cotton	24	1.87

Table 6

Adjusted Mean Surfactant Content
For Temperature
(mg/gm fabric)

Temperature	No. of Samples	Mean Surfactant Content
105 F	24	1.76
135 F	24	2.39

Table 7

Adjusted Mean Surfactant Content
For Laundering Cycle
(mg/gm fabric)

Laundering Cycle	No. of Samples	Mean Surfactant Content
3	24	1.48
8	24	2.67

resin-treated fabric retained more anionic surfactant than

the untreated fabric while the latter retained more nonionic

surfactant than the resin-treated fabric. The means are

shown in Figure 7.
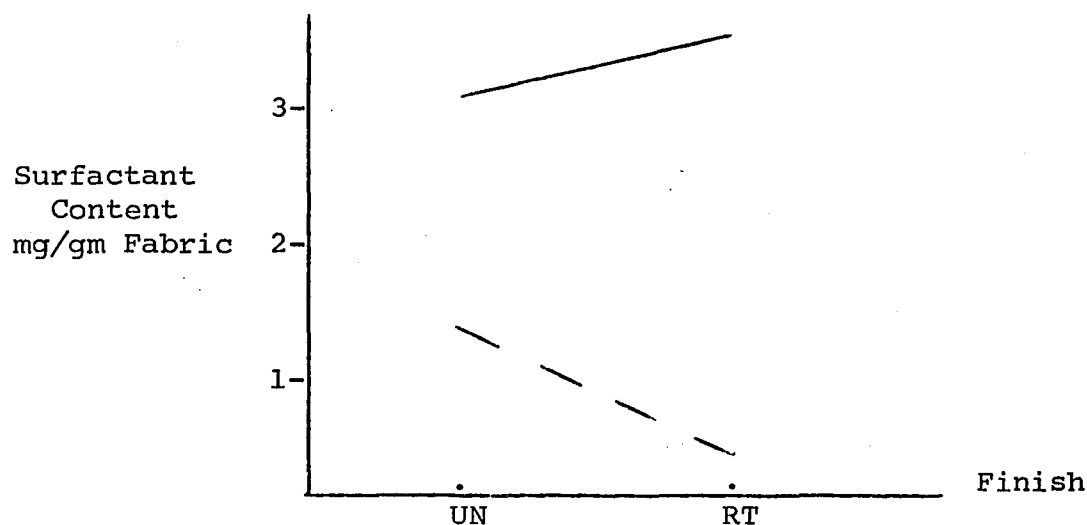
Figure 7

Adjusted Mean Surfactant Content for
Surfactant by Finish Interaction
(N=12)

Key:

UN = Untreated   ———————— Untreated

RT = Resin-Treated   — — — — Resin Treated

A highly significant interaction between surfactant

and laundering temperature was obtained. The slope of the

lines in Figure 8 shows that an increase in temperature

seemed to cause a greater increase in the retention of the

anionic surfactant than in the retention of the nonionic
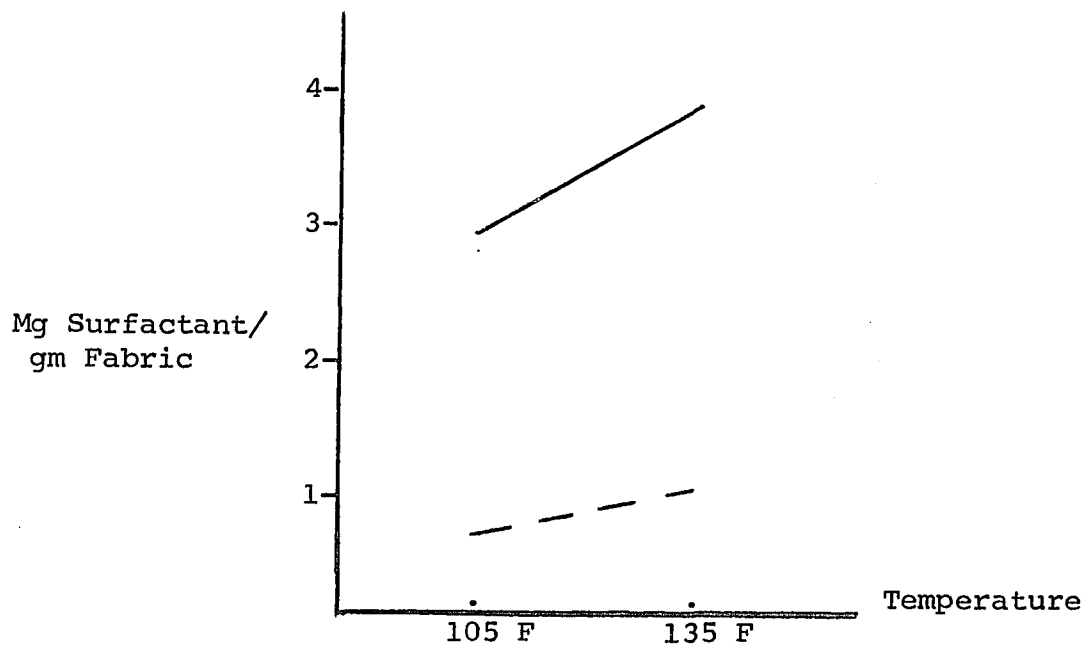
surfactant.

Figure 8

Adjusted Mean Surfactant Content for Surfactant
by Temperature Interaction
(N=12)

Key:

_____ Anionic Surfactant

___ ___ ___ Nonionic Surfactant

anionic surfactant than in the retention of the nonionic surfactant.

The surfactant content of the fabrics also varied with the different levels of surfactant and laundering cycle, as indicated by the significant interaction. The multiple comparisons were significant for all of the means. As in the case of the preceding interaction, the anionic surfactant increased at a faster rate than the nonionic surfactant as the number of times the fabric was laundered increased from 3 to 8. Figure 9 illustrates the nature of this interaction.
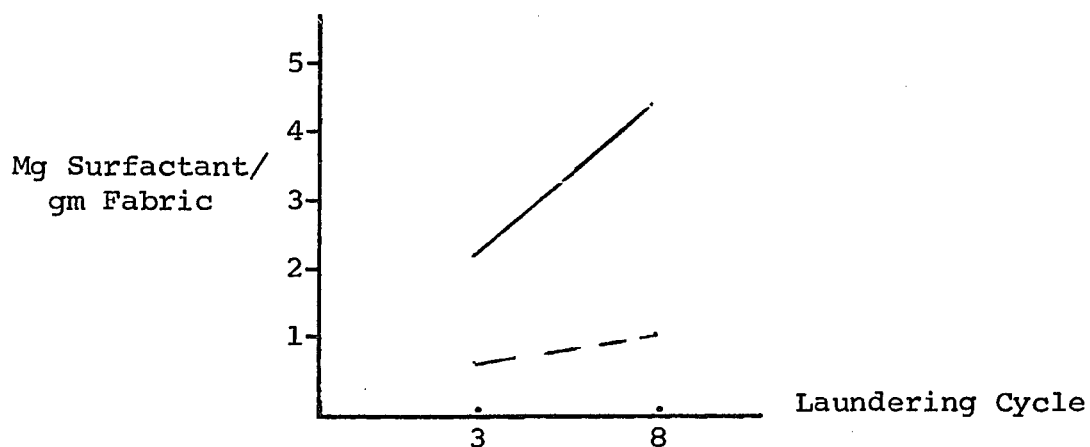
Figure 9

Adjusted Mean Surfactant Content for Surfactant
by Laundering Cycle Interaction
(N=12)

Key:

_____ Anionic Surfactant
___ ___ ___ Nonionic Surfactant

No significant effect on surfactant content was found for the interactions of finish with temperature, finish with laundering cycle, and temperature with laundering cycle.

A significant interaction was obtained between surfactant, finish, and temperature. A multiple comparison of the means showed that the two groups of fabric did not differ significantly in their anionic surfactant content, when laundered at 105 F. At 135 F however, the resin-treated fabric accumulated more anionic surfactant than the untreated fabric. The position was reversed for the nonionic surfactant. The untreated fabric retained more nonionic surfactant than the resin-treated fabric at both temperatures. Furthermore, while the amount of surfactant on the untreated fabric increased with temperature, the quantity left on the finished fabric remained stable. The means are shown in Figure 10.

The interaction between surfactant, finish, and laundering cycle was significant. The means, shown in Figure 11, revealed that both fabrics contained about the same amount of anionic surfactant at the third laundering cycle. At the eighth cycle, however, the resin-treated fabric had accumulated more of this class of surfactant. The reverse seemed to be the case for the nonionic surfactant. The
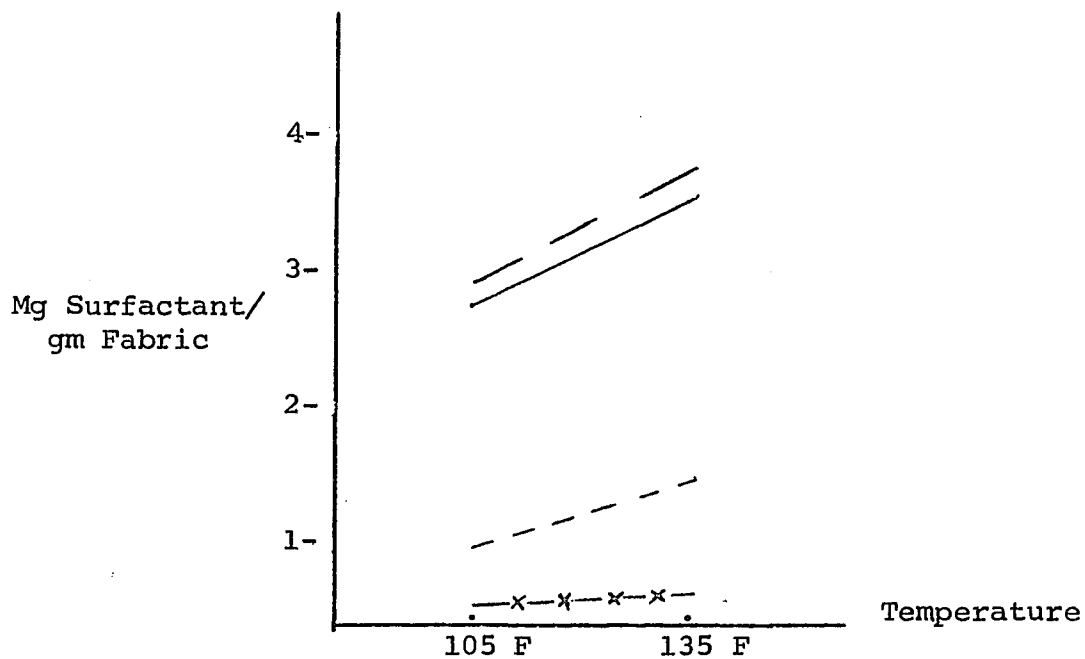
Figure 10

Adjusted Mean Surfactant Content for Surfactant
by Finish by Temperature Interaction
(N=6)

Key:

_____ Anionic Surfactant, Resin-Treated

__ __ __ Anionic Surfactant, Untreated

-------------- Nonionic Surfactant, Resin-Treated

-x-x-x-x-x-x Nonionic Surfactant, Untreated
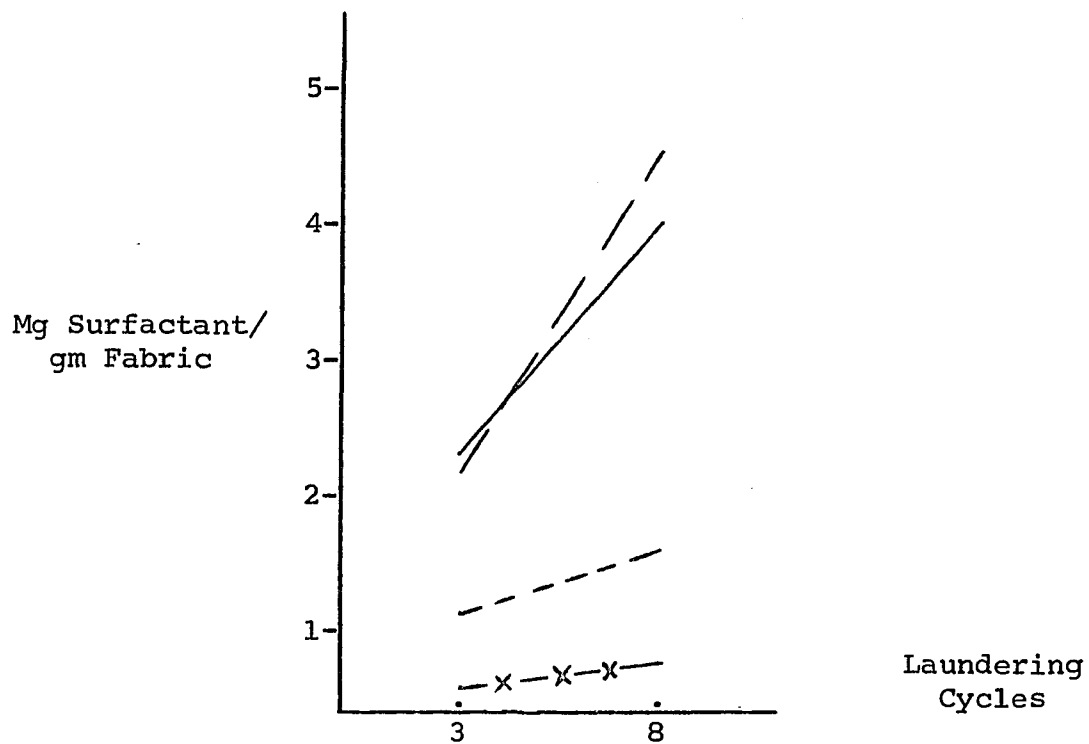
Figure 11

Adjusted Mean Surfactant Content for Surfactant
by Finish by Laundering Cycle Interaction
(N=6)

Key:

_____ Anionic Surfactant, Resin-Treated

___ ___ _____ Anionic Surfactant, Untreated

_____ Nonionic Surfactant, Resin-Treated

-x-x-x-x-x-x-x- Nonionic Surfactant, Untreated

untreated fabric contained more nonionic surfactant at the third laundering cycle than the resin-treated fabric and this quantity increased appreciably at the eighth cycle while the amount on the resin-treated fabric remained fairly stable.

A multiple comparison between the means for the surfactant by temperature by laundering cycle interaction showed that increases in temperature resulted in an increase in the quantity of anionic surfactant on the fabric. This held true for both laundering cycles. The fabric samples laundered in the nonionic surfactant behaved differently. Increasing the temperature resulted in an increase in the surfactant content of the fabrics only at the third laundering cycle. At the eighth laundering cycle, while the surfactant content of the samples laundered at 105 F had increased, that of the fabrics laundered at 135 F remained essentially unchanged, and approximately the same value as that of the fabrics laundered at 105 F. An illustration of this interaction is given in Figure 12.

The interaction between temperature, finish, and laundering cycle was not significant nor was the four-way interaction between the four independent variables.
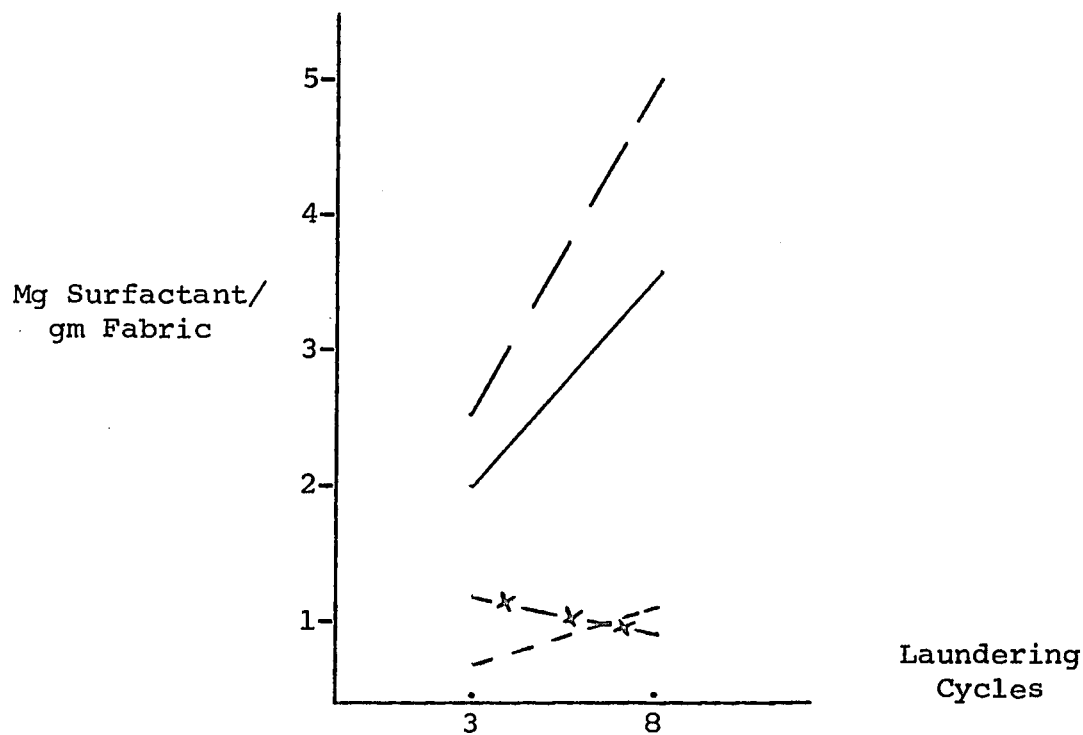
Figure 12

Adjusted Mean Surfactant Content for Surfactant
by Temperature by Laundering Cycle Interaction
(N=6)

Key:

_____ Anionic Surfactant, 105 F

___ ___ ___ Anionic Surfactant, 135 F

_____ Nonionic Surfactant, 105 F

-x-x-x-x-x-x- Nonionic Surfactant, 135 F

Warp Tensile Strength

A univariate analysis of covariance for the variable warp tensile strength yielded a significant F ratio for the main effect of surfactant and for the interactions between surfactant and laundering cycle, and surfactant, finish, and laundering cycle. The results are summarized in Table 9. Multiple comparisons were made to determine which of the means differed in cases where more than two means were involved.

On examination of the mean tensile strength for the variable surfactant, it was found that the fabrics laundered in anionic surfactant had a higher warp tensile strength than the fabrics laundered in nonionic surfactant. Table 8 shows the means.

Table 8

Adjusted Mean Warp Tensile
Strength for Surfactant

Surfactant	No. of Samples	Warp Tensile Strength
Anionic	24	1.51
Nonionic	24	1.39

Table 9

Analysis of Covariance Summary Table
for Warp Tensile Strength

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Covariates				
Surfactant Content	0.06	1	0.06	18.1
Warp Wrinkle Recovery	1.34	1	1.34	408.5
Filling Wrinkle Recovery	.06	1	.06	21.3
Abrasion Resistance	.01	1	.01	.62
Surfactant	.03	1	.03	8.5*
Finish	.01	1	.01	3.4
Temperature	.001	1	.001	.2
Laundering Cycle	.00	1	.00	.0
Surfactant x Finish	.00	1	.00	.0
Surfactant x Temperature	.04	1	.04	12.9*
Surfactant x Laundering Cycle	.001	1	.001	.4
Finish x Temperature	.00	1	.00	.0

Table 9 (continued)

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Finish x Laundering Cycle	.00	1	.00	.0
Temperature x Laundering Cycle	.001	1	.001	.1
Surfactant x Finish x Temperature	.001	1	.001	.2
Surfactant x Finish x Laundering Cycle	.02	1	.02	7.5*
Surfactant x Temperature x Laundering Cycle	.01	1	.01	1.6
Finish x Temperature x Laundering Cycle	.00	1	.00	.0
Surfactant x Finish x Temperature x Laundering Cycle	.00	1	.00	.0
Error	.09	28	.003	
Total	1.68	47		

*$p = .05$

A comparison of the means was made for the inter-
action between surfactant and finish. It was found that
the difference in the warp tensile strength of the two
fabrics was more pronounced in the fabrics laundered with
anionic surfactant.

The interaction between surfactant, finish, and
laundering cycle was significant. The mean warp tensile
strength of the fabrics did not change appreciably with
changes in laundering cycle. However, the difference in
the strength of the samples washed with the two surfactants
was more noticeable in the resin-treated fabric than in the
untreated fabric.

Filling Tensile Strength

The result of the univariate analysis for the filling
tensile strength, given in Table 10, showed that only the
interaction between finish and laundering temperature was
significant. Increasing the temperature caused an increase
in the tensile strength of the untreated fabric while the
resin-treated fabric remained essentially unchanged.

Warp Wrinkle Recovery

Only one of the fifteen effects was significant
for the variable warp wrinkle recovery. The resin-treated

Table 10

Analysis of Covariance Summary Table
for Filling Tensile Strength

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Covariates				
Surfactant Content	0.20	1	0.20	3.1
Warp Wrinkle Recovery	10.4	1	10.4	156.9
Filling Wrinkle Recovery	1.3	1	1.3	18.9
Abrasion Resistance	.17	1	.17	2.7
Surfactant	.01	1	.01	.2
Finish	.04	1	.04	.6
Temperature	.09	1	.09	1.4
Laundering Cycle	.01	1	.01	.1
Surfactant x Finish	.01	1	.01	.2
Surfactant x Temperature	.00	1	.00	.0
Surfactant x Laundering Cycle	.23	1	.23	3.5
Finish x Temperature	.36	1	.36	5.4*
Finish x Laundering Cycle	.01	1	.01	.1

Table 10 (continued)

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Surfactant x Finish x Temperature	.02	1	.02	.4
Surfactant x Finish x Laundering Cycle	0.01	1	0.01	0.7
Surfactant x Temperature x Laundering Cycle	.03	1	.03	.5
Finish x Temperature x Laundering Cycle	.00	1	.00	.0
Surfactant x Finish x Temperature x Laundering Cycle	.04	1	.04	.6
Error	1.86	28	.07	
Total	14.97	47		

$*p = .05$

fabric had a greater mean recovery angle than the untreated fabric. The results of the analysis are summarized in Table 11.

Filling Wrinkle Recovery

No significant main effect was obtained for the filling wrinkle recovery. It was however, found that the interactions of finish and laundering cycle; surfactant, temperature and laundering cycle; and finish, temperature, and laundering cycle produced significant changes in filling wrinkle recovery. The univariate results are shown in Table 12. Multiple comparisons were made in cases where more than two means were involved.

A comparison of the means for laundering cycle by finish interaction revealed that while the untreated fabric lost its wrinkle recovery as the laundering cycle increased, the resin-treated fabric did not change significantly. The significant interaction of surfactant with temperature and laundering cycle showed, on examination of the means, that the recovery angle of the fabrics laundered in nonionic surfactant was stable to changes in temperature and laundering cycle. For the anionic surfactant however, a significant increase in recovery angle was observed at the third

Table 11

Analysis of Covariance Summary Table
for Warp Wrinkle Recovery

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Covariates				
Surfactant Content	4.58	1	4.58	0.2
Warp Wrinkle Recovery	2299.90	1	2299.90	118.8
Filling Wrinkle Recovery	315.05	1	315.05	16.3
Abrasion Resistance	.52	1	.52	.0
Surfactant	44.92	1	44.92	2.3
Finish	258.51	1	258.51	13.4*
Temperature	7.48	1	7.48	.4
Laundering Cycle	20.47	1	20.47	1.1
Surfactant x Finish	4.72	1	4.72	.2
Surfactant x Temperature	.34	1	.34	.0
Surfactant x Laundering Cycle	10.50	1	10.50	.5
Finish x Temperature	61.77	1	61.77	3.2

Table 11 (continued)

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Finish x Laundering Cycle	2.97	1	2.97	.2
Temperature x Laundering Cycle	4.05	1	4.05	.2
Surfactant x Finish x Temperature	41.35	1	41.35	2.1
Surfactant x Finish x Laundering Cycle	27.23	1	27.23	1.4
Surfactant x Temperature x Laundering Cycle	.31	1	.31	.0
Finish x Temperature x Laundering Cycle	6.34	1	6.34	.3
Surfactant x Finish x Temperature x Laundering Cycle	57.09	1	57.09	3.0
Error	541.79	28	19.36	
Total	3709.91	47		

*p = .05

Table 12

Analysis of Covariance Summary Table
for Filling Wrinkle Recovery

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Covariates				
Surfactant Content	150.35	1	150.35	4.0
Warp Wrinkle Recovery	7205.99	1	7205.99	189.9
Filling Wrinkle Recovery	371.52	1	371.52	9.8
Abrasion Resistance	71.00	1	71.00	1.9
Surfactant	137.83	1	137.83	3.6
Finish	80.46	1	80.46	2.1
Temperature	19.76	1	19.76	.5
Laundering Cycle	17.52	1	17.52	.5
Surfactant x Finish	23.48	1	23.48	.6
Surfactant x Temperature	25.23	1	25.23	.7
Surfactant x Laundering Cycle	38.52	1	38.52	1.0
Finish x Temperature	100.34	1	100.34	2.6

Table 12 (continued)

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Finish x Laundering Cycle	187.23	1	187.23	4.9*
Temperature x Laundering Cycle	51.67	1	51.67	1.4
Surfactant x Finish x Temperature	62.11	1	62.11	1.6
Surfactant x Finish x Laundering Cycle	10.83	1	10.83	.3
Surfactant x Temperature x Laundering Cycle	231.44	1	231.44	6.9*
Finish x Temperature x Laundering Cycle	184.08	1	184.08	4.8*
Surfactant x Finish x Temperature x Laundering Cycle	14.96	1	14.96	.0
Error	1062.46	28	37.94	
Total	10046.80	47		

*p = .05

laundering for the temperature of 135 F. This increase was not observed at the eighth laundering.

Although a significant F ratio was obtained for the finish by temperature by laundering cycle interaction, no significantly different means were found using Newman Keul's method, beyond the fact that the difference in the wrinkle recovery of the untreated samples laundered at 105 F was more pronounced at the eighth laundering than the third.

Abrasion Resistance

Twelve of the fifteen effects for the univariate analysis of abrasion resistance were significant at the 5% level of significance. The results are summarized in Table 13. Multiple comparisons were made to determine the significance of the differences among the means in cases where more than two means were involved.

The fabric samples laundered in nonionic surfactant had a higher abrasion resistance than those laundered in anionic surfactant. The means are shown in Table 14. The untreated fabric exhibited a higher resistance to abrasion than the resin treated fabric. The samples that were laundered eight times also had a higher mean abrasion resistance than those laundered three times. The means are given in Table 15.

Table 13 (continued)

Source	Sum of Squares	Deg. of Freedom	Mean Square	F
Finish x Laundering Cycle	6211.21	1	6211.21	72.2**
Temperature x Laundering Cycle	3936.39	1	3936.39	45.7**
Surfactant x Finish x Temperature	752.08	1	752.08	8.7*
Surfactant x Finish x Laundering Cycle	370.30	1	370.30	4.3
Surfactant x Temperature x Laundering Cycle	1.81	1	1.81	.0
Surfactant x Finish x Temperature x Laundering Cycle	794.79	1	794.79	9.2*
Error	2409.59	28	86.05	
Total	83360.53	47		

*p = .05

**p = .001

Table 14

Adjusted Mean Abrasion Resistance
for Surfactant

Surfactant	No. of Samples	Mean Abrasion Resistance
Anionic	24	114.9
Nonionic	24	140.8

Table 15

Adjusted Mean Abrasion Resistance
for Laundering Cycle

Laundering Cycle	No. of Samples	Mean Abrasion Resistance
3	24	117.83
8	24	137.91

A multiple comparison for the significant surfactant by temperature interaction showed that an increase in the laundering temperature caused the abrasion resistance of the samples laundered in anionic surfactant to increase. The reverse situation was obtained for the nonionic surfactant where the resistance to abrasion decreased as the temperature was raised from 105 F to 135 F.

The significant interaction between surfactant and laundering cycle showed, after comparisons were made, that the fabrics laundered in the nonionic surfactant showed an increase in abrasion resistance from three to eight laundering cycles. The increase for the samples laundered in the anionic surfactant was not as pronounced. The means are given in Figure 13.

The interaction between finish and temperature was significant. When the means were compared, it was found that the increase in temperature caused an increase in the abrasion resistance of the untreated fabric while the abrasion resistance of the resin-treated fabric was relatively unaffected by changes in temperature. A similar result was obtained for the interaction between finish and laundering cycle. The resistance of the untreated fabrics to abrasion increased with laundering cycle while that of the resin-treated fabric did not change significantly.
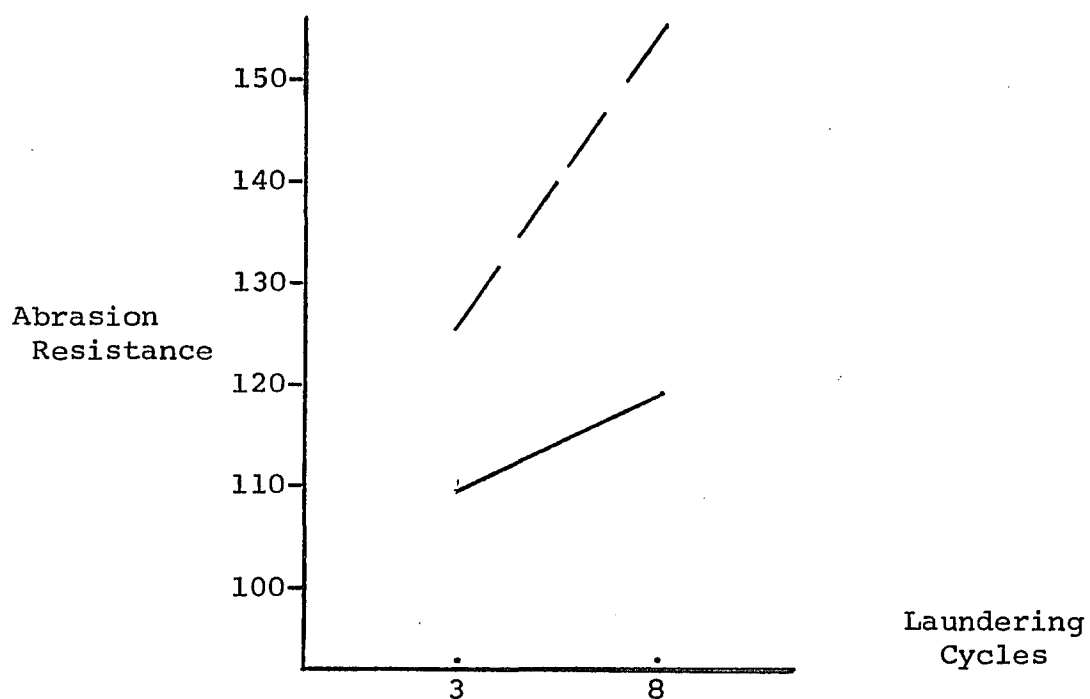
Figure 13

Adjusted Mean Abrasion Resistance for Surfactant
by Laundering Cycle Interaction
(N=12)

Key:

_____ Anionic Surfactant

___ ___ __ Nonionic surfactant

Resistance to abrasion also yielded different values
for the different levels of temperature and laundering
cycle. At the lower temperature, there was no significant
increase from three to eight launderings. At 135 F however,
abrasion resistance increased with the laundering cycles.

The same pattern was repeated in the interaction between

finish, temperature and surfactant. The untreated samples

laundered in anionic surfactant increased in abrasion

resistance as temperature increased. No significant changes

were observed for the resin-treated samples. No significant

changes were observed in the fabrics laundered in the non-

ionic surfactant. The means are shown in Figure 14.
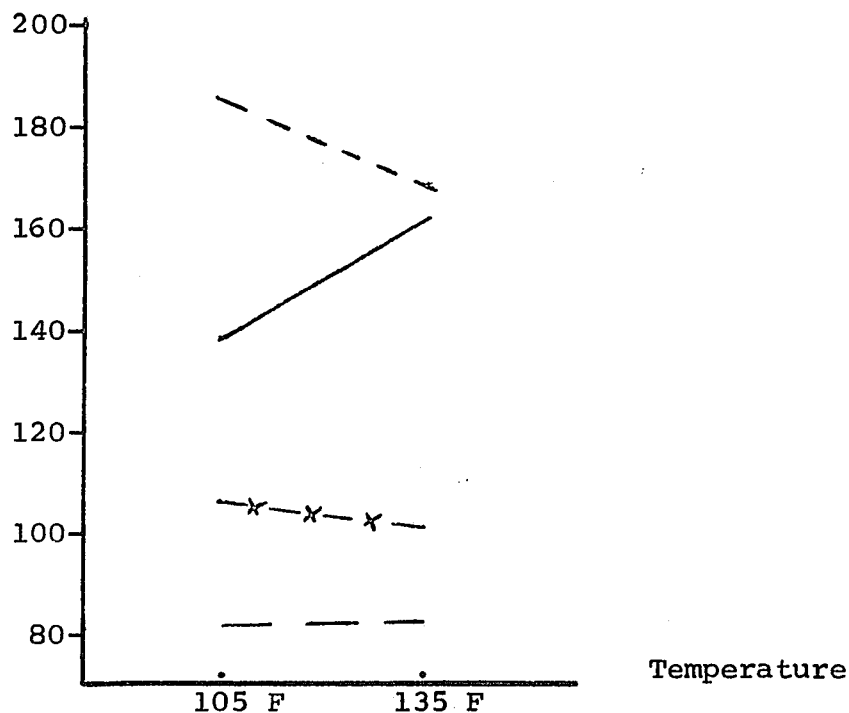
Figure 14

Adjusted Mean Abrasion Resistance for Surfactant
by Finish be Temperature Interaction
(N=6)

Key:

_____ Anionic Surfactant, Unfinished

___ ___ __ Anionic Surfactant, Resin-Treated

------------ Nonionic Surfactant, Resin-Treated

-x-x-x-x-x-x Nonionic Surfactant, Untreated

Comparisons were made to determine which of the means for the significant surfactant by laundering cycle by finish interaction differed. These means are shown in Figure 15. It was found that the abrasion resistance of the untreated fabric increased with laundering cycle, irrespective of the surfactant used, with the nonionic surfactant maintaining its superiority. With the resin-treated fabric, however, the fabrics laundered in both surfactants had comparable abrasion resistance at the third laundering cycle. At the eighth cycle, the abrasion resistance of the fabrics laundered in nonionic surfactant exceeded that of the fabrics laundered in anionic surfactant.

Summary

The multivariate analysis of covariance yielded significant results for 12 of the 15 effects at the .05 level of significance. The canonical correlations showed that surfactant content and abrasion resistance were responsible for most of the significance. However, surfactant content received the heavier weight of the two in most of the instances. The results of the univariate analysis of covariance were in agreement with the multivariate results.
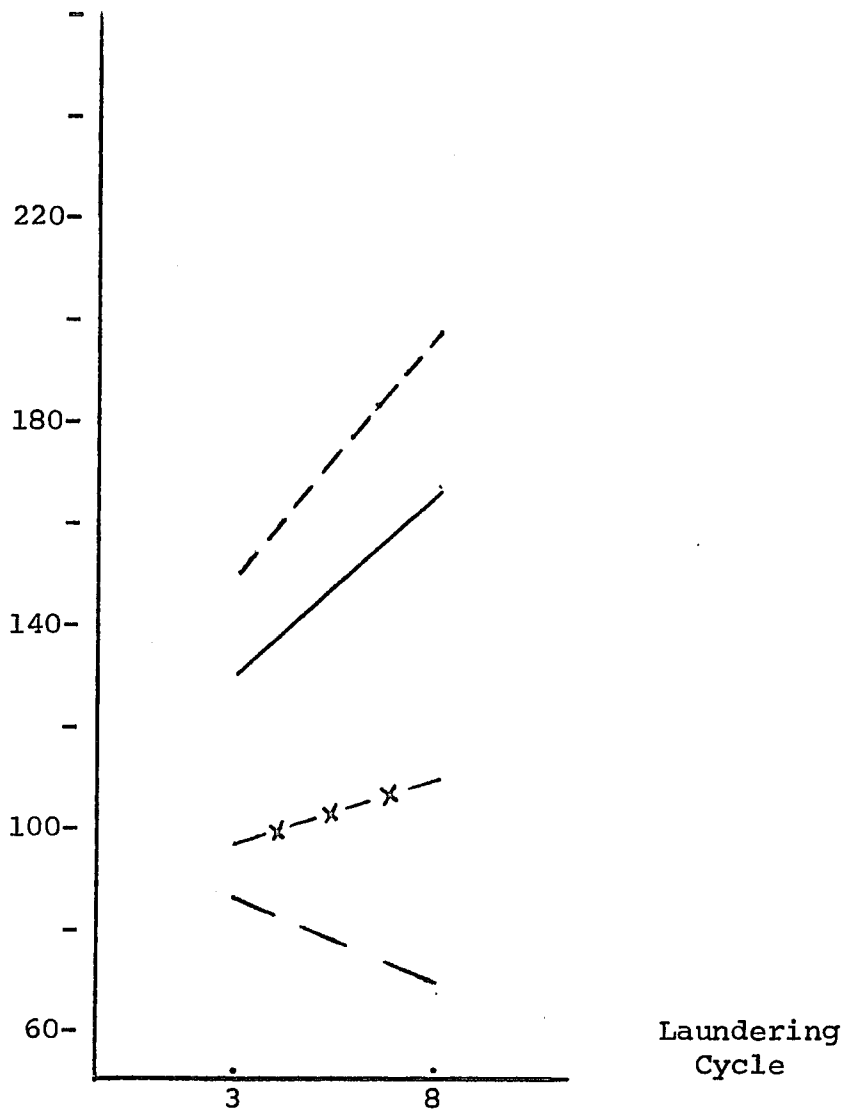
Figure 15

Adjusted Mean Abrasion Resistance for Surfactant
by Laundering Cycle by Finish Interaction
(N=6)

Key: _____ Anionic Surfactant, Untreated

___ _____ ___ Anionic Surfactant, Resin-Treated

_____ Nonionic Surfactant, Untreated

-x-x-x-x-x- Nonionic Surfactant, Resin-Treated

The univariate analysis for surfactant content indicated the significance of 12 of the 15 effects at the .02 and .01 levels of significance. Multiple comparisons of means showed that the fabrics retained more anionic than nonionic surfactant. The quantity of surfactant retained increased significantly with temperature and laundering cycle. On the whole, the untreated fabric retained more surfactant than the finished fabric but while the untreated fabric had a greater affinity for the nonionic surfactant than the resin-treated fabric, the position was reversed for the anionic surfactant. It was found that the anionic surfactant content of the fabrics was greate at 135 F than at 105 F. The rate of increase of the anionic surfactant as temperature and laundering cycle increased was greater than that of the nonionic surfactant. The rate of increase of the anionic surfactant content was also significantly higher for the resin-treated fabric than for the untreated fabric. The rate of increase of the nonionic surfactant was, however, higher for the untreated fabric than for the resin-treated fabric.

The univariate analysis for warp tensile strength gave three significant effects while that for the filling tensile strength showed only one significant effect at the

.05 level of confidence. The fabrics laundered in the anionic surfactant had a higher warp tensile strength than the fabrics laundered in the nonionic surfactant. The effect of surfactant was also more obvious for the untreated fabric than for the resin-treated fabric. The anionic surfactant gave a significantly higher warp wrinkle recovery than the nonionic surfactant. Three interaction effects were significant for the filling wrinkle recovery. The untreated fabric lost wrinkle recovery as the laundering cycle increased, and the temperature of 105 F contributed more to this decrease than the temperature of 135 F, especially for the fabrics laundered in the anionic surfactant. The filling wrinkle recovery of the fabrics laundered in the nonionic surfactant was stable to temperature and laundering cycle.

Twelve highly significant effects were obtained for the abrasion resistance. Multiple comparisons showed that the fabrics laundered in nonionic surfactant had a higher mean abrasion resistance than those laundered in anionic surfactant. The untreated fabric had the higher abrasion resistance of the two fabrics and abrasion resistance increased with laundering cycle. A highly significant interaction was obtained for surfactant and temperature.

Multiple comparisons showed that increases in temperature increased the abrasion resistance of the fabrics laundered in anionic surfactant. For the nonionic surfactant, the crucial factor was the laundering cycle, not temperature. The finish by laundering cycle interaction gave significant results. The untreated fabric was more susceptible to changes in laundering cycle than the finished fabric. The higher temperature also appeared to improve abrasion resistance as laundering cycle increased. The untreated fabric laundered in anionic surfactant showed increased abrasion resistance as temperature and laundering cycle increased while the resin-treated fabric laundered in anionic surfactant was stable to changes in temperature and laundering cycle. For the fabrics laundered in anionic surfactant, the beneficial effect of temperature on the abrasion resistance of the untreated fabric was more readily observed at the eighth laundering.

An examination of the correlation coefficients revealed only one significant correlation between surfactant content and the other dependent variables. This was a low correlation of .3 between surfactant content and warp wrinkle recovery. The correlation coefficients are shown in Appendix C.

CHAPTER V

SUMMARY, DISCUSSION AND RECOMMENDATIONS

SUMMARY

This study was concerned with the build-up of sur-
factant on untreated and resin-finished cotton fabrics.
The investigation was prompted by a personal interest in
cotton, a major product of Nigerian textile mills, and the
fact that soil removal by an aqueous solution of surfactants
is an important part of the wear life of a fabric. A
search of the literature revealed that the build-up of
surfactant on cotton had been studied. However, the con-
ditions under which this build-up occurred had not been
fully investigated nor were data found related to this
phenomenon on resin-treated cotton.

Specifically, this study focused on the build-up of
anionic and nonionic surfactants on untreated and resin-
treated cotton fabrics under two temperature conditions and
over eight laundering cycles. A secondary consideration
was the effect of this build-up on the tensile strength,
wrinkle recovery, and abrasion resistance of the fabrics.

The study was developed in the following sequence:

1. Formulation of hypotheses

2. Identification of the variables

3. Collection of data

4. Results of data analysis.

A summary of each aspect is given below, followed by the discussion of results and recommendations.

Formulation of Hypotheses

The following null hypotheses were developed for the study:

Hypothesis 1. There is no significant surfactant build-up attributable to the durable press finish.

Hypothesis 2. There is no significant surfactant build-up attributable to surfactant type.

Hypothesis 3. There is no significant surfactant build-up attributable to laundering temperature.

Hypothesis 4. There is no significant surfactant build-up attributable to any combination of fabric finish, laundering temperature and surfactant type.

Hypothesis 5. There is no significant difference in fabric properties attributable to surfactant build-up.

Identification of Variables

The variables identified for the study were the build-up of surfactant on untreated and resin-treated cotton fabrics under varying laundering conditions and the effect of the build-up on the tensile strength, wrinkle recovery, and abrasion resistance of the fabrics. The different laundering conditions were:

1. Surfactant - Anionic (Sodium Dodecylbenzene Sulphonate) and Nonionic (Slkyl Phenoxy Polyethoxy Ethanol)

2. Finish - Untreated and Resin-Treated

3. Temperature - 105 F and 135 F

4. Laundering Cycle - 3 and 8.

Collection of Data

Untreated and resin-treated cotton fabrics were obtained from the manufacturer and 54 samples were prepared. Three samples were assigned to each level of the factors and three samples of each fabric were left unlaundered and used as control. The fabric samples were laundered in an automatic home washer for 10 minutes and rinsed for 6 minutes. They were tumble dried for 30 minutes in an automatic home dryer at a high temperature setting.

The methylene blue indicator method was used to determine the anionic surfactant content of the samples and

the phosphomolybdic acid method was used for nonionic

determinations. The surfactant content per gram of fabric

was calculated using the formula:

$$\text{mg surfactant/} = \frac{\text{\% conc. x flask sol. vol. x 1000}}{\text{\% cotton solids x gm cotton}} [62]$$
$$\text{gm of fabric}$$

ASTM and AATCC standard methods were used to test the physi-

cal properties of the fabrics. Multivariate analysis of

covariance was used to determine the significance of the

results. Multiple comparisons were made between the means

of significant effects, using Newman Kuel's method.

Results of Data Analysis

The multivariate analysis of covariance yielded

significant results for all the effects but the surfactant

by finish interaction and the four-way interaction between

the variables. On examination of the canonical correlations,

it was found that the surfactant content and abrasion resist-

ance accounted for most of the significance.

The univariate analysis of covariance for surfactant

content yielded significant results for all but the finish

by temperature, finish by laundering cycle, and temperature

by laundering cycle interactions. Comparisons of individual

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[62] Ginn, Kinney, and Harris, op. cit., p. 138.

means showed that surfactant content increased with temperature and laundering cycle. On the whole, more anionic than nonionic surfactant was retained. However, the finished fabric retained more of the anionic surfactant while the untreated fabric retained more of the nonionic surfactant. The surfactant content of the resin-finished fabric was higher than that of the untreated fabric. It was found that temperature was a crucial factor in the build-up of the anionic surfactant while laundering cycle was more important for the nonionic surfactant. Hypotheses one to four were rejected as a result of the evidence.

No strong correlations were found to exist between surfactant content and the measured fabric properties. There were no grounds for rejecting hypothesis 5.

The univariate analysis for abrasion resistance yielded 13 significant effects. Comparisons of the means showed that the nonionic surfactant caused a greater resistance to abrasion than the anionic surfactant. The abrasion resistance of the resin-treated fabric displayed a stability to changes in temperature and laundering cycle while the abrasion resistance of the untreated fabric increased with temperature and laundering cycle. Increases in temperature resulted in an increase in the resistance to

abrasion of the fabrics laundered in anionic surfactant

while for those laundered in nonionic surfactant, laundering

cycle was the important factor.

DISCUSSION

This investigation was designed to answer specific

questions namely:

1.   Do fabric finish and surfactant type affect the

quantity of surfactant deposited on the fabric during laun-

dering?

2.   Under what laundering conditions does surfactant

build-up occur?

3.   Does surfactant build-up affect the physical

properties of the fabric?

To this end data were collected in a laboratory experiment.

The laundering procedure employed standard equipment and the

laundering conditions are replicable. The analytical method

used to determine the quantity of nonionic surfactant repre-

sents a method recommended by the AATCC for determining small

quantities of nonionic surfactant. The methylene blue method

for the anionic determination gives an end point, in a

titration, where colormetric changes are involved. In small

quantities of surfactant, the end point requires careful

interpretation. The procedure is used for assay purposes and here, the small changes in color on titration would not greatly affect the reliability of the results.

Surfactant Content

The univariate analysis of covariance showed a significant effect for the covariate, surfactant content. On examination of the original means, given in Appendix B, it was found that the fabrics contained more of the nonionic surfactant than the anionic surfactant. This was not surprising since if the anionic surfactant had been used in the scouring processes care would have been taken to ensure complete removal. Sodium salts of anionic materials cause yellowing on heating. The comparatively high nonionic surfactant content of the resin-treated fabric was also not surprising since nonionic wetting agents form a part of the resin system.

Hypothesis 1 stated that there was no significant surfactant build-up attributable to the durable press process. The univariate analysis of covariance yielded a significant finish effect. An examination of the means showed that the untreated fabric had a higher surfactant content than the resin-treated fabric. The quantity of

surfactant retained by both fabrics was on the low side and represented .23% and .19% of the fabric weights respectively. This is in keeping with the results of other investigators. Schwarz, Maple, and Aiken all found that cotton did not adsorb very large quantities of surfactant.[63] Unlike wool and other amine-containing fibers, cotton contains no polar groups capable of forming chemical bonds. The surfactant molecules are then held by purely physical forces. This also accounts for the fact that the resin-treated fabric retained less surfactant than the untreated fabric. The resin treatment results in a reaction of the resin with the hydroxyl groups of cellulose to form cross-linkages. This loss of the hydroxyl groups results in a reduction of the free energy and Van Der Waals forces which reduced the affinity of the fibers for the surfactant molecules. The evidence provided by the data led to a rejection of hypothesis 1.

Hypothesis 2 stated that there was no significant surfactant build-up attributable to surfactant type. The univariate analysis gave a significant surfactant effect.

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[63]Schwarz et al., op. cit., p. 37, and Maple, op. cit., p. 505, and Aiken, op. cit., p. 60.

The means on Table 4 showed the retention of a larger quan-
tity of the anionic than nonionic surfactant. This result
is in keeping with market expectations of the nonionic sur-
factant. Zika stated that nonionic surfactants had a low
substantivity.[64] Weatherburn and Bailey also found, in
their investigation of the adsorption of the different
classes of surfactant, that the nonionic surfactant was the
least adsorbed.[65] This can be explained by their nonionic
nature. Possessing no ionic groups, this class of surfac-
tants has little attraction for the fabric and the hardness
minerals in the wash bath. Hypothesis 2 was rejected on
the basis of the above evidence.

Hypothesis 3 stated that there was no significant
surfactant build-up attributable to the laundering temper-
ature. A highly significant effect was obtained for tem-
perature and the means, given in Table 6, showed that
surfactant build-up increased with temperature. Investi-
gators on the adsorption of surfactant on cotton found that
adsorption increased with temperature.[66] A number of

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[64]Zika, op. cit., p. 26.

[65]Weatherburn and Bailey, op. cit., p. 797.

[66]Ibid.

factors are responsible for this behavior. At higher temperatures, the surfactant in the wash bath exists in the monomolecular form rather than the aggregated form and so penetrates the fibers more readily. This in effect, increases the quantity of molecules involved in adsorption. Aiken and other investigators have shown that increases in concentration result in increased adsorption.[67] Further to this effect of temperature to the form of the surfactant in the wash bath, increases in temperature result in increased mobility of the fiber molecules. The opening up of the fiber that ensues makes the more remote areas of the fiber accessible to the hardness minerals in the wash water which are partly responsible for build-up. The overall result is increased adsorption and retention of surfactant. Hypothesis 3 was rejected as a result of the above evidence.

Hypothesis 4 stated that there was no significant surfactant build-up attributable to any combination of finish, surfactant and temperature. All but three of the interaction effects were found significant in the univariate analysis of covariance. A comparison of the means for the surfactant by finish interaction showed that the untreated

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[67]Aiken, op. cit., p. 60.

fabric retained more nonionic surfactant that the resin-
treated fabric while the resin-treated fabric retained more
anionic surfactant than the untreated fabric. Weatherburn
and Bailey came up with a result similar to the first portion
of the interaction. They found that their cotton fabrics
adsorbed more nonionic than any other category of surfac-
tant.[68] In this case, an explanation can be found in the
nature of the resin-treated fabric. The build-up of sur-
factant on cotton has been attributed to the presence of
waxes on the fiber surface, to hardness minerals in the
wash water, and to free energy forces within the fiber.
The durable press process involves an introduction of a
reactive resin into the fiber. The resin reacts with the
hydroxyl groups of cellulose to form crosslinkages. This
reaction reduces the free energy forces of the crosslinked
cellulose cutting down its affinity for several chemical
compounds. It was therefore not surprising that the resin-
treated fabric had a lower affinity for the nonionic sur-
factant which is not highly attracted to textile fibers in
the first place. The second part of the interaction showed
that the resin-treated fabric contained more anionic

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[68] Weatherburn and Bailey, loc. cit.

surfactant than the untreated fabric. The resin system

for the durable press finish contains polyethylene softeners

which react to surfactants in a manner similar to wax. Ginn

et al. found that wax-containing cotton adsorbed more anionic

surfactant than dewaxed cotton.[69] The softener then accounts

for the higher retention of the anionic surfactant.

A highly significant interaction was obtained for

the surfactant by temperature interaction. The comparison of

the means shown in Figure 9, indicated that the rate of

increase of the anionic surfactant as temperature increased

was greater than that of the nonionic surfactant. It was

observed in the discussion of the effect of temperature that

increasing the temperature of the wash bath increased the

single ion concentration as well as opening up the remote

areas of the fiber, thus providing opportunity for increased

retention of surfactant. It was also noted earlier in the

discussion, that nonionic surfactant had a low affinity for

the fibers. Increasing the opportunity would therefore have

little effect if there is no affinity for the fibers. Thus,

the anionic surfactant content increased as the opportunity

was created by increasing the temperature. The increase for

the nonionic was not as pronounced.

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[69] Ginn, Kinney, and Harris, loc. cit.

The interaction between surfactant and laundering cycle was significant. The means in Figure 9 showed a reaction similar to what was observed in the preceding interaction. The rate of increase of the anionic surfactant as laundering cycle increased was greater than that of the nonionic surfactant. It was expected that more hardness minerals which are partly responsible for surfactant build-up would be deposited on the fabric as the number of launderings increased. As in the case of temperature, increasing the mineral deposits on the fabric would not greatly affect the nonionic surfactant content since it possesses little affinity for these materials.

The means for the interaction between surfactant, finish and laundering cycle showed that the anionic surfactant content of the two fabrics did not differ significantly at 105 F but at 135 F the resin-treated fabric accumulated more surfactant than the untreated fabric. For the nonionic surfactant the untreated fabric retained more surfactant than the finished fabrics at both temperatures. This is a more complex illustration of the behavior already observed in the surfactant by finish and the surfactant by temperature interactions. The higher temperature increased the single ion concentration, making the fiber molecules

more accessible to the surfactant; this increased the quantity of anions retained by the softener.

A comparison of the means for the surfactant by temperature by laundering cycle interaction, illustrated in Figure 12, showed that increasing the temperature resulted in an increase in the quantity of anionic surfactant on the fabric. This held true for both laundering cycles. For the nonionic surfactant however, an increase in temperature resulted in increased build-up only at the third laundering cycle. At the eighth cycle, while the surfactant content increased for the fabrics laundered at 105 F, those laundered at 135 F remained essentially unchanged. The effect of temperature on the single ion concentration and the mobility of the cellulose molecule is evident in the anionic surfactant. The behavior of the nonionic surfactant is more difficult to explain. An examination of the individual components of this interaction suggested that the anomalous behavior was introduced by the resin-treated fabric which had a considerable drop in surfactant content when laundered eight times at 135 F. It is possible that a gradual removal of the softener was occurring at the higher temperature and this loss was neutralizing the increase that was occurring with laundering cycle.

In summary, several significant interactions were found to exist between surfactant type, fabric finish, and laundering temperature. The finished fabric built-up more anionic surfactant than the untreated fabric while the position was reversed for the nonionic surfactant. Increased temperature caused a greater increase in the build-up of anionic surfactant than the nonionic surfactant. In light of the above finding, hypothesis 4 was rejected.

Hypothesis 5 stated that there were no significant changes in fabric properties attributable to surfactant build-up. The correlation coefficients were examined for strong correlations between surfactant content and the variables. One correlation, between surfactant content and warp wrinkle recovery was significant. No explanation was found for this especially since the filling wrinkle recovery had a very low correlation with this variable. Enough evidence was not found to lead to a rejection of hypothesis 5.

Other Findings of Interest

It was found that the abrasion resistance of the fabrics was affected by the experimental variables. Some of these, like the effect of finish, were expected and so not of interest. The effect of surfactant and the

interactions between surfactants, temperature, and laundering cycles call for some mention.

The samples laundered in nonionic surfactant were found to possess an abrasion resistance superior to that of the fabrics laundered in anionic surfactant. Temperature had no effect on the abrasion resistance of these fabrics but laundering cycle caused appreciable increases. Three possible explanations can be advanced for this behavior.

1. Shrinkage occurred, resulting in increased abrasion resistance, and the nonionic surfactant caused a greater amount of shrinkage than the anionic surfactant.

2. The nonionic surfactant was causing a hydrolysis of the resin and this showed up as improved abrasion resistance.

3. The nonionic surfactant acted as a lubricant for fibers resulting in increased abrasion resistance.

It is known that higher temperatures cause greater shrinkage than the low temperature. If the nonionic surfactant was causing more shrinkage than the anionic surfactant it would have been observed in the surfactant by temperature interaction. Rather the reverse appeared to be the case. An examination of the surfactant by finish by temperature interaction showed that the increase in abrasion

resistance of the samples laundered in the anionic surfac-
tant was changed only for the untreated fabric. This fabric
was not treated for shrinkage control as was the resin-
finished fabric. The abrasion resistance of the fabrics
laundered in the nonionic surfactant increased with laun-
dering cycle. Shrinkage would hardly continue to eight
launderings. This then rules out the first explanation.
Resin hydrolysis is known to increase with temperature.
Yet, in the finish by temperature interaction, the abrasion
resistance of the finished fabric did not increase with
temperature. This also rules out hydrolysis of the resin,
leaving lubrication of the fibers as the only plausible
explanation.

In summary, the univariate analysis of covariance
yielded twelve significant effects which led to a rejection
of the first four hypotheses which stated that there was no
significant surfactant build-up attributable to the durable
press finish, surfactant type, laundering temperature, or
any combination of these factors. An examination of the
correlation between the dependent variables showed that there
were no grounds for rejecting the fifth hypothesis which
stated that there was no significant difference in fabric
properties attributable to surfactant build-up.

From the results of this investigation it was concluded that untreated and resin-treated cotton fabrics do not retain large quantities of surfactants. For the little that is retained, temperature and surfactant type are important factors. No relationship exists between the quantity of surfactant on the fabric and the tensile strength, abrasion resistance, and wrinkle recovery of the fabrics; rather, the lubricating action of the surfactant is of more relevance to the abrasion resistance of the fabric.

RECOMMENDATIONS

The fabrics were laundered eight times which was less than one-fourth the number of launderings a fabric is expected to go through in a normal wear life. Future research should be conducted over a larger number of launderings to allow for pronounced changes in fabric properties.

The quantity of surfactant retained was small in quantity but fairly large if considered in terms of surface action. Research should be undertaken to determine the effect of this quantity of residual surfactant on the soiling property and the ease of soil removal of the fabrics.

Finally, the effects of concentration and builders were controlled for this study. Research should be undertaken to determine the effects of these on surfactant build-up.

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APPENDIX A

CANONICAL CORRELATIONS
(N=48)

Source	Surfactant Content	Warp Tensile	Filling Tensile	Warp Wkl. Recovery	Filling Wkl. Recovery	Abrasion Resistance
Surfactant	0.90	0.19	−0.05	0.27	−0.25	−0.25
Finish	− .08	− .32	− .17	.66	.18	− .36
Temperature	.92	.04	.11	.04	− .07	.05
Laundering Cycle	.78	.01	.01	.04	− .03	.34
Surfactant x Finish	.93	− .02	− .11	.12	− .20	.03
Surfactant x Temperature	.57	− .61	.01	.02	.14	.61
Surfactant x Laundering Cycle	.94	.05	.14	− .05	− .07	− .23
Finish x Temperature	.32	.05	.47	.36	.33	.21
Finish x Laundering Cycle	− .16	.02	− .03	.04	− .23	.88

CANONICAL CORRELATIONS (continued)

Source	Surfactant Content	Warp Tensile	Filling Tensile	Warp Wkl. Recovery	Filling Wkl. Recovery	Abrasion Resistance
Surfactant x Finish x Temperature	-0.47	0.09	-0.12	-0.28	-0.25	0.58
Surfactant x Finish x Laundering Cycle	.68	.43	.04	- .18	- .08	- .32
Surfactant x Temperature x Laundering Cycle	.74	- .15	- .08	.01	.28	.23
Finish x Temperature x Laundering Cycle	.68	.03	- .01	.11	.42	.03
Surfactant x Finish x Temperature x Laundering Cycle	.61	.01	- .20	.41	.15	- .73

The header "Canonical Correlations" spans the six data columns.

Wkl. = Wrinkle

APPENDIX B

MEAN SURFACTANT CONTENT FOR THE VARIABLE SURFACTANT

Surfactant	No. of Samples	Surfactant Content
Anionic Control	6	.004
Nonionic Control	6	.33
Anionic	24	3.04
Nonionic	24	1.11

MEAN SURFACTANT CONTENT FOR THE VARIABLE FINISH

Finish	No. of Samples	Mean Surfactant Content
Untreated Control	6	.12
Resin-Treated Control	6	.21
Untreated	24	1.88
Resin-Treated	24	2.27

MEAN SURFACTANT CONTENT FOR THE
VARIABLE TEMPERATURE

Temperature	No. of Samples	Mean Surfactant Content
Control	12	.16
105 F	24	1.76
135 F	24	2.39

MEAN SURFACTANT CONTENT FOR THE
VARIABLE LAUNDERING CYCLE

Laundering Cycle	No. of Samples	Mean Surfactant Content
Control	12	.16
3	24	1.48
8	24	2.39

MEAN SURFACTANT CONTENT FOR SURFACTANT
BY FINISH INTERACTION

Surfactant	Finish	No. of Samples	Mean Surfactant Content
Anionic	Untreated Control	3	.002
Anionic	Resin-Treated Control	3	.01
Anionic	Untreated	12	2.62
Anionic	Resin-Treated	12	3.47
Nonionic	Untreated Control	3	.23
Nonionic	Resin-Treated Control	3	.42
Nonionic	Untreated	12	1.14
Nonionic	Resin-Treated	12	1.08

MEAN SURFACTANT CONTENT FOR SURFACTANT
BY LAUNDERING CYCLE INTERACTION

Surfactant	Temperature	No. of Samples	Mean Surfactant Content
Anionic	Control	6	.004
Anionic	3	12	1.20
Anionic	8	12	4.09
Nonionic	Control	6	.33
Nonionic	3	12	.96
Nonionic	8	12	1.2

MEAN SURFACTANT CONTENT FOR SURFACTANT
BY TEMPERATURE INTERACTION

Surfactant	Temperature	No. of Samples	Mean Surfactant Content
Anionic	Control	6	.004
Anionic	105 F	12	2.62
Anionic	135 F	12	3.47
Nonionic	Control	6	.33
Nonionic	105 F	12	.91
Nonionic	135 F	12	1.31

MEAN SURFACTANT CONTENT FOR SURFACTANT
BY FINISH BY TEMPERATURE INTERACTION

Surfactant	Finish	Temperature	No. of Samples	Mean Surfactant Content
Anionic	Untreated	Control	3	.002
Anionic	Resin-Treated	Control	3	.1
Anionic	Untreated	105 F	6	2.22
Anionic	Untreated	135 F	6	3.02
Anionic	Resin-Treated	105 F	6	3.01
Anionic	Resin-Treated	135 F	6	3.92
Nonionic	Untreated	Control	3	.23
Nonionic	Resin-Treated	Control	3	.42
Nonionic	Untreated	105 F	6	.80
Nonionic	Untreated	135 F	6	1.48
Nonionic	Resin-Treated	105 F	6	1.02
Nonionic	Resin-Treated	135 F	6	1.15

MEAN SURFACTANT CONTENT FOR SURFACTANT BY
FINISH BY LAUNDERING CYCLE INTERACTION

Surfactant	Finish	Laundering Cycle	No. of Samples	Mean Surfactant Content
Anionic	Untreated	Control	3	.002
Anionic	Resin-Treated	Control	3	.01
Anionic	Untreated	3	6	1.78
Anionic	Untreated	8	6	3.46
Anionic	Resin-Treated	3	6	2.22
Anionic	Resin-Treated	8	6	4.71
Nonionic	Untreated	Control	3	.22
Nonionic	Resin-Treated	Control	3	.42
Nonionic	Untreated	3	6	.89
Nonionic	Untreated	8	6	1.39
Nonionic	Resin-Treated	3	6	1.03
Nonionic	Resin-Treated	8	6	1.14

MEAN SURFACTANT CONTENT FOR SURFACTANT BY TEMPER-
ATURE BY LAUNDERING CYCLE INTERACTION

Surfactant	Temperature	Laundering Cycle	No. of Samples	Mean Surfactant Content
Anionic	Control	Control	6	.004
Anionic	105 F	3	6	1.78
Anionic	105 F	8	6	3.46
Anionic	135 F	3	6	2.22
Anionic	135 F	8	6	4.72
Nonionic	Control	Control	6	.33
Nonionic	105 F	3	6	.52
Nonionic	105 F	8	6	1.30
Nonionic	135 F	3	6	1.40
Nonionic	135 F	8	6	1.22

MEAN SURFACTANT CONTENT FOR FINISH BY TEMPERATURE
BY LAUNDERING CYCLE INTERACTION

Finish	Temperature	Laundering Cycle	No. of Samples	Mean Surfactant Content
Untreated	Control	Control	6	.12
Untreated	105 F	3	6	1.07
Untreated	105 F	8	6	1.95
Untreated	135 F	3	6	1.60
Untreated	135 F	8	6	2.90
Resin-Treated	Control	Control	6	.21
Resin-Treated	105 F	3	6	1.22
Resin-Treated	105 F	8	6	2.81
Resin-Treated	135 F	3	6	2.03
Resin-Treated	135 F	8	6	3.04

MEAN ABRASION RESISTANCE FOR SURFACTANT

Surfactant	No. of Samples	Mean Abrasion Resistance
Control	12	171.2
Anionic	24	126.4
Nonionic	24	129.3

MEAN ABRASION RESISTANCE FOR TEMPERATURE

Temperature	No. of Samples	Mean Abrasion Resistance
Control	12	171.2
105 F	24	127.2
135 F	24	128.6

MEAN ABRASION RESISTANCE FOR LAUNDERING CYCLE

Laundering Cycle	No. of Samples	Mean Abrasion Resistance
Control	12	171.2
3	24	117.9
8	24	137.9

MEAN ABRASION RESISTANCE FOR SURFACTANT
BY LAUNDERING CYCLE INTERACTION

Surfactant	Laundering Cycle	No. of Samples	Mean Abrasion Resistance
Control	Control	6	171.2
Anionic	3	12	120.8
Anionic	8	12	132.0
Nonionic	3	12	114.9
Nonionic	8	12	143.8

MEAN ABRASION RESISTANCE FOR SURFACTANT
BY FINISH BY TEMPERATURE INTERACTION

Surfactant	Finish	Temperature	No. of Samples	Mean Abrasion Resistance
Control	Untreated	Control	3	217
Control	Resin-Treated	Control	3	125.4
Anionic	Untreated	105 F	6	147.5
Anionic	Untreated	135 F	6	168.8
Anionic	Resin-Treated	105 F	6	94.7
Anionic	Resin-Treated	135 F	6	94.5
Nonionic	Untreated	105 F	6	175.0
Nonionic	Untreated	135 F	6	162.2
Nonionic	Resin-Treated	105 F	6	91.4
Nonionic	Resin-Treated	135 F	6	88.7

MEAN ABRASION RESISTANCE FOR SURFACTANT BY FINISH
BY LAUNDERING CYCLE INTERACTION

Surfactant	Finish	Laundering Cycle	No. of Samples	Mean Abrasion Resistance
Control	Untreated	Control	3	217.0
Control	Resin-Treated	Control	3	125.4
Anionic	Untreated	3	6	138.4
Anionic	Untreated	8	6	117.9
Anionic	Resin-Treated	3	6	103.2
Anionic	Resin-Treated	8	6	86.1
Nonionic	Untreated	3	6	145.6
Nonionic	Untreated	8	6	191.7
Nonionic	Resin-Treated	3	6	84.2
Nonionic	Resin-Treated	8	6	95.9

APPENDIX C

CORRELATION MATRIX
(N=48)

Source	Surfactant Content	Warp Tensile	Filling Tensile	Warp Wkl. Recovery	Filling Wkl. Recovery	Abrasion Resistance
Surfactant Content	1.0	−0.2	−0.2	0.3*	−0.2	−0.1
Warp Tensile		1.0	.8*	− .7*	− .9*	.8*
Filling Tensile			1.0	− .8*	− .8*	− .8*
Warp Wkl. Recovery				1.0	.8*	− .7*
Filling Wkl. Recovery					1.0	− .8*
Abrasion Resistance						1.0

*p = .05

Wkl. = wrinkle