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C O N T E N T S

Discussion and Review of Chemical Finishing of Cotton.
I. Flame Retardancy, Soiling and Soil Release, Cotton
Batting, Other Techniques in Cotton Finishing

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INTRODUCTION

I am indeed grateful for this privilege of being a part of this NRC/ACS Chemistry Work-
shop and for the opportunity to discuss some of the cotton utilization research being done
in our country, which we hope will, by transfer of technology, lead to the development of
new or improved products and processes that will increase the utilization of cotton. Many
textile fibers compete with cotton, primarily because they have attractive and useful prop-
erties not possessed by cotton in its natural state. The consumer has already demonstrated
that he will pay relatively high prices to obtain the fibers. It is essential to find
means of giving cotton these new and improved properties which only utilization research
can provide. The importance of this area of research to cotton cannot be overemphasized,
since cotton in the bale is of little value to the consumer unless it can be made into use-
ful textile products having properties that are competitive with other textile fibers.

Textile finishing today tends to impart functional qualities that provide consumers
with materials having improved performance characteristics. In many cases, finishes are
applied for aesthetic effect or for convenience, but in other cases protection of the con-
sumer is the goal. Finishes that have no protective or safety aspects need only to meet
vague performance standards that satisfy the individual consumer. A finish designed to pro-
tect the user must meet rigid legal standards to provide a margin of safety under extreme
conditions of use.

The first topic I will discuss will be flame retardancy, since flame resistance is the
protective finish that is receiving the most widespread attention by the textile industry.
The remaining topics to be discussed will be confined to chemical or finishing areas of
utilization research.

FLAME RETARDANTS

Nature of Cotton Cellose and Approaches
for Achieving Flame Retardancy

Cotton in the form of fabric is subjected to flame-retardant chemicals for reaction to
impart flame resistance. The physical state of the fiber has a very definite bearing upon
the degree of flame resistance one can obtain. Rowland has published a good description
of how cotton undergoes chemical modification (1).

The cotton fiber is a complex, well-ordered unit that is generated during the growth
cycle of the cotton plant in the form of a long, hollow tube, approximately 20 microns in
width by 25,000 microns (1 inch) in length. Each fiber has a twisted convoluted ribbon-
like structure, with a somewhat furrowed surface, a section of which is shown in A of
Figure 1. It is composed of a multitude of microstructural units which are packed in close
proximity and are microfibrils; these units become evident when an expanded portion of a
cross section of a cotton fiber is examined under high magnification, as in electron micro-
graphs B and C of Figure 1. The surface of a slab torn out of the cotton fiber (D of
Figure 1) shows the microfibrils, at high magnification, in an arrangement which they have
in the fiber. These microfibrils are composed from cellulose molecules, which in turn con-
sist of more than 3,000 D-glucopyranosyl units, such as shown in E of Figure 1, joined in

a linear chain.

The hydroxyl groups in cotton cellulose, upon which we depend for the cross-linking reactions and for the development of performance properties, are buried in a catacomb-like labyrinth in the cotton fiber. Only a fraction of these potential sites for chemical reaction are actually accessible to the reagent in conventional finishing operations. Moreover, there are two different types of hydroxyl groups in the fibers of cotton cellulose, i.e., secondary hydroxyls at carbon atoms 2 and 3, and primary hydroxyls at carbon atom 6 of each D-glucopyranosyl unit (E of Figure 1). These three hydroxyl groups react at different rates, and the linkages developed exhibit different stabilities.

How does the chemical reagent reach the hydroxyl groups in the bulk of the fiber? While the cross section of the native fiber, or a mercerized fiber, shows no pores or channels even at the high magnification of an electron micrograph, the cross section of a fiber, swollen as a result of wet embedment in methacrylate polymer (2), exhibits a selective concentric expansion with the development of a pattern such as shown in B of Figure 1. The expansion and pore development that the fiber undergoes in aqueous solutions of cross-linking agents are probably of this same type but considerably lesser in degree. The pores of decrystallized cellulose have been estimated by gel permeation chromatography to accommodate molecules of sugars having molecular weights ranging downwards from approximately 1800 (3). Sugars having molecular weights slightly below 1800 find very few pores of adequate size; however, with decreasing molecular weight of the sugar, an increasing number or volume, of pores becomes available to accommodate the sugar molecules. Preliminary assessment of pores in fibrous cotton by the same method has indicated a permeability in the range of 2800. It is quite evident, then, that the normal type of cross-linking flame-retardant agent, which has a molecular weight in the range of 100 to 200 finds many pores or channels through which it may reach the hydroxyl groups of the cellulose molecules in the microstructural units.

Application of Durable Flame Retardants and Commercial Finishes

There are four basic techniques used in the application of a flame retardant to cotton fabric. They are:

1. Direct reaction with cotton cellulose

2. The use of a thermoplastic polymer to coat the fibers

3. The use of a flame retardant polymer for deposition within the fiber

4. A combination of cellulose reaction and internal deposition of a polymer

The first technique has not been useful in obtaining durable flame retardancy, because it is often difficult to react enough of the hydroxyl groups of cellulose in order to obtain a high add-on. Also, compounds such as $ClCH_2P(O)(OH)$, which have been used in substitution reactions with cellulose, are subject to ion exchange and therefore lose flame retardancy during laundering. Likewise, the second technique has not been useful in the production of durable flame retardancy, because this technique will usually impart stiffness to the fabric since the polymer is located on the surface of the fibers. Therefore, techniques 3 and 4 are the ones most commonly used today for imparting durable flame resistance to cotton fabric.

To date, all successful flame retardants for cotton have been compounds containing the element phosphorus. Generally, the phosphorus compound is used in combination with a nitrogenous resin which polymerizes with the phosphorus compound and helps to bind the flame retardant to the fabric. In some cases, materials containing bromine or chlorine are also incorporated in the formulation, and the amount of phosphorus compound can be reduced. Therefore a typical flame retardant formulation will contain:
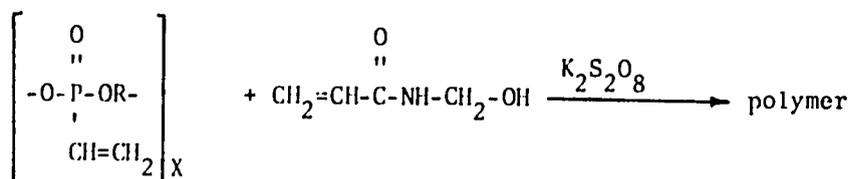
1. Reactive phosphorus compound

2. N-methylol compound

3. Catalyst and/or buffer

4. Softener and wetting agent (auxiliaries)

Durable flame retardants are mostly used for apparel, household goods, and some special items for military and industrial purposes. There are innumerable experimental flame retardant finishes, a few of which are being evaluated for commercial use. However, the best known durable flame retardant systems used commercially for cotton fabric are Pyrovatex CP, Fyrol 76, THPOH-Amide, Proban, and THPOH-NH$_3$.*

Pyrovatex CP is a finish developed by Ciba-Geigy (4) and is a typical flame retardant system as described above. The reactive phosphorus compound in this finish is a N-methylol dialkyl phosphonoprionamide, $(RO)_2P(O)C_2H_4C(O)NHCH_2OH$. A typical formulation consists of 40% Pyrovatex, 5% methylol melamine resin, 1% urea, 1% softener, 0.1% wetting agent, and approximately 0.5% of an acid catalyst such as phosphoric acid. This formulation is applied from a water solution by the conventional pad-dry-heat cure method. As in most chemical finishes, the treated fabric is given an afterwash to remove unreacted chemicals. This finish is low in toxicity and, when properly applied, gives an excellent hand to the fabric. The breaking strength of the fabric is reduced about 25%, and the tearing strength is reduced about 30%. This finish is durable to home laundering and has been used primarily in the production of children's flame-retardant cotton sleepwear, sizes 0-6X.

Fyrol 76 is a flame-retardant finish recently developed for cellulosics by Stauffer Chemical (5). The reactive ingredients in this formulation are shown in the equation:

$$\left[\begin{array}{c} O \\ \| \\ -O-P-OR- \\ | \\ CH=CH_2 \end{array} \right]_x + CH_2=CH-C-NH-CH_2-OH \xrightarrow{K_2S_2O_8} \text{polymer}$$

The vinylphosphonate monomer contains 22.5% phosphorus and is used in 20% concentration in the formulation. Approximately 22% methylolacrylamide, 0.5% potassium persulfate, 4% auxiliary agents, and water make up the remainder of the formulation. This formulation is also applied by the pad-dry-heat cure process in which curing is accomplished by a free radical mechanism. Reaction also occurs with the cotton cellulose which helps to make the finish durable to laundering and also makes the fabric wrinkle resistant. The treated fabric has a good hand, with about 15% loss in breaking strength and about 35% loss in tearing strength. A chemical add-on of 25-30% is needed to pass the DOC FF-3-71 standard for children's sleepwear.

The last three flame retardant finishes, THPOH-Amide, Proban, and THPOH-NH$_3$, all use the same reactive phosphorus compound, tetrakis (hydroxymethyl)phosphonium chloride (THPC). However, formulations of these processes differ in the use of the nitrogen compound and/or in processing techniques. THPC is produced by Hooker Chemical Co., Aceto Chemical Co., American Cyanamid Co., and Albright and Wilson, Ltd., England. The term THPOH is applied to the product obtained from the neutralization of THPC as shown in Figure 2. The neutralization of THPC has been the subject of great controversy and is adequately explained by Ellzey, Connick, and Boudreaux (6). Both THPC and THPOH will react with nitrogen compounds to form highly complex polymers. Many experimental flame retardant finishes based on THPC are thoroughly reviewed by Reeves and Drake (7).

The initial research on the development of the THPOH-Amide finish was conducted at SRRC (8). A standard formulation for use on an 8-oz. cotton fabric contains 17% THPC, 2.2% sodium hydroxide, 10.5% urea, 9.5% trimethylol melamine (TMM), about 1.5% auxiliaries, and the remainder water. The solution is prepared by adding dilute sodium hydroxide to a water solution of THPC to pH about 7. The other chemicals are added, and the fabric is treated

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* Use of a company or product name does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

by the pad-dry-heat cure process. A catalyst is not needed, since TMM is sufficiently re-active without it. The strength properties of treated fabric are about the same as with Pyrovatex or Fyrol 76, but wrinkle recovery is better. Because this finish gives a slightly stiffer hand than the other finishes, it has been used primarily on heavier weight fabrics such as that used for work clothing, tent lining, and curtains.

The Proban finish is based upon a precondensate of THPC and urea and is sold as such (8). The original Proban finish (before 1960) was also based on a heat cure process to fix the precondensate onto cotton cellulose. The process has since been modified by re-placing the heat cure with an ammonia gas cure (10), which has resulted in better efficiency and strength properties of the treated fabric. The fabric is impregnated with the precon-densate solution, dried at about 90° C., exposed to ammonia gas for approximately 20 seconds, and finally treated with an ammonium hydroxide solution to ensure complete reaction and fixation of the polymer on the fabric. The Proban finish is used primarily in Europe, and in 1973 more than 5 million yards were produced.

The THPOH-NH₃ process was developed by researchers at SRRC (11). It is not a typical flame retardant finish in that it does not use a N-methylol resin, it does not require a catalyst, and it does not use a heat cure. As a result, fabrics treated by the THPOH-NH₃ process have a good hand and very good strength properties. A schematic diagram of the process is shown in Figure 3. Fabrics are usually treated with a 30-35% solution of only THPOH plus auxiliary agents. After padding to approximately 80-90% wet pickup, the fabric is dried to about 5% moisture and then exposed to ammonia vapor to produce a polymer with-in the cotton fiber. The fabric is then oxidized to improve durability, eliminate odor, and improve color. A final after-wash, to remove unreacted material, is preceded by a final drying step.

The polymer produced from the THPOH-NH₃ process differs from the polymer in the Proban finish in that the phosphorus to nitrogen weight ratio is approximately 2:1 in the former and approximately 1:1 in the latter. Because of the higher percent phosphorus in the poly-mer, the THPOH-NH₃ polymer is a more efficient flame retardant per unit weight of polymer. The THPOH-NH₃ finish is now used commercially in the U.S. for children's sleepwear and other wearing apparel.

Factors Affecting Flame Resistance of Fibers

While phosphorus-containing flame retardants have some unique features such as glow resistance, these retardants require proper application and care to assure maximum effi-ciency and durability. Alkali and alkaline earth metal ions reduce or inhibit the flame resistance contributed by phosphorus. These ions need not be in direct union with the re-tardant to exhibit their effect; mere presence in the fiber or fabric is adequate. Calcium acetate is more detrimental to flame retardants than calcium phosphate. Calcium and mag-nesium can be picked up by flame-resistant fabric from wash water during laundering. This pickup can occur through ion exchange properties of the retardant and through precipitation in the fiber by combining with phosphate from detergents or fatty acids from soap. The amount of phosphate salts picked up by the fabric depends on the nature of the flame re-tardant and the amount of phosphate and calcium (or magnesium) in wash water. Pickup of these phosphates can lead to erroneous results when the phosphorus content of fabric is used as a measure of durability of the flame retardant. Calcium and magnesium soaps in a fabric similarly can offset flame tests that are often used to measure durability. The adverse effects of the foreign materials can be eliminated by rinsing the laundered fabric occasionally in dilute acid (Figure 4). Pickup of copper ions from solution has little effect on flame resistance.

The oxidation state of phosphorus in the finish affects the durability of flame re-tardant fabrics. THPC retardants with trivalent phosphorus are less durable to laundering than are the retardants that contain the corresponding phosphine oxide structure. Thus, the application of THPC-type retardants should include an oxidation step.

Retardants are generally degraded, at least to a small extent, when exposed to sun-light. This degradation becomes a significant problem for some retardants when the treated

fabrics are laundered and line dried. The unoxidized retardant based on the reaction of "TIIPOH" with ammonia is particularly sensitive to sunlight. A small amount of pigment can protect some flame retardants from the destructive action of sunlight. Pressing, which is sometimes part of the laundry cycle for apparel and household goods, also decreases the effectiveness of some flame retardants. The ester groups of alkyl phosphonates are hydrolyzed at the pressing temperature to produce sites for ion exchange, which is detrimental when the fabrics are laundered. Another factor affecting the durability of flame-retardant finishes is bleaching. None of the known commercial flame-retardant finished fabrics can pass the DOC FF-3-71 test after being bleached 50 times with hypochlorite bleaches.

SOIL RESISTANT FINISHES

The soil release problem attained considerable attention after garments made from durable-press fabrics had become established on the market. Most durable-press garments depend upon blending with man-made fibers and resin treatment of cotton fibers. Although the synthetic fibers are implicated most heavily, other factors are involved; that is, durable-press resins, softeners, catalysts, and even fabric geometry. Basically, textile scientists are trying to develop and refine chemical processes that overcome the hydrophobic, oleophilic, and electropositve properties of the chemically finished fabrics. A hydrophobic fabric prevents wash water from entering the spaces between the yarns; the fabric's positive charge attracts the negatively charged dirt particles; and the oleophilic nature of the material draws grease not only during wearing but also scavenges water-borne oils that accumulate during laundering. Other factors involved include the type and hardness of the finish, the nature of the soil, the method of soiling, the cleaning agent, the manner in which the soil is removed (laundering or dry cleaning), fabric structure, and the efficiency of detergent used. Unfortunately, in the late 1940's and early 1950's, the soiling problems grew because of two concurrent factors: (1) the greater cleaning problem of the resin-treated cotton in cotton/synthetic blends, and (2) the fall of efficiency of the homemaker's detergents. The newer synthetic detergents were much less effective at soil removal and soil suspension than the old-fashioned soap, so that other agents such as soil suspenders and optical bleachers had to be added.

Introduction of Durable Soil Resistant and Soil Release Finishes

It had been known for many years that carboxymethyl cellulose (CMC) could make soil removal from cotton fabric easier. This was accomplished by adding CMC to the last rinse water used in the laundering procedure. In that manner, 1% or 2% CMC was deposited on the surface of the fiber. According to earlier theories, the soiled fabric laundered easier because the CMC readily flaked off the surface of the fiber, carrying with it particles of soil. The loss of CMC from the surface of the fibers was considered a very important factor in the soil removal process.

Studies at SRRC revealed that CMC need not be removed from the surface of the fabric to provide ease of soil removal (12). It was found that the charge on the surface plus the hydrophilic nature of the CMC were the important factors contributing to the ease of soil removal. That it was not necessary for the CMC to be removed to be an effective soil release agent was demonstrated by bonding CMC to the surface of cross-linked cotton fabrics.

In studies with CMC as a durable soil release agent, cotton fabric was padded with an aqueous solution containing a cross-linking agent and CMC, then cured at about 150° C. The CMC, which contains cellulosic hydroxyl groups, remained mostly on the surface of the fiber because of its high molecular weight. The small amount of cross-linking agent normally present on the surface of the fibers after padding with a cross-linking agent reacted with the CMC and with the cotton, thus binding CMC to the cotton through a durable covalent cross-link. The wrinkle recovery angles of the treated fabrics ranged from about 260° to 290° (W + F) (12).

The resistance to aqueous soiling of untreated cotton was compared to that of cross-linked cotton and to cross-linked cotton that contained CMC fixed on the surface of the fibers. Samples were treated with DMEU-CMC and triazine-CMC solutions containing 5%

monomer, 2% CMC, and 1.5% Catalyst H-7. These treated fabrics along with DMEU and triazine treated controls and an untreated printcloth control sample were subjected to 25 laundering cycles. Samples of each fabric were taken from the washing machine after 5, 15, and 25 laundering cycles, and air-dried. Each sample was then padded through aqueous and oily carbon black soil dispersions and air-dried. Reflectance values of samples soiled after multiple launderings up to a total of 25 cycles are shown in Figures 5 and 6. The treated samples containing CMC were significantly more resistant to aqueous and oily soils than were the DMEU and triazine treated controls through 25 laundering cycles. Soil resistance of these samples closely resembled that of the untreated control fabrics.

Another set of samples, prepared exactly as those mentioned above, along with untreated control samples were evaluated with respect to soil removal through extended laundering. Reflectance measurements were made on these samples after soiling with aqueous and oily carbon black dispersions. The soiled samples were then laundered 25 consecutive times. After 1, 5, 10, 15, 20, and 25 laundering cycles, samples were taken from the washing machine, air-dried, and reflectance values were recorded for each. Figure 7 shows % reflectance of aqueous soiled samples through 25 launderings. It is readily seen that the triazine-CMC finished sample was best. However, aqueous soil was readily removed from fabric treated with triazine only. Both of these treated fabrics had higher reflectance values than the untreated control fabric through 25 launderings. Considerably higher reflectance values were measured for the CMEU-CMC samples in comparison to the DMEU treated fabrics. These data clearly indicate that soil removal from DMEU and triazine resin treated fabrics was improved when 2% CMC was incorporated in the treating solutions.

Figure 8 shows the results of laundering those samples soiled in oily carbon black dispersions. Again, the treated fabrics containing CMC had higher reflectance values through 25 laundering cycles, indicating better soil removal from these samples. Oily soil was more readily removed from the DMEU-CMC treated fabric than from all others.

This study demonstrated (a) the soil resistance imparted by CMC when bound to the cotton fiber, and (b) the good durability of the CMC to repeated laundering.

In a third comparison of this series of fabrics, 2% CMC was added to the cross-linking formulation to impart soil resistance and ease of soil removal properties. The reflectance values for these fabrics show that CMC imparted some soil resistance and significant improvement in ease of soil removal to the various fabrics and that the CMC is more effective on the resin-treated fabrics which contain the highest percentage cotton.

Effect of Surface Properties on Soiling and Soil Removal

Experimental cotton fabrics were prepared having a wide range of surface properties. This was accomplished by cross-linking with formaldehyde, chemically modifying to add anionic, cationic, or nonionic groups, or treating with various finishes. Additional fabrics were prepared by various combinations of cross-linking treatments, chemical modifications, or surface finishing.

The fabrics included in this study were desized, scoured, bleached cotton printcloth; cotton formaldehyde-treated in the "dry" state (Form D); and treated in the wet or swollen state (Form W). Thirteen chemically modified fabrics were also evaluated; these included each of the three basic fabrics mentioned above that were phosphonomethylated, aminized, sulfoethylated, or carboxymethylated. The untreated cotton was also hydroxyethylated.

All of the basic three fabrics were treated with the following: four acrylic finishes of varying hardnesses, two acrylic finishes with cationic groups or anionic groups; two fluorochemical finishes, fluroacrylate, or chrome complex of perfluorooctanoic acid; a hydrophilic finish, carboxymethyl cellulose; and an insoluble inorganic salt. The chemically modified cotton fabrics were also finished with a hard acrylic and fluoroacrylate. The phosphonomethylated cottons that had been cross-linked with formaldehyde (Form D and Form W) were also treated with the hard acrylic and fluoroacrylate finishes.

Studies were made of the soiling characteristics of these fabrics in both aqueous and

dry cleaning solvent media.

In an aqueous medium it was found that a high energy interface between the fiber substrate and water caused the deposition of oily soils onto the fabrics. Soft polymeric finishes on cotton were found to contribute to wet soiling, especially if they were thermoplastic and softened still further at elevated laundering temperatures. Fibers and finishes having positive zeta potentials in water were found to be associated with high levels of soiling. Thus, in water, the preferred fabric surface from the point of view of resistance to soiling and ease of soil removal would be a thin, hard hydrophilic, negatively charged surface (13).

Soiling in Stoddard solvent revealed:

1. Most of the finishes investigated increased the degree of soiling.

2. There appeared to be a definite trend toward increased soiling with charged groups, both cationic and anionic. The only exception was the aminized cotton, which soiled to the same extent as the unmodified control in Stoddard solvent.

3. There was a slight but definite trend towards greater soiling for cottons cross-linked with formaldehyde, especially in the "dry" state, when compared with the untreated control.

4. Of the three factors in combination treatments, the type of chemical finish, the character of the chemical modification, and the cross-linking with formaldehyde, the one having the largest effect on soiling was the type of finish.

5. The nature of the soil was important; there was more soiling with dry iron oxide than with oily iron oxide or vacuum cleaner dirt.

6. The hardness of the finish was a factor only with very soft finishes.

Under most conditions, the ease of soil removal was inversely related to the degree of soiling, i.e., those fabrics which soiled heavily retained a larger percentage of the soil during cleaning than those that were lightly soiled.

In all cases studied, much less soil was removed by dry cleaning than by laundering. One reason for this is that the aqueous detergent solution has much better antiredeposition properties than does the dry cleaning bath. This was demonstrated by the much larger amount of soil deposited on clean swatches (redeposition) during dry cleaning than during laundering. Another factor contributing to this may be the smaller size of the soil particles in dry cleaning solvent.

On the basis of the results of these studies, it was concluded that the treatment or modification of cotton to produce a fabric of low soiling characteristics should have the following properties: (1) thin, hard, nonswelling finish; (2) hydrophilic surface; (3) oleophobic surface; and (4) small negative surface charge, or small negative zeta potential.

Oleophobic-Hydrophilic Finishes for Soil Release

Fluorine-containing polymers have been used in large quantities over the past several years for treating textiles to impart water and oil resistant properties. These provide resistance to oil soils and stains, but once the oily soil or stain is rubbed in, it is very difficult to remove. As a result of the previous studies using CMC to incorporate a hydrophilic surface to the cotton, and of the soiling characteristics of fabrics having various surface properties, it was theorized that removal of the rubbed-in soil and most other types of soil would be easier if the finish had hydrophilic as well as hydrophobic properties. The idea was that the aqueous laundry detergent would wet the soiled areas in the more hydrophilic fabric and thus do a better job of cleaning the fabric. In 1966, Ellzey of our laboratory reported on the synthesis of some fluorocarbon finishes which, when

applied to cotton fabric, produced high oil repellency ratings of 100-120 but little water repellency instead of the usual 90-100 spray ratings exhibited by conventional fluorocarbon finishes. Since then, more complete studies have been conducted on the performance of these finishes with high oil repellency and low water repellency (15).

One of the finishes reported is based upon the reaction of ethyl perfluorooctanoate with ethylenenimine (EPO-EI) (16). This finish, when applied to fabric from an aqueous emulsion and dried at about 100° C., forms an insoluble polymer on the surface of the fiber. The treated fabric exhibits 3M oil ratings of 100-120 and spray rating of about 50 with a 2% add-on of the polymer. For comparison, untreated printcloth and printcloth treated with three commercial fluorocarbon finishes, and the EPO-EI finish were examined for oily soil release and oily soil redeposition properties.

In the soil release experiment, all of the fabrics were soiled with oily carbon black. After being laundered five times in separate Launder-O-Meter cups, fabrics with the three commercial fluorocarbon finishes were still heavily soiled. The EPO-EI treated fabric was only lightly soiled, and the untreated cotton fabric was essentially free of soil.

To determine soil redeposition properties of the experimental fluorocarbon finished fabrics, each nonsoiled sample was placed in a Launder-O-Meter cup with an oily-soiled cotton fabric. After five laundry cycles, two of the commercial fluorocarbon finished fabrics were heavily soiled, and one was moderately soiled, whereas an untreated cotton and the EPO-EI treated fabric were slightly soiled. These experiments indicated the potential value of imparting hydrophilic character to the oleophobic fluorocarbon finishes.

Another new fluorocarbon finish for cotton was based on the formation of a highly insoluble fluorinated bis-urea (31). The FEMU (fluorinated ethoxymethylurea) was applied from an ethanolic solution or an aqueous dispersion to give high oil repellency and moderate water repellency. Durability of oil ratings to laundering was better than that for the commercial fluorochemical finishes tested at comparable solids levels. Co-application with PR-183 (Permafresh Reactant 183) from ethanol-water solution additionally imparted wrinkle recovery properties of about 300° conditioned and 270° wet.

The FEMU finish had good stain resistance and offered easy removal of several common stains. Oily soil redeposition was intermediate between older commercial finishes and a newer commercial fluorocarbon soil release finish.

Ellzey and coworkers also reached THPC and 1,1-dihydroperfluorooctylamine (POA) in a 1:1 molar ratio, which when applied to cotton fabric from aqueous emulsions imparted a low degree of water repellency and high oil repellency after curing with gaseous ammonia (14). The oil repellency was not very durable to perchloroethylene extraction, but durability to home laundering was quite good. Using a simulated soiling procedure, the POA-THPC finish was about as effective as three commercial fluorochemical finishes tested in aqueous soil release and aqueous redeposition properties, although it was generally inferior in initial aqueous soiling. In oily soiling tests, the new finish had greater oily soil repellency, suffered less oily soil redeposition, and had slightly better oily soil release characteristics.

The POA-THPC formulation was combined with a typical permanent-press agent (again PR-183).

Fabric treated with the combined finish had good conditioned and wet wrinkle recovery in addition to high oil repellency and low water repellency. Soiling properties were approximately the same as those of the POA-THPC or PR-183 finishes alone. The combined finish behaved somewhat poorer in oily soil redeposition tests. Certain properties, notably tearing strength and abrasion resistance, were improved by adding the POA-THPC formulation to the permanent-press agent (15).

Research at SRRC, in industry, and in other research organizations continues toward a better understanding of the principles involved in soiling, soil release, and soil redeposition and toward the development of new formulations and processes for the production of the ideal soil release durable-press fabric. As with the flame retardants, there is now

no one soil release finish that is suited to all fabrics and to all end uses.

COTTON BATTING: A NEW NONWOVEN CUSHIONING MADE WITH LOW GRADE FIBERS

Commercial production of a new nonwoven product--an improved cotton batting--for cushioning uses has been made possible by the Cotton Flote process.

Experiments conducted by the U.S. Department of Agriculture's Southern Regional Research Laboratory in New Orleans show that the process permits profitable employment of low grade cotton fibers--a blend of first cut cotton linters and a mixture of textile wastes (60% linters--40% textile waste).

The fibers can be used as received without costly preprocessing (scouring, bleaching) even though they may be highly contaminated with waxes, pectins, oil, and other extraneous foreign matter.

This new nonwoven product can be produced in conventional cotton batting processing lines by adding two new unit operations--spraying and drying-curing.

In essence the Cotton Flote process involves spraying on a web of cotton fibers a formula containing both thermoplastic and thermosetting resins, a catalyst, and a buffer. After this, the spray-damp webs are lapped or laminated to the desired thickness and then the product is dried and cured.

The key feature is the simultaneous application of both thermoplastic and thermosetting resins from a single solution. Such an arrangement improves the resilience of the fibers and bonds the fibers together at points of contact to enhance dimensional stability, tensile strength, and integrity.

The spray in the laboratory's experiments was applied immediately following garnetting and preceding lapping. The treating formulations used for products with nominal density of 2 pounds per cubic foot consisted of about equal proportions of thermosetting resins of the urea-formaldehyde, melamine, or imidazolidone types with thermoplastic resins of the vinyl acetate, vinyl acrylate, or styrene butadiene types. The optimum solids concentration in the formula is 20% and the wet add-on is 100% by weight of the cotton fibers being treated.

Adequate but not excessive curing is needed to assure best product performance characteristics. Inadequate or overcuring can result in the formation of odorous by-products that would be objectionable in automobile seat cushions, furniture, or mattresses. The use of buffers or formaldehyde acceptors in the treating solution practically eliminates the possibility of odors in the product if they are properly cured.

Because the process is versatile, a wide range of products exhibiting various degrees of resilience, tensile strength, dimensional stability, and integrity can be engineered to meet end-use requirements for specific applications by altering one or more process conditions.

Density can be controlled over the range of 1.5 to 6 pounds per cubic foot or higher by varying the web weight, the speed of the lapping conveyor, the number of webs, the ratio of thermoplastic to thermosetting resin, and the amount of compression exerted on the products by the hold-down conveyor during drying and curing. In addition, such characteristics as hand can be varied by controlling the drying conditions. Where a harsh skin effect is desired, it can be achieved by providing conditions conducive to resin migration. Such conditions include drying air temperatures in excess of 225° F. at a humidity of less than 5% at velocities greater than 200 feet per minute during initial phases of drying.

For a soft hand, the following conditions (under which practically no resin migration occurs) would be appropriate: air temperatures of 180° F., a humidity of greater than 10% and air velocities up to 150 cubic feet of air per square foot per minute (17-20).

Cotton Batting Products that Comply with the Mattress Flammability Standard and the Proposed Upholstered Furniture Flammability Standard

On June 7, 1972, the U.S. Mattress Flammability Standard FF 4-72 issued. Legal and other considerations delayed the implementation of the standard until December 22, 1973. At present, a proposed standard for the Flammability of Upholstered Furniture is being considered by the U.S. Consumer Product Safety Commission. While the titles of these standards imply that the products resist flaming combustion, they only require that mattresses and upholstered furniture resist ignition by lighted cigarettes. Research at the Southern Regional Research Center disclosed that cotton batting products that had been impregnated with classical flame retardants, both inorganic and organic types, and which could easily pass a vertical flame test, would fail when installed in mattresses and subjected to a test where lighted cigarettes were the igniting source.

There are fundamental differences in the mechanism of oxidative degradation that results from open flame ignition and flaming combustion, and the mechanisms smoldering combustion that follows the cigarette induced combustion of mattress structures.

Flaming combustion is characterized by a rapid oxidation of degradable material. Flaming takes place in the gaseous phase. It involves the combustion of gaseous by-products from the degradation of the material and is visually observed by the light generated. Classical flame retardance theory envisions an interference with the course of pyrolysis by reducing the amount of flammable gases produced and concurrently increasing the amount of solid by-products such as char. Because the flaming reaction provides heat to degrade the material, suppression of the production of combustible gaseous by-products reduces the production of thermal energy. The combustion subsides, since there is insufficient thermal energy to sustain it.

Smoldering combustion is characterized by a direct oxidation of solid material in the solid state. It proceeds at a very slow rate in comparison with flaming combustion. In smoldering combustion, very little visual light is generated. The temperatures at which smoldering combustion takes place are usually about 200° F. higher than occur in flaming combustion.

It is important to recognize that the terminology applied to pyrolysis and combustion is sometimes misleading. For example, the term "afterglow" is frequently applied to smoldering combustion. This implies that smoldering combustion is a sequel to flaming combustion, whereas smoldering combustion is different from, and unrelated to, flaming combustion. Where smoldering combustion becomes apparent after flaming subsides, the flaming reaction simply provided the energy to initiate smoldering. Smoldering could be induced by a cigarette, an electrical probe, or other flameless source of thermal energy.

Chemical treatments that impart flame retardance by changing the course of pyrolysis to yield increased amounts of char and solid by-products are ineffective in the prevention of smoldering as it occurs in cotton mattresses. The inability to inhibit smoldering is due to the fact that such flame retardants provide more solid fuel for the smoldering combustion reaction.

When a lighted cigarette is placed in contact with a cotton mattress and ignition occurs, the combustion is of the smoldering type. Smoldering combustion in mattress structure is self sustaining in atmospheres containing as little as 1% oxygen if the temperature within the structure exceeds 750° F. This temperature is easily attained. In fact, localized temperatures in mattresses undergoing smoldering combustion frequently exceed 1100° F., even where conventional flame retardants have been used to treat the batting. Such high temperatures are sustained for long periods of time, because the mattress structure consists of an excellent insulator, the cotton batting, and the ticking cover which further reduces convection, conduction, and radiation of heat. Where the temperatures within a mattress undergoing smoldering combustion are consistently above 750° F., most conventional phosphorus-containing flame retardants are broken down chemically. Thus, they are unable to provide smolder or glow resistance. The ticking per se usually plays little part in the ability of a mattress to resist cigarette ignition. Certain polymers used as back-coatings for ticking fabrics can improve the resistance of the mattress structures

to cigarette ignition, particularly where treatment for the filling batting is marginal.

Thermal analysis and minimattress evaluations on cotton batting treated with chemical systems containing boric oxide donors showed that such compounds would impart smolder resistance to cotton batting sufficient to pass FF 4-72. An add-on of about 4% by weight of boric oxide was needed. Boric oxide is generated by the thermal degradation of such compounds as sodium borate (borax), boric acid, ammonium pentaborate, or zinc borate. Subsequent research showed that the use of borax (sodium borate) was undesirable, because the sodium ions catalyze the oxidation of carbon in the solid state, and that boric acid was the treatment of choice. A continuous wet-pad-dry process to impregnate fibers was developed.

Processing research showed that where the boric oxide donor was applied from a wet system, the drying operation was critical. The criticality of the drying operation stems from the relationship of the vapor pressure of the boric oxide donor (especially boric acid) to the humidity and the temperature of drying. For this reason, solvent systems using alcohols or alcohol-water mixtures were evaluated as a means of impregnating the fibers with boric acid. Methanol, ethanol, isopropanol, and glycerol as pure compounds or as water mixture were used as the solvent for the boric acid. The formulations were padded onto the rawstock or the finished batting and then dried, or alternatively the formulations were sprayed onto webs from garnetting which were lapped into batting and then dried. Problems were again encountered in the drying operation because of the formation of volatile borate esters.

An examination of the chemistry involved disclosed that boric acid readily forms highly volatile esters with both ethanol and methanol. Calculations showed that the losses of boric acid during the drying of batting treated with formulations containing methanol or ethanol and boric acid were probably due to the formation of esters which were in effect distilled off during the drying operation. This analysis of the physical chemistry provided a basis for the hypothesis that it might be possible to eliminate the wet processing of the fibers simply by exposing them to the vapors from methyl or ethyl borate and utilizing the reversible nature of the chemical reaction to accomplish the deposition of boric acid on and within the cotton fibers.

This concept was proved viable and feasible when samples of cotton batting or cotton batting rawstock were exposed to the vapors emanating from either methyl or ethyl borate formed by dissolving boric acid in either methanol or ethanol. In this procedure, the fibers were suspended above the solution that supplied the vapors. At no time were the fibers in contact with the liquid; consequently, no drying was needed. The boric acid add-on achieved by exposure of the fibers to the vapors of methyl or ethyl borate was found to be dependent upon their moisture content when they were first exposed to the vapors. Increasing the temperature of the vapors did not significantly improve the efficiency of the conversion of methyl borate to boric acid and methanol when the vapors contacted the moisture in the fibers.

The batch vapor phase procedure to impregnate cotton batting with boric acid was converted to a continuous process. A pilot plant processor was designed, constructed, and test operated. For continuous operation, methyl borate was found to be the most suitable source of vapors. Products containing 5% boric acid add-on obtained by the vapor phase process consistently pass FF 4-72. Conditions for this add-on at ambient temperature and pressure seem to require 0.149 gm./l. volume of boric acid in the vapor, a vapor velocity of 100 ft./min., an initial cotton moisture content of about 8 to 10%, and a residence time of about 2.4 minutes. Additional research is under way to investigate other process variables and to reduce the residence time.

Continuous treatment was carried out on both cotton batting and roughly opened rawstock. Boric acid add-on obtained was dependent upon exposure time, initial moisture content of the fibers, vapor concentration of methyl borate, and the amount of fibers being processed at any given time. Some gradient in the add-ons obtained were found with add-ons decreasing in the path of the vapor flow through the fibers being treated. If rawstock is treated the mechanical manipulation of the fibers will tend to even out the nonuniformity in add-on (21, 22).

OTHER TECHNIQUES IN COTTON FINISHING

Techniques for finishing cotton are too numerous to even try to mention in this short space, so I will limit my comments to four areas of finishing research: (a) mildew and rot resistant cotton, (b) stretch cotton yarns and fabric, (c) oxidation, and (d) multifunctional finishing.

Rot and Mildew Resistance

Although we already have many mildew and rot resistant finishes, they have weaknesses or limitations. Some are very expensive; some have disagreeable odors; some are not effective enough. Therefore, we have undertaken a study to develop better mildew and rot resistant finishes which are needed for many products used outdoors such as tents, tarpaulins, and awnings.

We have recently found that certain zirconium compounds can solubilize many normally insoluble antimicrobial agents. For best mildew and rot resistance these agents must be put into the cotton fabric in a form that resists removal by leaching. Thus, the antimicrobial agent is dissolved in an aqueous zirconium solution, padded in fabric, and finally heated to about 115° C. to decompose the solubilized compound and to deposit the antimicrobial agent and zirconia as an essentially insoluble product. This process has been used to treat cotton fabrics with several antimicrobial agents. The technique appears to have opened a new and attractive approach for finishing cotton fabrics.

Fabric treated with zirconyl ammonium carbonate and copper borate and subjected to weathering retained over 50% of its strength after 12 months exposure and was essentially free of mildew. Incorporation of this finish with a water repellent and suitable light-screening pigments should give outstanding weather resistance. The chemical cost of this finish has been estimated to be about one-third of the cost of a commonly used finish, copper 8-quinolinolate, and it is just as effective and just as easily applied. The market potential for cotton fabrics finished with antimicrobial agents is estimated to be equivalent to 265,000 bales of cotton. The major potential is for tarpaulins, shoe linings, and tents.

Stretch Fabrics

We have conducted research in a very broad spectrum with respect to both yarns and fabrics. I shall limit this discussion to only one approach for making yarns and one for fabrics. Stretch yarn is produced by wetting the original plied yarn with an aqueous solution of a crosslinking agent used to produce wash-wear properties, twisting the yarn to a very high degree, then heating to promote reaction of the chemicals with the cotton. Finally, the yarn is backtwisted to a considerable degree.

This stretch yarn can be woven into fabrics. Woven fabric can have about 70% stretch with good recovery. Such fabrics compete favorably with high stretch fabrics made from textured synthetic fibers. Fabrics woven from cotton stretch yarn have large potential market. Most of this potential is in apparel goods, although a small amount would go into household and industrial uses.

Now we shall discuss a process for treating fabric to impart stretch. This process, called slack or tensionless mercerization, is a very simple technique--at least it can be described very simply. The process amounts to immersing either woven or knit goods in a solution of sodium hydroxide of about 23% concentration, allowing the material to shrink, then washing and drying it at constant dimensions. The amount of shrinkage that occurs during the caustic treatment is closely related to the stretch properties that are later observed in the fabric. It is easy to get shrinkage; it's easy to get stretch; the difficulty is in producing a stretch fabric having good recovery properties. In other words, recovery is the important thing that had to be accomplished through research. This has been accomplished for woven cotton fabrics through use of the proper yarn and fabric structures and suitable processing.

Some of the more important points to keep in mind for the production of one-way stretch fabrics include the following:

1. Use singles yarn in preference to plied yarn.

2. Use high twist yarn in preference to low twist.

3. Reed out fabric 5-20%.

4. Increase the number of yarns per inch in the filling, rather than decrease.

5. Use larger warp yarn than filling yarn.

6. Use 23% NaOH at less than 50° C.

7. Maintain warp tension through the wet processing.

8. After mercerization, wash and dry fabric at constant dimension.

Stretch fabrics made by slack mercerization generally are significantly more resistant to abrasion than similar nonstretch cotton fabric--as much as a fourfold increase for some fabrics. However, tensile and tear strengths are generally unchanged by the slack mercerization process. For most apparel uses, a wash-wear finish must be applied to the stretch fabric not only to impart wash-wear properties but also to improve the recovery properties. On the average, apparel-type fabrics have about 15% stretch after slack mercerization and the application of a wash-wear finish. The term "stretch" is the elongation obtained when a 2-inch strip of the fabric is loaded with a 4-pound weight.

Total operating costs for producing fabrics with filling stretch have been estimated at about one cent per square yard while two-way stretch fabrics are estimated to cost about four cents per square yard. These figures include direct costs, indirect costs, fixed costs, and general expenses based on an annual production of 20 million yards of filling stretch fabrics and 5 million yards of two-way stretch fabrics.

All-cotton stretch hose can be made by slack mercerization. The method being investigated consists of slack mercerizing very loosely knit hose. The hose are knit about twice the normal length but with the same number of courses. For best results, the hose should be knit on a cylinder approximately 25 to 30% narrower than normally used, as there is little or no shrinkage in the width of the hose during slack mercerization. The loosely knit hose is then slack mercerized, bleached, and dyed. A softer hand is obtained by mercerizing in 15% caustic and by applying a softener after dyeing. Low twist yarns spun from long staple cotton are also recommended to give a softer hand. Approximately 50% shrinkage in the length occurs during mercerization of grey hose.

These cotton socks have the properties of a good cotton. They are absorbent; they feel good; they do not bind the leg; they merely cling lightly to the leg. The socks grow somewhat during the day's use but it returns to its original size each time it is washed.

Sculptured cotton lace can also be prepared by the differential shrinkage treatment using slack or tensionless mercerization (24, 25, 26). Almost all laces with any raised or three-dimensional effects are made by first weaving the design in a flat figured fabric and then reworking by hand or machine with thread, cord, tape, ribbon, etc., over parts of the design. This is an expensive process, adding considerably to the price of the finished lace, but necessary for the rich, three-dimensional effect.

The results of recent research at this laboratory show that heavy three-dimensional laces with a reembroidered, textured appearance may be produced from relatively flat inexpensive laces by differential shrinkage treatments. This should be of great importance to the high fashion lace industry. In addition to having a richer, handsomer, and more expensive appearance, the laces have increased toughness, improved dimensional stability, and comfort stretch properties.

The basic requirement of the slack mercerization process is that the lace be permitted to shrink in both lengthwise and widthwise directions without restrictive tensions. Lace is permitted to shrink in a 22-25% NaOH solution at 110° F. for 3 to 5 minutes and washed to remove the caustic.

In wearing apparel, most laces can only be dry cleaned, and for lace this is an expensive process. Laundering is preferable for cotton laces but can very rarely be done without irreparable damage due to shrinking. However, a slack mercerized, resin-finished cotton lace garment can be safely home laundered.

Oxidation

Since the discovery by Criegee that saturated alcohols are oxidized by lead tetraacetate, this reaction has been applied intensively in the field of carbohydrate chemistry (23). However, very few oxidations of polysaccharides with lead tetraacetate are reported in the literature, and in all these cases the consumption of the oxidant was very small. By optimizing the reaction conditions, we have increased significantly the rate of oxidation of cotton by lead tetraacetate. Acetic acid solutions of lead tetraacetate are very stable under the conditions used. Use of sodium acetate as catalyst, elevation of the temperature at which the reaction was carried out, and increasing the concentration of lead tetraacetate increased the rate and amount of oxidation of the cotton (from 1.1% to as high as 33.5% oxidized). Samples which were 13% oxidized were completely soluble in 10% aqueous NaOH. This could be done in within 15 minutes. Oxidized cotton samples, after treatment with 3% NaBH4 which converts carbonyl groups to hydroxyl groups, showed no ion exchange capacity. The solubility of the fabric is attributed to the presence of aldehyde groups with concurrent carbon bond scission in the cellulose. In contrast to periodate oxidation of cotton, the fabric imparted no increase in dry wrinkle recovery angle. The wet wrinkle-recovery angle for the oxidized cotton was 38 to 40° higher than the control (27).

Multifunctional Finish for Cotton

A simple means of combining color and crease resistance to cotton fabric using conventional dyeing or finishing equipment has been the object of several recent investigations. We have found that color and wrinkle resistance, which is not removed by acid or alkaline treatment, can be imparted to cotton simultaneously by treatment with aqueous solutions of compounds containing aziridinyl groups and mono- or dichlorotriazine dyes. The reactions take place in an acid system, and the reaction with aziridinyl derivatives is believed to be in two steps. One involves the formation of an immonium ion by protonation, and in the second step the ring is opened by a suitable nucleophilic agent yielding the colored addition product. Simultaneous application of the dye and the crosslinking agent, both in the laboratory and the pilot plant, has resulted in brightly colored crosslinked fabrics which have durable colorfastness and wash-wear properties.

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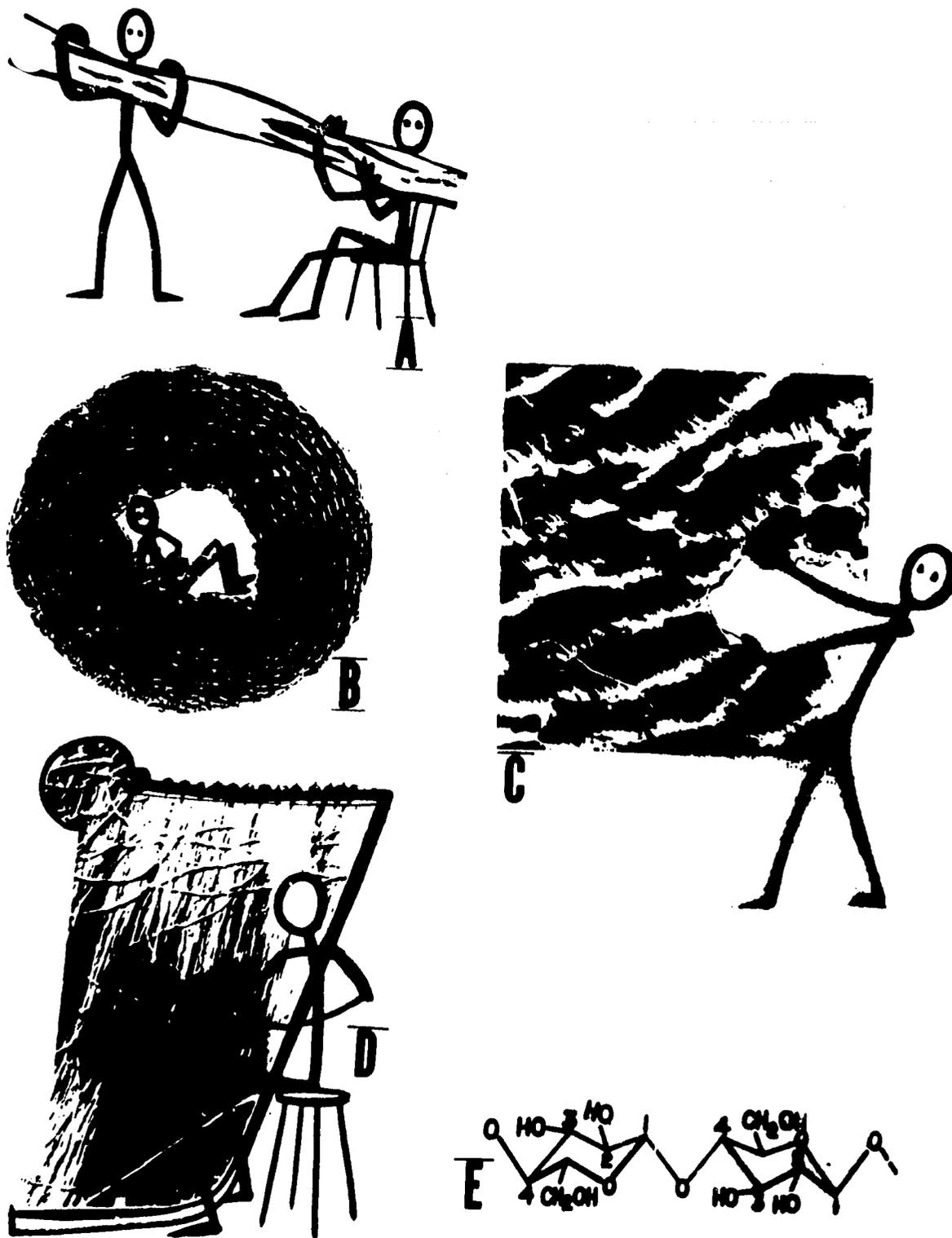
Figure 1

Features of the cotton cellulose fiber that are involved in the cross-linking reaction: A--a section of a fiber; B--an electron micrograph of an expanded cross section of a cotton fiber; C--a portion of the expanded cross section under highest magnification; D--an electron micrograph view of the longitudinal structure and microfibrils in a slab torn from a cotton fiber; and E--two D-glucopyranosyl units which constitute a portion of the molecular chain of cellulose.

$$(HOCH_2)_2PCH_2OCH_2OH$$

$$(HOCH_2)_4PCl + NaOH \longrightarrow (HOCH_2)_3P + CH_2O$$

$$(HOCH_2)_3P^+CH_2O^-$$

Figure 2. Neutralization of THPC.

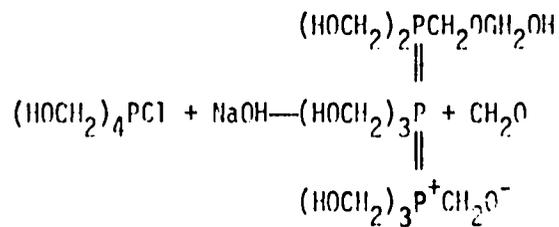| PAD ON THPOH | TENTER (TO DRY) | NH_3 CHAMBER (TO PRODUCE POLYMER) | WASH AND OXIDIZE | DRIER |
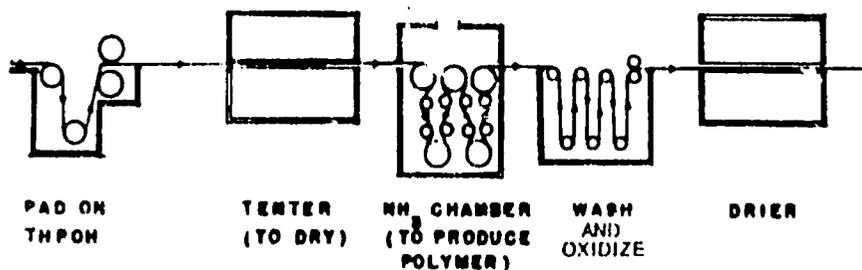
Figure 3. Schematic diagram showing the basic steps in the THPOH-NH_3 process.
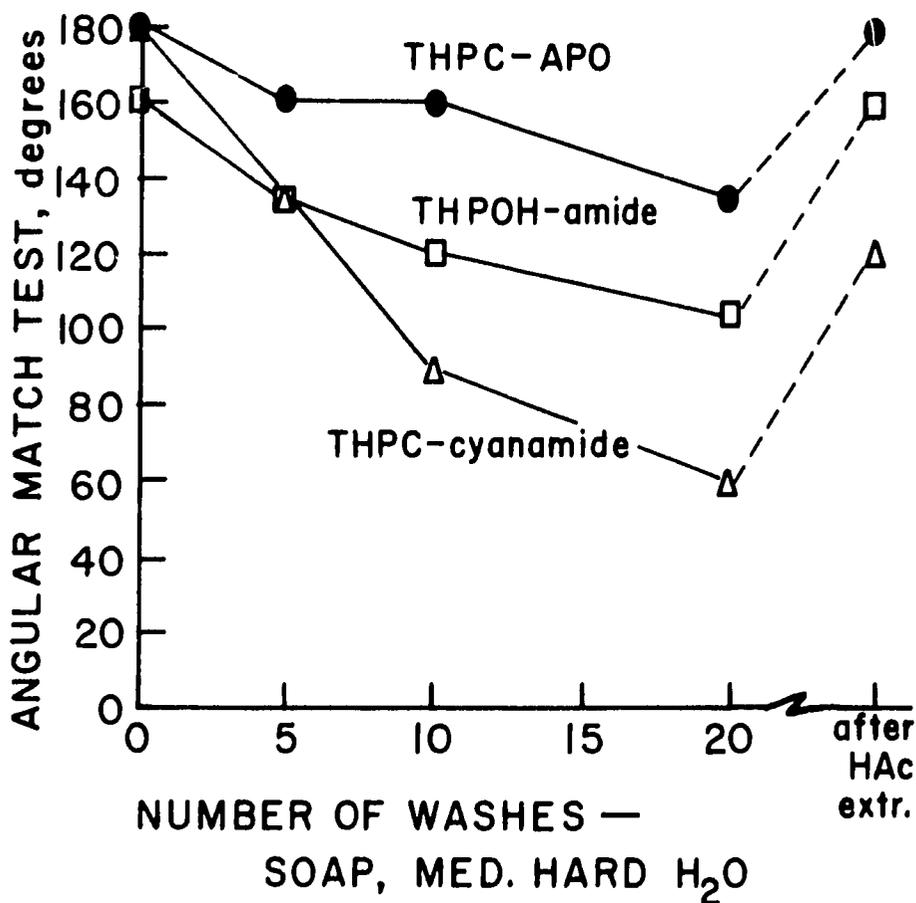
Figure 4. Flame resistance of three cotton fabrics after repeated laundering and after acetic acid extraction.

Figure 5. Effect of multiple laundering on aqueous soil resistance of
cross-linked CMC fabrics.

Figure 6. Effect of multiple laundering on oily soil resistance of cross-linked CMC fabrics.

Figure 7. Effect of multiple laundering on aqueous soil removal from cross-linked CMC fabrics.

Figure 8. Effect of multiple laundering on oily soil removal from cross-linked CMC fabric.

Studies on Chemically Modified Celluloses

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Chemical modification of cotton to impart new and improved properties to it while retaining its fibrous character has lon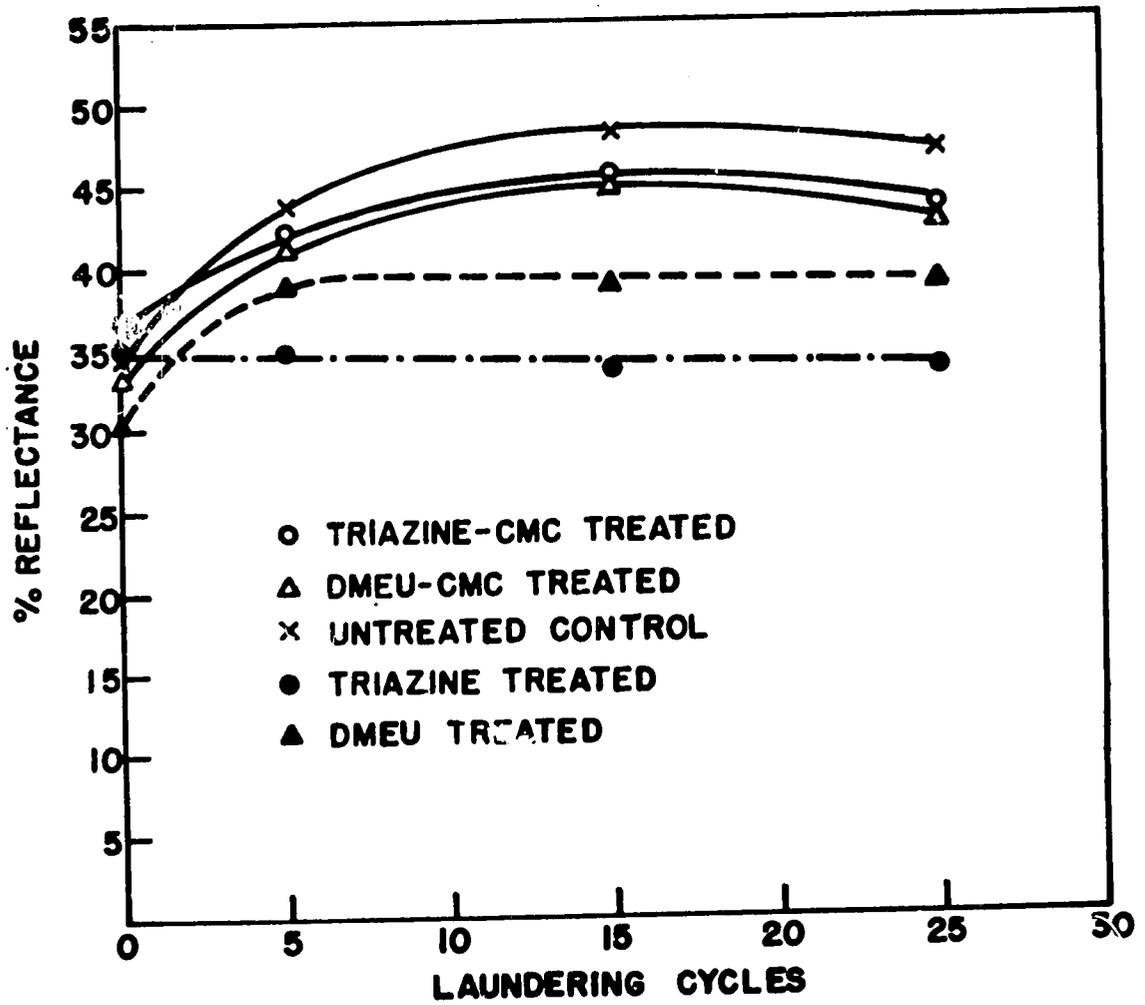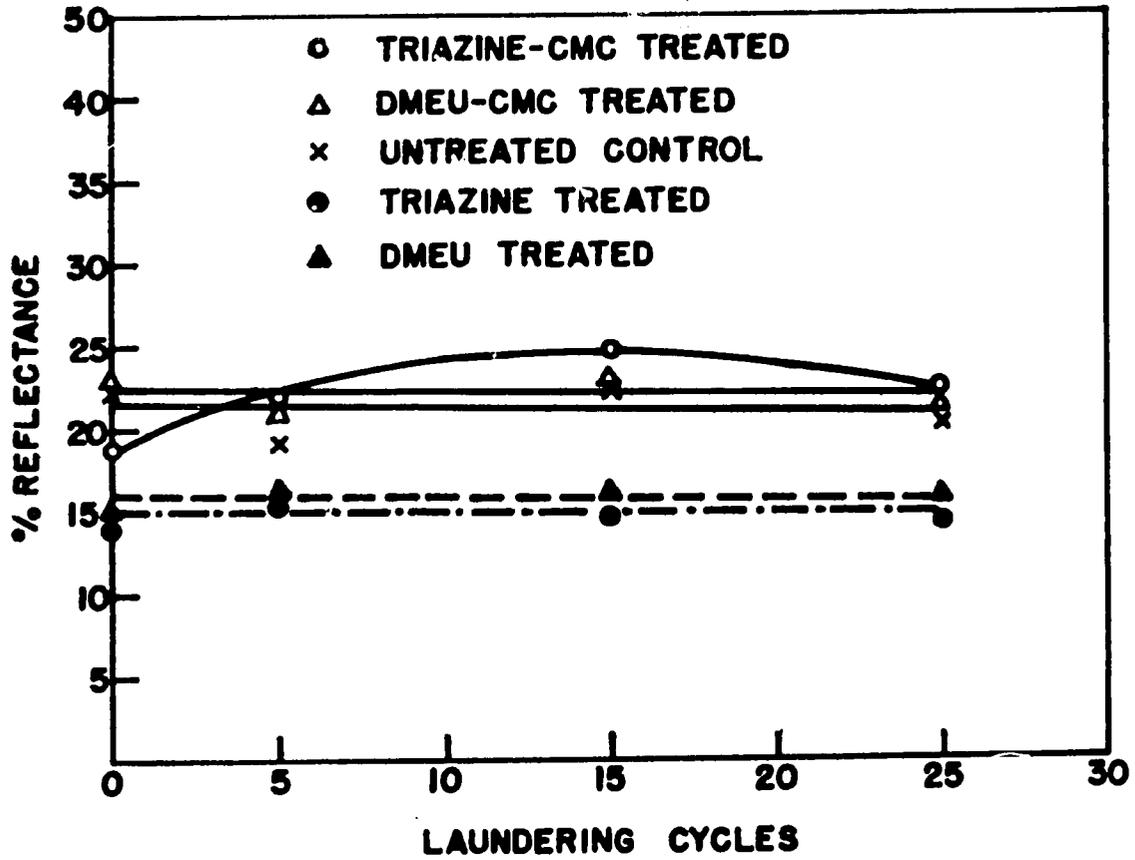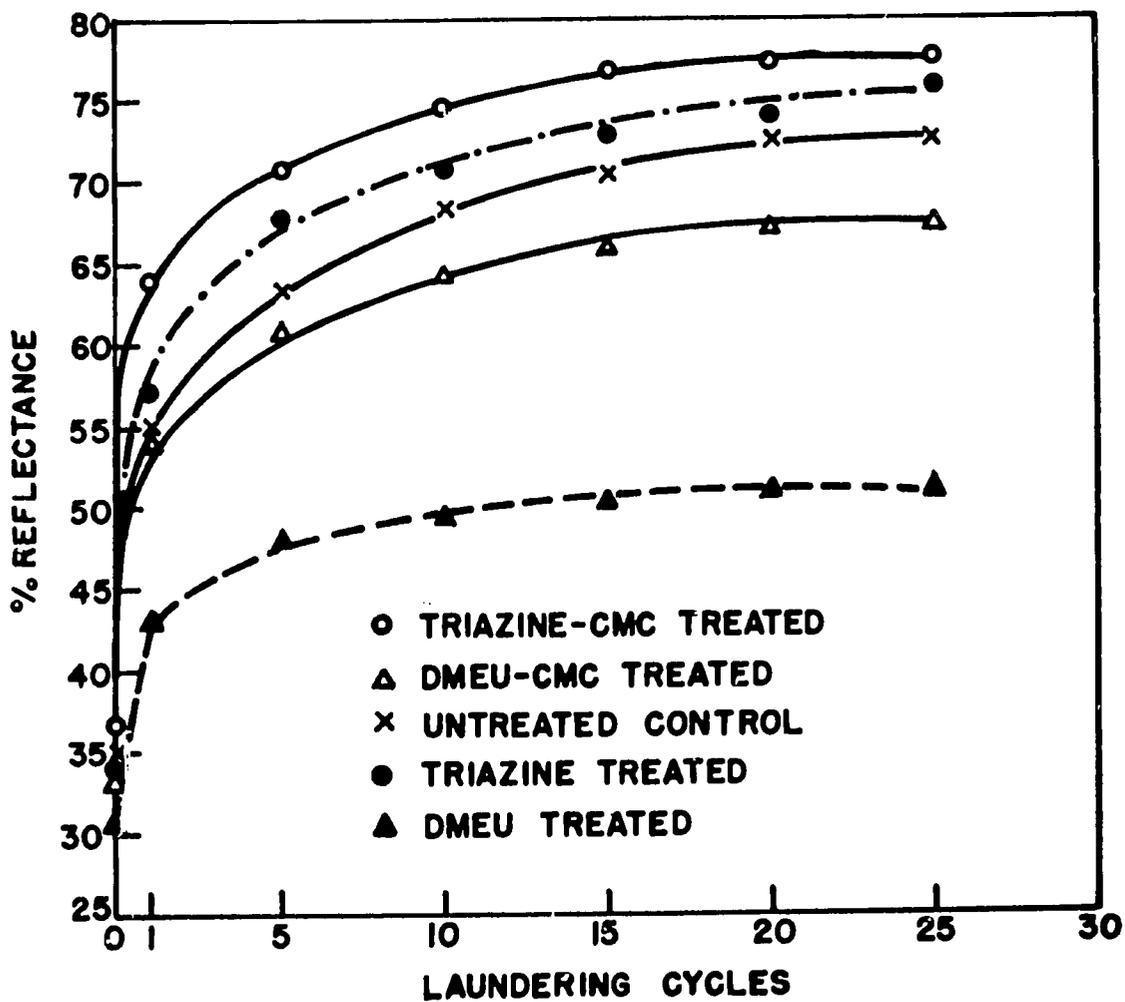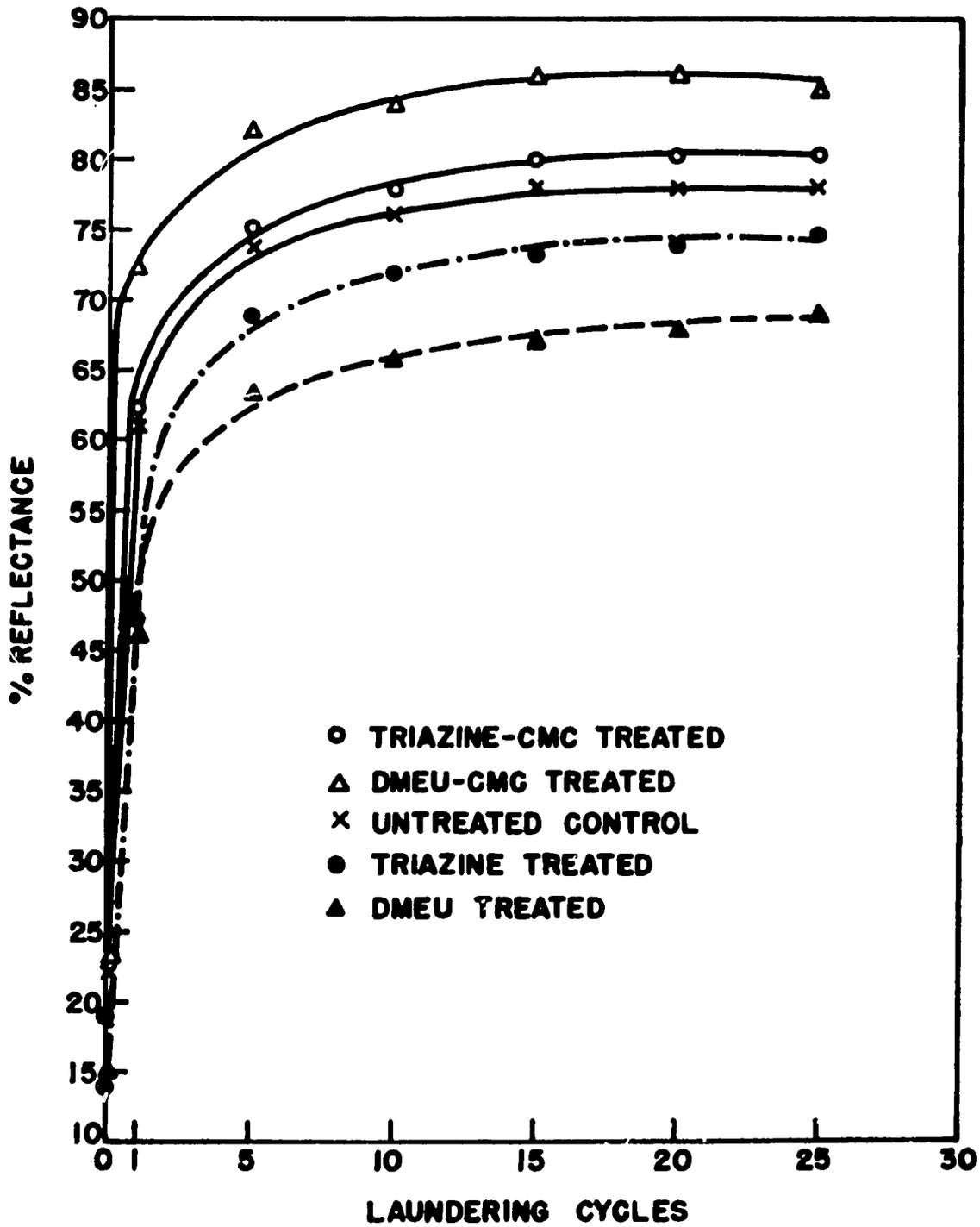g been the objective of many investigators. This report presents a summary of and main conclusions arrived at from the major studies on chemical modification of cellulose that have been carried out in the Textile Research Division, National Research Centre, during the past 15 years.

PARTIAL CARBOXYMETHYLATION

Semicontinuous and continuous methods (1-3) have been introduced for the preparation of partially carboxymethylated cotton (PCMC) with adequate degree of substitution (DS). The general procedure involved padding with chloroacetic acid or sodium chloroacetate followed by padding with sodium hydroxide. Thus, the dry cotton fabric was padded with chloroacetic acid or its sodium salt of specified concentration (0.5-6N) to a wet pickup of about 75%. The fabric was padded again with sodium hydroxide solution of different concentrations (9, 12, and 16N) to a wet pickup of about 140%. Completion of the reaction was achieved by any of the following methods: (1) the padded fabric was rolled and stored at room temperature for varying periods (1-24 hrs.); (2) the padded fabric was wet steamed for 5 min., the other conditions being the same as in method (1); (3) the fabric was given the same treatment as in (2) but was used as such without storage; (4) the fabric after storage for varying periods was placed between two hot plates and then kept at 100°-160° C. for 5 min.; (5) the fabric was subjected to the same treatment as in (4) but was used as such without storage; (6) the fabric was padded with chloroacetic acid as in (1-5) and then treated in a laboratory jigger with sodium hydroxide solution (material-liquor ratio 1:25) for 1 hr. at room temperature. The fabric was then squeezed, washed, neutralized with 1% HCl for 5 min., washed, treated with 2% NaHCO$_3$, washed again to neutrality, and finally dried.

Factors affecting the partial carboxymethylation of cotton were investigated (4). The DS of PCMC increased by increasing the chloroacetic acid concentration up to 3N. Beyond this no increase in DS was observed. In contrast, the DS increased by increasing sodium chloroacetate concentration. The effect of increasing sodium hydroxide concentration was to bring about considerable enhancement in DS of PCMC. The DS was also dependent on the method used for preparation of PCMC.

The effect of the nature of the padding techniques followed and the different variables involved (concentration of reagents, duration of storage, and temperature) on the degradation of cotton cellulose during its partial carboxymethylation have been investigated, taking the degree of polymerization (DP) and copper number as the criteria for the extent of degradation (5). Whatever the padding technique followed, there was a slight decrease in the DP and slight increase in the copper number of PCMC. Increase in sodium hydroxide concentration caused a decrease in the DP and an increase in the copper number. Increase in chloroacetic acid and its sodium salt concentrations was accompanied by a slight increase in the DP and a slight lowering in the copper number. Increasing the storing period was accompanied by a gradual decrease in the DP and a gradual increase in copper number. Baking temperature had practically no effect on the DP and copper number values.

Partial carboxymethylation of a polyester/cotton blended fabric was studied under a variety of conditions using the padding techniques and aforementioned methods (6). Partial carboxymethylation was accompanied by a decrease in the polyester component of the blend. The decrease was influenced favorably by the increase in the concentration of

carboxymethylating agents, storage time, and conditions of baking. The modified blend fabric showed a significant improvement in moisture regain and a substantial loss in tensile strength (6).

Trials have been made to introduce the partial carboxymethylation in the wet processing of cotton fabrics with a view of omitting desizing and mercerization and thereby reducing conventional operations commonly used in the wet processing (7). Furthermore, partial carboxymethylation of scoured cotton fabric was carried out so as to give PCMC having different DS's. These modified cotton samples were bleached with sodium hypochlorite and sodium chlorite and compared with bleached scoured and alkali-treated controls. The bleached substrates were analyzed for total size, carboxyl content, copper number, DP, tensile strength, elongation at break, degree of whiteness, and wettability. The comparison indicated that the properties of PCMC were comparable, if not superior, to alkali-treated control. The same situation was encountered with respect to dyeing with reactive dyes and easy care finishing with dimethylol ethylene urea (8).

The behavior of PCMC towards acid hydrolysis, oxidation, acetylation, and nitration was studied (9). PCMC resisted acid attack to a greater extent than alkali-treated controls, and the resistance to acid attack increased with increase in DS. Acid hydrolysis of PCMC was accompanied by a decrease in the carboxyl content, which increased with the increase in the duration of hydrolysis. The resistance of PCMC samples to oxidation by sodium metaperiodate was more than that of alkali-treated samples; oxidation by sodium metaperiodate did not affect the carboxymethyl content of the samples. The carboxyl content increased to the same extent in both modified and alkali-treated controls for the same amounts of oxygen consumed. The rate of acetylation of PCMC was much lower than that of alkali-treated control. The extent of esterification of PCMC decreased with increase in DS. Nitration of PCMC was accompanied by a decrease in its carboxyl content, but acetylation had no such effect. The decrease in carboxyl content of PCMC as a result of nitration was explained on the basis of decarboxylation reaction.

ACRYLAMIDOMETHYLATION

The pad-dry-cure method and the pad-wet-batch method have been applied to preparation of acrylamidomethylated cellulose (AMC). The latter was prepared by reacting cotton cellulose with N-methylolacrylamide or its ethers in acidic medium under a variety of conditions (10). The extent of the reaction, expressed as a mole double bond per 1g cellulose, increased by increasing the concentration of N-methylolacrylamide or its ethers. However, the pad-dry-cure technique produced AMC with greater amounts of double bonds than the pad-batch technique. Also, the reactivity of the etherifying agents follow the order N-methylolacrylamide > N-methoxymethylolacrylamide > N-methoxymethyl-methacrylamide.

The behavior of AMC in neutral, alkaline, and acidic media was studied (10). No change in the amount of the pendent double bonds of AMC occurred in neutral medium regardless of the conditions employed. On the contrary, disappearance of the double bonds took place in alkaline medium. The extent of disappearance depends on the kind of alkali used as well as on the conditions implemented. It was disclosed that consumption of the pendent double bonds of AMC occurred mainly via addition of the cellulose hydroxyls to yield a crosslinked cellulose. Treatment with hydrochloric acid, on the other hand, resulted in partial splitting of the acrylamidomethyl groups as well as addition of the acid on the pendent double bonds of AMC.

ACETYLATION

Fibrous acetylation of the cotton component in the polyester/cotton blend was carried out at room temperature using a mixture of acetic anhydride and benzene (6:94) for 1 hr. and a liquor ratio of 1:30. Perchloric acid in glacial acetic acid (1%) was used as catalyst (11). The modified substrates were dyed under various conditions with a number of disperse dyes by either the exhaustion method or the pad-thermofixation method. It was found that the values of color strength for the modified substrate were much greater than the corresponding values for the unmodified blend. The overall fastness properties of the

dyed blend before and after modification were comparable, indicating that acetylation prior to dyeing had practically no adverse effect on the fastness properties of the dyed goods.

INTRODUCTION ON AROMATIC AMINO GROUPS

A novel method for preparation of cellulose bearing aromatic amino groups by reacting cotton cellulose with 2,4-dichloro-6-(P-nitroanilino)-S-triazine in presence of alkali and subsequent reduction of nitro groups to amino groups was described (12). The technical procedure adopted was as follows: The cotton fabric was padded in an acetone solution containing 1% of the triazine and 2% NaOH to a wet pickup of about 80%. The fabric was then heated for 5 min. at 90° C. After being thoroughly washed and dried, the fabric was treated with thiourea dioxide (5%) at pH 8 at room temperature. The temperature was then raised to 80° C. and the treatment was continued at this temperature for 5 min. The fabric was then thoroughly washed, dried at ambient conditions, and analyzed for nitrogen.

Factors affecting the extent of the reaction, expressed as percent nitrogen, were also studied. The extent of the reaction was found to depend upon alkali concentration, duration of heating, and reaction temperature as well as reaction medium.

INTRODUCTION OF CARBAMATE GROUPS

Cellulose carbamate was prepared by reacting urea with cotton cellulose (13). Cotton fabric samples were impregnated in aqueous urea solutions (5-80%) for 10 min. at room temperature using a liquor ratio of 1:30. Following this, samples were squeezed to give a wet pickup of about 100%. They were then air dried and subjected to heat treatments (80-180° C.) for 30 min. After that period, the samples were thoroughly washed and dried.

The behavior of cellulose carbamate toward acid, alkali, and thermal treatments was examined (13). Cellulose carbamate having a nitrogen content of 1.6% withstands boiling in 2% sulfuric acid for up to 2 hrs. and was stable to thermal treatment at 180° C. for up to the same time. In contrast, boiling in dilute alkali causes hydrolysis of the carbamate groups. The extent of hydrolysis depends on alkali concentration and temperature of the treatment.

Reaction of cellulose carbamate with p-nitroaniline was investigated by adopting three techniques (13). The first involved padding of cellulose carbamate with p-nitroaniline dissolved in acetone and then drying and baking at 180° C. The second entailed padding cotton fabric in an aqueous urea solution, drying, then padding in a solution of p-nitroaniline in acetone, drying, and baking. The third technique consisted of padding cotton fabric in a solution containing urea and p-nitroaniline dissolved in an acetone/water mixture, then drying and baking. The three techniques were found to bring about identical extent of reaction. The latter relies on concentrations of urea and p-nitroaniline as well as on the temperature and duration of baking. While a concentration of 60% constituted the optimal urea concentration, the extent of the reaction increased as p-nitroaniline concentration increased. No reaction occurred below a temperature of 120° C. Above this the extent of reaction increased by raising the baking temperature to 180° C., which was the highest temperature used. The same holds true for reaction time, except that the rate of the reaction does slow down with time. A tentative mechanism of the reaction was suggested. Reaction of cellulose carbamate with p-nitroaniline seems to occur via direct condensation of the amino group of p-nitroaniline with the carbamate groups of cellulose carbamate.

The reaction product of cellulose carbamate with p-nitroaniline could be used to bring about a set of different colors by subjecting it to reaction, diazotization, and coupling with different coupling agents. Trials to replace p-nitroaniline with o-nitroaniline and aniline were also made (13).

GRAFTING

Work on vinyl graft polymerization onto cotton and modified cottons deals with the following aspects:

1. Effect of the fine structure of cellulose on the grafting reaction.

2. Effect of changes in the physical and/or chemical structure of cotton cellulose brought about by etherification, esterification, crosslinking, and oxidation.

3. Feasibility of a number of initiators which have been suggested or actually used for vinyl polymerization in inducing graft polymerization of vinyl monomers onto cotton and modified cottons.

4. Characterization and properties of cellulose graft copolymers.

Fine Structure

The effect of the fine physical structure of cellulose on the general kinetics of the grafting reaction has been studied (14-15). No direct relation could be obtained between the accessibility of cellulose and the graft yield per cent when grafting was induced by both the chemical (15) and the radiation method (17). A linear relation could only be obtained by suitably modifying the grafting method to suppress homopolymerization.

Substrate Structure

The behavior of chemically modified celluloses, brought about by etherification, esterification, crosslinking, and oxidation toward grafting was shown to depend essentially upon the influence of newly created or introduced groups on the properties of cellulose. Among these are:

A. Variation in the fine structure (perhaps the cellulose is held in an open state).

B. Swelling of cellulose.

C. Availability and accessibility of the cellulose hydroxyls to reaction.

D. Reactivity of the cellulose hydroxyls in the presence of the newly created or introduced groups.

E. Specific localization of the newly created or introduced groups on the anhydroglucose unit of cellulose.

F. The type of reaction between the cellulose and initiator (whether specific or or nonspecific).

G. Reactivity of the introduced group with the initiator.

H. Affinity of the monomer to modified cellulose.

In general, if the introduced groups increase the magnitude of A, B, C, and D or if they act as additional sites for grafting (i.e., G), grafting would be greatly enhanced. Among the modified cottons which constituted examples of this were partially carboxymethylated cotton (PCMC) (18, 19), cyanoethylated cotton (19, 20), carbamoylethylated cotton (19), and cellulose carbamate (21). Conversely, lower grafting would occur if the introduced groups adversely affect the reactivity of cellulose hydroxyls. The same situation would be encountered if the groups of the chemically modified cellulose take place at the same carbon atom in the anhydroglucose unit of cellulose, the hydroxyl groups of which are liable to react specifically with the initiator. These were exemplified by grafting on acetylated cellulose (22), crosslinked cellulose (23), as well as acrylamidomethylated cellulose and its reaction products with mercaptoethanol or hydrogen sulfide (24).

Vinyl graft polymerization onto modified celluloses has evoked considerable interest in the graft yield. Indeed, grafting of synthetic polymer chains onto the modified celluloses has proved of value in getting a good understanding of the kinetics and mechanisms of grafting as well as in obtaining basic information needed for improvements to be made in the properties of the product. Somewhat detailed information about the susceptibility of modified cottons to grafting using different initiators are given below.

Initiators

The capability of a number of initiators to initiate vinyl graft polymerization onto cellulose and modified celluloses has been investigated. Among these initiators were ceric ammonium nitrate, ceric ammonium sulfate, potassium permanganate, azobisisobutyronitrile, potassium bromate-thiourea, dimethylaniline-benzyl chloride mixture, dimethylaniline-cupric ion, and hydrogen peroxide-thiourea dioxide.

Ceric Ion (Ce^{iV}). Ce^{iV}-induced graft polymerization of various vinyl monomers on cotton and modified cottons under different conditions has been extensively studied (14-16, 18-20, 23, 25). Graft yield and monopolymer formation as well as ceric consumption during grafting and oxidation were found to depend upon the nature of the substrate, concentration and reactivity of monomer, concentration of Ce^{iV}, reaction temperature, and reaction time. By way of example, mention is made of the following:

Grafting of PCMC with acrylonitrile, methyl methacrylate (MMA), and acrylamide was effected using Ce^{iV} as the initiator (18). Under similar reaction conditions, the graft yield increased by increasing the DS of PCMC up to 0.124, beyond which the grafting decreased. However, the graft yields for PCMC were significantly higher than those for native cotton and alkali-treated control. Reactivities of monomers were in the order AN>MMA>AM. Increasing the monomer concentration caused a substantial increase in the graft yields. The same effect was found with initiator up to a certain concentration, but beyond it there was a reversal. The Ce^{iV} consumption during grafting increased with rising concentration of Ce^{iV} but decreased with rising monomer concentration. Comparison of Ce^{iV} consumption during grafting and oxidation showed that their magnitudes depend on the nature of the substrates, monomer, and initiator as well as the reaction condition. Grafting had practically no effect on the carboxymethyl (expressed as carboxyl group) of modified cotton.

Ce^{iV}-induced grafting of MMA and AN on cellulose bearing different substituents was investigated (19). While cellulose bearing either cyanoethyl or carboxymethyl groups showed higher graft yields, cellulose bearing both groups showed lower yields. Presence of acrylamidomethyl groups in the cellulose molecules reduced its reactivity to grafting. The same holds true for cellulose bearing acrylamidomethyl groups along with carboxymethyl groups. On the other hand, introducing carbamoylethyl groups in the cellulose molecule enhanced significantly the susceptibility of cellulose to grafting. This was also observed with cellulose bearing cyanoethyl and carboxyethyl groups. Treating cellulose with N-methylolacrylamide in alkaline medium seemed to produce a crosslinked cellulose with lower reactivity to grafting. The results obtained with the different substrates were discussed on the basis of the change in the physical and/or chemical structure of cellulose brought about during its modification as well as on the nature of the substituent groups introduced. The mode of Ce^{iV} attack on cellulose was also classified.

Ce^{iV}-induced grafting of MMA and AN to cotton cellulose crosslinked in either the wet or dry state has been also studied (23). It was found that the graft yields obtained with dry crosslinked cellulose were much lower than those of the control, whereas the yield obtained with wet crosslinked cellulose and the control were comparable. Dry crosslinking prior to grafting seemed to cause a significant structural change, particularly in the disordered region, reducing the accessibility of these regions to grafting. Wet crosslinking, on the other hand, appeared to stabilize the uncollapsed state of the cellulose, thereby leaving its susceptibility toward grafting practically unaltered. The consumption of Ce^{iV} during grafting was higher than that during oxidation, probably because of homopolymer formation. This was observed with the crosslinked cellulose as well as with the controls. The Ce^{iV} consumption during oxidation of crosslinked cellulose was comparable to that of the controls regardless of the crosslinking

method. The bound formaldehyde in crosslinked cellulose decreased after Ce^{iv} treatment, indicating some cleavage of the crosslinks.

Manganese (iv). The ability of potassium permanganate in the presence of different acids to induce grafting of MMA and AN onto sodium hydroxide-treated cotton (control) PCMC partially cyanoethylated cotton, and partially acetylated cotton was investigated (20). The copolymerization reaction was carried out under a variety of conditions. The graft yields were greatly enhanced by increasing concentration of monomer, reaction time, and temperature. The opposite holds true for initiator at higher concentrations. The effectiveness of the acids was nitric acid > sulfuric acid > perchloric acid > hydrochloric acid. The change in the physical and/or chemical structure of cellulose by its modification via etherification reaction or esterification reaction had a significant effect on the susceptibility of cellulose toward grafting. While partial carboxymethylation or partial cyanoethylation of cellulose prior to grafting increased the graft yield partial acetylation caused a decrease.

Azobisisobutyronitrile (AIBN). Grafting of MMA on cellulosic materials by chain transfer under the catalytic influence of AIBN was extensively studied (27). The graft yield was influenced by reaction time, temperature, monomer and initiator concentration, reaction medium, and nature of the substrate. In general, the grafting reaction showed an induction period after which the polymerization proceeded rapidly. The graft yield increased and the induction period decreased by rising the reaction temperature from 50° to 70° C. This was also the case when the monomer concentration was increased from 2 to 6%. Increasing the AIBN concentration up to 0.01M caused a significant enhancement in grafting, while further increase brought about a marked fall in the graft yield. Of the reaction media studied, a water/solvent mixture containing 25% of methanol, ethanol, propanol, butanol, or acetone seemed to constitute a reaction medium where the monomer and initiator were completely miscible and the swelling of cellulose by water was not hindered by the presence of the solvents. Increasing the solvent ratio in the water-solvent mixture caused a considerable decrease in the graft yield. The polymer content of the cellulosic materials, i.e., the graft yield, followed the order PCMC > cotton treated with 12N sodium hydroxide > cyanoethylated cotton > cotton treated with 0.5N sodium hydroxide > purified cotton. In addition, proof of grafting was provided by the fractional precipitation method.

Dimethylaniline (DMA)-Cu^{2+} Ion. Graft polymerization of MMA on viscose fibres induced by the DMA-Cu^{2+} ion system was investigated under different conditions (28). Variables studied included concentration of DMA, Cu^{2+} ion, and MMA, reaction times and temperature. There were optimal concentrations of DMA and Cu^{2+} ion. Below or above these concentrations, lower grafting occurred. Within a reaction time of 4 hr., the grafting reaction showed an initial fast rate followed by a slower one at 80° C. At 70° C., on the other hand, the graft yield increased in proportion to the increase in reaction time. Increasing the monomer concentration did not have a significant effect on the graft yield during the first 15 min. of reaction. Beyond this, the effect of monomer concentration was marked.

Dimethylaniline(DMA)-Benzyl Chloride (BC). The feasibility of DMA-BC mixture to initiate graft polymerization of MMA on PCMC was examined (29). The graft yield relied on the nature of solvent used along with water. Ethanol proved to be the best at a water: ethanol ratio of 90:10. Considerable grafting occurred in presence of acetic acid at a concentration of 200 m mole/l. Higher concentrations of this acid decreased the grafting significantly. The graft yield obtained in the presence of formic acid was much lower than acetic acid, whereas inclusion of hydrochloric acid or sulfuric acid in the graft polymerization system prevent grafting. DMA-BC mixture at a concentration of 0.08:0.087 mole/l. constituted the optimal concentration for grafting. This contrasted with 0.32:0.35 mole/l. for total conversion. The rate of grafting increased by raising the polymerization temperature from 50° up to 75° C. Furthermore, increasing the monomer concentration caused a significant enhancement in the graft yield and total conversion.

Hydrogen Peroxide-Thiourea Dioxide. Cotton cellulose was independently oxidized with potassium periodate, potassium dichromate-sulfuric acid, and potassium dichromate-oxalic acid and the resulting oxidized celluloses were further modified by treatment with chlorous acid or sodium borohydride. The various modified celluloses so obtained were grafted with 2-methyl-5-vinyl pyridine using thiourea dioxide-H_2O_2 redox system (30). It was found that the initiation characteristics of the cellulose samples varied widely with oxidizing agent used. Further modification of the oxidized celluloses by treating them with chlorous acid enhanced considerably their susceptibility toward grafting. The opposite held true when these oxidized celluloses were modified by sodium borohydride treatment. Excluding thiourea dioxide from the polymerization system offset grafting into cellulose, while considerable grafting took place on the various oxidized celluloses and their further modified samples. The work was also extended to study the factors which affect the graft yield, homopolymer formation, and total conversion. In addition, the reactions involved in initiation of grafting were elucidated.

Characterization and Properties of Cellulose Graft Copolymers

Various cellulosic substrates, viz., native cotton, sodium hydroxide-treated cotton, viscose, and ramie were grafted at 20° C. with AN by the Ce^{iV} method. Ramie was also grafted with the same monomer at 40° C. and 60° C. Isolation of PAN side chains of the graft copolymers was performed by acetolysis of the cellulose backbone. Number average molecular weight ($\overline{Mn}$) of the graft as well as the homopolymer was determined viscometrically (31). It was found:

A. That $\overline{Mn}$ of homopolymers were considerably higher than those of grafted polymers.

B. That $\overline{Mn}$ of the grafts as well as homopolymers depended upon the nature of the substrate and followed the order Native cotton ⟩ viscose ⟩ sodium hydroxide-treated cotton ⟩ ramie.

C. That $\overline{Mn}$ of grafted polymers were comparable at 20° C. and 40° C., while at 60° C. they were significantly lower.

Determination of moisture regain of grafted products was also carried out (31). The moisture regain of polyacrylonitrile-cellulose graft copolymers was less than the theoretically calculated value of physical mixture of cellulose and PAN. Also, the moisture regain values based on weight of cellulose content only were less than those of untreated celluloses.

The mechanical properties of cotton fabrics grafted with methyl acrylate, MMA, AN, and mixture of these monomers were examined (32). Properties examined included tensile strength, breaking elongation, tear strength, abrasion resistance, crease recovery, flexural rigidity, and tensile recovery. It was found that some of these properties were improved by grafting, some were unchanged, and others were slightly deteriorated, the changes being dependent on the nature of polymer and extent of grafting.

The behavior of cellulose grafted with poly(MMA) and poly(AN) toward some direct and reactive dyes was investigated (33). Exhaustion rate of the dye onto fibers was governed by the amount and nature of the polymer grafted. In general, the dye affinity for cellulose and dye exhaustion onto fibers decreased as the graft yield increased. Dye affinity for the PAN-cellulose graft copolymers was greater than that found with PMMA-cellulose graft copolymers. Except in few cases, the tendency of cellulose graft copolymer of about 13% graft to accept direct dyes was more than that of the untreated cellulose, whereas the affinity of reactive dyes for cellulose graft copolymers of up to about 43% polymer was more than that of the untreated cellulose. The dye fixation, based on the weight of cellulose component, increased as the graft yield increased.

DYEING

Dyeing of modified celluloses and their corresponding controls (unmodified celluloses) was performed under identical conditions using some reactive dyes (34). The modified celluloses examined were partially acetylated cellulose, partially carboxymethylated cellulose, cyanoethylated cellulose, carbamoylethyl cellulose, and PAN-cellulose graft copolymers. Partial acetylation up to 7% combined acetic acid prior to dyeing caused an enhancement in dye fixation. Above this value, no perceptible shade could be obtained. A decrease in dye fixation was observed with partially carboxymethylated cellulose and PAN-cellulose graft copolymers, particularly at higher extents of modification. On the other hand, increasing the extent of chemical modification via cyanoethylation or carbamoylethylation was accompanied by an increase in dye fixation.

Fading studies (34) revealed that at the same dye concentration on partially acetylated cellulose and its corresponding control, the former showed decreased fading. The opposite holds true for partially carboxymethylated cellulose, cyanoethylated cellulose, carbamoylethyl cellulose, and PAN-cellulose graft copolymers. It was also found that chemical modification of cellulose prior to dyeing did not alter the fading order of the dye. Furthermore, the characteristic fading curves of the reactive dyes on the modified celluloses and the controls showed that chemical modification of cellulose prior to dyeing had no significant effect on the change of the dye distribution with its concentration on the substrate.

Similar studies have been carried out using some direct dyes (35, 36).

CROSSLINKING

The literature relevant to easy care cotton finishing has been reviewed (37, 38). A new catalyst system based on a mixture of boron trifluoride-acetic acid complex ($BF_3 \cdot 2CH_5COOH$) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6 H_2O$) has been examined (39). It provides strong catalysis in crosslinking cotton with a series of N-methylol finishing agents when the pad-dry-cure process was applied. Curing could be carried out at a temperature of $130^\circ-150^\circ$ C. for a period of 1-3 min. depending on the temperature used. The resilience and abrasion resistance as well as the degree of polymerization (DP) of the crosslinked cotton so obtained were equivalent or slightly better than those of crosslinked catalyzed by conventional catalysts. The influence of the new catalysts as well as a number of conventional catalysts (viz., ammonium chloride, ammonium dihydrogen phosphate, magnesium chloride hexahydrate, and zinc nitrate hexahydrate) on some properties of cotton was also investigated. The behavior of these catalysts in the presence of the N-methylol finishing agent was quite different from their behavior in its absence. With the exception of ammonium salts, the DP of crosslinked cotton was much higher than that of cotton treated with the catalyst only. The opposite holds true for the abrasion resistance.

CONCURRENT DYEING AND FINISHING

Preparation of a methylolated dye that could react with cotton cellulose under acidic conditions was described (40). This dye was applied to cotton fabric by continuous and semicontinuous methods. Optimal conditions for application were examined. Incorporation of N-methylol finishing agents in the dyeing bath to establish a one-step process for dyeing and finishing was outlined. Evaluation of dyeings and dyed-finished goods were assessed by determination of dye fixation, crease recovery, tensile strength, and the overall fastness properties.

Dyeing of polyester-cotton blend with reactive-disperse dyes and finishing with N-methylol compounds in the presence of $MgCl_2 \cdot 6 H_2O$, NH_4Cl, or $NH_4H_2PO_4$ as the catalyst has been successfully carried out in a single step process (41, 42). Properties of the simultaneously dyed and finished fabrics relied on concentration and nature of both the N-methylol finishing agent and the dye mixture, concentration and type of catalyst, and the conditions of curing. Color strength, crease recovery, tensile strength, and the overall fastness properties were comparable to or better than those of fabrics dyed and finished in two separate steps.

Reaction of reactive dyes with cellulose in alkaline medium is well-known, but reaction of N-methylol finishing agents with cellulose is still obscure. That is why dyeing and finishing are usually carried out in two separate steps because the finishing agent requires an acid catalyst. Recent reports, however, postulate that reaction of N-methylol compounds with cellulose is possible provided that the former are able to form activated imines. Work (43, 44) in this division offers experimental results which confirm the proposed mechanism and signify the advantages of simultaneous dyeing and finishing under the influence of alkaline catalyst. Three N-methylol compounds (viz., monomethylol urea, dimethylol urea, and N-methylol acrylamide) were independently incorporated in a dyeing bath containing reactive dye, urea, and alkaline catalyst. Cotton fabrics treated with such solutions by applying the pad-dry-cure method or pad-cure method showed dye fixations which were higher than those of fabric dyed in absence of the finishing agent. Dye fixation, crease recovery, and tensile strength were governed by the nature and concentration of the N-methylol compound, of the dye, and of the catalyst as well as by the conditions of curing. The simultaneously dyed and finished fabrics showed considerable improvement in conditioned crease recovery and outstanding enhancement in wet crease recovery. Their losses in tensile strength and elongation were not so striking, and their fastness to washing and to light were comparable to those of dyed fabrics.

A new approach for simultaneous dyeing and wash-wear finishing of textile materials by using acrylamidomethylated cellulose has been reported (45). Excellent dye fixation and wash-wear properties could be achieved with dyes containing nucleophilic groups as well as reactive dyes. In alkaline medium, presence of acrylamidomethyl groups allowed fixation of dyes containing nucleophilic groups as well as crosslinking of cellulose.

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Discussion and Review of Chemical Finishing of Cotton

II.   Durable Press; Differential Dyeing and Printing;

Practical, Simplified Bleaching; Degradation of Mercerized Yarns

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INTRODUCTION

I have spent 45 years of my life in the field of textile research, and it is a real pleasure now to discuss such research in the land which was the birthplace of textile chemistry. The ancient Egyptians had woven cloth when the Europeans were still running around in animal skins. The first dyer was probably an Egyptian who began his career by daubing colored berry juice onto a linen fabric.

The textile chemist who does research on cotton has one important factor working in his favor and that is that cotton is of universal interest. Cotton is used by everyone from the cradle to the grave. What the chemist does to cotton affects everybody without exception. There are so many millions of yards of cotton used that a very slight decrease in cost per yard is multiplied millions of times to total great savings.

In any discussion of research on textiles, we find that there is often a considerable variance in emphasis from country to country, depending upon the availability of cotton compared to other fibers, economic considerations, and political considerations.

For my first and principal subject, I plan to discuss what we call "durable press" or "permanent press." In the past, it was called "wash-and-wear," "no iron," "smooth drying," and similar names. As you know--aside from the dyeing of textiles--durable press is the most important textile chemical modification in the United States and probably in the world. In our country, about 60% of the adult women do some type of work outside of the home in offices, schools, or factories. Garments which do not need ironing after launder-ing effect a savings of about one day of labor per family per week--the labor of ironing clothes. This represents a tremendous savings per year of labor which otherwise would reduce our gross national product.

Ironing is the household chore which is most disliked by housewives, and it is difficult to sell a garment in the United States which requires ironing. This requirement that a garment be smooth drying after laundering has greatly affected our development of textiles. For example, there has been a tremendous acceptance by the consumer of knit garments, not only of cotton and wool but especially knit fabrics made of polyester fibers. Because of this easy-care feature, semitransparent knit garments are acceptable today which would have been rejected only a few years ago.

J. T. Marsh has estimated that there are more than 7,000 publications and 3,000 patents relating to durable press. Considering the high quality of Egyptian research, it is probable that Egyptian textile chemists are more familiar than I am with the details of many of the processes covered. I have decided, therefore, to discuss durable-press re-search in a more general manner, with my main emphasis on points that I consider to be important. Furthermore, I shall use the story of the development of durable press in our country to illustrate some of my comments on our philosophy of research.

DURABLE PRESS

The research leading to the present stage of development of durable press started approximately 50 years ago when Foulds, Marsh, and Woods, working for Tootal Broadhurst Lee Co., Ltd., in Manchester, England, began investigating means to give cotton the crush resistance of wool (1). By 1940, the process was a mild commercial success in several

areas of the world, but interest in such finishes in the United States was largely limited to methods of producing shrink resistance in cotton during finishing. That is, the greater yardage production in the mill more than offset the cost of the shrink-resistance treatment. However, the introduction and popularity of nylon no-iron garments generated interest in no-iron cotton among textile finishers.

By 1955, considerable yardage of wash-and-wear fabrics was being sold, but the product was in great difficulty in the American market because it was not able to withstand the prevalent rigorous laundering procedures--that is, chlorine bleaching in the home and acid souring in commercial laundries. Chlorine bleaching caused formation of an acid which degraded the cloth. Garments were sent occasionally to commercial laundries, and the acid souring removed the no-iron finish. Furthermore, most of the fabrics also had a very bad soiling problem in that they scavenged soil particles from the wash water during laundering (2).

I joined the staff of the Southern Regional Research Laboratory when it was established in 1940 in New Orleans, Louisiana. A main objective for the establishment of this laboratory--now known as the Southern Regional Research Center--was to do research to increase the use of cotton and, thus, to help the American farmer by providing him with new markets. It was obvious to us at the laboratory that more satisfactory no-iron cotton garments would greatly increase the use of cotton. An extensive program of research was begun to aid industry in both the practical and theoretical aspects of the work. One of our first papers relating to creaseproofing was published in 1952 by Daul, Reinhardt, and Reid (3).

Achievements in Fundamental Research

In attacking a problem such as the development of durable press, the textile chemist must choose whether his research will be fundamental or applied. Fundamental or theoretical research can be subdivided into several categories. One of the most important of these divisions is fundamental research to explain why a reaction works. For example, in the early days of no-iron cotton, most chemists were thoroughly convinced that the no-iron feature was due to what was called then--and still is in a colloquial manner--the "resinification" of the cotton. That is, they believed that the fabrics returned to their smooth state after washing because urea-formaldehyde or some other polymer had been resinified (polymerized) inside the fiber. They thought the fabric had been given what amounted to a sort of permanent starching. Or, to put it another way, if a hollow straw is filled with sand, it will resist bending. We showed that this idea was not right. We supported the hypothesis that crosslinking of the cellulose molecules was the cause of the permanent set of the fibers.

The average cotton fiber in the U.S. is about 1,500 times as long as it is wide. It is made up of thousands of fibrils composed of long chains of several thousand anhydroglucose units each. Some chains lie parallel to each other in a crystalline arrangement, so that it is almost impossible to cause reaction in these areas because reagents cannot penetrate these areas. In other areas of the fiber, chains are jumbled together in a random arrangement which gives flexibility to the fiber and accessibility of that area to chemical agents. It is in these accessible areas that reaction can take place. When water entered these areas, as in laundering cotton clothes, the accessible areas became swollen and the long molecules could slide by each other. When the fiber dried, hydrogen bonding occurred and wrinkles became fixed in the fiber. If cotton cloth is smooth and kept completely dry in a desiccator, it has remarkable resilience and is difficult to wrinkle. When cloth is moistened and then ironed, the cloth can be made smooth.

The crosslinking theory mentioned above held that, if the chains were permanently crosslinked to each other through chemical bonding, there would be no slippage during laundering, and each individual fiber would retain its original configuration which it would return to after washing and drying.

We showed (4) that crosslinking was the mechanism by which the cloth was made crease resistant by reacting both a monofunctional and a difunctional derivative of ethyleneurea

with cotton. At that time, dimethylol cyclic ethylenurea was being used commercially to
make cloth crease resistant. Reaction of 3% of this reagent with cotton gave excellent
wrinkle resistance to the fabric. However, the reaction and addition of twice as much of
the monofunctional reagent gave practically no change in the properties of the fabric.
This showed that crosslinking and not resinification was the basis for wrinkle resistance.

It is obvious that fundamental research such as this to establish the theoretical
basis for wrinkle resistance greatly accelerated the practical development of finishes.
There is a second area in which fundamental work is often of great value. In this area,
the theoretical chemist develops a hypothesis that something can be done and then does re-
search to prove the validity of his hypothesis. That is, the chemist is carrying out re-
actions which he considers might conceivably occur to yield a new product. Most original
synthesis results from this type of fundamental research.

For example, we thought that a certain compound would be a good crosslinking agent
for cotton (5). This was 1,3-bis(hydroxymethyl)-tetrahydro-2(1H)-pyrimidone, a compound
which is known more simply as dimethylol propylenurea.

$$HOH_2C\text{-}N\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}N\text{-}CH_2CH$$
$$H_2C \diagdown_{\displaystyle C} \diagup CH_2$$
$$H_2$$
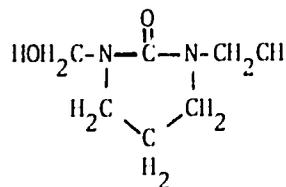
As we had anticipated, this was an excellent crosslinking agent with many good proper-
ties except that it cost about $500 per pound because of the high cost of the diaminopro-
pane from which it was made. At that price, our work was definitely fundamental rather
than practical. However, we described our work in a publication (5). The German company
Badische Anilin- und Soda-Fabrik picked it up and sold the agent all over Europe because
it had an inexpensive way to make the diaminopropane. It called it "Fixapret PH" (PH for
propylene harnstoff). This is an example of fundamental work which was apparently im-
practical but became of commercial use because of further developmental work.

I shall give one more example of this type of fundamental work which was not success-
ful. We made some partially carboxymethylated cotton fabric. That is, acid carboxyl
groups were attached here and there along the cellulose chain, but the modified cotton re-
tained its fabric properties. We knew that some metal salts, such as the aluminum salt of
carboxymethylcellulose, are almost insoluble. We wondered if we could add aluminum to link
the carboxyl groups together and thus crosslink the cellulose chains to make the fibers
wrinkle resistant. It didn't work. The product was not wrinkle resistant.

It is possible that we might have anticipated this failure if we had done a consider-
able amount of theoretical calculation. However, I have observed that it is often much
more economical to do a short pilot experiment than to attempt to make a decision based on
theory. For example, I have seen projects fail which were apparently sound, and conversely
I have seen successful projects which appeared to be unsound.

There is a third area of fundamental research which consumes many more hours of re-
search time that it should. This is the area where the chemist is pursuing research which
has the single objective of producing a publication for that chemist. The product of the
research can have no conceivable use except for extending human knowledge an infinitesimal
bit. Sometimes there is a very narrow line between research that is useless and that which
is potentially useful. I said I would use durable-press research for examples, but this
time I am not going to embarass researchers--myself included--by spotlighting examples of
this type of research. However, I have tried to avoid this type of research. We were paid
by public tax money, and I felt that the country could not afford the luxury of paying
chemists to follow their own hobbies without regard for the production of useful knowledge.
Surely these chemists could utilize their time to better advantage.

Achievements in Applied Research

We come now to the other type of research--applied or developmental research. Sometimes it is called practical research. In general, this type of research has one of three objectives:

A. To make a specific product for less cost.

B. To make a better product for the same cost.

C. To develop methods of manufacture for a new product. (The new product may
    have been the result of fundamental research.)

I mentioned the soiling problem in which no-iron clothes scavenged dirt particles from the wash water during laundering. This drawback could have retarded the whole durable-press development for several years if it had continued, because housewives who encountered this phenomenon became highly prejudiced against the development. White shirts became a dingy gray which got worse with each laundering. Fortunately, we observed this fault very early in the game.

The problem was due to the softener used. When cotton is crosslinked, the treated fibers have an unpleasant hand because of their crispness. Therefore, an additive softener is used which not only improves the feel of the fabric but also lubricates the fibers so that they slide more easily one on another. This improves both crease recovery and tearing strength. In those first no-iron shirts, a softener was used which was a mixture of an acrylic polymer and a silicone. Only 2 or 3% was used, but the large polymers filtered out on the surface and completely covered each fiber. Through microscopic examination we determined that the soiling was due to black particles which adhered firmly to the softener on the surface of each fiber. Through experimental work, we determined that both the silicone and the acrylate became tacky at laundering temperatures and picked up the soil particles which then could not be removed by laundering, bleaching, or drycleaning (2). We suggested that emulsified polyethylene be substituted as the softener, and the problem was solved. Also, the polyethylene cost less than the previous softeners, so the textile finishers were very willing to adopt its use.

We obtained a United States public service patent on this development (6). This patent is interesting because in it we described the durable-press treatment of a garment rather than the cloth before the garment was made. That is, we would soak a cotton shirt or trousers in the crosslinking solution, centrifuge it, and then iron it dry on a commercial press. After that, we would cure the garment in an oven. In this manner, seams, pleats, and trouser creases were set into the finished garment. Later, a patent issued which superseded ours because it had been filed at an earlier date. However, there were a considerable number of garment treated in this manner for a number of years in the United States and in Great Britain.
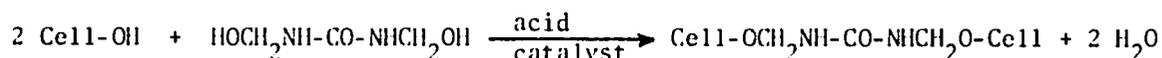

Development of Carbamate Agents

To return to the discussion of types of applied research, it can be seen that in the example just given we accomplished the first two objectives listed; that is, we made a better product at a lower price.

As an example of the development of a new product, I will describe our development of the carbamate finishing agents.

A considerable number of types of crosslinking agents for cellulose have been tried and used for the commercial production of no-iron cotton. For example, these include formaldehyde, epichlorhydrins as in the Belfast process, disodium trissulfatoethylsulfonium inner salt as in the Tebexel process, divinyl sulfone as in the Ganalok process, and other unusual compounds. However, commercial processes in the United States almost always use some type of nitrogenous crosslinking agent. An example of such crosslinking with dimethylolurea is shown in the following equation which portrays a simplified, idealized

representation of the reaction:

$$2 \text{ Cell-OH} + \text{HOCH}_2\text{NH-CO-NHCH}_2\text{OH} \xrightarrow[\text{catalyst}]{\text{acid}} \text{Cell-OCH}_2\text{NH-CO-NHCH}_2\text{O-Cell} + 2 \text{ H}_2\text{O}$$

Many other nitrogenous compounds such as cyclic ethyleneurea, triazone, melamine, uron, dihydroxyethyleneurea, alkyl carbamates, and others are employed as their formaldehyde adducts in durable-press finishing. Many factors bear upon the finishing agent selected, such as cost, difficulty of applicatio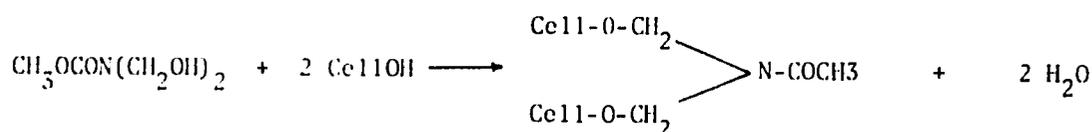n, formaldehyde odor evolved, susceptibility to chlorine bleach, hydrolysis during use, yellowing with chlorine, and degradation because of difficulty in crosslinking.

The carbamate class of finishing agents was developed at the Southern Regional Research Center and first introduced to industry in 1961 (7). Formaldehyde was reacted with a carbamate such as methyl carbamate to give the dimethylol compound. These dimethylol compounds are extremely difficult to isolate, but they do exist in solution.

$$2 \text{ HCHO} + \text{CH}_3\text{OCOCONH}_2 \longrightarrow \text{CH}_3\text{OCON(CH}_2\text{OH)}_2$$
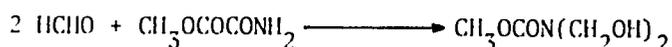
The crosslinking of cellulose proceeds through a condensation reaction as follows:

$$\text{CH}_3\text{OCON(CH}_2\text{OH)}_2 + 2 \text{ CellOH} \longrightarrow \begin{array}{c} \text{Cell-O-CH}_2 \\ \\ \text{Cell-O-CH}_2 \end{array} \hspace{-0.5em} \Big\rangle \text{N-COCH3} + 2 \text{ H}_2\text{O}$$

The finish imparts wrinkle-resistance properties and is resistant both to chlorine bleaching and to mild acid hydrolysis. At present, carbamate agents are used mainly on fabric for sheets and pillowcases because of the resistance of the finish to the hard laundering these items receive (8).

Shortly after introducing the carbamate agents to industry, we carried out toxicity tests and cautioned that dimethylol ethyl carbamate should not be used because ethyl carbamate itself produces lung cancer in mice (9). Methyl and hydroxyethyl carbamates have been used commercially, but the present choice of agents appears to be dimethylol isopropyl carbamate and dimethylol methoxyethyl carbamate.

The development of the carbamate agents illustrats the point I made previously about the difficulty of predicting reactions with cotton cellulose. The fact that the monomethylol methyl carbamate is a crystalline solid while dimethylol methyl carbamate was unknown at that time might well have discouraged us from trying to make it. Furthermore, it would seem logical that, even though it were formed in solution, it should break up when the solution was dried and heated on the fabric. Also, all other nitrogenous agents, with the possible exception of certain melamines, crosslinked cellulose through substituents on separate nitrogens rather than through two methylol groups on a single nitrogen atom. When the work was first presented, some chemists doubted that the bond existed. They insisted that it must be a simple formaldehyde methylene crosslink with the carbamate agent merely serving as a formaldehyde donor. However, we showed later that the crosslink through a single nitrogen did exist. The practical man in the textile finishing plant, of course, did not care about the theoretical basis as long as the finishing agent gave a superior product at a satisfactory price.

The Role of Catalysts

The selection of catalysts is very important in durable-press finishing. Catalysts have always fascinated the chemist, and the work done at the Southern Laboratory on catalysts to promote the crosslinking of cotton would fill a small book. These catalysts are generally acidic. The more acidic they are, the more efficient the reaction is but

also the more that degradation occurs. Similarly, both reactions are more complete at higher temperatures. The fascination occurs because there is always the hope that the ideal catalyst will be found--one that causes crosslinking to take place at a low temperature with no degradation of the cellulose.

One of the most interesting catalyst systems is the phase-equilibrium catalyst of Tootal Broadhurst Lee. In this system the bath is only slightly acidic with a solution of magnesium dihydrogen phosphate. However, as the solution dries on the fabric, full acidity is developed by the deposition from solution of the less acidic salt (10).

In the United States, magnesium chloride, zinc nitrate, and zinc chloride were popular catalysts with the cure temperature in the range of 150°-160° C. However, three factors have effected changes in the choice of catalysts. First, the introduction of polyester and cotton blends has allowed the use of a more active catalyst, because there is not so much concern about slight degradation of the cotton. That is, the strength of the fabric lies mainly in the polyester. Secondly, concern about the cost of energy has led to studies of activated catalysts which allow the curing to proceed at a lower temperature. For example, a 1:1 molar mixture of citric acid and magnesium chloride hexahydrate has been found to provide such catalysis (11).

The third factor, more lately, has been the discovery of trace amounts of bis(chloromethyl) ether--a powerful carcinogen--in the vapors above some pad baths. This is presumed to come from the interaction of formaldehyde and hydrogen chloride. Because of fear of legal action by employees, some companies have banned the use of magnesium chloride or any other chloride in their operations. However, Bernard North of Sun Chemical Co. recently has examined a considerable number of crosslinking agents and determined the amount of formaldehyde released during curing with various catalysts. He concluded that the low levels of formaldehyde which would be expected when the released formaldehyde is diluted with the air in the ovens may be the reason that recent tests show no bis(chloromethyl) ether in textile finishing plants (12).

The three factors mentioned above have fostered a deepened interest in new catalysts throughout the world. At the Southern Regional Research Center, studies have been carried out that indicate the usefulness as catalysts of hydroxymethanesulfonic acid (the adduct of formaldehyde, sulfur dioxide, and water); certain of its salts; salts of other alkyl and arylsulfonic acids; aluminum chlorhydroxide $(Al_2(OH)_5Cl)$; combinations of $Al_2(OH)_5Cl$ and various salts, organic acids, inorganic acids, and peroxides; mixtures of ammonium chloride and phosphoric acid or certain organic acids; strong Lewis acid salts, in particular various aluminum salts; aluminum phase separation-type salts, such as aluminum dihydrogen phosphate, aluminum hydrogen tartrate, and the like; moderated mineral acids; and zirconyl hydroxychloride. An inexpensive, halide-free, heavy metal-free catalyst which is effective at lower-than-conventional curing temperatures is sodium bisulfate. Magnesium and aluminum bisulfates are even stronger and, as such, require more careful control in finishing. A recent publication (13) describes a systematic study of pad-dry-cure finishing with a variety of salt catalysts and details the factors that contribute to and control catalytic activity.

Blends for Durable Press

I wish now to discuss the present situation in the United States with regard to durable press.

In the early days of durable press, we found that 100% cotton fabric could be treated to give a smooth drying garment with excellent appearance. There was some trouble at first with seams shrinking and puckering, but the garment manufacturers soon developed techniques which produced smooth seams after laundering. However, the garment showed evidence of abrasive wear after 20 to 30 launderings. The strength of the cotton had been reduced to about 60%. Seams, edges of creases and pleats, and collar points wore out first. Therefore, most garments in the United States today are made from fabric with a blend of polyester fiber and cotton to give sufficient strength for good wear life. Woven fabrics of 100% polyester are not comfortable and do not present a good appearance if they are ironed.

The blends are best. Cotton, Incorporated, a research agency to promote cotton, recommends what it calls the "natural blend" of 60% cotton and 40% polyester. Although we did much research to produce a durable-press all-cotton fabric, we were not able to overcome the problem of severely reduced strength and abrasion resistance. Certain finishing formulations and special weaves gave fabrics with moderate wear life, but we were not able to compete in cost with the use of blends.

Because of the shortage of oil in our country, the raw ingredients and the energy required for making polyester fiber have increased in price. However, in a paper by T. E. Miller and H. L. Hergert, presented at the 1977 Chicago meeting of the American Chemical Society, it was estimated that the petroleum required for $5 worth of gasoline could be made into polyester fiber worth $76 which, in turn, could be made into garments worth $500. So, it is evident why polyester is still a very popular fiber in the United States and research continues on the treatment of cotton-polyester blends.

To look at the picture more broadly, India, for example, is short not only of oil to make polyester fiber but is short of cotton as well. Therefore, India has decreed that output of all cotton mills must contain 10% of rayon fiber. This has created problems for the textile chemist, particularly when ordinary viscose rayon is used. Polynosic rayon is preferred. It has been necessary, then, for the Indian textile chemist to modify his research to fit this new picture.

At the Chicago meeting mentioned above, there was speculation that, as the population continued to increase in countries such as India, farm acreage now used to grow cotton will have to be devoted to the production of food. Speculation was that woods will be raised in tropical countries to make rayon. It is possible that in the future, then, textile research must be tailored, country by country, to support those goals that will be most beneficial to the needs of that country.

In the United States many farmers are changing from growing cotton to growing soy beans, because they find that soybean oil and meal is more profitable than cotton grown on the same acreage.

Research at Southern Regional Research Center

There is no time here to review all the work which has been done at the Southern Regional Research Center. I myself have approximately 115 articles and 16 patents on the subject. However, as a reminder for you, I shall list some of the main areas of durable-press work with which I have been concerned:

- Development of detailed practical information for industry on crosslinking agents and their use.

- Fundamental information on crosslinking agents and processes.

- Treatment of cotton garments in the laboratory and in commercial dry-cleaning plants.

- Wet soiling studies and methods of avoiding soiling of DP garments during laundering.

- After mercerization of DP cotton to improve resistance to abrasion.

- Chlorine resistant blends of triazone and urea for DP use.

- Release of formaldehyde from DP treatments and control of release from garment and fabric.

- Development of new finishing agents, including alkyl and hydroxyalkyl carbamates, urons, propyleneurea, triazones and triazines.

- Finishing of cotton with formaldehyde.

- Effects of mercerization and tension on the properties of DP cotton fabric.

- Effects of structure of agents on acid hydrolysis of DP cotton.

- Effect of additives such as polymeric agents or reactive softeners on abrasion resistance and other important properties of DP cottons.

- DP by wet fixation.

- Stabilization of knitted cotton fabrics.

- Vapor cure finishing systems.

- A mild cure process (essentially a more rapid version of the European moist crosslinking process).

- Mixed catalysts.

- Low energy catalysts.

- Steam curing and steam fixation.

- Solvent finishing systems.

- Curing creasing techniques.

In addition to the above, other research groups at the Southern Regional Research Center have investigated many other phases of DP treatments of cotton.

Recent Advances in Durable Press

I shall conclude my remarks on durable press research at the Center by a brief description of two projects which have been presented recently.

At the Chicago 1977 meeting of the American Chemical Society, a paper was presented which was co-authored by R. M. Reinhardt and J. C. Arthur. It was entitled, "Photo-initi ed Grafting of N-Methylolacrylamide with Cotton in a Process for Producing Wrinkle Resistant Fabrics." N-methylolacrylamide (CH_2= $CHCONHCH_2OH$) was grafted to cellulose rapidly and efficiently with ultraviolet light as the radical initiation source. There was little or no dry-crease resistance. However, high levels of dry wrinkle resistance were achieved in processes that included a catalyst and heat treatment to react the methylol group with the cellulose. This fundamental work is continuing in an effort to develop pilot plant photoinitiation.

Practical areas of research which are being investigated at the Center are those which lead to savings in energy, as announced May 4, 1977. A very promising approach is that of using minimum moisture application techniques for applying chemical to cotton and thus saving energy because there is less water to evaporate during the drying step. Such methods have been reviewed by Schwemmer, Bors, and Götz (14).

At the Center it has been found that transfer padding techniques can be used to prepare durable-press fabrics which are equivalent in performance to conventionally finished fabric. The wet pickup could be greatly reduced with consequent savings of energy. The work has been described by Dr. Harper and his associates (15). Modifications of the standard kiss-roll technique have been used as illustrated in the Figure 1 entitled "Various Indirect Padding Techniques." The method shown in A is essentially a controlled kiss-roll technique. The second application method, illustrated in B, is called a loop transfer method. A more sophisticated approach, shown in C and D, controls the wet pickup more closely and gives a more even distril ion. The pressure between rolls 1 and 2 and between rolls 2 and 3 can be individually controlled, thereby achieving a wide range of pickups.

Figure 2 shows a pad transfer method in which the fabric being treated provides its own loop. The fabric has the advantage of being fully padded.

These minimum moisture applications would seem to be applicable in many areas besides that of durable press.

DIFFERENTIAL DYEING AND PRINTING

For the chemist who thinks in a creative manner, it is often possible to adapt the techniques used in one field of textile chemistry for use in another field of textile chemistry. Observations made on the crosslinking of durable-press cotton have been used in the development of techniques for dyeing and printing cotton.

As an example of the benefits of DP research in another textile field, let us consider the use of active catalysts in saving energy in pigment dyeing.

This particular work was done by Dr. D. V. Parikh--who worked with my group for 2 1/2 years before returning to India. While there, working at Kesoram Industries of Calcutta, he utilized the citric acid-magnesium chloride hexahydrate active catalyst in pigment dyeing. The work is so new it is still in press (16).

Pigment dyeing has captured 60-70% of the Indian textile market and is still gaining in popularity because of the low cost of dyeing and the ease of coloration. Pigment dyes are fixed to the cloth by means of a resin system which holds the dye to the fiber. Thus, the fastness of the dye depends upon proper curing and stability of the resin. With the usual catalyst of diammonium phosphate or ammonium chloride, a cure of 3 mins. at 140°-150° C. is required. By substitution of an equimolar mixture of citric acid and magnesium chloride hexahydrate, the time could be reduced to 40 sec. and the temperature of cure to 85°-95° C. Furthermore, it was possible to use economical steam drying cans for the cure. Fastness properties such as wash fastness and wet and dry crock fastness were not impaired.

At the Kesoram mills, Dr. Parikh was able to achieve a considerable savings in the cost of pigment dyeing by use of the active catalyst. It was also possible to combine a durable-press finish with the pigment dyeing by a one-bath, one-step operation through a tenter frame. In this case, drying was done on a tenter frame and curing was accomplished on drying cans as before. Of course, this meant that clip marks would show on the finished selvedge, but the selvedge is normally discarded anyway. Ordinary finishing could also be accomplished in the same manner, except that starch is not compatible with the finish.

I quote this as a commercially successful example of the adaptation of knowledge from one field of textile chemistry to another.

In another example of the use of durable press-techniques, differential dyeing of cotton has been achieved to give special effects and novelty fabrics. It is well known that the crosslinking of cotton changes its dyeing characteristics, so that the crosslinked portion of the cloth will resist dyeing with many dyes.

In my group at the Center, Blanchard, Harper, Bruno, and Gautreaux (17), produced multicolored cotton pile fabrics by dye-resist techniques. A crosslinking formulation containing dimethylol ethyleneurea (DMEU) and catalyst and thickened by a suitable agent such as hydroxyethyl cellulose or alginate was applied to one side of a towel fabric and the fabric dried and cured. It was then dyed with a reactive dye, such as Procion Orange M-2R, or with a combination of vat and naphthol dyes. The DMEU was then removed by mild acid hydrolysis and the fabric overdyed with a lighter shade such as Procion Yellow MX-8G. An attractive bicolored fabric was produced.

Other work in this area has been done lately. For example, an economical kiss-roll padding has been developed to apply the thickened crosslinking solution to one side of the fabric (18).

At the October 1977 National Meeting of the American Association of Textile Chemists and Colorists, a paper was presented in which a chambray effect was obtained by preparing fabric with dye-resist filling yarns. The dye-resist in this case was obtained by phosphorylating the filling yarns prior to weaving with, for example, dibasic sodium phosphate (Na_2HPO_4). The chambray effect was obtained because only the untreated yarns absorbed dye. This method allows production of chambray by piece dyeing of treated fabric, a less expensive process than warp beam dyeing (19).

An economical variation of the above-mentioned dye-resist principle has been used commercially in India to produce beautiful tone-on-tone cotton fabrics in various patterns. A fabric is printed with designs in the usual manner, except that a small percentage of crosslinking agent with catalyst is used in the printing paste, and the fabric is dried, cured, and washed. When the fabric is dyed in the usual manner, the pretreated areas dye a lighter shade than the untreated areas. Thus, an attractive two-tone effect is achieved.

Before I leave the subject of dyeing and printing, I would like to comment on the subject of printing cotton-polyester blends.

The introduction of polyester fabric into the United States caused problems in dyeing and printing, because the relatively inert, solid, plastic fiber did not react with or absorb dyes as cotton and wool do. In general, this problem was solved by application of dyes with a very brief, high temperature heating period which caused the surface of the polyester fiber to soften so that the dye could be absorbed or dissolved in the softened surface layer of the individual fiber.

An interesting variation of this method is the process known as heat transfer contact printing. This method of printing has increased greatly since commercial transfer printing was introduced in 1965. At present, it has captured approximately 19% of the printed fabrics market in Great Britain, and it is estimated that transfer printing will account for 16% of the total world market by the early 1980's.

In this method of printing, a roll of paper is printed economically with the desired pattern in much the same manner as magazines are printed with colored pictures. However, certain disperse dyes are used instead of the usual printing colors. These dyes are ones which sublime at a high temperature, say 200° C. When the paper and cloth are pressed together and run through hot rollers, the dye sublimes directly from paper to fabric. This technique allows beautiful and complicated, clear, sharp patterns to be printed. Furthermore, short runs of fabric can be made which would be uneconomical if the usual expensive engraved printing rollers were necessary.

However, this process was not applicable to cotton or cotton-polyester blends because the sublimed dyes washed off of the cotton. Therefore, a project was initiated at the Center to modify the cotton, so that cotton or cotton-polyester blends could be transfer printed. Cotton and cotton-polyester blends were chemically modified to allow transfer printing with disperse dyestuffs (20). Successful treatments included the use of glycols with crosslinking agents to attach them to the cellulose, interfacial polymerization techniques for in situ polymer formation, and acetylation of the cotton. The most effective method for achieving excellent prints with good print durability to laundering was through partial acetylation.

Transfer printing of cotton textiles has been investigated further, and the results have just been reported as the subject of a Gulf Coast Section contest paper at the October AATCC meeting referred to above. The paper is by George L. Drake, et al, and the paper was presented by Eugene J. Blanchard (21). It was found that the affinity of disperse dyes for acetylated cotton vary greatly. Although acetylation improves the affinity of cellulose for disperse dyes, the washfastness is insufficient for high-quality transfer prints. The durability can be improved substantially by treating acetylated fabrics with 5% of hexamethoxymethyl melamine crosslinking agent using 0.05% of p-toluenesulfonic acid catalyst. The resin shows good affinity for disperse dyes and does not yellow, even at the 200° C. transfer printing temperature.

PRACTICAL SIMPLIFIED BLEACHING

As I have indicated previously, I believe the research scientist should devote at least part of his effort toward research benefiting the people or industry of his country. Therefore, I would like to devote part of my discussion to a subject which may be of special interest and benefit the textile finisher who has grey fabric to bleach. At many mills in the United States, bleaching is carried out at high speeds, perhaps 200 yards per minute with several strands of cloth treated simultaneously in what is called a high speed, continuous process. However, not all mills have the expensive machinery needed, and many mills in the U.S. and around the world use a variation of the older discontinuous process which may require from three to seven days to complete.

In India, it is very difficult to receive permission to spend money for expensive imports such as equipment for continuous bleaching. I would like to give you a brief description of how one Indian mill has modified its desizing and bleaching process from the old fashioned slow process to take advantage of newer methods without investment in new equipment. This work is described in a paper by Dr. D. V. Parikh (22). It is so new that it has not yet been published but it has been submitted to one of the Indian textile journals for publication.

This work was done at the Kesoram Cotton Mills, Ltd., Calcutta, India, which mill processes about 200,000 yards per day. The savings in desizing and bleaching were from 20 to 40%, which amounted to about 50,000 rupees or about $6,000 per month, with very little investment in new equipment. The improvements were high-speed production, faster movement of goods, less stock in the bleachery, and significant savings in chemicals, water, steam, power, and labor.

In general, bleaching of cotton consists of three major phases: (a) a pretreatment of desizing and possibly mercerizing, (b) scouring, and (c) bleaching. Each of these steps consists of three parts: (a) saturation, (b) storage during reaction time, and (c) washing. All are batch operation.

In sizing of yarns, there is some modern use of polyvinyl alcohol or carboxymethyl-cellulose, and such fabrics need only be washed to remove the size. However, starch is still the major sizing agent, and this fabric must be desized. At the Kesoram mill, instead of an 8 to 24-hr. treatment with enzyme, desizing is done by passing the fabric, directly after singeing, into a quench box containing about 8 to 9 grams per liter of hydrochloric acid. After 2 hrs., the cloth was thoroughly washed through a pair of synchronized washers. The washers were synchronized as closely as possible, but about 250 meters of cloth were allowed to pile up between the washers to allow for errors. Reaction time varied from 1 1/2 hr. in summer (30-35° C.) to 2 1/2 hr. in winter (20-25° C.). If some type of J-Box were constructed, the process could be made continuous by elevating the bath temperature to 45°-50° C. and allowing only a few minutes reaction time. There must, of course, be no drying of the fabric at any time before afterwashing because of the acid on the cloth. However, acid desizing was used at Kesoram Mills for 20,000 pounds per day of grey fabric for eight months without a single instance of degradation. The mill then planned to expand acid desizing to its total production of 36,000-40,000 pounds per day. Advantages are savings in time, the cloth is partially cleaned, it is economical, metal contaminants are removed, factory inventory is cut down, and a uniform product is obtained which lessens defects during dyeing.

Dr. Parikh describes a number of operations in which synchronized washing machines can be used to effect savings in time and labor with increased production. He recommends short sequence weak hypochlorite bleachings with about 0.5 to 1 gram per liter of available chlorine.

In Indian mills an open peroxide boil is often used. However, greater economies can be obtained by use of a pressure boil, provided air is properly and completely removed. Of course, safety precautions must be observed to make sure that the kier boiling equipment can safely withstand a pressure of about 15 to 20 pounds per square inch.

Removal of air is extremely important, and it must be properly done to avoid air pockets in the cloth. One method recommended is to give the load a "rest pause" of 10 min. after it has been heated to 60-65° C. and another pause at 80-85° C.

The above is only a summary of Dr. Parikh's paper. Through the courtesy and coopera- tion of Dr. Parikh, I shall be glad to attempt to furnish more explicit details of what he calls an "intermittingly continuous process."

I think the research chemist should give consideration to standard processing methods with the objective of improving them in the light of modern knowledge. The above example shows how a well-trained, modern chemist has modified an ancient process with considerable savings in time, energy, and money.

DEGRADATION OF MERCERIZED YARNS

My last subject is concerned with the degradation of mercerized yarns. In the prelim- inary notes on this workshop, a question was asked as to "resolving the apparent contradic- tion in why treated cotton retains more strength than untreated cotton such as before and after mercerization."

In 1941, in my first work at the Southern Laboratory, I treated mercerized and unmer- cerized cotton yarns with formaldehyde in acetone for 20 hr. at 40° C. with use of a sul- furic acid catalyst. I noted that there was considerably less loss of strenth in the mer- cerized yarns.

At that time the Laboratory established a research suggestion system that I recommend very highly to you for consideration in your own organization. Anyone who had a suggestion for future research on any aspect of the Laboratory's program was encouraged to describe the idea briefly in a written report and submit it to the Director's office. The suggestion was reviewed, revised, given a number, and copies of it were sent to research leaders for filing. The person submitting the suggestion received credit for it and, if the idea were activated, received further acknowledgment. Eventually, the book of suggestions became very large, and a system was developed to modernize and combine similar suggestions. This book often furnished ideas for new research and proved helpful in setting up new research projects.

I submitted a suggestion about the mercerized and unmercerized yarns and forgot about it until one day, about 25 years later, I received a notice that I had been appointed sponsoring scientist on the subject on a PL-480 project which had been granted to India. You may know that PL-480 funds were blocked funds which could be used to support research projects in that country. These funds are now called "SFC" for special foreign currency funds.

The project was numbered UR-17-(20)-227 and was granted to Shri Ram Institute for Industrial Research, Delhi, India, and it was activated on October 8, 1970. The project title was "Fundamental study of differences in degradation and reason therefor between mercerized and unmercerized cotton in the presence of acid and basic catalysts to provide basic information needed to improve durable press finishes for cotton fabrics and to in- crease the utilization of cotton".

A final report of about 100 pages on this project was submitted in October 1977. It is, of course, impossible to give all the details in this space. Briefly, however, a com- prehensive study was made of the effect of various types of mercerization, including ten- sion-mercerized, slack-mercerized, slack-mercerized and restretched, mercerization with simultaneous steaming, and a comparison of caustic soda and ammonia mercerization. Tensile strengths were determined, x ray diffraction diagrams were made to determine con- version of cellulose I to cellulose II, barium numbers were used to determine absorption, and fluidities run to determine degradation. Yarns and fabrics both were studied, and some knitted fabrics were examined. Woven fabrics of different constructions were used, and these fabrics and the knitted fabrics were treated to make them crease resistant.

Very briefly, it was found that although mercerized cotton undergoes higher chemical degradation, it retains higher tensile strength as compared to unmercerized cotton for identical treatments such as acid hydrolysis, thermal degradation with or without basic catalysts, and resin treatments for imparting durable-press finishes. Furthermore, among the mercerized yarns, the slack-mercerized and restretched yarns retain higher strength than the normal tension-mercerized yarns. The susceptibility to chemical degradation was found to decrease with the increase in tension applied during the stretching of the slack-mercerized yarns beyond their original length.

To quote from the report:

"The results of the degradation studies on mercerized yarns clearly bring out the anomalous behavior of mercerized and unmercerized yarns toward chemical degradation. The mercerization treatments have increased the accessibility and reactivity of the cotton and this increased reactivity is shown by the higher values of fluidity, bonds broken and higher rates of hydrolysis in case of all mercerized yarns. The better retention of strength properties has been attributed to certain supermolecular changes brought about by mercerization treatments. Correlation of x ray data with the retained breaking strength values shows that of all of the changes brought about by mercerization, increase in the orientation of the crystallites along the fiber axis is the single factor largely responsible for the retention of higher strength by mercerized yarns after degradation. Thus the yarn with an orientation factor of 0.069 retains as much as 86% of breaking strength even after 64 hours of hydrolysis as compared to only 66% strength retention in the case of yarns with an orientation factor of 0.058.

"Thus, the slack mercerized and overstretched yarns (stretched beyond their original length) have reduced susceptibility to degradation as a result of the increased orientation which increases with increasing strength. The higher degree of orientation has possibly helped in reducing the size of the crystallites and in making these crystallites more crystalline in nature. The voids in between the crystallites will also be reduced."

The Indian researchers were very interested in the improvement in mercerization when the fabric was steamed during the first stage of mercerization. They found in the laboratory and in the mill that this treatment was beneficial in giving an acid resistant fabric and that it minimized strength loss substantially when the fabric was given a durable press treatment. They recommended that further work be done along these lines.

It now appears that further work on this project will be done in Egypt in the Textile Research Division of the National Research Centre by Dr. A. A. Hebeish. The Sponsoring Scientist at the Southern Regional Research Center will be Dr. Stanley P. Rowland. The project is titled, "Mechanism of degradation of cotton and mercerized-stretched cotton." Degradation by ultraviolet light, hypochlorite bleach, acid hydrolysis, thermal exposures, and weathering will be studied.

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VARIOUS INDIRECT PADDING TECHNIQUES

(A)

KISS ROLL PROCESS
(TWO-ROLL PAD)

FABRIC

AGENT
SOLUTION

(B)

LOOP TRANSFER PROCESS
(TWO-ROLL PAD)

FABRIC

←LOOP

(C)

LOOP TRANSFER PROCESS
(THREE-ROLL PAD)

1 2 3

(D)

LOOP TRANSFER PROCESS
SHOWING TRANSFER
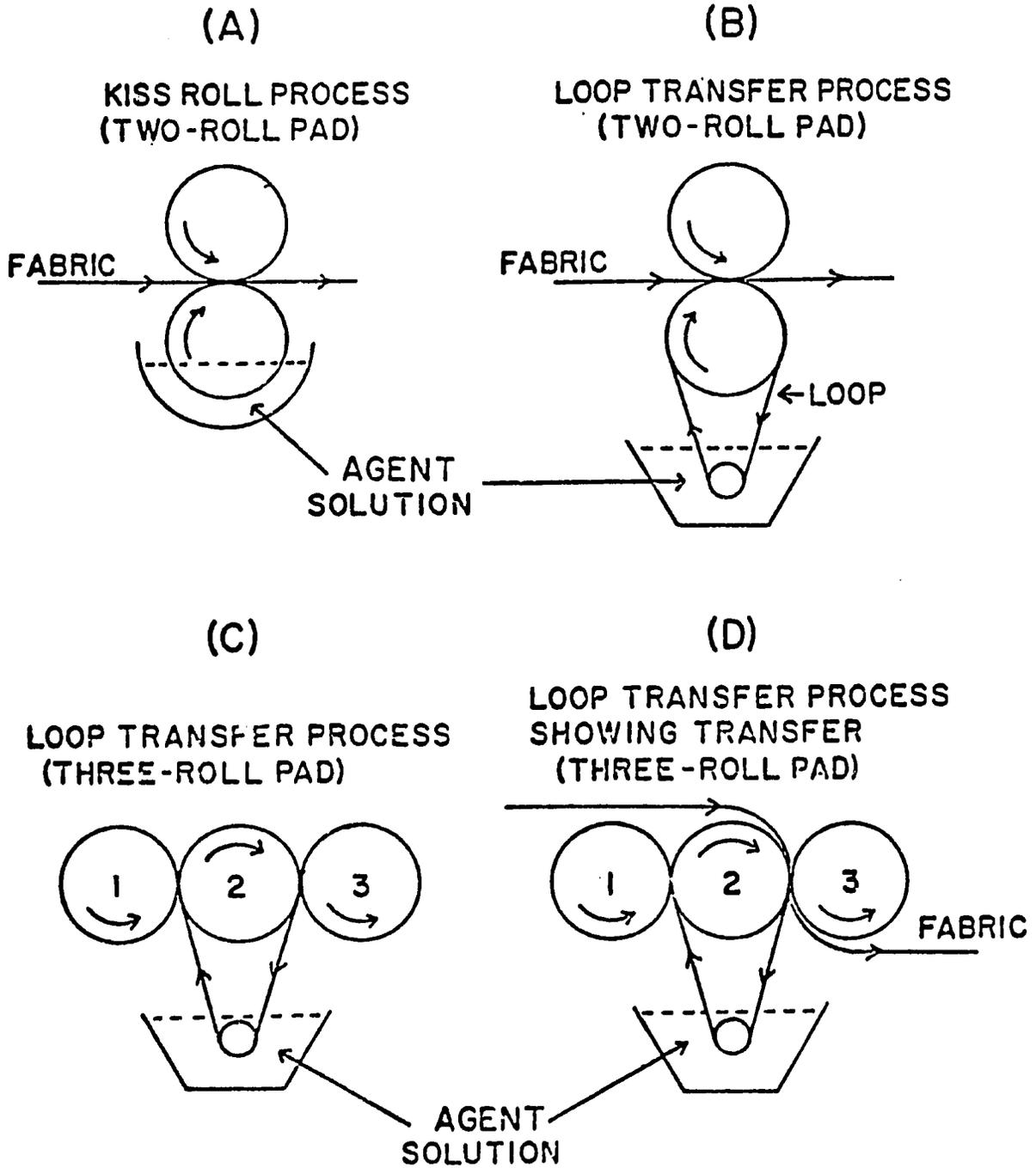(THREE-ROLL PAD)

1 2 3

FABRIC

AGENT
SOLUTION

Figure 1
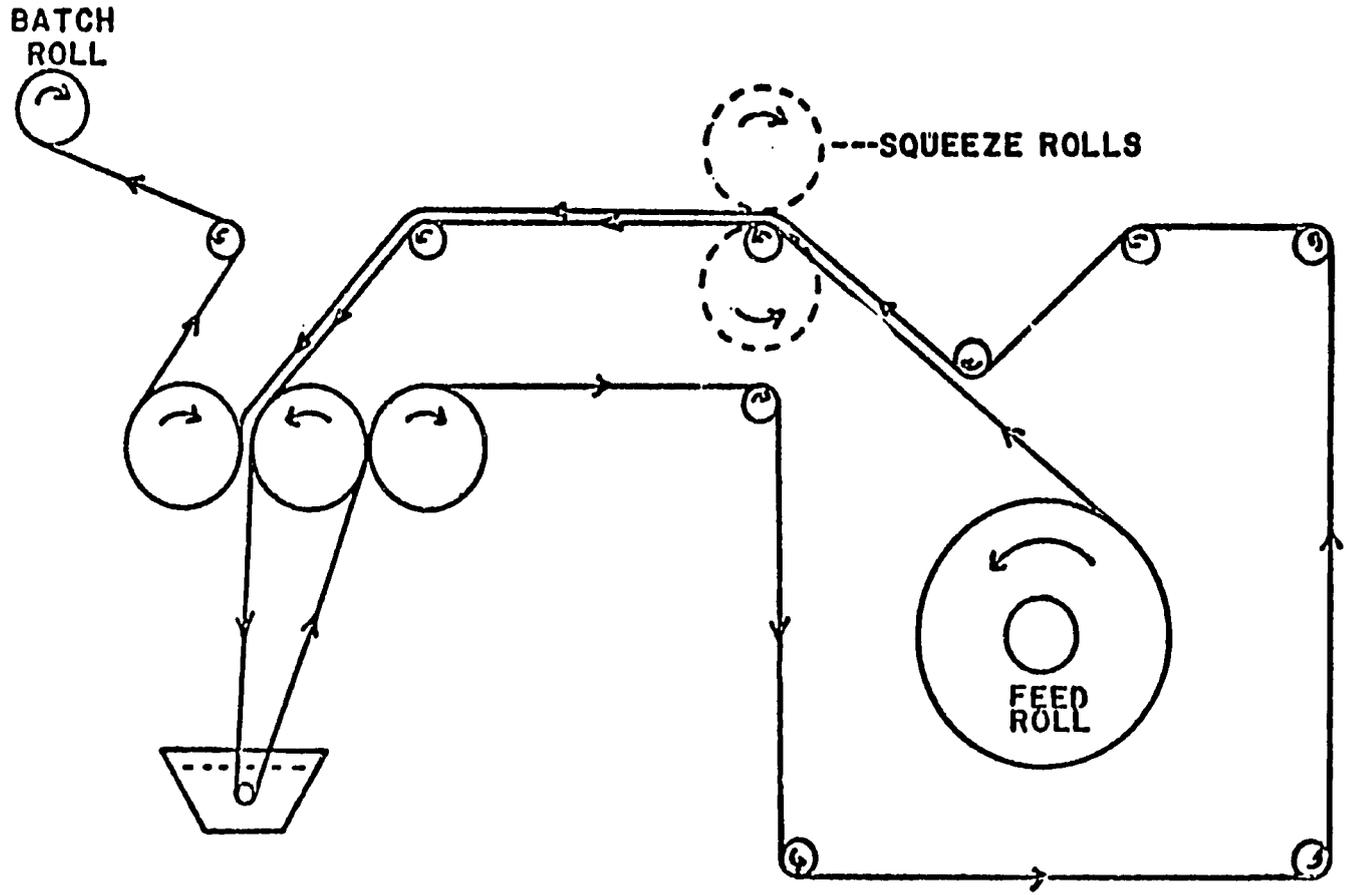
PAD TRANSFER TECHNIQUE

Figure 2

Radiation--Chemical Modification

of Cotton and Its Blends

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National Research Centre

INTRODUCTION

The application of high energy radiation has been successfully developed in several industrial processes during the past decade. In the textile industry, electron accelerators are currently being used in a process which imparts durable-press and stain-release properties to a polyester-cotton blend fabric. For this, Deering Milliken Co. is applying a continuous delayed-heat cure/mutual irradiation process using five ICI-500 electron accelerators for the finishing of millions of yards per year (1, 2), while Cone Mills produces the same type of finish through a delayed radiation-cure/mutual irradiation process based on the work of Walsh and Rutherford of North Carolina State University (3, 4).

It should be emphasized that the application of high energy radiation to textiles is essentially concerned at this time with the efficient utilization of the free radicals that result from the radiolysis to promote reactions which lead to beneficial property changes in textile fibers. Radiation-induced graft copolymerization of many different vinyl monomers with polymer fibers constitutes by far the largest volume of the research publications in the field of radiation modification of polymers to obtain new and interesting properties leading to better performance. These properties, which can in principle be built into a fiber by radiation grafting include crease recovery (5, 6), better wettability and adhesion, stain-release (7), dyeability (8), antistatic behavior, increased comfort, rot and mildew resistance, high thermal stability, nonflammability (9), and others.

RADIATION-INDUCED FINISHING OF TEXTILES AT NRC

To keep pace with recent advances in science and technology, a group of research scientists was recently formed in the textile department of the NRC to study the application of high energy radiation in textile finishing operations. The team tackled finishing aspects of importance dealing with different textile substrates, mainly cotton, cotton/polyester, wool, wool blends, polyester, and polyamide. Results are summarized in the following abstracts.

RADIATION MODIFICATION OF COTTON FABRICS

PART I: CROSSLINKING COTTON USING MULTIFUNCTIONAL MONOMERS (5)

Ionizing radiation (gamma rays from a Co-60 source) combined with a chemical treatment using two multifunctional monomers (HHTAT and N-methylol acrylamide) successfully cross-linked cotton cellulo e, thus imparting easy-care properties. Improvements of 50% were obtained in both dry a id wet crease recovery when irradiating fabrics in a single monomer system. In mixed mono, or systems, irradiation followed by a delayed heat cure plus chemical catalysis gave cotton an easy-care finish with a 72% improvement in the dry crease recovery and a 70% improvement in wet crease recovery properties. All fabrics finished in the foregoing manner remarkably retained their tensile strength in contradiction with great losses encountered with conventional chemical crosslinking type of finishes.

PART II: CATALYTIC EFFECT OF GRAFTED ACIDS (6)

This paper reports the catalytic effect in crosslinking reactions of grafted acids as substitutes for conventional inorganic ones.

Unsaturated mono- and/or dicarboxylic acids were radiation-grafted on cotton cellulose during crosslinking using multifunctional monomers. In a delayed heat cure, the grafted acids catalyzed the condensation of available cellulose hydroxyls with the methylol groups of grafted polymethylol acrylamide. This further crosslinking gave an additional improvement in wrinkle resistance with negligible loss in tensile strength. The catalytic effect of used acids was studied singly or/and combined.

GAMMA RAYS FOR THE PRODUCTION OF AMPHOTERIC COTTON
WITH IMPROVED DYEING AND WRINKLE-RESISTANCE PERFORMANCE (10)

Gamma rays successfully grafted a copoly (acrylic acid + allylamine) on the cellulosic chains of cotton fabrics. This radiation-chemical modification of cotton imparted to it new, valuable properties by introducing an amphoteric character through the fixation of both carboxylic and amino groups permitting cotton to be dyed with both basic and acid dyes to which originally it has no affinity. In addition, the radiation/chemically-treated cotton fabrics gained a significant improvement in wrinkle or crease-recovery performance through formation of crosslinks between cellulose chains.

Parameters dealt with in this investigation are radiation dose, composition of treating monomer systems, effect of pH, and effect of type of neutralizing acids. Textile evaluations investigated for the radiation-produced ampholytic cotton are dyeing affinity, crease resistance, and tensile strength.

COTTON/POLYESTER BLENDS WITH IMPROVED DYEABILITY AND
PHYSICAL PERFORMANCE VIA GAMMA RAYS (8)

A cotton/polyester blend is radiation grafted with a copolymer (allylamine + acrylic acid) to varied add-ons at different doses of Co-60 gamma rays. The amphoteric character imparted to this radiation/chemically-treated blend is due to the fixation of carboxyl and amino groups on the polyester and cotton cellulose chains by a radiation-induced free radical mechanism. The treated blend acquires new, remarkable dyeing affinity toward basic dyes, to which originally the untreated blend components both have no affinity. Hence, dyeing the blend with a single dye to a desirable solid color by a one-bath process is feasible. Moreover, an additional improvement in the wrinkle-resistance performance of the treated blended fabrics is recorded because of the formation of crosslinks between the components chains accompanied by a significant increase in tensile strength and elongation at break.

Parameters investigated during this work are radiation dose (0.2-1.6 Mrad. for 1 to 4 hr.), composition of treating monomer solutions, effect of pH, and role of neutralizing acids. Textile evaluations reported are visual dyeing affinity, crease recovery, tensile strength, and elongation at break.

FLAME-RETARDANT COTTON FINISHING THROUGH GAMMA RAYS (9)

Co-60 gamma rays were used to radiation-cure a flame-retardant finish on a drill-type cotton fabric to impart the property to the substrate. The radiation-induced grafting of flame-retardant components was effected via two methods. Method A involves the grafting of 3-methyl-5-vinylpyridine (MVP) onto cotton fabrics followed by reacting the formed polypyridinomethyl cellulose separately with three phosphorous compounds; namely, ortho-phosphoric acid (OPA), B-chloroethylphosphonic acid (CPA), and tetrakis (hydroxymethyl) phosphonium chloride (THPC). In Method B, equimolecular mixtures of MVP and each of the three phosphorous compounds were prepared followed by radiation grafting of the mixtures on cotton through a mutual technique.

Method A resulted in cotton with durable flame retardancy (in case of CPA and THPC) accompanied by acceptable loss in tensile strength and elongation at break. Method B led to fabrics with better performance in both flame retardancy (10-25% improvement) and tensile strength (22-136%) when compared to Method A. The durability of the finish being as with Method A.

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Some Commercial Successes and Failures
in Chemical Modification of Cotton

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Those of us who have had industrial experience would define "successful" research as that research which results in a product which can be produced in commercially acceptable quantities. Generally, economics is the important issue. Is the product desired, i.e., is there a market or must one be created? Is the result of the process worth the cost? These are simple questions and quite obvious, but sometimes we overlook their importance in our enthusiasm for our successes in the laboratory. I would like to discuss a few chemical modifications of cotton which were successful in the laboratory and pilot plant and which did not always succeed in commercial development.

Cellulose has long been an interesting chemical raw material, and over the years we have studied many of its reactions. However, cotton is a relatively expensive form of cellulose and the only kinds of chemical modification which would be of value would be those in which the fibrous form of the cotton was preserved and required. If we agree that the fiber must be preserved, we can consider three stages where the proposed modifications might take place.

First, we may carry out the chemical treatments in the fiber form. Some of the early cyanoethylation work was done in a stock dyeing machine (1, 2, 3) but the kind of equipment needed is seldom available in mills and is usually not readily adapted to chemical treatment. Laboratory or small scale units were devised for the production of cyanoethylated and hydroxyethylated linters (4), but the processes were not commercialized. In any event, the most prominent reason why such systems are not popular is the difficulty in getting the modified fibers through the normal mechanical processes such as carding, drawing and spinning.

The second stage at which treatments might take place is when the cotton is in the form of sliver, roving, or yarn. Of these three, yarn is normally preferred. Cyanoethylation of yarns was carried out on a large scale in package dyeing machines (1, 2, 3) and on a small scale in a continuous system (5), and although the process appeared to be commercially successful, there was no demand for the product, which will be discussed later.

Some other yarn processes which either failed or had very limited success might be mentioned. Soluble yarns to be used as stuffing yarns in towel borders were prepared in package dyeing machines by reaction with acrylamide, but rayon proved to be a better substrate than cotton. Ultimately, the small demand did not make the process worthwhile, and readily available alginate yarns were successfully substituted. Carboxymethylated cotton yarns met with some limited success, and I am certain that you will hear more about this from one of the other speakers. Also, there was some interest in yarns which were resin-treated and then untwisted to provide a kind of texturized yarn, but the process was never utilized on a commercial scale.

FABRIC TREATMENT

The third approach to chemical modification of cotton is the most popular--the treatment of fabrics. Certainly the popularity of this approach is based on the availability and flexibility of equipment found in most chemical finishing plants, and the majority of our successes and failures have taken place in the fabric form. Therefore, I would like to examine a few of these processes in depth.

One of the earliest attempts at the Southern Regional Research Laboratory of the U.S. Department of Agriculture dealt with partial acetylation of cotton fabrics to produce products which were heat- and rot-resistant (6). Some interest was shown in this fabric for covers for steamheated presses in the apparel and laundry industries. Although the acetylated fabrics were shown to have a much longer life than those untreated fabrics normally used, press operators elected to continue using untreated fabrics rather than pay the necessary increase in cost or to use more expensive man-made fibers with even longer life.

Partial cyanoethylation has already been mentioned. One property of this modified fabric which aroused the most interest was its resistance to rot or microbial attack. In spite of this interest, no commercial products resulted except a brief output of fabric for the manufacture of sandbags for the erection of protective barricades. This sandbag market was eventually taken over by man-made fibers which were inherently resistant and were lighter (which resulted in easier transportation of the empty bags).

Partially carboxymethylated cotton was used for a while in scaffolding fabrics for Schiffli embroidery, but these have been replaced by fabrics of oxidized cellulose.

A good example of how unforeseen events can affect a market is the failure of Deering Milliken's "Belfast" treatment for wash-wear cotton fabrics. You will remember that this involved the formation of a bis ether from dichloropropanol and cellulose in the presence of concentrated sodium hydroxide.

$$Cell-O-CH_2-C(OH)-CH_2-O-Cell$$
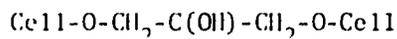
Since the cross-link was established in the wet condition, the fabric had good wet wrinkle recovery, but this required that the fabric be hung to dry in the wet condition, i.e., it had to be "drip dried." The hand of the finished fabric was silky, and the resistance to chlorine bleach made the product attractive. Shortly after this finish was introduced commercially, however, tumble dryers for home use became popular in the U.S., and "drip dry" finishes would not perform satisfactorily in these appliances. The finish quickly disappeared from the marketplace.

RADIATION CURING

A more elaborate sequence of events first stimulated our interest in radiation methods for producing durable-press apparel and then destroyed it.

In 1964, Levi Strauss Co. built the first oven for commercializing the Koret patent which had been issued to Warnock and Huebner on March 14, 1961. This patent dealt with the delayed cure concept in which a fabric was treated with a cross-linking agent and a catalyst, dried, cut, and assembled into a garment which was shaped and finally cured in an oven (7). Because the use of the patent required a fee and royalties, searches for alternate methods were conducted on many fronts. Two of these alternates involved the use of radiation with electron beams (8).

Deering Milliken Co. had devised a method for grafting N-methylol acrylamide onto cotton presumably through the unsaturated segment of the molecule by the use of radiation. The grafted fabric which contained a normal Lewis acid catalyst could then be cut, sewn, shaped, and cured to give durable-press apparel. This was considered to be substantially different from the specifications of the Koret patent which prescribed the kinds of cross-linkers to be used. The DM fabric also had soil-release properties.

During the same time, researchers at North Carolina State University had been working on a similar process (9, 10). The NCSU process was reversed, however, That is, the N-methylolacrylamide was applied to the fabric with a catalyst and thermally cured. The fabric was then washed and sent to the apparel manufacturer who was expected to cut, sew, and shape the garment and then complete the cross-linking by means of electron beam radiation. This approach met with substantial resistance on the part of the apparel manufacturers, who objected to the cost of the irradiation equipment, and the process was never commercialized.

Meanwhile, complicated legal proceedings were developing which culminated in a long, multifaceted trial in the U.S. Federal Court in San Francisco in 1973. The trial involved two textile manufacturers, at least a dozen apparel manufacturers, and Koret Co. The court's decision in 1974 upheld the validity of the Koret patent but confined the coverage only to the precise wording in the patent claims "...the fabric (is) partially dried at a temperature below the polymerization temperature of the resin so as to maintain the contained resin in an unpolymerized state and approximately 2% to 8% of moisture is retained in the fabric..." This confinement liberated the apparel manufacturers from the restraints of the patent, because they had been using partially or lightly cured fabrics all along (which they preferred because of their improved stability during the manufacturing process). Therefore, they were free to use these fabrics already available to them and cure them in their ovens without paying royalties.
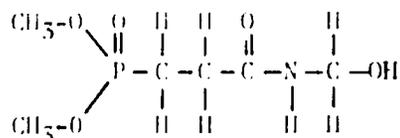
The interest in radiation curing disappeared overnight.

RESISTANCE TO FLAMMABILITY

Nevertheless, this early experience in radiation curing of textile finishes prepared us for a more recent development. Flammability legislation has promoted our interests in flame-retardant finishes for cotton, and it has now been shown that Fyrol 76, a finish which we will discuss later, can be successfully grafted onto cotton to produce durable flame-retardant products with good hand, strength retention, and resistance to chlorine bleaching (11).

Flammability legislation, which we just mentioned, led to a commercial failure for reasons which we did not anticipate and to two successes which required considerable development.

First, let me discuss the failure. Pyrovatex CP (12) was introduced to textile

$$CH_3-O \diagdown \diagup \overset{O}{\underset{CH_3-O}{P}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{O}{\underset{H}{C}} - \overset{H}{\underset{H}{N}} - \overset{O}{C} - OH$$

finishers in 1967. By the middle of 1968, development had proceeded to several pilot plant trials of a few hundred yards each. A major apparel retailer decided to test market the finish on cotton flannel sleepwear, and a substantial order was placed for delivery of treated fabric in late 1968. When the mill began to process the order on continuous pad-dry-cure equipment, an unforseen problem arose. Some kind of adhesive substance collected on the rollers in the curing oven and gradually built up to the point where the range had to be shut down for cleaning. Since this happened every 10,000 yards or so, the processing time was excessive and the production effort was abandoned. A second mill succeeded in completing the contract by using a loop, or festoon dryer, for curing instead of a roller oven (13).

This retail offering of FR sleepwear, although it was rejected by consumers because of higher cost, probably convinced government agencies that flame-retardant children's sleepwear was possible, and the first law covering sizes from 0 to 6X was issued in 1971. Meanwhile, difficulties with Pyrovatex CP continued. This time, the problem was unreliability, probably caused by the poor shelf life of the finish. Since it was produced in Switzerland (for patent reasons), substantial time elapsed between the time of manufacture and the use of the reagent. Apparently, the instability was caused by cleavage of the methyl ester to produce a free acid with subsequent lowering of the pH and an increased rate of decomposition. These new problems led to abandonment of the finish, to be revived only when no other substitute was available in 1973 when the sleepwear law became fully effective. By 1974, more reliable substitutes were offered for development, and by 1975 the use of Pyrovatex had sharply declined.

During the development period between 1971 and 1975, the unpredictable results from Pyrovatex CP, coupled with the difficulty in applying it to cotton fabrics because of the

sticky residue and the interference with stabilization of cotton knits, led to a decline in cotton's share of the 50 million pounds-per-year children's sleepwear market. In 1967, 87% of this market was cotton. By 1973, it was 19%, in 1974 13%, in 1975 11%, and in 1976 it was 10% (14).

It is important to note that one of the unforseen events which contributed to the decline in the use of FR finishes for cotton was the requirement that the product be tested for flammability before and after 50 mechanical wash-and-dry cycles. Fibers considered to be "inherently flame retardant," such as modacrylics, do not require such durability tests. The long delay before goods could be shipped--more than a week in a one-shift laboratory--made these products unpopular in the finishing plant.

Currently, attempts are underway to produce a more stable version of Pyrovatex in order to recapture the market which it helped to create, but for the moment this process must be considered a short-lived success but a long-range commercial failure.
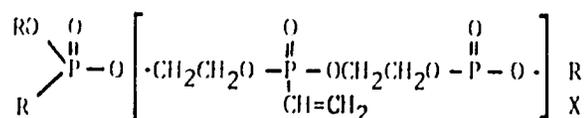
Although knitted cotton sleepwear for children almost entirely disappeared in 1973 and is only now beginning to return to the marketplace, woven fabric still required FR treatment and Pyrovatex CP was replaced by two newcomers which so far have divided the cotton sleepwear market almost equally between them.

The finish which took longer to develop was somewhat different from conventional finishes, which depend on a chemical bond to cellulose and may therefore be considered a chemical "modification." This process, THPOH-ammonia, depended on the deposition of an insoluble substance inside the fiber--somewhat like the formation of napthol dyes. The idea of using gaseous ammonia originated in Southern Regional Research Laboratory around 1956 (15), but something like 10 years passed before attempts were made to commercialize such a finish. In 1967, pilot plant trials indicated that the treatment was feasible, but development was difficult. The primary obstacle was the control of the diffusion of the ammonia gas into the fiber, and there were many false starts until successful systems were devised around 1974 or early 1975. The deposition of the polymer inside the fiber without chemical attachment to the cellulose bulks the fiber but does not cause reduction in its strength. In fact, there is a slight increase in the breaking load. Bulking of the amorphous regions does lead to some rigidity and a loss in tearing strength but not as much as is normally experienced with cross-linkers. Unfortunately, these good strength characteristics are paid for by a lack of wash-wear or smooth drying ability.

The other successful FR agent also depended on a new approach, vinyl polymerization. When Fyrol 76 was introduced commercially by Stuaffer Chemical Company in 1974, the structure was revealed as (16):

$$\left[-O -\underset{\underset{CH=CH_2}{|}}{\overset{\overset{O}{\|}}{P}} -O -R \right]_X$$
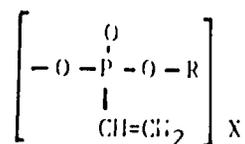
Later, the structure was modified to reduce the number of vinyl groups and therefore the number of bonding sites, which gave improved strength retention (17):

$$\underset{R}{\overset{RO}{\diagdown}}\hspace{-0.5em}P-O\left[\cdot CH_2CH_2O -\underset{\underset{CH=CH_2}{|}}{\overset{\overset{O}{\|}}{P}} -OCH_2CH_2O -\overset{\overset{O}{\|}}{P} -O \cdot \right]_X R$$

R = alkyl, usually CH_3

This finish is made durable by polymerization of the vinyl group brought about by peroxide catalysts. Attachment to cellulose can be achieved by including a co-reactant, usually N-methyloacrylamide, which provides a vinyl group to react with Fyrol 76 and a methylol group to react with the cellulose. Fyrol 76 can also be applied as a homopolymer which presumably is bulked inside the fiber like the THPOH-ammonia product with the same results; that is, better strength retention at the expense of wash-wear appearance.

An added benefit of this homopolymer is its resistance to chlorine bleach, probably because of the absence of basic nitrogen groups, which requires a higher phosphorus content.

Both of these systems with insoluble polymers and an absence or minimum of crosslinks give fabrics which have better sewability; that is, with less needle heating and less needle cutting of yarns.

A final success story is more recent: the commercial production of cotton fabrics "mercerized" in liquid ammonia. Southern Regional Research Laboratory has studied the transformation from Cellulose I to Cellulose II and III for more than a generation, and a recent paper (18) outlines some of this work and indicates these new interests. This process has been commercially successful for more than a year in an area that we would not have predicted from laboratory studies on 12-to-14-ounce denim. This cloth usually comes off the loom with about 14% shrinkage in the warp direction, and this amount of shrinkage cannot be eliminated in one pass through a Sanforizer or other compactor. Ammonia mercerization eliminates about 40% of this shrinkage in 14-ounce denim, less in lighter fabrics. The remaining potential shrinkage can then be handled by conventional means. In addition, the treatment appears to eliminate progressive shrinkage.

As a bonus to shrinkage control, the swelling of the fibers gives a fabric which dries almost as smooth as one which is resin treated, without the usual loss in tearing strength.

The financial success of one large apparel producer last year (19) was attributed largely to this process, and several of its competitors have now adopted it. Other major apparel manufacturers are depending on a small amount of polyester to produce a competing product, and an interesting commercial battle is taking place.

ENVIRONMENTALISM

I cannot end this discussion without mentioning some influences in the U.S. which may create new opportunities for chemical modifications of cotton but will probably cause a large number of commercial failures of successful laboratory processes. As you know, we have entered an age of "consumerism" and "environmental protection." In 1969, the U.S. Congress endorsed the National Environmental Policy Act which led to the establishment of several agencies empowered to restrict or prohibit any agent which might interfere with acceptable environmental qualities.

One of these agencies is the Environmental Protection Agency, whose main efforts have been in the areas of air and water contamination. Clearly, its regulations can control the use of many chemical reagents now being used or proposed for use on cotton.

The specific impact of chemical reagents on the worker falls under the authority of the Occupational Safety and Health Administration. One of its concerns has been the cancer-causing potential of materials used in manufacturing. Textile people in the U.S. are well aware of the problems caused by the possibility of bis-chloromethyl ether in finishing baths and of the restrictions put on exposure to vinyl monomers. Proposed regulations on noise and dust in cotton mills are expected to increase the cost of manufacture of cotton fabrics by some 20%.

The Consumer Product Safety Commission has focused attention on the effect of chemical reagents on the consumer. Its most widely publicized effort has been the so-called "Tris" incident in which tris(dibromopropyl)phosphate was banned from use as a flame retardant in polyester and acetate fibers because it caused cancer in animals.

A new addition to the many government controls is the Toxic Substances Control Act, a blanket law which "clearly places the burden of proof on the manufacturer that a chemical will not lead to significant adverse effects to health or the environment" (20).

Six weeks ago, several speakers at the annual Technical Conference of the American Association of Textile Chemists and Colorists speculated on the future. One of them (20) said:

Because textiles rank with food, drugs and cosmetics in human exposure, it is foreseeable that the EPA, as well as public interest groups, will spend an increasing proportion of their resources on close scrutiny of textile fabrics as possible vehicles for public exposure to toxic materials.

In spite of these dismal prospects I am, like most of you, still infatuated with cotton 40 years after my first exposure to cellulose chemistry. I don't believe that cotton will disappear from the Universe, nor do I believe that the science of chemistry will be abolished. My logical conclusion is that cotton chemistry will survive.

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Chemical Modification of CMC:

Possible Paste for Printing with Reactive Dyes

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Carboxymethyl cellulose in the sodium form (CMC) is one of the most important materials used in the printing pastes of pigments, vat dyes, and dispersed dyes. In printing with reactive dyes, which combine chemically with cellulose, one of the first problems encountered was that of finding a suitable thickener. Since it was reported that most of the common thickening agents are carbohydrate, it is only to be expected that under any conditions which will lead to fixation of these dyes on the fiber, reaction with the thickener will also occur. This is, in fact, observed. The effect is either to give a poor color yield, since some of the dye is not available to combine with the fiber and is removed in a bound form when the thickener is washed off, or else to insolublize the thickener, so that it cannot be readily removed from the fabric and gives prints with a harsh, stiff hand (1, 2, 3).

The absence of any reaction between sodium alginate and reactive dyes for cellulosic fibers makes it the most suitable thickener for use with these dyes (1, 2, 3, 4, 5, 6). The observation that sodium alginate does not react with reactive dyes has been interpreted as evidence that the secondary hydroxyl groups of cellulose do not react with these dyes. However, experiments on the dyeing of oxidatively degraded cellulose indicate that both primary and secondary hydroxyl groups undergo reaction (2, 7). The reason for the nonreactivity of sodium alginate toward reactive dyes is not fully understood but is probably a consequence of the ionized groups in the alginate. It seems probable that the value of this product lies in the carboxyl groups in the polymer, which ionize and repel the similarly charged dye ions and so prevent reaction. This effect will also promote the transfer of the dye from the thickener into the cellulose. With some dyes, an alginate gives a better transfer of color from the paste to the fabric than other materials. This again is attributed to the negative charge on the alginate ion (8).

However, it was found that solid calcium alginate reacts with reactive dyes of the triazine type. The reaction product is readily decomposed with alkali washing treatments (2). The fact that viscous solutions of sodium alginate form, in the cold, primary valence bonds with reactive dyes in the presence of OH^- was proved by dyeing tests followed by oxidative cleavage, diazotization, and coupling with a phenol before and after precipitation of the acid with $Ca(OAc)_2$ (9).

Although it is generally known that the failure of employment of CMC in the printing paste of reactive dyes could be traced back to the reaction of CMC hydroxyls with reactive dyes (1, 2, 3), yet no systematic study has been carried out so far on the extent of reaction of reactive dyes with CMC. It is believed that such studies would be quite useful to find out whether CMC could under certain conditions be used for the printing paste of reactive dyes without impairing the prints.

The work carried out in this division (10, 13-18) aims to fill this gap and presents the results of investigations on possible use of CMC in reactive dyes print paste.

Judging from what is revealed in the literature (loc. cit.) and from experimental results obtained in this laboratory (10), it is certain that carboxymethyl cellulose reacts with Cibacron Brilliant Red B. Yet, it is likely that in presence of cellulose, CMC may react with the reactive dye as well as may act as a transferring medium for the dye, thereby facilitating its penetration to the cellulose for a reaction to occur. In order to check the validity of this and in order to ascertain whether the amount of the

dye which reacts with CMC in absence of cellulose would be influenced by its presence, two parallel experiments were carried out under similar reaction conditions using the same paste. In the first experiment, the reaction was conducted, as previously described, by making a thin film of the paste on a glass plate. This is followed by drying and thermofixation at 150° C. for 5 minutes. These operations constitute the steps of the second experiment except that the glass plate was replaced by a cotton fabric. The latter, after being treated, was washed with cold water to remove the thickener, which was then precipitated, purified, and dried. The cellulosic fabric was soaped at the boil with an alkali soap solution (pH 11) to remove the loosely adhering dyed CMC.

The data reveal that CMC reacts with Cibacron Brilliant Red B in the presence and absence of cellulose. However, the extent of reaction is much lower in the presence of cellulose. This is expected, since reactive hydroxyl groups are available along the cellulose chain molecules, so that reaction of the dye with cellulose is possible in addition to the normal reaction between the dye and CMC. This is substantiated by the significant amount of the percentage of reacted dye observed with the cellulose. Thus, during printing of the cotton fabric with the reactive dye in question using CMC as a thickener in the print paste, there are two reactions which operate simultaneously. The first reaction is responsible for the significant amount of percentage reacted dye observed with the thickener, i.e., CMC, whereas the second reaction accounts for the substantial amount of percentage of reacted dye obtained with the cellulose. In other words, CMC in the print paste reacts with the dye as well as behaves partly as a thickening agent, depending on the nature of CMC used. Evaluation of CMC as a thickener will be discussed later.

CMC VERSUS SODIUM ALGINATE

It has been shown from the experimental results that CMC is able to act as a thickener in the print paste which can be used in printing of cotton fabric with Cibacron Brilliant Red B. It is therefore of interest to study the efficiency of CMC as a thickening agent in the print paste. For this purpose, pastes containing different CMC samples and another one containing sodium alginate, as thickeners, were prepared under identical experimental conditions. The pastes were applied to the cotton fabric either by just making a thin film or through a screen, i.e., screen printing.

Results from these experiments may be summarized as follows:

A. The percentage of dye reacted with cellulose when the printing paste was applied as a thin film is marginally higher than when the paste was applied through a screen. This is observed with both CMC and sodium alginate.

B. The percentage of dye reacted with cellulose is nearly equal for the paste of commercial CMC (D.S. = 0.62) and of sodium alginate. However, the samples which have been printed with CMC have a harsh hand, while those which have been printed with sodium alginate have soft hands.

C. It is believed that the harsh hand of the samples which have been printed with CMC is probably due to the adherence of some dyed CMC on the cellulose which cannot be removed by washing.

It is clear now that the problem of using CMC in printing cellulose with reactive dyes is the harsh hand. Hence, it is believed that the oxidation of CMC would reduce its reactivity toward reactive dyes by oxidizing some of the -OH groups and increasing its solubility via glycosidic bond cleavage. This may improve the hand of the printed goods.

OXIDATION OF CMC WITH SODIUM HYPOCHLORITE

A number of patents (11, 12) have outlined the utilization of sodium hypochlorite as a bleaching agent for CMC. These patents disclosed that CMC treated with hypochlorite showed lower viscosity than similar but untreated one.

A detailed study of the action of sodium hypochlorite on water-soluble CMC was carried out in this laboratory (13). It is believed that the results of this investigation would prove of value to the utilization of oxidized CMC in the printing paste of reactive dyes.

To start with, oxidation of CMC having D.S. 0.62 with sodium hypochlorite was examined under a variety of conditions. Variables studied include concentration of the oxidant, pH of the oxidizing medium, and temperature of the reaction. The influence of a catalyst with the oxidant was also investigated.

It has been found that increasing the hypochlorite concentration and/or the reaction temperature favorably affects the rate of oxidation. The latter is very slow in alkaline solution, while it is only slow in the earlier stages of the reaction when the oxidation was conducted in acidic medium. On the other hand, the rate of oxidation is very rapid in neutral medium.

By carefully controlling the oxidation process, it has been possible to prepare oxidized CMC which has a viscosity suitable for use in the printing pastes of reactive dyes. The printed goods acquire a soft hand with a color yield equal to that obtained when alginate was used as a thickener (14).

Furthermore, CMC with D.S. 3 was also prepared according to a method described elsewhere. This sample is not soluble in water. However, it was solubilized by oxidation with hypochlorite solution (13). Use of the oxidized product as a thickener in the printing paste of reactive dyes produces printed goods with excellent results in respect to color yield and hand. The thickener does not also react with Cibacron Brilliant Red B (14).

Furthermore, the suitability of oxidized CMC as a possible base for reactive dye print pastes has been technologically evaluated (15). The color yields and overall fastness of prints are somewhat comparable to those thickened by sodium alginate. Oxidized CMC has been successfully applied on a semi-industrial scale using both roller and screen printing methods. Furthermore, storage of oxidized CMC in paste form has practically no effect on printing efficiency (15).

CYANOETHYLATION OF CMC

The cyanoethylation of CMC in aqueous sodium hydroxide solution was investigated (16). The extent of reaction, expressed as nitrogen content, increases by increasing the concentration of acrylonitrile and then levels off, whereas the percent nitrogen decreases by increasing the cyanoethylation temperature. Cyanoethylated CMC samples are water-soluble, and their viscosity depends upon the degree of cyanoethylation.

Cyanoethylated CMC of different degrees of cyanoethylation was reacted with a reactive dye, Cibacron Brown 3 GR-A in the presence and absence of a cotton fabric (17). The extent of the reaction is much greater in the absence than in the presence of the fabric. The degree of cyanoethylation does affect the magnitude of the color yield on the thickener (modified CMC) as well as on the fabric. Generally, increasing the degree of cyanoethylation is accompanied by a decrease in the color yield on the fabric. Screen printing was performed by making use of pastes containing cyanoethylated CMC. The prints showed appreciable color yield and soft hand, reflecting the potential value of using this modified CMC in printing with reactive dyes.

Finally, the suitability of cyanoethylated CMC as a thickener for printing with reactive dyes has been technologically evaluated (18). The color yields and overall fastness of the prints are somewhat comparable to those thickened by sodium alginate.

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Chemical Modification of Cotton (Cellulose)--Carboxymethylation

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My introduction to cellulose chemistry began in 1945 when I joined Dr. J. David Reid's Chemical Properties of Cotton Section at Southern Regional Research Laboratory (now Southern Regional Research Center, U.S. Department of Agriculture) in New Orleans. The primary mission of this laboratory was to increase the utilization of cotton and cotton products. The first assignment given to me by Dr. Reid was to find a different approach to making modified cotton which would be swellable in water while retaining its fibrous state.

Goldthwait (1), a SRRL scientist at the time, had patented a treatment for cotton which involved impregnation with the alkali-soluble water-insoluble hydroxyethyl ether of cellulose. The object was to make a cotton substitute for linen fire hose because of the shortage and high price of linen during World War II. While Goldthwait's solution to the problem involved a surface application with no chemical modification as such, work by Stallings (2) followed with the same objective, which involved true chemical modification with acrylonitrile in the presence of sodium hydroxide. This treatment gives a partially substituted carboxyethyl ether of cellulose which yields swellable fibers and according to the patent fire-proof, leak-resistant fire hose. Why such a product would be expected to be fire-proof is not apparent, unless sufficient moisture is available from the hose to prevent ignition (a wet fire hose wouldn't burn!).

Our approach was similar to Stalling's except the mechanism would be carboxymethylation. The preparation of carboxymethylcellulose, using chloracetic acid and sodium hydroxide had been patented in Germany in 1921 (3). Lilienfeld (4) then patented the treatment of cellulosic fabrics with chloracetic acid followed by mercerization to obtain different finish and dyeing effects.

Our experiments were performed first on purified cotton fibers, then yarns, and finally fabrics. Although a single-stage treatment using sodium chloroacetate in sodium hydroxide appeared more logical, the problem of insolubility of the former in strong sodium hydroxide and its rapid hydrolysis led to the use of the treatment of cotton with a solution of chloroacetic acid followed by impregnation with sodium hydroxide. It was found that by varying the concentration of these two reagents, rather good control over the substitution of the hydroxyls in cotton by carboxymethyl groups could be obtained.

The initial objective being swellable cotton fabric as a substitute for linen, partially carboxymethylated cotton yarns were woven into fabrics and tested for water holding capacity. It was found that while the desired swelling was evident, most of the water transferred through the fibers in the fabric, not necessarily through the interstices which had been sealed effectively. So the original purpose of the research was not successful.

Since research must never be discouraged by initial failure, other possibilities for the PCMC reaction with cotton were investigated. The initial work involved in making cotton more swellable resulted in two publications and a patent (5,6,7) which described the conditions necessary to obtain the desired effects. Also resulting from this research were rapid methods for estimating the degree of substitution; converting to heavy metal-COOH salts, some of which conferred a degree of rot resistance; a stiffening surface effect resembling starching (which was not fully exploited); and highly absorbent material for uses such as kitchen towels.

To test the potential for commercialization, full width 80-square cotton cloth was padded on pilot plant equipment with 17.6% MCA and a wetting agent, followed by padding

with 42% NaOH. The fabric was collected on a roll, allowed to stand for 45 min. and then washed free of excess NaOH and dried on cans. CM-substitution was 1 cm group/15 anhydro-glucose units and found to be very uniform.

This PCM fabric was characterized as being more water absorbent, having increased resistance to soiling and ease of soil removal, being easier to iron and having a starched feel after ironing, offering improved light-fastness with azoic dyes, and having altered dye acceptance with substantive and vat dyes. While I am not aware of any present commercialization, it was reported by Decossas (8) in 1960 that CM-cotton was in production in the U.S. on a commission basis. It is interesting to note that monochloracetic acid was quoted at 19¢/lb. and NaOH at 2.8¢ at that time. No comment is needed as to the effect inflation has had on those prices since 1960.

As most researchers must agree, one never knows where a project will lead if time, money, and an understanding project director are present. In our case, the research led rather far afield of the original intent. Interest turned to the possibility of producing alkali soluble yarns which might compete with the rather expensive soluble alginate fibers produced in England. These fibers (yarns) were used for special effects in weaving, knitting, lace making, or for any product in which a thread is needed only temporarily and can be readily removed at some later stage of processing, such as in string-sock-knitting.

Attempts were made to duplicate the claim of Dreyfus (9) that by carboxymethylating cellulose to a D.S. of 2, acetone solubility could be obtained. The exact procedures of Dreyfus' patent were used without success, and multiple treatments of PCMC and commercial CMC were necessary to obtain this degree of substitution. The free acid of CMC with a D.S. of 2.05 was not soluble in acetone as claimed by Dreyfus. Unless I have missed something in the literature, I don't believe an acetone-soluble CMC has ever been produced, and I wonder if one should expect the carboxyl group on cellulose to impart such solubility.

Two approaches were used to imitate the properties of alginate fiber. In one, commercial water-soluble Na-CMC was used to make solutions which could be spun into metal-salt baths to produce filaments which, considering the crude methods used, were surprisingly strong (10,11). Blend fabrics of cotton and CMC yarns were made again in an attempt to obtain swellable structures or to dissolve the metal-CMC yarns to make lack-like materials. I am grateful to Dr. Reid and Dr. Ward (another member of the American team) that this newcomer to research was not ordered to discontinue this line of endeavor, since it was highly unlikely (on reflection), that it would ever lead to increased utilization of cotton. It was, however, intensely interesting and fueled the fires of the imagination which persuaded me that research on cellulose could be exciting.

Almost simultaneously with the fiber spinning project, it was found that cotton yarns could be carboxymethylated in two stages to impart water-solubility (12,13). The success of this development depended upon two properties of the finished product -- insolubility in strong alkali and in alcohol. CM-cotton yarns were produced which retained most of the tensile strength and other physical properties and yet would disintegrate in water. This development achieved more publicity and commercial interest than any prior work the author had done. Samples of CM-cotton yarn were supplied to shirt manufacturers, lace makers, meat packers, sock knitters, and placed in science kits which were widely distributed. Newspaper publicity queried whether the inventors had thought of making bathing suits from soluble cottons (we had, but only in jest). Unfortunately the interest waned when costs of production were considered (estimated at 40-50¢/lb.)

To me, one of the more interesting properties of CM-cotton is its ability (in the acid form) to self-catalyze cross-linking agents. Dr. Reid has described the development of durable press in the United States and the important contributions made by the Southern Regional Research Center. Recently, however, the "Environmentalists" in the U.S. have been getting wide publicity by casting suspicion on the more important reagents being used to make cellulosic durable-press fabrics as being carcinogenic or mutagenic. Several of the most important chemicals used as finishing agents have been cited as being under suspicion (14). They are formaldehyde, trimethylol melamine, tri-ethylene melamine, epi-chlorohydrin, di-biepoxybutane, acrolein, glycidol, di(2,3 opoxypropyl)ether, aceteldehyde, diethyl sulfate, and others. To meet stringent restrictions on these chemicals will mean vast outlays of money to protect workers and the environment or discontinuation of their commercial use. Substitutes would therefore have to be found.

In preparing for this presentation, I found an old notebook in which I had recorded (on 2/10/49) the idea for self catalysis of cross-linking resins by the COOH group in CM-cotton and a footnote, "it will probably work on phosphorylated cellulose also." Attached to the notation was the first piece of CM-cotton which had been treated with dimethylol urea resin without a catalyst. At that time the methylol resins were notably unstable in that their molecular weight increased on standing and especially in warm, acid-catalyzed pad bath. They were, however, successfully used on rayon fabrics or for stiffening agents (hand-builders) but were not especially good for cotton because the large molecules could not penetrate sufficiently the multiwalled layers of cellulose in the cotton fibers. With CM-cotton, however, there are two advantages: higher swellability and absorptivity of the larger molecules and a self-contained acid environment (the CH_2COOH group) which might possibly cross-link the resin with the cellulose. It had been determined by Hoffpauir and Guthrie (15) that the pH at half capacity of CM-cotton in the acid form is 3.65. This was expected to be more than adequate for the cross-linking reaction with amino resins.

When laboratory-prepared dimethylol urea and methylol melamine (Resloom HP) were applied respectively to CM-cotton fabrics and dried and cured, it was found that the finished, once-washed crease resistant fabric retained over 80% of its breaking strength, compared to 65% for the catalyzed resin treatment of mercerized cloth. In later experiments, improvements in tear strength and abrasion resistance were found over mercerized control fabric treated to equivalent resin contents.

This work was extended to phosphorylated cotton (16), which was made by the reaction of urea and phosphoric acid with cotton fabric. After conversion to the acid form, it was resin treated without catalyst. In this case, a rather good degree of fire retardancy was also obtained in addition to crease resistance.

My personal involvement in the research work at SRRL came to a conclusion in 1953 when I accepted a position with Courtaulds (Ala.) to do research on rayon modifications. However, the interest in PCM-cotton continued at SRRL and research on this subject was continued by my friend and co-worker, R. M. Reinhardt, and others

The nonaqueous carboxymethylation of cotton was described by Reinhardt and co-workers (17) in 1957. By using solvent exchange techniques to increase accessibility to reactivity, optimum conditions were obtained when prepared cotton was soaked in 5% monochloroacetic acid in isopropanol, take-up adjusted to 100%, and then treated to reflux with 0.3% excess of NaOH. a mixture of 12.5% methanol -- 87.5% isopropanol. A DS of about 0.075 was reached. With this treatment, however, some loss in breaking strength was obtained.

As a side observation of this work, they found that different varieties of cotton resulted in different degrees of substitution. This correlated very well with the Micronaire fineness of the cotton -- the lower the Micronaire the more substitution occurred. For example, SxP cotton gave twice the reactivity of Rowden 41B (fineness 3.85 and 6.07 respectively). This probably reflects the higher surface area of the finer cotton.

When compared with the aqueous treatments with higher concentrations of acid and alkali, however, the nonaqueous treatment gave less uniform carboxymethylation, as evidenced by dyeing with methylene blue. This was attributed to the comparatively lower amount of swelling in alcohol.

A rather extensive study on the effects of partial carboxymethylation on the physical properties of chemically modified cottons was done by Grant and co-workers (18). Six different varieties of cotton were used (Acala 1517, Coker 100 wilt, Deltapine 14, Rowden 41B, Stoneville 2B, and SxP) to determine the degree of CM-substitution obtained from identical (aqueous CM) treatments, and the effects of those treatments on such physical parameters as density, moisture regain, fiber length, linear density, breaking load and tenacity, elongation, and secant modulus. Fibers, fiber bundles, and yarns were used and untreated and mercerized cottons served as controls.

As in the Reinhardt study mentioned above, significant changes in physical properties were found for the six different cotton varieties investigated, with some giving larger or smaller changes from the untreated and control cottons. Density and moisture regain

increased, the latter to about twice that of normal untreated cotton. Fiber length was shortened and linear density increased, as did cross-sectional area and moisture absorptive capacity. Breaking loads of yarns increased more than that of individual fibers, and tenacities of both fibers and yarns were increased but not to the same extent as the breaking load. The smallest change was found in elongation at break. This is attributed to the use of controlled tension during the caustic soda treatment, following MCA or for the controls.

Of the six cotton varieties studied, the largest percentage of increases in breaking loads, tenacity, and elongation at break were found for the Stoneville cotton. The smallest increases in breaking load and tenacity and the largest decrease in elongation at break were found for the SxP sample.

These studies on different varieties of cotton indicate that one might pay some attention to the selection of cotton used for chemical treatment or that the cotton geneticists might be encouraged to develop cotton varieties with enhanced propensity for chemical treatment, including resin finishing.

In an investigation which might be termed rather more fundamental research than practical, Reinhardt and co-workers (19) described the posttreatment of partially carboxymethylated cotton to determine whether the unique physical and chemical properties of this material would contribute to secondary reactions of chemical reagents with the cellulosic hydroxyl or with the carboxy groups. Some of the secondary treatments involved use of phenylmercuric and mercuric salts to give bactericidal and fungistatic activity, beta-propiolactone to introduce carboxyethyl, hydroxypropionic acid ester, and graft polyester substituents; cyanoethylation with acrylonitrile; cross-linking with a diepoxy finishing agent without added catalyst; a triaziridinyl compound to impart flame resistance; and oxidation with chromic acid or nitrogen dioxide to yield fibrous products with alkaline solubility. Results showed that the CM pretreatment of cotton enhanced the rate and extent of many of the subsequent reactions as compared to native or mercerized cotton.

Another fundamental study was conducted by A.C. Bullock, et al (20), in which cross-linking by vapor-phase formaldehyde was carried out on cotton fabric before and after partial carboxymethylation. The major conclusion reached was that the location of the cross-links was different in the two sample fabrics. Differences were noted in the water of imbibition (water retention) and in the ratios of wet-to-day crease recovery angles.

To improve the commercial viability of the PCM-cotton process, Reinhardt and Fenner (21) took a different approach which more closely approximated techniques used for textile finishing. They found that application to cotton fabric of a solution about 25% MCA and only 5% NaOH followed by tenter-frame drying, and baking at 140° C. would give a D.S. of 0.11. Breaking strength of the etherified cotton was about the same as that of the untreated fabric, but tearing strength was lower. In addition, they found that other strong alkali and etherifying agents (α halocarboxylate salts) could be used as well to give the corresponding ethers.

MORE RECENT RESEARCH ON CARBOXYMETHYLATION OF CELLULOSE

It would be presumptious of me to try to describe here the many contributions to science on this subject by Drs. Fahmy, Hebeish, Kamel, Mansour, El Thalough, and their co-workers. Some of them will no doubt have the opportunity to do this during our panel discussions.

There has been some more recent work than I have already mentioned in the U.S. and other countries as well which should bring this review as up-to-date as our receipt of publications allows.

Perrier and Benerito reported (22) and recently patented (23) a rather involved but unique series of steps to produce CM-cotton in nonaqueous media. The chemical and physical properties of this material are different from those of the CM-cotton fabric prepared in an

aqueous system. The series of steps involved are:

1. Swelling (mercerization) with 23% NaOH.

2. Solvent exchange by neutralization, washing with water and then with anhydrous methanol.

3. Reaction with 2M sodium methoxide solutions in anhydrous methanol to form sodium cellulosate.

4. Wash with anhydrous t-butanol to rid excess sodium methoxide.

5. React with 2.5% sodium monochloroacetate in DMSO at room temperature under agitation with N_2 gas for 0.1 to 24 hours.

6. Wash in excess DMSO, then with deionized water.

7. Iron dry and air equilibrate.

After 24 hours of reaction time at 25° C., a D.S. of 0.30 was reached. At 60° C., a D.S. of 0.24 could be reached in 2 hours. Wet wrinkle recoveries of these fabrics were 275° and 289° (WxF). Surprisingly, the CM fabrics did not become gelatinous or dissolve as would be expected from multiple treatments by aqueous methods. It is entirely possible that the CM substitution occurs at different C-positions in the two different reaction procedures.

The treated fabrics could be converted to the free acid form at pH 2.5 and used for the self-catalysis of cross-linking resins described earlier.

As an extension of this development, Ward, Benerito, and Perrier (24) patented the reaction of propylene or ethylene carbonate with CM-cotton prepared by the above nonaqueous procedure to give fabric with high conditioned- and wet-wrinkle recovery by ester cross-linking. When this process was used on aqueous reacted CM-cotton, only the conditioned wrinkle recovery was improved.

While the above developments leave much to be desired by way of practical application, they do show that it is possible to get good wrinkle recovery in cellulosic fabric without the use of formaldehyde-based resins or any of the environmentally hazardous catalysts.

To show that interest in carboxymethylation of cotton is not confined to the United States and Egypt, two references to work done at Kyoto University (25, 26) were found but unfortunately only title descriptions were available in the retrieval. They are simply "Carboxymethylation of Cotton Fabrics by Glycolic Acid" and "Carboxymethylation of Cotton Fabrics by a One-Step Method."

POSSIBILITIES FOR FUTURE WORK

In the original discussion of workshop topics, the question was asked "whether it would be possible to carry out the partial carboxymethylation process in a manner similar to mercerization." To address myself to this question, I would say not on a conventional, continuous mercerizing range in which large volumes of caustic soda are used with multiple padding operations. It would be more economical to use techniques such as those described by Dr. Reid in his earlier presentation, using indirect padding techniques or perhaps better to use the pad transfer technique for the mercerization step to use only the amount of caustic soda necessary and not contaminate a large volume of liquid.

When a wetting agent was used with the monochloroacetic acid, we found rapid and complete penetration by the caustic soda. At the time of my work, we did not thoroughly investigate the effect of initial temperature of the alkali on the reaction. It was rather observed that a temperature of 50° C. was reached in the rolled up CM-fabric during reaction. It is of course necessary to prevent alkaline hydrolysis of the chloroacetic acid, and

this reaction is more rapid at higher temperatures. However, if proper precautions are used, as mentioned in the report on the pad-dry-bake method of Reinhardt, et al (mentioned above), this effect can be minimized. It would be of interest to use NaOH at less than ambient temperatures, and perhaps lower concentration than used in the earlier work might be as effective.

Heretofore, I have avoided those reactions which did not involve cotton or which resulted in a completely water-soluble CMC such as is used extensively in commerce. However, a worldwide interest in finding new routes to dissolving cellulose has been developed as a result of environmental difficulties with the viscose process. Among the more interesting of the new solvent systems involves DMSO and HCHO which gives very clear solutions in a short time. D. C. Johnson describes the mechanism as a methylolation of the cellulose.

At the recent ACS meeting in Chicago (27) he described a rather exotic method of preparing CMC from solutions of methylol cellulose in DMSO, using sodium hydride and methyl bromoacetate. He explains the reaction as the hydride promotes the loss of methylol groups which in turn liberates nucleophilic cellulose anions. Subsequent etherification with methyl bromoacetate leads to a homogeneous solution of CMC followed by precipitation of the salt form.

By analysis, Johnson showed that much of the CM substitution occurred at the C-3 position, indicating that the C-6 had previously been occupied by methylol groups.

On the other hand, when he used a solution of cellulose in N-methyl morpholine oxide diluted with DMSO, he achieved carboxymethylation using sodium hydride and methyl chloroacetate at 70° C. In this case, most of the CM substitution occurred at the C-6 position. It would, of course, be of interest to see whether CM-substitution at C-6 would confer different properties to CM cellulose than at other substitution sites.

Russian scientists recently described (28) the reaction of CMC with the enzyme urea in the presence of N,N,dicyclohexyl carbodiimide as a catalyst. The enzymatic activity of the CMC-urease was 12 to 85% of the natural enzyme, depending on the amount of reaction obtained. There may be potential uses for this CM-enzyme derivative in cotton fabric form. Other enzymes may be suited to this type of reaction using CM-cotton fabric as a substrate.

As one who thought back to his early work on carboxymethylation in 1945, that surely most of the "cream had been skimmed off the milk," after his eight years at SRRL, you can see from this report that I have been badly mistaken, and there is still a lot of research to do on this and other cellulose reactions. Cellulose being nature's only large-scale renewable polymeric resource, we cannot, as scientists, overlook any road which leads to new knowledge or new uses for old knowledge about this fascinating material.

I am deeply honored to have been invited to participate in this workshop and thank you for your kind attention.

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Studies on Fixation of Different Dyes

Using Hexahydro-1,3,5,-Triacryloyl-s-Triazine

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Dye fixation by means of polyfunctional crosslinking agents is a relatively new principle in dyeing practice, since the first articles relating to this process appeared in the 1960's (1, 2). A range of dyes applying this principle has become available commercially under the name Basazol dyes (BASF), while the crosslinking agent is known as fixing agent P100 (hexahydro-1,3,5-triacryloyl-s-triazine (I). These dyes and the new method of application are employed primarily in textile printing. The majority of these dyes possess only slight substantivity and consist mostly of 1:2 metal complex dyes.

Although in the dyeing sector several patents appeared describing methods for the application of the new principle using direct dyes (3) and acid dyes (4, 5), no systematic study has been published pertaining to the feasibility of these methods. To fill this gap, members belonging to direct dyes, acid dyes, and reactive dyes have been chosen for this study.

Direct Dyes

C.I.	22150	Benzo Congo Rubine
C.I.	29160	Chloramine Scarlet SE
C.I.	24555	Coprantine Pure Blue 2RLL
C.I.	25200	Posanthrene Orange P

Acid Dyes

C.I.	17770	Supramine Orange R
C.I.	42080	Xylene Blue AS
C.I.	22895	Supranol Orange G
C.I.	61570	Alizarine Fast Green G
C.I.	18065	Kiton Fast Red B2R

Reactive Dyes

C.I.	18165	Cibacron Brilliant Red B
C.I.	13245	Cibacron Yellow R
C.I.	18157	Cibacron Violet 2R
		Cibacron Brilliant Blue C4GP

Hydrolyzed Reactive Dyes

Hydrolyzed Cibacron Brilliant Red B
Hydrolyzed Cibacron Yellow R
Hydrolyzed Cibacron Brilliant Blue C4GP

Bazasol Dyes

Basazol Red Brown PL
Basazol Bordeaux B
Basazol Brilliant Blue R

The following three compounds were used as polyfunctional crosslinking agents: I, hexahydro-1,3,5-tris (β -chloro-propionyl)-s-triazine (II), and the addition product of diethylamine with I (III).

Two methods for application were used: the padding method and the application of (I) as an after-treatment for direct dyes. For experimental details see Reference 6.

FIXATION OF DIRECT DYES

To improve the washfastness properties of this class of dyes, several methods are common, including after-treatment with metal salts, HCHO, or synthetic resins. It is possible to achieve the same goal with excellent results by applying the new principle of dye fixation using I, II, or III as additives to the padding liquor or as an after-treatment. After such a treatment, the washfastness at the boil is always 5, compared with gradings 1-2 for dyeings without any after-treatment. The improvement in washfastness properties renders these dyeings comparable to reactive dyeings. It was also found that the percentage of dye fixation after soaping depends upon several factors, including the type of dye, type of fixing agent, and method of application. These factors will be discussed later in more detail.

FIXATION OF ACID DYES

Although it is generally known that acid dyes have little or no affinity for cellulose fibers, several trials were undertaken to apply them on cotton (7-10). Kamel, et al (11) also described a new method of dyeing cotton fabrics using some acid dyes and resin precondensate in one bath.

An attempt was undertaken to bind some selected acid dyes on cotton using the previously mentioned polyfunctional crosslinking agents. Dyeing experiments have revealed that the acid dyes used can be classified into three main categories as far as color yield is concerned when the new method is applied:

A. Dyes which give high color yield, e.g., Supramine Orange P.

B. Dyes which can be moderately fixed on cotton, e. g., Xylene Blue AS.

C. Dyes which cannot either be bound to cotton or which give very poor color yields (below 10%), e.g., Alizarine Fast Green G and Kiton Fast Red B2R.

It is believed that the high fixation of Category A is due to their moderate affinity to cellulose as well as to the presence of certain groups which react readily with the polyfunctional crosslinking agents, as will be shown later.

Trials to increase the percentage dye fixation of Category C by addition of NaCl to increase dye exhaustion or by addition of Levalin CB, which is known to increase diffusibility of dyes, failed.

REACTIVE DYES

Cibacron Dyes. Covalent bonds linked between carbon atoms of the reactive dyes and the oxygen atoms of cellulose in alkaline medium. It must be considered that the aqueous alkaline solvent also provides hydroxyl groups which take part in the dyeing process. As a result of this reaction, some of the dye is hydrolyzed in the course of the process, the extent of the hydrolysis reaction being dependent on the structure of the dye. It has been reported (12) that up to 10% of the dye may be lost in the dyeing process.

In view of these considerations, it was thought that it would be interesting to try the addition of I to the bath of reactive dyes with the objective of fixing the hydrolyzed dye via the crosslinking agent.

The addition of the polyfunctional crosslinking reagent does in fact cause an increase of the color yield which amounts sometimes to an increase from 66 to 99.5%. As a result of this, the soaping process which constitutes an essential step in normal reactive dyeing

can be either simplified or in some cases completely eliminated, since the hydrolyzed dye could also be made fast to washing at the boil.
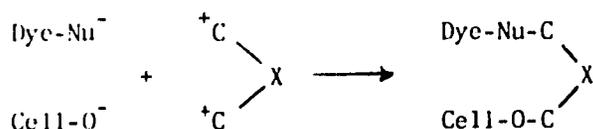
In the light of these results and in order to prove whether the main dye fixation is due to normal covalent bonds or to crosslinking via the fixing agent, the Cibacron dyes were first hydrolyzed and then applied by the padding procedure. It was found that the principal dye fixation in the case of monochlorotriazinyl dyes applied by the new procedure is due to the covalent linkages formed between the unhydrolyzed dye the the fibers.

Basazol Dyes. This range of dyes is considered here as reactive, since dye fixation using I is the usual practice in their application. The color yield in this case reaches 59.0 to 83.2% after extraction.

A consideration of the above results reveals that two factors related to the structure of the dyes are decisive regarding the degree of fixation after soaping; namely, affinity to the cellulosic fibers and the presence of suitable nucleophilic groups.

A moderate affinity is an essential prerequisite for high color yield after soaping by the new method. The low color yields obtained in case of most acid dyes as compared to direct dyes can undoubtedly be explained on this basis.

Another important condition for high dye fixation is the presence of certain nucleophilic groups suitable for reaction with the crosslinking agent. It was previously shown by Lützel (2) that polyfunctional crosslinking agents (e.g., I) contain several reactive groups are capable of forming stable chemical bonds with both the cellulose and the dye molecules under alkaline conditions. The reaction is of the following type:

$$\text{Dye-Nu}^- \quad + \quad \overset{+}{\underset{+}{\text{C}}}\diagdown_{\diagup}^{\diagdown} \text{X} \quad \longrightarrow \quad \text{Dye-Nu-C}\diagdown_{\diagup}^{\diagdown}\text{X}$$
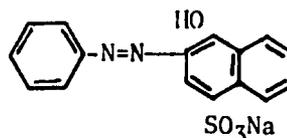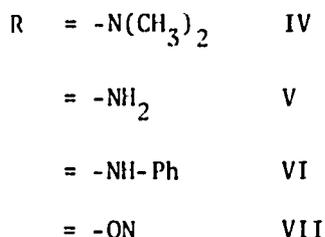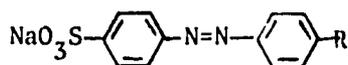$$\text{Cell-O}^- \qquad\qquad\qquad\qquad \text{Cell-O-C}$$

Where   Nu = a nucleophilic group

X = a polyfunctional crosslinking agent

It is now found that aromatic amino groups (e.g., Bonzo Congo Rubine), aromatic secondary amino groups (e.g., Chloramine Scarlet SE), -CO-NH- and hydroxyl groups (e.g., Rosanthrene Orange R) are effective in this type of fixation. The increase of number of nucleophilic groups seems also to favor this type of reaction.

The high color yields of the acid dye Supramine Orange P is undoubtedly due to the presence of the reactive -NHCOCH$_2$Cl group. Increase in percentage of dye fixation in the case of the reactive dyes (Cibacron Brilliant Red B, etc.) should also be attributed to a similar reason. However, other factors related to the structure of the dye molecule as a whole such as steric configuration and diffusibility should not be excluded.

In order to gain more information on the role played by the basic skeleton of the molecule, the type, and the number of nucleophilic groups, Amin, Hashem and Kamel (13) first synthesized the similar compounds IV-VII representing simple benzene and which differ only in the type of nucleophilic groups:

NaO$_3$S—⟨C₆H₄⟩—N=N—⟨C₆H₄⟩—R

R = -N(CH$_3$)$_2$ IV

= -NH$_2$ V

= -NH-Ph   VI

= -ON   VII

⟨C₆H₅⟩—N=N—⟨naphthalene with HO⟩

SO$_3$Na

VIII

The first example, IV, is devoid of active hydrogen atoms and thus would be expected to be inert in the process. In fact, this was found to be the case, thus confirming the assumption that dye fixation takes place by covalent bonds. Compound VIII was chosen to reveal the effect of an ortho-hydroxy-azo group. The results of dye fixation after soaping and after treatment with 50% dimethylformamide (DMF) indicate that fixation of dyes IV-VII depends upon the type of nucleophilic group and follows the order -NH$_2$ > -NH > -OH. However, it is found that no fixation takes place in case of VIII. This is un- doubtedly due to the hydrogen bonding between the OH and the o-azo group (14) which re- sults in the difficulty of removal of the proton from the OH group and formation of the nucleophilic anion as well as the steric hindrance caused by the bulky ortho -N=N-R moiety.

It can generally be stated according to the tables in Reference 13 that the presence of one nucleophilic group seems to be incapable of yielding a high degree of fixation. So, IX-X and another 14 compounds were synthesized with the objective of revealing the effect of presence of two nucleophilic groups (-NH$_2$, -OH, heterocyclic imino, and/or -SO$_2$NH$_2$):

R'

NaO$_3$S—⟨C₆H₄⟩—N=N-⟨C₆H₄⟩-R

Where R = R' = -NH$_2$ IX

= -OH   X
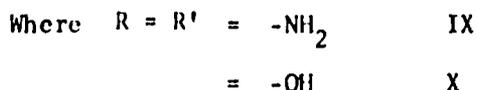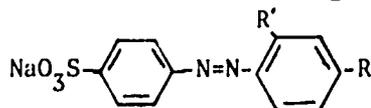
The results of fixation of these dyes indicated that the presence of two nucleophilic groups generally increases the percent fixation of dyes, and in some cases as high as 86% fixation is obtained. The overall structure of the molecule (type and position of the nucleophilic groups) was found also to play a significant role in the percent of dye fixation (13).

If the number of nucleophilic groups was increased to three, still higher values of dye fixation were obtained. In this connection, higher values of fixation obtained with some direct dyes (e.g., Benzo Congo Rubine, etc.) can be attributed to the presence of two or three nucleophilic groups in the molecule.

EFFECT OF THE CHEMICAL STRUCTURE OF THE CROSSLINKING AGENT

This factor seems also to play an important role. Compounds I and II give comparable results of dye fixation in most cases (15). On the other hand, the diethylamine addition product III usually gives lower color yields. This may be attributed to the fact that the reactive groups in the latter compound are partially (or totally) saturated with the

strong nucleophilic diethylamino groups which are not easily eliminated under the conditions of alkaline fixation.

NATURE OF REACTIONS INVOLVED

The chemical processes involved in dye fixation using I are expected to be very complex in nature, since the three acryloyl groups of this compound have three co-reactants: dye, cellulose, and water. In addition, the compound itself may undergo polymerization (16) and/or hydrolysis reactions. In fact, it has been proved by Valk, Kamel, and Abou-Zeid (17) using thin layer chromatographic analysis that the hexahydro-s-triazine ring is hydrolyzed under alkaline conditions to give a series of products including acrylamide, N-methylolacrylamide, and N,N-methylene-bis-acrylamide in addition to ammonia and formaldehyde.

Evidence that hexahydro-1,3,5-triacryloyl-s-triazene under the conditions of dye fixation can react with dyes containing active hydrogen is now furnished by the fact that it reacts with Posanthrene Orange R, as also proved by thin layer chromatographic analysis.

Similarly, the possibility that I can be chemically fixed on cellulose is proved by the fact that when cotton is treated with this reagent under conditions similar to dye fixation for different baking times at 150° C., the obtained fabric contains nitrogen values which are only slightly lowered by extraction with 50% DMF. This reaction seems to depend upon temperature and attains a maximum at 170° C.

It was proved (17) that I can react with cotton in 2% NaOH solution at 40° C., as proved by the increase in wet wrinkle recovery of the fabric as well as by the fact that on hydrolysis of the treated fabric using 72% H_2SO_4 followed by thin layer chromatographic analysis, O-glucopronionic acid is among the hydrolysis products.

Recently, Kamel, Abou-Zeid, Amin, and Hashem (18) studied the mechanism of reaction of cotton with I and proved that the reaction between I and cotton cellulose in the presence of aqueous sodium hydroxide solution may proceed in two steps: (a) hydrolysis of I in this medium to give an equimolecular mixture of acrylamide, N-methylolacrylamide, and N,N-methylene-bis-acrylamide followed by (b) an in situ polymerization of the latter mixture inside the fabric to yield an insoluble, high-molecular-weight product containing free double bonds.

In order to gain more insight into this complex problem, the dyed and soaped samples were extracted with 50% DMF. The results obtained indicate that, in contrast to normal reactive dyes, the percentage of dye fixation after soaping using I or its derivatives is composed of two values:

A.   A value which represents the covalent dye fixation via the crosslinking agent.

B.   A value which represents a fixation resistant to soaping but not to extraction with DMF (no covalent linkage).

The question as to whether one or the other of these two values predominates depends undoubtedly as already mentioned on the structure of the dye molecule as a whole, since substituents, steric configuration, and diffusibility play a large role.

The percentage of extracted dyes represents that fraction of the dye which has re-acted solely with the fixing agent or its reactive decomposition and/or partially poly-merized products. As a consequence of this reaction, the new complex, bigger molecules or aggregated molecules formed are relatively less mobile, causing the increased stability to soaping at the boil. This decreased mobility, however, lowers the probabilities of the reaction of the dye-fixing agent complex with cellulose. This holds true if the dyeing process is carried out in two steps instead of one (19). In this case, I is let to react with cotton cellulose in the presence of Na_2CO_3 at 60° C. for 1 hr. to yield reactive cotton cellulose containing reactive double bonds. When the latter was dyed with some

selected dyes (19) using the pad-dry-cure method, the fixation percentage of these dyes was found to increase by increasing the double bond content on the fabric. This indicates that here, too, a nucleophilic addition of the dye with the active hydrogen on modified fabric takes place. A comparison of dye fixation using the one-step and the two-step method has been carried out (19). From this study, it was found that fixation of the dye in a one-step process is much higher than that in the two-step process. This could be explained on the assumption that in the one-step process the polymerized hydrolysates of I and the dyes are both in solution and therefore their ability to react together is higher compared to the two-step process where the dye reacts with the solid polymer inside the fibers.

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ندوة الكيمياء

ينظمها

المركز القومي للبحوث

والجمعية الكيميائية الأمريكية

٢٨ نوفمبر ـ ٨ ديسمبر ١٩٧٧

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