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PORTUGAL UNIVERSITY INSTITUTES DEVELOPMENT PROJECT

(Contract AID/NE-C-1701)

REPORT ON
SHORT-TERM STAFF ASSIGNMENT

Submitted by
DR. STEPHEN B. SELLO
Department of Chemistry
Polytechnic Institute of New York
Brooklyn, New York

February 28 - May 1, 1985

PORTUGAL UNIVERSITY INSTITUTES DEVELOPMENT PROJECT

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REPORT ON

SHORT-TERM STAFF ASSIGNMENT

AT THE

INSTITUTO UNIVERSITARIO DA BEIRA INTERIOR (IUBI)

COVILHA, PORTUGAL

February 28 - May 1, 1985

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SUMMARY

Area of Consultancy:

Textile Chemistry

Specific Objectives:

a) Course for the faculty and students on "Recent Developments in Textile Finishing"

b) Development of quality control methods in dyeing auxiliaries

c) Lectures on a conference to be held for the Portuguese textile industry

d) Assistance on research projects

Portuguese Counterpart:

Dr. J. Miguel Fiadeiro, Coordinator, Textile Department; Chairman, Textile Chemistry Department

REPORT ON SHORT-TERM STAFF ASSIGNMENT

Submitted by
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INTRODUCTION

The Portuguese textile industry employs approximately 200,000 persons representing a very substantial proportion of the total work force employed in the industry. Since textile manufacturing is a major industry in Portugal, higher education in the field of textile technology and textile chemistry is indispensable.

The Instituto Universitario da Beira Interior (IUBI) in Covilha is a relatively young, 10 year old school which went through a remarkable development in the last several years, and further growth is scheduled for the future. Presently the number of students is approximately 600, which will double in the next three years and an eight-fold increase is planned within a 10 to 15 year period. Although the number of textile students is relatively small, approximately 10 percent of the total student body, the education of the textile students is of utmost importance to assure the growth of the textile industry.

Textile engineering degree is given by IUBI after five years of study in Covilha. The curriculum includes basic sciences, textile technology and textile chemistry and some textile mill practice. The textile chemistry curriculum puts greater emphasis on dyeing than on preparation and finishing. It is probably due to the background of the senior staff.

The Textile Chemistry Department is headed by Dr. J. Miguel Fiadeiro, who has an excellent background in chemistry and specialized in the theory and practice of textile dyeing. He has one assistant with a basic degree who is assisting him in the dyeing laboratory.

The textile dyeing laboratory is well equipped with the most necessary modern laboratory dyeing and printing equipment; several new testing instruments are still at a different location (Acondicionamento) in Covilha, but they are being moved in the near future to the IUBI building into a conditioned laboratory which is close to completion. The Department also has a color laboratory with an ACS computerized color matching system. Most of this laboratory equipment was obtained through the USAID program.

Consequently, the Textile Chemistry Department of IUBI has the capability not only to educate the students, but also to carry out development and service work for the textile industry. Such applied research and development work would be beneficial for both the staff and students, but it should not be considered as a substitute for the training of the students in textile mills.

ACCOMPLISHMENTS

Course for the Faculty and Students

I gave a series of lectures on "Recent Developments in Textile Finishing." Members of the staff of the Textile Chemistry, Textile Technology and Chemistry departments, staff of the Acondicionamento and Laboratory of the Textile Institute, and several students participated in the course.

The course covered the basic principles and the recent developments in textile preparation and textile finishing procedures. The following areas were reviewed:

1. Warp sizing, desizing, size recovery
2. Preparation (scouring, bleaching, mercerization, etc.)
3. Easy-care finishes for cellulose and cellulose blends
4. Antistatic, water and oil repellent, soil release finishes
5. Flame resistant textiles
6. Shrinkproofing of wool
7. Elastomeric fabrics
8. Energy saving approaches in textile finishing

Copies of publications covering the above subjects were given to the participants. The most relevant publication was:

S. B. Sello. Functional Finishes for Natural and Synthetic Fibers. Journal of Applied Polymer Science: Applied Polymer Symposium 31, 229-249 (1977). (Copy of publication attached to this report as Appendix B.)

More details and bibliography should be found in the four volumes of the book:

M. Lewin, S. B. Sello. Chemical Processing of Fibers and Fabrics. Vol I Part A and B: Fundamentals and Preparation; Vol II Part A and B: Functional Finishes. Published by Marcel Dekker Inc, 1983-1984.

The above materials should be the outline of a course (2 terms) on Textile Preparation and Textile Finishing.

Laboratory Development Work for Senior Textile Students

The suggested laboratory development work will be of great interest for the Portuguest textile industry.

1. Compare the effectiveness of the carriers most widely used in the dyeing of polyester and polyester blends. Investigate the possibility of the replacement of carriers with nonionic surfactants as migrating agents in high temperature dyeing.

The work started already with the participation of two students under the supervision of Dr. Mona Arif, Department of Chemistry, and Francisco Franco, Department of Textile Chemistry.

2. Study the surface saponification of polyester. Use batch and continuous method in the absence and in the presence of quaternary ammonium salt as accelerator. Determine the correlation between weight loss and fiber degradation; study the effect of saponification on fabric hand, luster and moisture related properties. Similar experimentation should be carried out on polyester-cellulosic blends.

The work started already with the participation of two students under the supervision of Francisco Franco, Department of Textile Chemistry.

3. Study the supercontraction of woven pure wool fabrics in moderately alkaline medium using anionic surfactant. Carry out the supercontraction under warp tension to attain stretch characteristics in weft direction.

The work started already with the participation of two students under the supervision of Francisco Franco, Department of Textile Chemistry.

4. Study the simultaneous reactive dyeing and resin finishing of cotton fabric. Study the effect of such combined treatment on the brightness of the shade and also on light and wet fastness properties. Consider the possibility that not the fiber but the resin present on the fiber is dyed with the reactive dyes.

5. Study the simultaneous sizing and dyeing of 100% cotton warp yarns using napthol dyes with the objective to attain denim-type fabric in various colors.

6. Set up laboratory methods for the identification of fibers, fiber blends and also of dyestuff groups present in textiles. This work should be carried out as described in the book, "Analytical Methods for Textile Laboratory," edited by W. Weaver, published by the American Association of Textile Chemists and Colorists in 1984.

All of the above projects should be carried out under the direction of Professor Fiadeiro, Chairman of the Textile Chemistry Department.

Seminar for the Textile Industry

Presented lectures at a seminar held on April 26 and 27, 1985, for the technical people of the Portuguese textile industry. Subjects of the lectures were:

1. Dye Assistants
2. Chrome Dyeing of Wool Under Optimized Conditions

The program of this seminar is included in this report as Appendix C.

Research Projects

Assisted the Textile Chemistry Department with a project on the "Yellowing of Polyester on Reduction." It was demonstrated that the yellow color cannot be removed by solvent extraction; the X-ray crystallinity is the same before and after reduction; no excessive oligomer deposition was observed by transmission electronmicroscopy. It seems that the ingredient changing color on reduction and oxidation might be an integer part of the polymer backbone.

Further work is scheduled to continue this investigation.

Plant Visits and Consultation

Visited Francisco Fino LDA wool plant in Portalegre, where I discussed with director Guy Fino, commercial director Ruy Borges and technical director Eugenio Lopes Fazenda such problems as wool shrinkproofing and stretch wool.

Visited Fabrica Textil Riopele SARL in Farmilicao where consultation was carried out with the technical director for finishing,

Eng. Domingos Barbosa, on many subjects of common interest. Such subjects were: Easy-care finishing of 100% cotton fabric, low formaldehye finishing, simultaneous dyeing and resin finishing, single stage bleaching, etc. The discussion was continued on April 25 in Covilha. It included new mercerization process and reduction of migration in continuous dyeing.

Visited Adalberto Pinto de Silva LDA print works in Santo Tirso. Discussions were held with the commercial director, Arthur Braga Teixeira about problems on discharge printing and pigment printing.

In addition, visits were made to Finicisa Synthetics SARL polyester manufacturing plant in Portalegre for discussions with Dr. Vladimir Spohr, manager, and also to Fisipe SARL acrylic manufacturing plant in Barreiro where discussions were held with Ioao Carlos Duarte David, marketing manager.

IDENTIFICATION OF PROBLEMS

1. The textile dyeing laboratory of IUBI has all the necessary laboratory and pilot equipment, but their glassware and fabric supply is insufficient.
2. The textile dyeing laboratory does not have the necessary safety equipment, such as safety glasses, eye washer, shower, and fire extinguisher.
3. The students do not learn any foreign language at IUBI, although technical and scientific literature is very limited in Portuguese.
4. The dyeing course is three semesters, but it does not include dye group identification on textiles.

5. In the curriculum of the textile students, the area of sizing, preparation and finishing is much less emphasized than dyeing.
6. The Department of Textile Chemistry needs an additional educator with an advanced degree or at least another assistant.
7. The Textile Department, which includes Textile Technology and Textile Chemistry, needs more secretarial and typing help.
8. The knowledge of the educators will be outdated in several years if they do not obtain short-term training.

RECOMMENDATIONS

1. Assure laboratory glassware and fabric supply for the textile dyeing laboratory.
2. Supply the laboratories with safety equipment, such as safety glasses, eye washer, shower, and fire extinguisher.
3. Give a course in foreign language, preferably in English.
4. Set up a fiber and dyestuff group identification laboratory course.
5. Put greater emphasis on preparation and finishing. Give a two-term course with a senior lecturer.
6. Set up a finishing laboratory course.
7. Assure more typist help for the Textile Department.
8. Increase the number of educators in the Department of Textile Chemistry, preferably with at least one person who has an advanced degree.
9. Assure funds for the short-term training of the senior staff to keep their knowledge updated. Their participation in international conferences would be desirable.

10. Carry out with the assistants and students experimental laboratory work on projects of interest to the Portuguese textile industry.
11. Organize continuing education courses for the technical people of the industry. People from the universities as well as from the industry should lecture on these courses.
12. Set up cooperative research and development work with Fabrica Textil Riopele in the field of textile finishing.

ACKNOWLEDGEMENTS

Thanks are due to many people who contributed to the success of this assignment.

Dr. C. M. Passos Morgado, Rector of IUBI, Dr. J. Miguel Fiadeiro, Coordinator of the Textile Department and his staff, Dr. Mona Arif, Chemistry Department, were very helpful in the planning and implementation of the work described in this report.

Dr. Hassan Behery at Clemson University, Ms. Vivian L. Rider at Purdue University and the staff of the USAID program at the American Embassy in Lisbon gave very useful advice and guidance.

Special thanks are due to Prof. Joao Lisboa, Mrs. Maria Manuel and the administrative staff of IUBI for their help and assistance during my two month stay in Covilha.

APPENDIX A

Daily Itinerary

DAILY ITINERARY

February 28	Travel from Cedar Grove, New Jersey to New York JFK airport, leaving for Lisbon, Portugal
March 1	Arrival in Lisbon, visit to the U.S. Embassy, traveled to Covilha
March 4-5	Introduction to the faculty of IUBI, discussions with Rector Morgado, visit of the facilities of IUBI
March 6-8	Discussions with the members of the faculty, planning
March 9	Meeting with the technical directors of the local wool mills (Manuel Masquita, Complexo Industrial de Lanificios; Rui M. Esgalhado de Oliveira, Lanofibril; Roman Macedo, Ninafil)
March 11-15	Gave seminars to the faculty and students on textile chemistry
March 18-22	Gave seminars and discussed thesis work for senior textile students
March 25-26	Discussions on research projects and preparation for the conference to be held for the industry
March 27	Visited Francisco Fino wool mill and Finicisa Synthetic SARL polyester plant in Portalegre
March 28	Visited Ministry Administration Interne Servicio de Estrangero in Lisbon to obtain an extension of the stay in Portugal beyond 60 days.
March 29	Visited Fisipe SARL acrylic plant in Barreiro
April 1-2	Discussions on thesis projects and on textile chemistry curriculum
April 3	Visited USAID personnel at U.S. Embassy, Lisbon
April 4-5	Preparation of the lectures to be held for the textile industry
April 8	Discussion with Rector Morgado as preparation for the project review meetings with USAID
April 9-10	USAID review meeting at Covilha

April 11	Visited University of Coimbra and Fabrica Textil Riopele SARL in Farmilicao
April 12	Visited Adalberto Pinto da Silva LDA print works in Santo Tirso
April 15-19	Discussion with faculty members and with the students on the thesis work suggested
April 22-23	Meeting with Professor Refega at the University of Lisbon and with Prof. Dr. V. Meira Soares, Secretary of State for Higher Education. Subject: USAID program
April 24	Meeting with Dr. Maria Jose Constancio, Director General for Industry
April 25	Consultation with Eng. Domingos Barbosa, Technical Director for finishings, of Fabrica Textil Riopele. Preparation of final report
April 26-27	Conference for the industry, presented two seminars
April 29	Discussion with students, completion of final report
April 30	Final discussions. Travel to Lisbon, visit to USAID office
May 1	Left for New York, travel from JFK airport to Cedar Grove, New Jersey

APPENDIX B

Publication

"Functional Finishes for Natural and Synthetic Fibers"

FUNCTIONAL FINISHES FOR NATURAL AND SYNTHETIC FIBERS

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SYNOPSIS

Diverse bulk and surface properties are imparted to natural and synthetic fibers through chemical finishing. Durable finishes are attained by several routes: chemical modification of the fiber surface; covalent bonding with the reactive groups of the fiber molecules; *in situ* polymerization; insolubilization of preformed polymers; deposition of chemicals of low surface tension; insolubilization of appropriate chemicals in thermoplastic fibers by thermosol treatment. While crosslinking of cellulose imparts dimensional stabilization and increased resilience, the formation of hydrolytically stable crosslinks in wool results in permanent setting, but modification of the surface scale structure is required for shrinkage control. Phosphorus compounds acting in the condensed phase are the most efficient flame retardants on 100% cellulosic substrates, but flame retardants possessing both condensed and vapor-phase activity are the most suitable for polyester/cellulose blends. Water repellency is attained with long-chain hydrocarbons, fluorochemicals, and silicones. Surface treatment of hydrophobic fibers with hydrophilic finishes results in improved soil release and redeposition properties, and treatment with hydrophilic electroconductive polymers leads to the dissipation of accumulated electrostatic charges. The chemistry and mechanism of these bulk and surface modifications are reviewed.

INTRODUCTION

In the last three decades, extensive work has been carried out for the purpose of developing new textile products using new fibers and fiber blends as well as treating textiles with chemical finishes to impart specific functional properties. Many investigations have been reported which were designed to lead to a better understanding of the mechanism by which the various finishes act, and progress has been made to replace the empirical approaches with those developed by systematic scientific studies. It is beyond the scope of this paper to give detailed chemical finishing procedures, but it is an objective to consider the various possibilities of attaining certain functional properties through the selection of appropriate finishing chemicals and procedures.

The functional properties included in this report can be categorized as arising from bulk and surface characteristics. While the crosslinking and flame-retardant treatment of cellulosic substrates should be considered as bulk modifica-

Journal of Applied Polymer Science: Applied Polymer Symposium 31, 229-249 (1977)
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tions, water- and oil-repellent finishes and stain release and antistatic treatments of hydrophobic fibers are surface modifications.

Only those chemical finishing procedures are being discussed which are capable of assuring improved functional properties to the textile for a prolonged period of time, which includes multiple launderings and dry cleanings. Such durable finishes can be attained by several routes, such as modification of the fiber surface (e.g., chlorination or bromination of wool to minimize felting and laundering shrinkage); insolubilization of appropriate chemicals via covalent bonding with the reactive groups of the fiber molecules (e.g., crosslinking of cellulose to attain dimensional stabilization and crease resistance or reacting cellulose with organophosphorus compounds to reduce its flammability); insolubilization of monomers or oligomers by *in situ* polymerization (e.g., flame-retarding treatment of cellulosic substrates by the free-radical polymerization of organophosphorus oligomers or by the condensation polymerization of appropriate phosphorus- and nitrogen-containing monomers); insolubilization of preformed polymers (e.g., wool shrinkproofing with preformed polymers or the antistatic treatment of hydrophobic fibers via the crosslinking of preformed water-soluble electroconductive polymers); deposition of specific insoluble polymers (e.g., water- and oil-repellent treatments with flourochemicals).

Since many of these durable textile finishes have undesirable side effects (e.g., crosslinking of cellulose reduces the extensibility of the fiber which contributes to its strength, or the high level of modification required to render cellulose substrates self-extinguishing alters the physical and aesthetic properties of the textiles), it is of great importance to select the appropriate chemicals and processes which impart the permanent improvement in the desired functional properties without substantial impairment of the other aesthetic and wear characteristics.

MODIFICATION OF BULK PROPERTIES

Cellulose Crosslinking

Permanent press cellulosic or cellulose-containing fabrics are produced by setting the fabric in the desired configuration via a crosslinking reaction between hydroxyl groups on adjacent cellulose chains. Such a crosslinking imposes restraints on the movement of the chains and thus imparts to the fabric a tendency to recover from any subsequent deformation and to return to the state in which the crosslinks were introduced. The extent of changes in fiber and fabric properties resulting from the crosslinking reaction depends on the degree of crosslinking and also on the condition of the fiber at the time the crosslinks were introduced. Low levels of crosslinking are capable of imparting dimensional stability, while higher degrees of modification are necessary to attain wash/wear properties. The retention of set creases or pleats requires the highest level of crosslinking [1].

Only those crosslinking reactions can be considered suitable for textile applications which proceed with satisfactory rate under relatively mild conditions.

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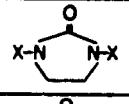
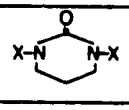
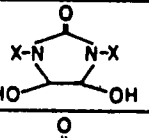
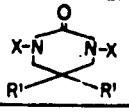
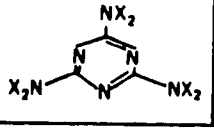
Crosslinking agents penetrate the fiber but do not enter the crystalline portion of the cellulose; thus, the crosslinking takes place exclusively in the amorphous region. The crosslinking can be carried out in the collapsed state of the fiber by heat-curing and by vapor-phase reactions or in its swollen state by wet-curing techniques. Cellulose fabrics crosslinked in the collapsed state exhibit high dry crease recovery, low moisture regain, and low water imbibition. Those crosslinked in the swollen state possess high wet and low dry crease recovery, high moisture regain, and high water imbibition [2].

Dry Cure

The most widely used method is the dry cure process, which is the most economical, imparts the highest level of dry crease recovery and crease retention, but causes the greatest losses in strength and abrasion properties. Both pre- and postcure processes have gained commercial acceptance, and acid-catalyzed reactions are utilized almost exclusively. The structure and reactivity of the customary crosslinking agents are shown in Table I [3].

TABLE I
Structural Formulas of Customary Reactants for Dry Cure Process

CUSTOMARY REACTANTS	REACTIVITY	DURABILITY TO			LIGHTFASTNESS OF REACTIVE AND DIRECT DYESTUFFS
		LAUNDERING	CHLORINE	HYDROLYSIS	
X-HN-GO-NH-X	INCREASING REACTIVITY ↑	+(+)	—	+	++
		+++	+	+	+
		+++	+++	+	+
$ROCONX_2$		+++	++(+)	++(+)	+++
		+++	+	+++	+++
		+++	++(+)	++(+)	+++
		+++	+(+)	++	+(+)

Note: X = CH_2OR, R = H, alkyl, R^1 = alkyl, hydroalkyl, alkoxyalkyl; R = alkyl; +++ very good, ++ good, + fair, − bad.

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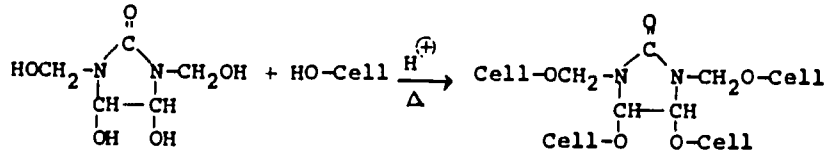
If high acid stability is required, crosslinking agents of low reactivity should be employed. Bis(hydroxymethyl) or bis(alkoxymethyl) derivatives of carbamates, 4,5-dihydroxy-(or dialkoxy-)ethylene ureas, and 4-hydroxy-(or alkoxy-)5,5-dialkylpropylene ureas are the most important reactants in this group.

Interestingly, there is a correlation between the hydrolytic stability of the reactant and its effect on the lightfastness of direct and reactive dyeings. The crosslinking agents possessing high hydrolytic stability do not impair the lightfastness, while those of low hydrolytic stability have an adverse effect on the lightfastness of direct and reactive dyeings [4].

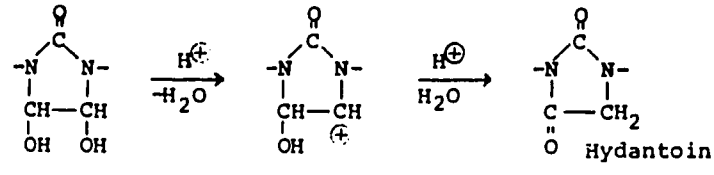
N,N'-Dimethylol-4,5-dihydroxyethylene urea (DMDHEU) is the most widely used crosslinking agent. It exhibits high acid hydrolytic stability and relatively low reactivity, while *N,N'*-dimethylolethylene urea (DMEU) possesses high reactivity and only limited hydrolytic stability. It is generally accepted that all the four reactive groups of DMDHEU react with cellulose [eq. (1)], but the 4,5-dihydroxyethylene ureas undergo also conversion to hydantoins [eq. (2)] which are responsible for the increased chlorine retention of the crosslinked cellulose since the free N-C groups combine readily with chlorine. The dimethylol derivative of 4,5-dialkoxyethylene urea yields a less chlorine-retentive cellulose ether than the 4,5-dihydroxy derivative [4]. In addition, DMDHEU yields some colored products under strongly acidic curing conditions in the presence of zinc nitrate catalyst, but by buffering the impregnating solution, the discoloration can be minimized [3].

The reaction of cellulose with formaldehyde has been well documented in the literature [2, 5, 6]. Formaldehyde condenses with cellulose to form inter- and intramolecular crosslinks with the loss of water. The reaction can be carried out in substantially anhydrous solvent media, in the wet swollen state, by dry-cure process or in the vapor phase. The latter process, employing SO_2 as catalyst, has gained some commercial acceptance for the treatment of garments made of cotton or cotton blends [7].

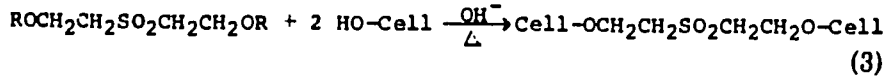
The alkali-catalyzed elimination of water or alcohol from bis(2-hydroxyethlyl) or bis(2-alkoxyethyl) sulfones at elevated temperatures under anhydrous conditions is also an effective way to crosslink cellulose [eq. (3)] [8].



(1)



(2)



(3)

where R = H or lower alkyl groups. Alkali-catalyzed reactions have not gained commercial acceptance, however, because of discoloration of cellulose in alkaline heat-curing. It should also be considered that the cellulose ethers formed have higher acid, but lower alkaline hydrolytic stability than those formed with *N*-methylol crosslinkers under acidic conditions.

Wet Cure

By crosslinking cellulose with the wet-cure method in the swollen and with the moist-cure technique in the partially swollen state, high wet crease recovery can be attained without undue reduction in strength properties. By adjusting the residual moisture content, the ratio of wet and dry crease recovery can be varied.

Since the crosslinking with *N*-methylol crosslinkers takes place under strongly acidic conditions, reactants of high acid hydrolytic stability should be used which resist the low pH for a prolonged period of time. The yield of crosslinking reaction is generally lower under these conditions than in the dry-cure process. It should be considered that some hydrolysis of the reactant takes place in the acidic medium, leading to the release of formaldehyde and to the subsequent crosslinking of cellulose through methylene ether bonds and to the formation of free NH groups which are responsible for higher chlorine retention [3].

Epihalohydrin, dihalopropanol, and the saturated derivatives of divinyl sulfone and of vinylsulfonium compounds are suitable for alkaline wet-curing at ambient temperature. Ionic derivatives of divinyl sulfone [9] and bis(vinylsulfonyl) compounds [10] containing various leaving groups (pyridinium, sulfate, thiosulfate, acetate) have been successfully utilized for cellulose crosslinking. The rate of elimination depends on the structure of the leaving group, but the addition of the activated vinyl groups to the cellulosic hydroxyl groups is the rate-determining step [eqs. (4) and (5)] [2].

Elimination:

$$SO_2(CH_2CH_2Y)_2 + 2\ NaOH \longrightarrow SO_2(CH{=}CH_2)_2 + 2\ NaY + H_2O \qquad (4)$$

where $Y = (-N^+C_5H_5)Cl^-$ $-OSO_3Na$, $-SSO_3Na$, $-OOCCH_3$

Addition:

$$SO_2(CH{=}CH_2)_2 + 2\ HO\text{-}Cell \xrightarrow{OH} SO_2(CH_2CH_2O\text{-}Cell)_2 \qquad (5)$$

The activating effect of the sulfonium group is similar to that of the sulfone group, but that of the sulfoxide group is insufficient for reaction with cellulose under mild conditions. The disodium tris(2-sulfatoethyl) sulfonium inner salt has been used for cellulose crosslinking in Europe [11].

$$(NaO_3SOCH_2CH_2)_2S^{\oplus}{=}CH_2CH_2OSO_3^{\ominus}$$

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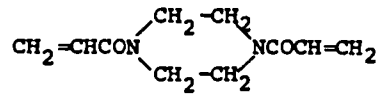

Lower reactivity activated vinyl compounds (e.g., acrylamides) and their ionic saturated derivatives can be employed by use of an alkaline steaming technique. A good example of this type of reactant is 1,4-diacrylic piperazine [12]. The lower the reactivity, the higher is the alkaline hydrolytic stability of the crosslinked cellulose ether formed.

The base-catalyzed reaction of epihalohydrin gives a crosslinked product, but many side reactions lead to the formation of polymeric crosslinks and side chains [13]. The crosslinking reaction of dihalopropanol with cellulose [14] proceeds through an epihalohydrin intermediate [15] and leads to the formation of similar complex products.

The wet-curing techniques in alkaline medium have failed to gain any commercial acceptance.

Unsymmetrical Crosslinking Agents

The characterization of crosslinked cellulose by direct chemical methods is extremely difficult because the crosslinked products—especially when covalent crosslinks are introduced in the nonswollen fibers—cannot be penetrated by chemical reagents. It should also be considered that many side reactions (e.g., single-ended reaction with cellulose, polymer formation) occur when polyfunctional crosslinking agents are employed. The use of unsymmetrical agents which have two groups capable of reacting with cellulosic hydroxyl groups under widely different conditions has been the most feasible approach to establish the extent of the formation of true crosslinks. Examples of such reagents are *N*-methylolacrylamide (NMA) and 2-methoxyethylvinyl sulfone (MVS). Both of these chemicals can be reacted with cellulose stepwise which makes it possible to characterize the single-ended product prior to the formation of crosslinks in the second reaction step.

In the case of NMA, while the single-ended reaction takes place by acid-catalyzed heat-curing, the crosslinking occurs when the activated vinyl group reacts with cellulosic hydroxyl groups at room temperature in the presence of an alkaline catalyst [Eqs. (6) and (7)] [16].

In the case of MVS, the formation of single-ended reaction product takes place

$$CH_2{=}CHCONHCH_2OH + HO\text{-}Cell \xrightarrow[\Delta]{H^+} Cell\text{-}OCH_2NHCOCH{=}CH_2 \quad (I.) \tag{6}$$

$$I. + HO\text{-}Cell \xrightarrow{OH^-} Cell\text{-}OCH_2NHCOCH_2CH_2O\text{-}Cell \tag{7}$$

$$CH_3OCH_2CH_2SO_2CH{=}CH_2 + HO\text{-}Cell \xrightarrow{OH^-} \underset{(II.)}{Cell\text{-}OCH_2CH_2SO_2CH_2CH_2OCH_3} \tag{8}$$

$$II. + HO\text{-}Cell \xrightarrow[\Delta]{OH^-} Cell\text{-}OCH_2CH_2SO_2CH_2CH_2O\text{-}Cell \tag{9}$$

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at room temperature in the presence of an alkaline catalyst, while the crosslinking step can be effectuated by alkaline heat-curing [eqs. (8) and (9)] [17].

It has been reported earlier [18] that in cotton, the maximum crease recovery is attained at D.S. = 0.04–0.08 which is equivalent to 1 crosslink for 2–4 anhydroglucose units in the accessible region (estimated at about 20%).

Location of Crosslinks

The great increase in wrinkle recovery and the severe losses in strength properties of cotton crosslinked with formaldehyde are attributed to the formation of short methylene crosslinks. It has been postulated that crosslinking cellulose with longer-chain, more flexible, difunctional reactants might lead to a more favorable ratio between increases in crease recovery and losses in tensile strength [19], but the improvement has been found to be only moderate. It has also been established that reagents of functionality greater than 2 are not necessarily more effective than difunctional ones [12].

It has been attempted to minimize the losses in strength properties by controlling the location and distribution of the crosslinks. Skin crosslinking has been obtained by applying the reagent and catalyst from a nonswelling solvent such as ethanol [20]. Core crosslinking is achieved by applying the reagent and catalyst uniformly from aqueous medium and after drying, employing a nonswelling solvent to apply a catalyst poison [20] or to remove the reagent and catalyst from the surface [21]. The improvement in relationship between fabric crease recovery and strength has been only moderate.

In recent years, it has been reported that by using a controlled minimum wet pickup (MA process) for the treatment of cellulose or cellulose-containing substrates, a more uniform distribution of the crosslinking agents can be attained due to a lower degree of migration in drying. Better relationships between permanent press performance and losses in abrasion resistance are attributed to this improved crosslink distribution [22].

Wool Modification

Dimensional Stabilization

In the case of cellulosic substrates, both the dimensional stabilization and setting can be attained by crosslinking; however, in the case of protein fibers, which contain disulfide crosslinks, even the introduction of nonreversible crosslinks does not aid in reducing the shrinkage in laundering. Felting shrinkage is caused by an irreversible, unidirectional movement of the fibers during the laundering of the wool fabric [23] and is attributed to the scale structure and shape of the wool fiber. It can be reduced by chemical procedures such as oxidation with halogens, hypohalites, or peroxy compounds, which degrade the scales or otherwise modify the surface of the fiber to reduce the directional friction effect. These oxidative procedures result in some loss of mechanical properties.

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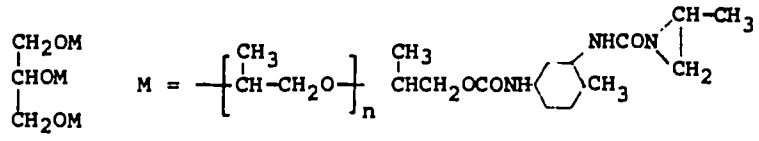
The elimination or reduction of the felting shrinkage can be obtained by depositing polymers on the fiber surfaces. Such a procedure does not cause weight or strength losses, but might lead to stiffening or alteration of the hand of the wool fabric. Therefore, it is of great importance to use such polymers which are efficient in low concentration and are capable, for instance of masking the scales with a thin layer of polymer coating or of spot-welding the fibers at only a small number of places [24].

The formation of polyamides from diamines in aqueous solution and dicarboxylic acid chlorides in a water-immiscible organic solvent or polyureas from diamines and aromatic diisocyanates *in situ* the fiber have been promising approaches to eliminate felting shrinkage in laundering [25, 26]. Later, the formation of polyamide was suggested by a single-step emulsion process using a mixture of diamine and activated dicarboxylic acid ester [27]. The two monomers do not react at low temperatures, but do form polyamide at ambient temperature or above. Similarly, polyurea can be formed *in situ* the fiber by a single-step process using long-chain aliphatic diisocyanates which possess low reactivity and can be employed from aqueous emulsion in combination with appropriate polyamines. The polyurea is formed at elevated temperature, preferably in steam-curing. The aliphatic diisocyanates can be replaced with hindered aromatic ones, but their activation requires very severe heat-curing conditions. By using a combination of aliphatic diisocyanates and polyols in the presence of appropriate catalysts, polyurethane can similarly be formed *in situ* the fiber [28].

An alternative approach is the use of preformed polymers. The early procedures with hard resins, such as urea–formaldehyde or melamine–formaldehyde precondensates [29], required high concentrations of the polymers to give a reasonable shrinkage control. Among the softer polymers, the most interesting are the linear *N*-alkoxymethyl polyamides [30], polyethylene-imines [31], water-dispersible self-crosslinking polyacrylates [32], isocyanate- [33, 34], aziridine-, and epoxy-terminated [35, 36], and thiolated polymers [37]. The polymers must spread over the fiber surface and adhere to ensure durability in wear, laundering, and dry cleaning. The spreading of the polymers can be greatly improved by preliminary modification of the wool, such as halogenation, to increase the critical surface tension of the fiber [38].

The polymers formed or deposited within the wool fiber can effectively yield the desired fiber properties, and greater changes in properties can be attained with smaller amount of polymers if it is anchored to the fiber as a graft polymer [39]. The dimensional stabilization of wool with water soluble basic polyaziridines, specifically with alkylene imine-terminated poly(ethylene oxide) [40] and with amidoaziridine- or epoxy-terminated polyurethanes derived from poly(propoxylated glycerol) [35] are such approaches. The functional groups of these reagents possess reactivity with the nucleophilic centers in the wool fiber. The reagents are also prone to polymerization as new reactive sites are formed in ring opening. While the aziridine-terminated polymers are effective shrinkproofing agents alone, the epoxy-terminated ones are effective only in the presence of coreactants such as polyamines.



The stiffening effect of the polymers with poly(propylene oxide) backbone is less than that of the polymers with poly(ethylene oxide) structure. Polymer treatments do not impair the abrasion resistance of wool and may even improve it.

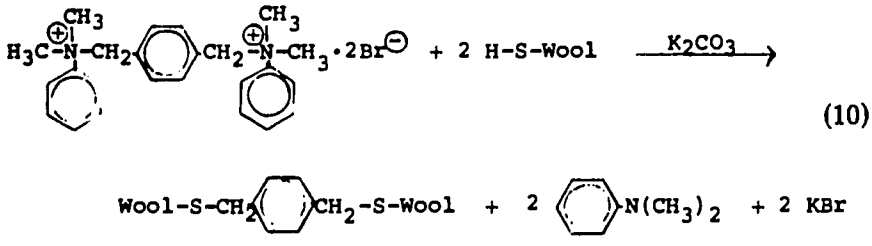
Wool Setting

Processes for setting wool fabrics or garments with creases or pleats stable to wear, wetting, or dry cleaning depend primarily on hydrogen bond and disulfide bond rearrangements which are inherently reversible [41] and thus not stable to washing or hot water exposure.

An effective approach to permanently set wool is by combining the cleavage of the disulfide bonds with the formation of hydrolytically stable thioether crosslinks [42]. It can be achieved in a single-step steampressing operation using alkali reactive difunctional crosslinking agents, e.g., activated vinyl or cleavable onium compounds. Among the activated vinyl compounds, 1,4-diacrylic piperazine [12] and among the cleavable onium compounds, xylylene-bis(dimethylanilinium bromide) [43] are preferred because of their stability in aqueous alkaline solutions and high reactivity in alkaline steaming.

The cleavable onium compounds must of course be applied at higher concentrations than the activated vinyl compounds due to the high molecular weight of the group eliminated in the course of reaction. The alkali concentration must also be higher because stoichiometric amounts of alkali are required for the elimination [eq. (10)].

Inhibition of shrinkage and felting is essential if the set fabrics are to withstand vigorous washing. When curing of the shrinkproofing polymer takes place simultaneously with or subsequent to the setting, stabilization of set is superior compared with that obtainable when the polymer treatment preceeds the setting. The improved effect is due to fiber encapsulation and bonding [44]. The crease retention performance is improved by moistening the fabric prior to steam setting. This wetting step may be avoided by adding hygroscopic agents to the sensitizing solution, but satisfactory conditions for this approach have not yet been established.



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Flame-Retardant Finishes

While textile treatments such as permanent press, water repellency, stain release, etc., are attained at <5% weight increase, most of the durable flame-retarding finishes are effective only at 15–25% weight gain. Therefore, the durable flame-retarding treatments are costly and it is a special problem to attain self-extinguishing properties without significant alteration of the mechanical and aesthetic characteristics.

Nonmelting Fibers

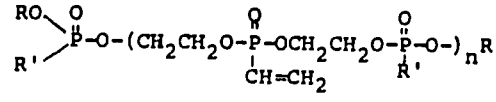
Cellulosics. Cellulosic fibers can be rendered flame-resistant by phosphorus chemicals which generally act in the substrate by altering the route of thermal decomposition in such a manner that the proportion of flammable volatile products to the amount of carbon and water formed is reduced. They also divert the oxidation of carbon residue from CO_2 to CO, and thereby produce insufficient energy to sustain the afterglow.

The esterification of cellulose with phosphoric or sulfamic acid or the ammonium salts of these acids are known methods for rendering cellulose flame-resistant [45, 46]. The severe afterglow of cellulose sulfate and the ion exchange of cellulose phosphate with alkaline earth salts, which destroy its flame resistance, has inhibited the commercial acceptance of these procedures. A single-step process based on simultaneous sulfation and phosphorylation overcomes these drawbacks. The combined process involves the use of ammonium sulfamate and phosphoric amide [$O{=}P(NH_2)_3$] [47, 48]. The utilization of phosphoric amide as phosphorylating agent is related to its limited hydrolytic stability.

The introduction of substituents on the amido groups of phosphoric amide increases the hydrolytic stability of the P—N bond. By coreacting *N,N′,N″*,-trialkylphosphoric amide with trimethylol melamine *in situ* the fiber, excellent durable flame resistance is attained whenever the reactants are used in such a proportion that all the amide hydrogens are substituted [49, 50].

Hydrolytically stable phosphonate derivatives of cellulose can be obtained by reacting cellulose with *N*-methyloldialkylphosphonopropionamide [$(RO)_2$-$P(O)CH_2CH_2CONHCH_2OH$] [51, 52]. It can be applied by an acid-catalyzed heat-curing technique in conjunction with aminoplast resins. The hydrolytic stability of dialkyl phosphonates depends on the alkyl substituents.

Another approach to obtain a phosphonate derivative of cellulose is via the free-radical polymerization of a vinylphosphonate oligomer [53] *in situ* the fiber. It can be homopolymerized or copolymerized with acrylamides.



Polymers containing the hydrolytically very stable phosphine oxide structures are obtained by insolubilizing tetrakis(hydroxymethyl)phosphonium chloride (THPC) with amines and amides.

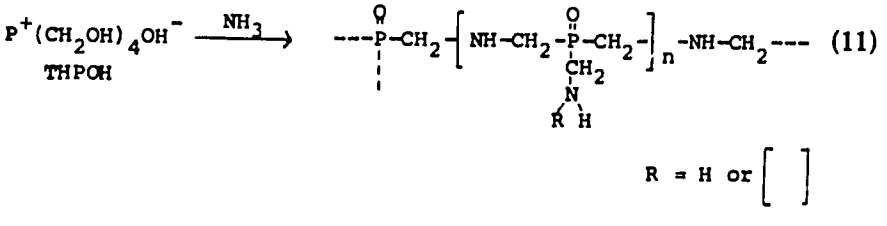
$$(HOCH_2)_4P^+Cl^-$$

The THPC-amide heat cure finish [54, 55] or the coreaction of the THPC/urea precondensate with ammonia vapor [56] as well as the THPOH-amide heat cure [57] or the THPOH-ammonia vapor-phase reaction [eq. (11)] [58] are excellent approaches to obtain flame-resistant cellulosic textiles. Oxidation of the intermediate trivalent phosphorus in the polymer to the pentavalent state is essential to achieve the maximum durability of the polymer. In all these reactions, the THPC and THPOH can be replaced with other tetrakis(hydroxymethyl)phosphonium salts, such as the sulfate, oxalate, phosphate, etc. [59].

In most of the procedures designed to flame-retard cellulosic substrates with organophosphorus chemicals, nitrogen is present, in some cases derived from the nitrogen content of the phosphorus compound, in other cases from the addition of a nitrogen-bearing component to the flame-retardant formulation. It has been established that nitrogen contributes to the flame-retarding effectiveness of organophosphorus compounds [51, 60-62], although its efficiency depends on the source of nitrogen [63]. While nitriles are ineffective, amides, especially in the form of urea and melamine, are the most effective. The nitrogen/phosphorus synergism is demonstrated experimentally, but its mechanism is still unresolved.

Although the flame retardants acting in the condensed phase are the most effective on 100% cellulosic substrates, halogen-containing compounds which function in the vapor phase can also be used as flame-retarding agents. They function mainly by reducing the flammability of the mixture of air and vapor distilled from the heated cellulose. Bromine is more effective than chlorine, and antimony oxide possesses a synergistic effect with the halogen-containing chemicals. The evolution of HCl or HBr from the halogenated compound and its interaction with Sb_2O_3 to yield SbOCl and $SbCl_3$ to form a free-radical trap in the vapor phase explain the enhanced flame retardance [64]. An example of this approach is the coating of cellulosic or cellulose containing fabrics with a composition consisting of decabromodiphenyl oxide, antimony oxide, and an acrylic binder [65].

Protein Fibers. Wool possesses relatively high ignition temperature, low flame temperature, and low heat of combustion. These characteristics are due to the morphological and chemical structure of the wool fiber. The relatively low flammability level of wool is also connected to its high moisture content, and thus under bone-dry conditions—as required in certain flammability standards—wool might fail the flame test.



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The flame resistant treatments of wool are based on the exhaustion of negatively charged metal complexes, treatment with halogenated acids and with phosphorus chemicals.

Negatively charged complexes of titanium and zirconium with fluorides, citrates, or other α-hydroxycarboxylic acids are exhausted on positively charged wool fiber (pH < 3) at elevated temperatures. Titanium complexes are more effective than the zirconium ones, probably because of better penetration of the fiber with the smaller titanium complexes. However, the zirconium compounds do not affect the color. The F/Ti or F/Zr ratio of the complexes has to be at least 5 but preferably 6 to improve the natural flame resistance of wool effectively. Only negatively charged penta-, hexa-, or heptafluorozirconate or titanate can be exhausted onto the positively charged wool. For washable wool, zirconium–tungsten complexes are preferred [66].

The metal complex in the wool fiber must form an insoluble acid residue that is volatile or decomposes at temperatures below the ignition temperature of wool. The acid residue is probably responsible for the increased amount of char, and for the formation of acid fragments on mild heating which trap the flammable volatiles so that the flame is extinguished.

Chlorendic acid [67] and tetrabromophthalic acid or anhydride [68] can also be exhausted onto the wool to improve the flame resistance of the wool fabric. Organophosphorus compounds are also effective flame retardants for wool fibers; e.g., the homopolymerization of oligomeric vinyl phosphonate or its copolymerization with acrylic compounds renders wool flame-resistant. Such a treatment can be combined with appropriate shrinkproofing finishes [28].

Thermoplastic Fibers (Polyester and Nylon)

Thermoplastic fibers are considered less flammable than the cellulosics because they possess a relatively low melting point and the melt drips rather than remains to propagate the flame when the source of ignition is removed.

The most common approach of flame-retarding polyester is the application of tris(2,3-dibromopropyl)phosphate (TDBP) [$(BrCH_2CHBrCH_2O)_3P{=}O$] by a thermosol or exhaustion technique [69]. It should be considered that polyester fiber cannot retain permanently more than 4–5% TDBP calculated on the weight of the fiber.

Interestingly, halogens are less effective flame retardants on nylon than on polyester, and most of the flame retardants effective on cellulosic or polyester substrates have only insufficient effectiveness on nylon. Thiourea appears to be the most effective on nylon [70]. Some durability can be imparted by employing methylolated thiourea or by applying aminoplast resins in conjunction with thiourea [71]. The effectiveness of thiourea and of certain other chemicals in flame-retarding nylon is related to their ability to depress the melting point

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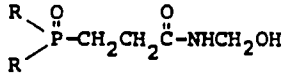
of the polymer and to increase the ease with which the melt drips away [70].

Blends of Thermoplastic and Nonmelting Fibers

Among the blends of thermoplastic and nonmelting fibers, polyester/cellulosic blends have the greatest commercial importance. It has been shown that the flammability behavior of the blends cannot be predicted from the flammability of the single-fiber structures [72–75]. The treatment of one of the fiber components with a flame-retarding agent specifically effective for that component does not necessarily render the two-component blend flame-resistant [72, 74] unless the treated component comprises at least 85% of the blend [73]. An effective flame-retarding treatment must reduce the flammability of each of the components. It has also been established that it suffices to flame-retard only one fiber component while the second one can be completely free of finish if a flame-retarding agent is used which is effective on both types of fibers [76].

While phosphonates are the more effective flame retardants on 100% cellulosic substrates, phosphine oxides exhibit higher effectiveness on polyester/cellulosic blends. This observation was confirmed with specially designed analogous structures [77].



where R = CH_3O (Phosphonate)
CH_3 (Phosphine Oxide)

Phosphonium compounds show similar effectiveness as the phosphine oxides because they are converted to phosphine oxides in the course of insolubilization.

It should be considered that chemicals employed from aqueous medium to the blend fabric are deposited preferentially onto the hydrophilic cellulosic component, and the adhesion of the polymer is significantly better to the cotton than to the hydrophobic polyester fiber. Thus, the extremely high chemical add-on on the cellulosic component results in significant impairment of the aesthetic and mechanical properties. Therefore, it would be desirable to employ booster flame-retarding chemicals to the polyester component (e.g., brominated compounds which can be thermosoled into the fiber) or to use inherently flame-resistant fiber in order to accommodate a portion of the chemical load on the polyester fiber and to reduce it on the cotton component. It should also be considered that the thermally more stable aromatic bromo compounds seem to be more effective on the blend fabric than the aliphatic counterparts. Antimony enhances the effectiveness of bromine compounds, but its synergistic effect is diminished when phosphorus is present [78].

Although the flame-retardant finishing of polyester/cellulosic blends is not a commercially solved problem, the investigations in the last five years have succeeded in determining the main requirements of a finish which should be anticipated to be effective on the blend fabric.

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SURFACE MODIFICATIONS

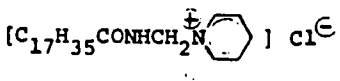
Water- and Oil-Repellent Finishes

The deposition of hydrophobic films consisting of saturated hydrocarbon or fluorocarbon chains attached to the fiber surface by reactive polar groups is the most usual technique by which water repellency is attained on textiles.

The treatment of synthetic textiles with wax dispersion in conjunction with melamine- or urea-formaldehyde resin results in water repellency with limited durability. Aluminum salts and zirconium and chromium complexes of fatty acids have been combined with these waxes to improve the durability of the treatment [79].

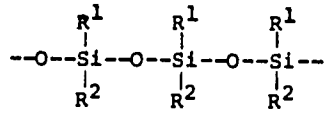
A very significant development has been the introduction of fatty alkyl derivatives containing groups capable of reacting with cellulosic hydroxyl groups [80]. It should be considered that the yield of cellulose etherification drops rapidly with increasing chain length of the agent. The maximum water repellency is attained when the hydrocarbon chain is about 16–20 carbon atoms long. Longer chains tend to coil, and shorter chains exhibit reduced water repellency because of the proximity of the terminal polar groups.

Fatty alkyl derivatives containing Y-CH_2Cl moiety, where Y is a —O—, —S—, —NH—, —CONH— group, are reactive and can be solubilized as the quaternary halides of tertiary amines, particularly pyridine. A successful example of this is the stearamidomethyl pyridinium salt [81].



The extent of the reaction with cellulose is limited to about 1 stearamidomethyl group per 150 anhydroglucose units; the formation of some methylenedistearamide *in situ* the fiber is also a possibility. The durability of the finish in laundering is very good.

The water repellency of silicones [82] is due to the low surface tension of the methyl-on-silicone groups; e.g., the critical surface tension of a polydimethylsiloxane film is approximately 22 dyne/cm. The structure of the siloxanes used for these treatments can be represented as follows:

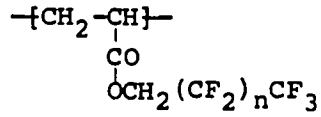


When R_1 and R_2 are both methyl groups, the silicone is the nonreactive type; when R_1 is methyl and R_2 is hydrogen, the silicone is the reactive type.

The nonreactive polydimethylsiloxanes are added to the fiber with titanium or zirconium compounds which, on curing, hydrolyze to metal oxide films and then coordinate with the siloxane structure. The reactive poly(methyl hydrogen siloxanes), which account for most of the silicone textile water repellents, crosslink on the fiber surface via the reaction of the residual Si—H bonds with

water or other sources of hydroxyl to give crosslinked structures. Tin and zinc catalysts are generally used and, interestingly, in this case titanium and zirconium catalysts are ineffective. Such silicone finishes are durable and possess thermal and oxidative resistance because of the inherent stability of the siloxane chain.

Fluorochemicals have revolutionized both oil- and water-repellent finishing. Two basic types of perfluoro compounds are used. These are the perfluorocarboxylic acids and polymers of perfluoroalkyl esters of acrylic acids [83].



Poly(perfluoroalkyl acrylates) exhibit increasing oil repellency as the number of fluorine atoms increases. A fluorochemical possessing satisfactory oil repellency should contain at least one perfluorogroup as large as C_7F_{15}. The water-repellent property is less affected by the size of the perfluoro chain than is the oil repellency. The CF_3 end group present in a fluorochemical film gives the surface a very low critical surface tension (approx. 6 dyne/cm). This low CST explains the fact that selected fluorochemicals are the most effective organic compounds in rendering textiles oil-repellent [84].

It is interesting to note that by combining a fluorochemical with other selected water repellents (e.g., stearamidomethylpyridinium chloride) in well-specified proportions, a less expensive oil- and water-repellent finish with superior durability can be obtained [85].

The surface roughness of the fluorine-containing film influences its surface tension. When the fluorochemical is deposited onto a fabric surface, the fluorochemical is present as an uneven film which is expected to have slightly higher CST than a smooth film. Any mechanical action which roughens the fabric and/or the fluorochemical surface film, reduces the effectiveness of the treatment. This explains why the oil repellency of a cotton fabric treated with a fluorochemical is diminished in laundering but is at least partially restored by hot ironing, which serves to smooth out increased roughness of the thermoplastic fluorochemical film caused by abrasion in laundering [84].

Soil Release Finishes

The oleophilic character of synthetic fibers increases their tendency to retain oily soils and their hydrophobic character impedes the penetration of the detergent solution and the solubilization of the oily stains in the course of laundering.

We must differentiate between three terms: (1) soil repellency is the ability of the textile to resist soiling or staining; (2) soil release is the ability to remove the soil in laundering; (3) soil redeposition is the pickup of soil suspended in wash water and results in greying of the textile [86]. Since all these properties are associated with the surface of the polymer, it is feasible to modify the surface characteristics of the fiber without altering its mechanical properties.

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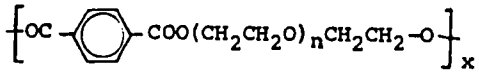
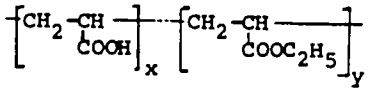
An early method used to improve soil release and prevent soil redeposition was treatment of polyester textiles with polyglycols. Sodium polyglycolate is capable of reacting with poly(ethylene terephthalate), the ester interchange leading to the chemical bonding of the polyglycolate to the fiber surface. Since the ester-interchange reaction is very sensitive to time, temperature, and moisture, this approach has been abandoned [87].

The alternative method for the surface modification of polyester fiber has been the application of a hydrophilic polyester derived from terephthalic acid and poly(ethylene glycol) [88]:



This is designed to form a surface coating, the adhesion of which is claimed to be enhanced by a "co-crystallization" mechanism. The hydrophilic surface impedes wetting by oily stains and enhances wettability in aqueous launderings, thus preventing soil redeposition and improving soil release properties.

Acrylic polymers employed as stain release finishes to permanent press polyester/cellulosic blends provide the fiber surface with a polar wettable coating to impart hydrophilic, oleophobic character. Copolymers of ethylacrylate and acrylic acid, e.g.,



are examples of such finishes [89].

Acrylic acid can also be grafted onto the fiber surface by radiation techniques. The preparation of nylon 6,6-acrylic acid graft copolymer by high-energy electron-beam radiation has been reported [90]. A newer approach which has reached commercial acceptance employs an electrical discharge in argon gas to graft acrylic acid onto a polyester surface and thereby provides improved wettability with enhanced soil release and reduced soil redeposition characteristics [91, 92]. Typical hydrophilic polyester generated by this process has a poly(acrylic acid) add-on of 0.05–0.10%. The grafted product retains its wettability through 50 launderings although there is a gradual loss of graft due to abrasion, about half of it being lost after 20 washings.

Another route to soil release finishing has been based on imparting soil repellency by the use of fluorochemicals [93]. The use of conventional fluorochemical soil-repellent treatments proved to be unsuitable for soil release finishing. While the soil-repellent treatment prevents penetration of oil under some conditions, it impedes the release of any oily stain which has succeeded in reaching the fiber.

"Dual action" fluorochemicals were developed to overcome this deficiency; these are soil repellent, soil releasing copolymers containing alternating hydrophilic and fluorochemical segments [94].

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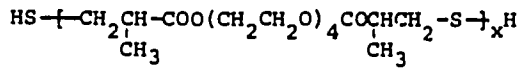
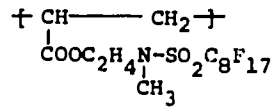
Hydrophilic segments:



Fluorochemical segments:



These finishes form continuous films which possess low surface energy in air and low interfacial energy in water. It has been postulated that the fluorinated segments lie on the fabric surface in air, and the hydrophilic ones lie on the surface in water.

Antistatic Finishes

Whereas most of the natural fibers are composed of strongly hydrogen-bonding polymers and exhibit hygroscopicity, some synthetic polymers such as polyolefins, polyamides, polyesters, and polyacrylonitriles are comparatively hydrophobic. The presence of water in the polymeric material increases the electrical conductance and therefore, under identical conditions, synthetic fibers are better electrical insulators than the natural fibers [95]. The only chemical mechanism by which accumulation of electrical charge by synthetic fibers can be prevented effectively is by increasing their electrical conductivity to a level comparable to that shown by hydrophilic fibers [96–98].

A textile fiber (other than the metal fibers) must contain water in order to be static-free. Electrolytic conductance requires the presence of a medium of high dielectric constant, and water is the only such medium which can be replenished from the atmosphere when lost. In order to assure the presence of water in or on the fiber, a hygroscopic compound must be associated with the fiber, either as an integral part of the fiber or added to it as a finish. With durable antistatic finishes hygroscopicity, while increasing their efficiency, will tend to reduce durability, since it causes swelling of the finish in laundering. The swollen finish shows reduced resistance to wet abrasion. The ideal durable antistatic finish should thus combine the highest possible moisture regain at medium and low relative humidities with the lowest possible swelling in water.

Since every ionizing group is hygroscopic, antistatic finishes can be prepared without the presence of nonionic hygroscopic groups in the molecule. Quaternary ammonium polymers retain more water at low relative humidity than other polymers. This suggests why these types of polymers are more conductive as a group than other polyelectrolytes [99]. Ionizing antistatic agents are, in general, more efficient antistats than mere nonionic hygroscopic ones. The latter serve as a conductive vehicle for the ions present in the fabric and rely solely on tramp electrolytes, e.g., the impurities present in the last rinse water. Only a finish

composed of an ion-exchange resin of suitable structure can establish its efficiency level independently of the nature of the rinse water.

Effective durable antistatic finishes can be generally obtained by forming *in situ* a crosslinked polymeric network containing ionic and hygroscopic groups, thus providing the fiber surface with an insoluble conductive sheath. Durable antistatic finishes obtained according to this general principle from crosslinked polyamine resins were first reported in 1959 [100], and many subsequent developments have been based on related reactions yielding polymers of similar structure [101–104]. For instance, insoluble polymers were formed on a polyester fabric surface by reacting *in situ* [eq. (12)] a trifunctional crosslinking agent, e.g., 1,3,5-tris(3-methoxypropionyl)-*s*-perhydrotriazine (TMPT), with a polyhydroxy polyamine (PHPA) [105]. The polymer formed contains a varying number of oxyethylene groups, contributing to hygroscopicity, and also ionizable amino groups. The tightness of the crosslinked polymeric network can be altered by varying the polyamine/crosslinker ratio and the average molecular weight of the PHPA reagent by controlling the reaction conditions used for its preparation.

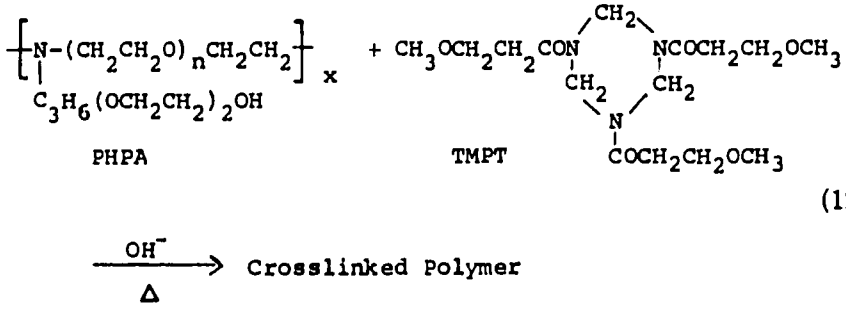
It has been established that crosslinked polymers formed *in situ* on the surface of hydrophobic fibers impart more effective antistatic properties to the fabric if they contain both hydrophilic moieties and ionizable groups than if they contain only one of these.

CONCLUSIONS

Diverse functional properties can be imparted to natural and synthetic fibers by chemical finishing procedures. In many cases, a compromise should be made because certain functional properties can be attained only by impairing other aesthetic and wear characteristics.

The introduction of new fibers and fiber blends has made chemical modifications, especially the flame-retarding treatments, more complex. For instance the flammability behavior of the blend fabric and the effectiveness of a flame-retardant finish on the blend cannot be predicted from the flammability behavior of the individual fiber structures or from the efficiency of a specific flame retardant finish on the individual fiber component.

It is a special problem to attain a uniform distribution of chemicals on blends of hydrophilic and hydrophobic fibers. For instance, while in the permanent press



(12)

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treatment of polyester/cellulosic blends the crosslinking agents should be deposited exclusively on the hydrophilic cellulosic component, flame-retarding chemicals should be uniformly distributed on the hydrophilic cellulosic and hydrophobic polyester components to avoid the undesirable side effects of an extreme chemical load on one of the fiber components.

For many end uses multiple chemical modifications are required, and it is not practical or possible to subject a textile to a sequence of finishing operations. Thus, some of the chemical finishing and dyeing procedures should be combined in a single-step operation. It is known that water repellents, such as the quaternary pyridinium types, silicones, or fluorochemicals, can be combined with *N*-methylol resins to attain permanent press and water repellency in a single step. Permanent press resins can also be employed together with stain release finishes, such as the acrylic acid copolymers or the "dual action" fluorochemicals. The combination of a flame-retarding treatment with pigment dyeing and a permanent press finish on cellulosic textiles, or simultaneous wool shrinkproofing and flame retarding are possible approaches to attain multifunctional properties in a single-step operation.

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REFERENCES

[1] G. C. Tesoro, *J. Amer. Oil Chem. Soc.*, *45*, 351 (1968).
[2] G. C. Tesoro and J. J. Willard, in *Cellulose and Cellulose Derivatives*, N. Bikales and L. Segal, Eds., Wiley, New York, 1971, pp. 835–875.
[3] W. Ruemens, G. Burkhardt, H. Petersen, and W. Ruettiger, *Amer. Dyest. Reptr.*, *62*, 43 (1973).
[4] H. Petersen, *Text. Res. J.*, *38*, 156 (1968).
[5] W. J. Roff, *J. Text. Inst.*, *49*, T646 (1958).
[6] J. T. Marsh, *J. Soc. Dyers Col.*, *75*, 244 (1959).
[7] R. Swidler and J. P. Gamarra, *Text. Chem. Col.*, *3*, 41 (1971).
[8] G. C. Tesoro, *Text. Res. J.*, *32*, 189 (1962).
[9] G. C. Tesoro, P. Linden, and S. B. Sello, *Text. Res. J.*, *31*, 283 (1961).
[10] G. C. Tesoro, *J. Appl. Polym. Sci.*, *5*, 721 (1961).
[11] F. H. Burkitt, *Text. Res. J.*, *34*, 336 (1964).
[12] G. C. Tesoro and S. B. Sello, *Text. Res. J.*, *36*, 158 (1966).
[13] J. B. McKelvey, R. R. Benerito, R. J. Berni, and B. G. Burgis, *J. Appl. Polym. Sci.*, *7*, 1371 (1963).
[14] D. M. Gagarine (to Deering Milliken Research Corp.) U.S. Pat. 2,985,501 (1961).
[15] A. Fairbourne, G. P. Gibson, and D. W. Stephens, *J. Chem. Soc.*, *1965* (1932).
[16] J. L. Gardon, *J. Appl. Polym. Sci.*, *5*, 734 (1961).
[17] G. C. Tesoro and A. Oroslan, *Text. Res. J.*, *33*, 93 (1963).
[18] G. C. Tesoro, *Text. Res. J.*, *30*, 192 (1960).
[19] E. I. Valko, B. Bitter, and R. S. Perry, *Text. Res. J.*, *34*, 849 (1964).
[20] C. J. Gogek and E. I. Valko, *Textilveredlung*, *2*, 423 (1967).
[21] J. J. Willard, G. C. Tesoro, and E. I. Valko, *Text. Res. J.*, *39*, 413 (1969).
[22] M. Schwemmer, H. Bors, and A. Goetz, *Textilveredlung*, *10*, 15 (1975).
[23] G. F. Flanagan, *Text. Res. J.*, *36*, 55 (1966).
[24] O. C. Bacon and D. E. Maloney, *Amer. Dyest. Reptr.*, *56*, 319 (1967).
[25] R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Text. Res. J.*, *31*, 704 (1961); *ibid.*, *32*, 743 (1962); *ibid.*, *33*, 440, 752 (1963).
[26] R. E. Whitfield, *Appl. Polym. Symp. No. 18*, 559 (1971).

32

[27] H. K. Rouette, H. Zahn, and M. Bahra, *Textilveredlung, 2,* 474 (1967).
[28] S. B. Sello, C. V. Stevens, and R. O. Rau, Paper presented at the 5th International Wool Research Conference, Aachen, West Germany, Sept. 1975.
[29] P. J. Alexander, *J. Soc. Dyers Col., 66,* 349 (1950).
[30] D. L. C. Jackson, *Text. Res. J., 24,* 624 (1954).
[31] C. E. Pardo, Jr., (to the U.S. Dept. of Agriculture), U.S. Pat. 2,817,602 (1957).
[32] H. D. Feldtman and J. R. McPhee, *Text. Res. J., 35,* 150 (1965).
[33] F. Reich, *Mell., 50,* 305 (1969).
[34] Deering Milliken Research Corp., Brit. Pat. 1,181,373 (1970).
[35] S. B. Sello and G. C. Tesoro, *Appl. Polym. Symp. No. 18,* 627 (1971).
[36] S. B. Sello, G. C. Tesoro, and R. Wurster, *Text. Res. J., 41,* 556 (1971).
[37] I. W. S. Nominee Co., Ltd. and Ciba A.G., Ger. Offen. 1,934,678 (1970)
[38] H. D. Feldtman and J. R. McPhee, *Text. Res. J., 34,* 634 (1964).
[39] J. B. Speakman, *J. Amer. Leather Chem. Assoc., 53,* 492 (1958).
[40] G. C. Tesoro and S. B. Sello, *Text. Res. J., 34,* 523 (1964).
[41] J. B. Caldwell, S. J. Leach, J. Meschers, and B. Milligan, *Text. Res. J., 34,* 627 (1964).
[42] S. B. Sello and G. C. Tesoro, *Text. Res. J., 43,* 309 (1973).
[43] H. Rath, *Mell., 38,* 181 (1957); *ibid., 38,* 656, 1406 (1957).
[44] J. R. Cook and J. Delmenico, *J. Text. Inst., 62,* 27, *62,* 438 (1971).
[45] M. Sander and E. Steininger, *J. Macromol. Sci.-Rev. Macromol. Chem., 2,* 57 (1969).
[46] E. E. Gilbert, *Sulfonated and Related Reactions,* Interscience, New York, 1965.
[47] P. Isaacs, M. Lewin, C. Stevens, and S. B. Sello, *Textilveredlung, 8,* 158 (1973); *Text. Res. J., 44,* 700 (1974).
[48] M. Lewin and P. Isaacs (to the State of Israel), Ger. Offen. 2,127,188 (1972).
[49] S. B. Sello, I. E. Pensa, and R. Wurster, *Textilveredlung, 10,* 183 (1975).
[50] S. B. Sello (to J. P. Stevens & Co., Inc.), U.S.Pats. 3,632, 297; 3,681,060, (1972).
[51] G. C. Tesoro, S. B. Sello, and J. J. Willard, *Text. Res. J., 39,* 180 (1969).
[52] R. Anishaenslin, C. Guth, P. Hofmann, J. Maeder, and H. Nachbur, *Text. Res. J., 39,* 375 (1969).
[53] E. D. Weil (to Stauffer Chemical Co.) U.S. Pat. 3,695,925 (1972).
[54] W. A. Reeves and J. D. Guthrie, *Text. World, 104,* 101 (1954).
[55] G. L. Drake, Jr., R. M. Perkins, and W. A. Reeves, *J. Fire Flamm., 1,* 78 (1970).
[56] W. A. Reeves and J. D. Guthrie (to the U.S. Dept. of Agriculture), U.S. Pat. 2,772,188 (1956).
[57] J. V. Beninate, E. K. Boylston, G. L. Drake, Jr., and W. A. Reeves, *Text. Res. J., 38,* 267 (1968).
[58] J. V. Beninate, R. M. Perkins, G. L. Drake, Jr., and W. A. Reeves, *Text. Res. J., 39,* 368 (1969).
[59] G. Hooper, in *Proceedings of the 1973 Symposium on Textile Flammability,* E. Greenwich, Ed., R. I. LeBlanc Research Corp., 1973, p. 50.
[60] G. C. Tesoro, *Textilveredlung, 2,* 435 (1967).
[61] G. C. Tesoro, S. B. Sello, and J. J. Willard, *Text. Res. J., 38,* 245 (1968).
[62] S. B. Sello, B. J. Gaj, and C. V. Stevens, *Text. Res. J., 42,* 241 (1972).
[63] W. A. Reeves, R. M. Perkins, B. Piccolo, andG L. Drake, Jr., *Text. Res. J., 40,* 223 (1970).
[64] J. Lyons, *The Chemistry and Uses of Fire Retardants,* Wiley-Interscience, New York, 1970.
[65] V. Mischutin, *Text. Chem. Col., 7,* 40 (1975).
[66] L. Benisek, *J. Text. Inst., 65,* 102, 140 (1974).
[67] M. Friedman, J. F. Ash, and W. Fong, *Text. Res. J., 44,* 555 (1974).
[68] M. Friedman, J. F. Ash, and W. Fong, *Text. Res. J., 44,* 994 (1974).
[69] E. Baer, in *Proceedings of the 1973 Symposium on Textile Flammability,* E. Greenwich, Ed., R. I. LeBlanc Research Corp., 1973, p. 117.
[70] D. Douglas, *J. Soc. Dyers Col., 73,* 258 (1957).
[71] H. Stepnicka, *Ind. Eng. Chem. Prod. Res. Devel., 12,* 29 (1973).
[72] G. C. Tesoro and C. Meiser, Jr., *Text. Res. J., 40,* 430 (1970).
[73] W. Kruse and K. Filipp, *Mell., 49,* 203 (1968).

33

[74] W. Kruse, *Mell.*, *50*, 460 (1969).
[75] G. C. Tesoro and J. Rivlin, *Text. Chem. Col.*, *3*, 156 (1971).
[76] P. Linden, L. G. Roldan, S. B. Sello, and H. S. Skovronek, *Textilveredlung*, *6*, 651 (1971).
[77] G. C. Tesoro, *Text. Chem. Col.*, *5*, 235 (1973).
[78] C. V. Stevens and S. B. Sello, in *Proceedings of the Third Symposium on Textile Flammability*, LeBlanc Research Corp., New York, 1975, p. 186.
[79] J. M. May, *Amer. Dyest. Reptr.*, *58*, 15 (1969).
[80] H. A. Schuyten, J. D. Reid, J. W. Weaver, and J. G. Frick, Jr., *Text. Res. J.*, *18*, 396 (1948).
[81] F. V. Davis, *J. Soc. Dyers Col.*, *63*, 260 (1947).
[82] J. K. Campbell, *Text. Chem. Col.*, *1*, 370 (1969).
[83] E. J. Grajeck and W. H. Petersen, *Text. Res. J.*, *32*, 320 (1962).
[84] D. C. M. Dorset, *Text. Mfr.*, *96*, 112 (1970).
[85] C. G. DeMarco, A. J. McQuade, and S. J. Kennedy, *Mod. Text.*, *41*, 50 (1960).
[86] G. C. Tesoro and J. J. Willard, *Tenside*, *6*, 258 (1969).
[87] D. A. Garrett and P. N. Hartley, *J. Soc. Dyers Col.*, *82*, 252 (1966).
[88] Imperial Chemical Industries, Ltd., U.S. Pat. 3,416,952 (1968).
[89] Deering Milliken Research Corp., U.S. Pat. 3,377,249 (1968).
[90] E. E. Magat, I. K. Miller, D. Tanner, and J. Zimmerman, *J. Polym. Sci.*, *8*, 615 (1964).
[91] J. D. Fales, paper presented at the Radiation Processing of Textiles Conference, North Carolina State University, Raleigh, N.C., May 1975.
[92] S. M. Suchecki, *Text. Ind.*, *3*, 91 (1975).
[93] R. E. Read and G. C. Culling, *Amer. Dyest. Reptr.*, *57*, 881 (1967).
[94] P. O. Sherman, S. Smith, and B. Johanessen, *Text. Res. J.*, *39*, 449 (1969).
[95] E. I. Valko and G. C. Tesoro, in *Kirk Othmer Encyclopedia of Chemical Technology*, *Vol. 2*, 1963, p. 204.
[96] E. I. Valko and G. C. Tesoro, *Mod. Text.*, *38*, 62 (1957).
[97] J. W. S. Hearle, *J. Text. Inst.*, *48*, P40 (1957).
[98] G. J. Sprokel, *Text. Res. J.*, *27*, 501 (1957).
[99] R. J. Dolinsky, and W. R. Dean, *Chem. Technol.*, 1971, 304.
[100] E. I. Valko and G. C. Tesoro, *Text. Res. J.*, *29*, 21 (1959).
[101] E. I. du Pont de Nemours & Co., U.S. Pat. 3,021,232 (1962).
[102] Onyx Oil and Chemical Co., U.S. Pats. 3,063,870; 3,070,552 (1962).
[103] Imperial Chemical Industries Ltd., Brit. Pat. 985,325 (1965).
[104] Millmaster Onyx Corp., U.S. Pat. 3,553,111 (1971).
[105] G. C. Tesoro, S. B. Sello, and W. K. Lee, *Textilveredlung*, *1*, 208 (1966).

APPENDIX C

Program of Seminar held April 26-27, 1985

PROGRAMA

MODERADOR: ENGº F. PINTO FERREIRA

SEXTA-FEIRA DIA 26 DE ABRIL DE 1985

ABERTURA

15H00 -"DIFERENÇA DA AFINIDADE TINTURIA DA LÃ"

PROF. J. CEGARRA

15H45 - DISCUSSÃO

16H15 - INTERVALO PARA CAFÉ

16H30 - "OS PRODUTOS AUXILIARES NO TINGIMENTO DE FIBRAS TEXTEIS"

PROF. S. SELLO

17H15 - DISCUSSÃO

SABADO DIA 27 DE ABRIL DE 1985

9H30 - "ASPECTOS FUNDAMENTAIS DO TINGIMENTO EM BARCA E EM JET DE TECIDOS DE LÃ E SUAS MISTURAS"

PROF. J. CEGARRA

10H15 - DISCUSSÃO

10H45 - INTERVALO PARA CAFÉ

11H00 - "OPTIMIZAÇÃO DO TINGIMENTO DA LÃ COM CORANTES AO CRÓMIO"

PROF. S. SELLO

11H45 - DISCUSSÃO

INSTITUTO UNIVERSITÁRIO DA BEIRA INTERIOR

DEPARTAMENTO

DE

CIÊNCIA E TECNOLOGIA TÊXTEIS

SEMINÁRIO

ASPECTOS FUNDAMENTAIS DO TINGIMENTO INDUSTRIAL

- INFLUÊNCIA DA MÁQUINA NO TINGIMENTO DE TECIDOS
- APLICAÇÃO E FUNÇÃO DOS PRODUTOS AUXILIARES
- INFLUÊNCIA DAS CARACTERISTICAS DA FIBRA DE LÃ NA IGUALIZAÇÃO:
  - CAUSAS
  - DETECÇÃO
  - CORRECÇÃO
- OPTIMIZAÇÃO DO TINGIMENTO DA LÃ COM CORANTES AO CRÓMIO

ESTE SEMINÁRIO INTEGRA-SE NO PLANO DE ACTIVIDADES DO D.C.T.T. DE APOIO À INDÚSTRIA E É REALIZADO COM A COLABORAÇÃO DA ASSOCIAÇÃO NACIONAL DOS INDUSTRIAIS DE LANIFICIOS.

OS TEMAS SERÃO APRESENTADOS PELO PROF. JOSÉ CEGARRA DA ESCUELA TÉCNICA SUPERIOR DE INGINIEROS INDUSTRIALES DE TERRASSA - - BARCELONA E PELO PROF. STEPHEN SELLO DO POLYTECHNIC INSTITUTE OF NEW YORK E ACESSOR TÉCNICO DA EMPRESA J. P. STEVENS.

FUNCIONAMENTO

O seminário será apresentado em espanhol e português sendo fornecida documentação aos participantes.

DESTINATÁRIOS

- Docentes e Investigadores
- Quadros Superiores e Intermédios
- Gestores
- Técnicos Comerciais de Produtos Químicos para a Indústria Textil
- Técnicos Comerciais de Máquinas a Tingir
- Estudantes

INSCRIÇÃO

A INSCRIÇÃO SERÁ DE 4.000$00 DEVENDO SER ENVIADA ATÉ AO DIA 23 DE ABRIL.

Se houver na sua Instituição outras pessoas interessadas em participar no Seminário é favor usar fotocópias da Ficha de Inscrição destacável.

TEMAS

O SEMINÁRIO TRATARÁ ASPECTOS TECNOLÓGICOS DO TINGIMENTO INDUSTRIAL QUE INFLUENCIAM DE FORMA IMPORTANTE A SUA QUALIDADE. DAR-SE-Á ESPECIAL RELEVO AO TINGIMENTO DA LÃ E SUAS MISTURAS EM PARTICULAR NO QUE DIZ RESPEITO À INFLUENCIA DA MÁQUINA E DA FIBRA NA CONDUÇÃO PRÁTICA DO TINGIMENTO COM VISTA À OBTENÇÃO DE TINTOS IGUALIZADOS.

TRATAR-SE-Á DE DEMONSTRAR A IMPORTÂNCIA DOS DIVERSOS PRODUTOS AUXILIARES NO TINGIMENTO DE FIBRAS TÊXTEIS ATRAVÉS DO SEU MECANISMO DE ACTUAÇÃO ASSIM COMO SE PROCURARÁ DEFINIR AS CONDIÇÕES PRÁTICAS QUE EXIGEM A SUA UTILIZAÇÃO.

PROPOR-SE-Á UM MÉTODO DE TINGIMENTO COM CORANTES AO CRÓMIO QUE DIMINUA A QUANTIDADE DE CRÓMIO RESIDUAL E QUE PERMITA, SIMULTÂNEAMENTE, AFECTAR MORFOLOGICAMENTE O MENOS POSSIVEL A FIBRA COM VISTA À OBTENÇÃO DE MAIOR EFICIÊNCIA NA SUA FIAÇÃO SEM, EM QUALQUER DOS CASOS, ALTERAR O RENDIMENTO E A QUALIDADE DO SISTEMA DE TINGIMENTO.

(CORTE, PREENCHA E DEVOLVA)

FICHA DE INSCRIÇÃO

PARA ASSISTIR AO SEMINÁRIO, AGRADECEMOS QUE PREENCHA ESTA FICHA E A REMETA, COM O VALOR DA RESPECTIVA INSCRIÇÃO À ORDEM DO INSTITUTO UNIVERSITÁRIO DA BEIRA INTERIOR, PARA O SEGUINTE ENDEREÇO:

INSTITUTO UNIVERSITÁRIO DA BEIRA INTERIOR
DEPARTAMENTO DE CIÊNCIA E TECNOLOGIA TÊXTEIS
RUA MARQUÊS DE ÁVILA E BOLAMA
6200 COVILHÃ

VALE DE CORREIO Nº .....
CHEQUE Nº .....
(S/BANCO .....)

NOME: .....FUNÇÃO .....
ORGANISMO/EMPRESA .....
DIRECÇÃO: .....TELEFONE .....
DATA: ..../..../.... ASSINATURA: .....