# Cellulose Mercerization: Use of Amino Acid-Glycerol Ethers as Wetting Agents

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**ABSTRACT:** The action of a new nonconventional series of (tryptophan-phenylalanine-histidine and tyrosine)-glycerol-ether surfactants as wetting agents in hot cotton mercerization was studied. The mercerization result was evaluated with the barium hydroxide absorption number, water absorbency and moisture regain, and mechanical properties of fibers; the dyeability of the mercerized samples with a direct and reactive dye was also studied. An improvement was observed for all the above parameters in the presence of the aforementioned wetting agents despite their being used in very low concentrations. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1120–1124, 2009

**Key words:** cotton mercerization; amino acid-glycerol-ether; wetting agent; nonconventional surfactant; barium absorption number (BAN); mechanical properties; dyeability of mercerized cotton; water absorbency; moisture regain

## INTRODUCTION

Cellulose is a natural polymer synthesized to a great extent by plants[1,2] and to a minor extent by some bacteria and marine animals.[2,3] As a textile material (cotton, flax, ramie, etc.), it is still very popular and the various finishings of the material are very important.

A very old and effective finishing is mercerization, which is defined as the treatment of cellulose or cellulose polyester blends with caustic soda, ammonia, or ammonium salt concentrated solution.[1,4] Depending on the temperature, the work may last from a few minutes to several days at a time, with or without tension.[1,4–11] During this finishing, the fibers do not lose their identity, but some important changes take place, such as swelling, an increase of the amorphous region with a consequent decrease of the crystalline one, and a simultaneous change of the geometry of the crystallites from parallel cellulose I to antiparallel cellulose II.[1,12–18] Simultaneously, chain folding occurs with an extensive intermolecular hydrogen bonding.[12,19,20] Moreover, when the mercerization process is taking place, an increase of tensile strength under tension is observed that may be due to an additional consolidation of weak points as well as the removal of fractions of cellulose with a very low degree of polymerization.[21] The effect of all the above is an improvement in dye uptake,[5,9–11] in moisture regain and water absorbency,[11] and sometimes in the fiber strength and the luster, depending mostly on the conditions of mercerization.

It is clear then that all the above properties are some of the parameters that one can use to evaluate both the degree and the quality of mercerization, as well as the barium hydroxide absorption value.[22]

Apart from the conditions mentioned, that is, the temperature, the time, and the tension, wetting also plays an important role in the whole process as it spreads and/or penetrates the liquid into the fibers. This is enhanced with the use of a proper wetting agent. The most common agents used are alkyl sulfates, alkyl sulfonates, alkyl aryl sulfonates, and phosphoric acid derivatives.[21] However, an extensive investigation of the wetting agents' role has not been done until now. The aim of the present work is the study of the hot mercerization of cotton under tension by using nonconventional surfactants (Scheme 1) as wetting agents.[23,24] The new compounds have many properties required for mercerization such as their solubility in alkaline media without decomposition of the molecule, due to the stable ether bond between the glycerol moiety and the alkyl chain, in contrast to the hydrolysable ester bond of the conventional surfactants, absence of affinity to the cellulose fiber, and efficiency at low concentrations.[25]

The degree of mercerization was evaluated by using the barium hydroxide absorption value.[22] The

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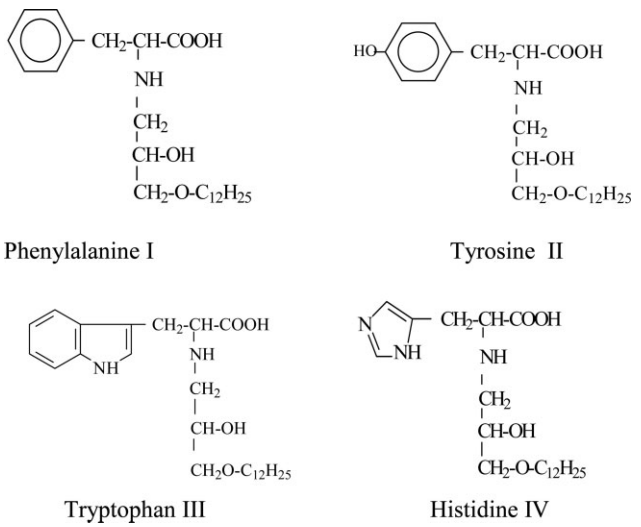


**Scheme 1** The chemical formulas of the new non-conventional series of surfactants 4I-4III.

effect of mercerization on the dyeing and the mechanical properties of the cotton fibers as well as on the water absorbency and the moisture regain of those fibers was studied in comparison with the corresponding mercerized fibers (i.e., those mercerized in the presence of a conventional wetting agent and/or those mercerized without any wetting agent).

## EXPERIMENTAL

### Materials

Unbleached Greek cotton fabric without any treatment was used. Quadrangular frames of glass sticks were used for the mercerization process under tension. The dyes, CI Direct Red 81 and CI Reactive Red 270, were used for the dyeings.

Leophen MC (Ciba-Geigy), an alkyldiol-containing preparation of a sodium alkanol sulfate and 1-*N*-L(phenylalanine, tyrosine, tryptophan, histidine)-3-dodecyloxy-2-propanols (condensation products of the above amino acids with dodecylglycerine ether I–IV) (Scheme 1), was used as conventional and nonconventional wetting agents, respectively.

### Methods

#### Mercerization

The cotton samples were immersed in a solution of 25% NaOH at 90°C under tension achieved by the quadrangular glass frames for 10 min, rinsed, neutralized with 2% acetic acid, and rinsed again.

Three mercerization experiments were performed under the following conditions: (1) without any wetting agent; (2) with 0.02% w/v of the nonconventional wetting agents (I–IV) with 0.6% w/v of the conventional wetting agent.

All samples were weighed before and after mercerization and the percentage weight loss was calculated (Table V).

#### Moisture regain and water absorbency[11]

The nonmercerized and the mercerized in the presence of 1-*N*-L-tryptophan-3-dodecyloxy-2-propanol (Compound III) samples were immersed in distilled water for 24 h and weighed after centrifuging at 3000 $min^{-1}$ ($W_1$). The samples were then dried for 1 h at 70°C, kept for 24 h at 65% relative humidity, weighed again ($W_2$), and dried for 2 h at 105°C ($W_0$). Moisture regain (MR) and water absorbency (WA) were calculated as per eqs. (1) and (2):

$$\mathrm{MR} = \frac{W_2 - W_0}{W_0} \times 100 \quad (1)$$

$$\mathrm{WA} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

#### Determination of barium absorption number AATCC 89-1998[22]

Two grams of the mercerized sample were treated with 30 mL of 25*N* barium hydroxide solution and kept for 2 h at an ambient temperature under stirring, and the solution was then titrated with 0.1*N* hydrochloric acid by use of phenolphthalein as an indicator.

#### Dyeing

Dyeings were carried out in a Zeltex apparatus with a liquor ratio 1 : 30 and a depth of shade 2% o.m.f. in the presence of 20 g/L sodium chloride and 12 g/L sodium carbonate for the direct and reactive dyes, respectively. The temperature was raised gradually (in the duration of 1 h) to 95°C and 85°C, respectively.

Dyeing continued at 85°C for the reactive dye for 45 min, while for the direct dye, the temperature gradually decreased from 95°C to 80°C in 50 min, marking the end of the dyeing process.

In the case of the reactive dyeing, the dyed samples were washed in standard soap solution (2 g/L) in a liquor ratio 1 : 30 and 15 min at boiling temperature for the elimination of the hydrolyzed dye.

#### Colorimetric measurements

K/S values of the dyed samples were obtained by using a Macbeth CE 3000 (England) coloreye spectrophotometer (PC Software Matchprobe 200, UV

and specular component included, large area view, 25.4 mm diameter).

### Surface tension measurements

The surface tensions were determined by using a KSV Sigma 70 (Finland) tensiometer (Dü Noüy ring method).

### Mechanical properties

Tenacity and elongation at break were measured according to ASTM D 2256-90 by using an SDL–UT 250 Micro Standard Universal Tester (Stockport, England). Pilling was measured according to ISO 12945-1 with a QM 227A/B ICI Pilling Tester (Halifax, England).

## RESULTS AND DISCUSSION

The Compounds I–IV were selected as wetting agents after preliminary experiments made with the homologous series of tryptophan glycerol ethers with 10–16 carbon atoms in their lipophilic alkyl chain. It was concluded that there is no negligible effect of the number of carbon atoms of the alkyl chain R on all the parameters under estimation. This could be explained by the assumption that, due to low concentrations (below their critical micelle concentrations), the surfactants are present as independent molecules and can easily reach the water–cellulose interface, thus enhancing the wettability of cellulose. In this case, the length of the alkyl chain would not have a dominant effect as in the case of micelle formation. Thus, the members with 12 carbon atoms in the hydrophobic alkyl chain R (Compounds I–IV) were selected as representatives. Preliminary experiments were also made with mercerization time varying from 5 to 60 min, indicating that under the conditions used (90°C, 25% NaOH, tension) the conversion of cellulose progressed as far as possible in 10 min. Further treatment had no effect on mercerization. This is in agreement with literature data.[12]

To compare the Compounds I–IV regarding their wetting ability, the surface tension of their solutions was measured.

If we consider a capillary system as consisting of parallel fibers in contact with a liquid, then the rate $k$ at which the liquid migrates into the capillary system depends on the surface tension $\gamma$ of the liquid according to the integrated Washbourn equation (3)[26]

$$k = \left[\frac{\gamma r \cos\theta}{2n}\right]^{1/2} \quad (3)$$

where $r$ is the radius of the capillary formed by the fibers, $\theta$ is the contact angle between the liquid and the fiber wall in the capillary, and $n$ is the viscosity of the liquid.[27]

**TABLE I**
**Surface Tension Values γ of the Wetting Agents Used and B.A.N. of Cotton Samples Mercerized in the Presence of the Same Wetting Agents**

| Wetting agent | Surface tension (γ mN/m) | BAN |
|---|---|---|
| Phenylalanine glycerol ether (0.02% w/v) | 36 | 204 |
| Tyrosine glycerol ether (0.02% w/v) | 56 | 195 |
| Tryptophan glycerol ether (0.02% w/v) | 30 | 160 |
| Histidine glycerol ether (0.02% w/v) | 54 | 193 |
| Lyophen MC (0.6% w/v) | 24 | 228 |
| – | | 140 |

Thus, measuring the surface tension of the surfactant solutions, a satisfactory approximation of the wetting rates of the Compounds I–IV can be made. In Table I the surface tension $\gamma$ values of the surfactants used as wetting agents are presented.

Given that 10 min of time is sufficient for mercerization to progress as much as possible, as concluded from the preliminary experiments, the final degree of the sample mercerization would be correlated to the barium absorption number (BAN) rather than to the wetting rate of the Compounds I–IV. In Table I, the BAN of a mercerized sample in the presence of the conventional wetting agent Leophen MC and the samples mercerized in the presence of the Compounds I–IV as wetting agents are presented. The BAN is a measure of the reactive amounts of accessible salt forming hydroxyl groups left after cellulose has been swollen and washed. BANs 100-105 indicate nonmercerized fiber, with numbers up to 150 showing incomplete mercerization, while BANs over 150 indicate a conventionally complete mercerization reaction.

Table I shows that significant mercerization improvement is observed with the use of both conventional and nonconventional wetting agents. The conventional agents proved to be the most efficient followed by the condensate phenylalanine-glycerol ether I and tyrosine–glycerol ether II, the amino acids with hydrophobic phenyl and hydroxy phenyl side chains, respectively, and the condensates of glycerol ethers with the amino acids with basic side chains histidine and tryptophan. In any case, Table I shows that all the nonconventional surfactants I–IV as wetting agents gave satisfactory results regarding the mercerization process. In Table II the % moisture regain and water absorbency values of the unmercerized sample and a sample mercerized in the presence of tryptophan-glycerol ether II as wetting agent are presented.

Moisture regain as well as water absorbency are attributed to a swelling of mercerized cotton due to

**TABLE II**
**The % Moisture Regain and Water Absorbency Values of the Unmercerized Sample and a Sample Mercerized in the Presence of Tryptophan-Glycerol Ether III as Wetting Agent**

| | Nonmercerized | Mercerized 3 |
|---|---|---|
| Moisture regain (%) | 4.5 | 6.6 |
| Water absorbency (%) | 48 | 55.8 |

the interruption of hydrogen bonds of cellulose chains.[1,11,21,25]

K/S values for the unmercerized sample 1 and the mercerized samples in the absence of any wetting agent 2 in the presence of a conventional wetting agent 3 and in the presence of the nonconventional wetting agents 4.1–4.4 dyed with the dyes CI Direct Red 81 and CI Reactive Red 270 C.I. Direct Red and C.I. Reactive Red one direct are given in Table III. For the evaluation of dyeability, the K/S value of the samples is measured according to Kubelka–Munk equation

$$\frac{k}{s} = a \times c = \frac{(1-R)^2}{2R}$$

where $k$ is the absorption (%), $s$ is the scattering (%) depending on the surface, $\alpha$ is the constant depending on the color, the wavelength, and the surface, $c$ is the color concentration on the surface, and $R$ is the reflectance (%).

From Table III the following can be concluded: mercerization always results in an increase in K/S value directly related to the dye absorbed on the fiber (Kubelka–Munk law). This is attributed to the increase of the amorphous region with a simultaneous decrease in the crystallinity of cellulose fibrils that consequently permit the water-soluble dyes to be incorporated into the cellulose structure.[1,5,10,11,21] The presence of wetting agents, both conventional or nonconventional during the mercerization process, is

**TABLE III**
**K/S Values of Cotton Samples Dyed with Dyes CI Direct Red 81 and CI Reactive Red 270 Non-Mercerized 1, Mercerized in the Absence of a Wetting Agent 2, Mercerized in the Presence of Conventional Leophen MC 3, Mercerized in the Presence of the Non-Conventional Surfactants 4.I-4.IV**

| Sample | C.I. Direct Red | C.I. Reactive Red |
|---|---|---|
| 1 | 16 | 12 |
| 2 | 22 | 19 |
| 3 | 22 | 19 |
| 4.I | 22 | 19 |
| 4.II | 23 | 19 |
| 4.III | 23.2 | 27.7 |
| 4.IV | 24 | 20 |

**TABLE IV**
**Tenacity and Elongation at Break Values of Yarns (Fibres) and Pilling Test Scores of Fabrics**

| Sample | Tenacity (mN/tex) | Elongation at break (%) | Pilling test |
|---|---|---|---|
| 1 | 170 (680) | 5.1 (12.1) | 2–3 |
| 2 | 196 (720) | 5.0 (11.6) | 2–3 |
| 3 | 210 (745) | 6.1 (12.6) | 3–4 |
| 4 | 210 (740) | 6.3 (12.8) | 4 |

advantageous with respect to the dye absorption. Despite their very low concentration, 0.02% w/v, the nonconventional surfactants I–IV have satisfactory wetting action compared to the conventional ones with multiple concentration 0.6% w/v as indicated by the K/S increase.

Similar results can be observed for the C.I. Reactive Red 270, indicating that the ease of dye penetration in the cellulose structure due to the increase of the amorphous region is responsible for the improvement of dye absorption rather than for the development of additional reactive sites for covalent bonding between reactive dye cellulose during mercerization.

The highest K/S values are observed for the samples 4.III and 4.IV mercerized in the presence of condensates of glycerol ether with tryptophan and histidine, and in the amino acids with basic side chain and dyed with both the direct and the reactive dye. This can be explained by assuming that Compounds III and IV were not thoroughly eliminated after mercerization but remained in the cellulose structure attracting the anionic dye.

In Table IV, the results of the tenacity and elongation at break measurements, as well as the pilling test scores of nonmercerized yarns 1, mercerized in the absence of a wetting agent 2, mercerized in the presence of Leophen MC 3 and mercerized in the presence of tryptophan glycerol ether 4, are presented.

From Table IV, we can conclude that mercerization results in improvement in the mechanical properties of cotton yarns mainly in the presence of a wetting agent. This was expected because the surfactants facilitate the wetting and the penetration of alkali with a consequent increase of swelling.[1,21] It is also obvious that the surfactant molecules during the final washing make the elimination of the sodium atoms conjugated to the cellulose hydroxy groups as Na-cellulose[7,21] more convenient, thus enhancing the changes of the crystallites' orientation, which takes place during this step of the mercerization process. There is either no difference or a very slight difference between the conventional and nonconventional wetting agent. The waving of yarns to fibers results in a significant increase of the

**TABLE V**
**Percentage Weight Loss After Merceization of the Samples Mercerized : 2, in the Absence of a Wetting Agent; 3, in the Presence of Leophen MC; 4, in the Presence of the Compounds I-IV**

| Sample | Weight loss (%) |
|---|---|
| 2 | 5.89 |
| 3 | 6.07 |
| 4.I | 6.14 |
| 4.II | 6.62 |
| 4.III | 4.70 |
| 4.IV | 6.18 |

mechanical properties of cotton; as expected, the order remains the same.

Pilling tests were also performed and showed a slight improvement for the samples after mercerization in the presence of a wetting agent (Table IV). This can be correlated to the fact that under the conditions used (90°C, 25% NaOH), a scouring of the cotton fiber takes place due to saponification of oils, waxes, and the like of the cotton surface[1,10,21] and elimination of the saponified derivatives evaluated by percentage weight loss after the mercerization of the samples mercerized in the absence of a wetting agent 2 in the presence of Leophen MC 3, and the presence of the compounds (4.I–4.IV). The results of the percentage weight loss measurements of those samples are presented in Table V.

From Table V, it is concluded that scouring is expressed as the percentage weight loss of the sample improved in the presence of both a conventional (Leophen MC) and a nonconventional (Compounds I–IV) wetting agent. Nonconventional wetting agents seemed to be more advantageous than Leophen MC with the exception of tryptophan–glycerol ether III regarding cotton scouring.

## CONCLUSIONS

The use of a wetting agent, both conventional and nonconventional, results in an improvement in the degree of mercerization as concluded from all the parameters studied: BAN, cotton dyeability, moisture regain, water absorbency, elongation at break, and tenacity.

The new nonconventional surfactants amino acid-glycerol ethers are advantageous because these are applied in submultiple concentrations compared to the conventional one with similar results. The hot mercerization of cotton under tension progresses as far as possible up to 10 min as concluded for the experimental study.

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