

## MASS COLORATION OF REGENERATED CELLULOSICS – A REVIEW

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### Abstract

Regenerated cellulosic fibers constitute a significant segment of the man-made fibers industry. This manuscript offers a critical review of the various methods available for their mass coloration; with 42 references.

**Keywords:** mass coloration, spun-dyeing, regenerated cellulosics.

### Introduction

Regenerated cellulosic fibers are obtained from wood pulp by dissolution and reshaping of the cellulose via physico-chemical processes. Of the many methods available for producing regenerated cellulosics [1-3], the viscose, cuprammonium, and lyocell processes may be regarded as being most prevalent in commercial industrial-scale operations [3]. Brief descriptions of these processes, excerpted from more detailed information in literature, are given below:

#### *Viscose Process* [4]

Cellulose pulp is converted to alkali cellulose by immersion in alkali solution. The alkali cellulose is mixed with CS<sub>2</sub> to form cellulose xanthate, which is dissolved in a dilute solution of sodium hydroxide to form the 'viscose' dope, and wet-spun in a solution of sulfuric acid to form fibers.

#### *Cuprammonium Process* [5]

Cellulose pulp is dissolved in cuprammonium solution (prepared by dissolving copper hydroxide in a concentrated ammonia solution), and wet-spun in acidic aqueous solutions to form fibers.

#### *Lyocell Process* [6]

Cellulose pulp is shredded and wetted in an aqueous solution of amine oxide followed by removal of excess water, which results in the disso-

lution of cellulose. The resulting solution, which is very viscous, is extruded via an air-gap into a water/amine oxide bath to form fibers. The process is characterized by a near complete recovery of the amine oxide, N-methyl-morpholine-N-oxide (NMMO), after fiber production.

Mass coloration, spun-dyeing or dope dyeing may be defined as "a method of coloring manufactured fibers by incorporation of the colorant in the spinning composition before extrusion into filaments" [7]. One of the primary considerations in any mass coloration process is to ensure chemical and physical stability of the polymer-colorant mixture. This is especially important with regard to regenerated cellulosics as their manufacturing processes involve treatment of the cellulose with strong oxidizing/ reducing agents, which may militate against the stability of colorants. But, mass coloration of regenerated cellulosics has been found possible, and the different methods reported for its achievement are summarized below.

### **Mass Coloration of Viscose or Cuprammonium Rayon**

#### *Vat Dyes*

Many of the techniques proposed for mass coloration of viscose or cuprammonium rayon involve the addition of vat dyes to spinning dopes, wherein the vat dye is reduced to its leuco form

and oxidized back to its parent form in the course of manufacturing the substrate. Some techniques involve addition of reduced vat dye to the spinning dope [11, 12]. In others, it is proposed that the vat dye be reduced in spinning dope either by utilizing the chemical reagents already present in the system [8], or by addition of reducing agents such as sodium hydrosulphite [13]. Yet others involve dispersing the vat dye in spinning dope as a pigment, forming the regenerated substrate, and treating the formed substrate with reagents to reduce the vat dye within [9, 10, 14]. In all these techniques, the oxidation of the vat dye back to its parent form is achieved, in general, by treating the formed substrate with oxidizing agents.

There are limitations to these techniques. Adding reduced vat dyes to the spinning dope may result in stabilization of the spinning dope [9]. Proper aging and coagulation of the spinning dope is hindered, which affects the development of suitable viscosities for fiber/filament spinning. The reduced vat dyes are also susceptible to premature oxidation, which results in a non-uniform distribution of dye in the substrate [15]. Many vat dyes are not reduced under conditions that exist in the spinning dope [16], and the addition of reducing agents to the system renders the dope liable to gel formation [13]. The technique of dispersing vat dyes in the spinning dope and reducing them in the formed substrate is not without challenges; firstly because a uniform distribution of the dyestuff in substrate is difficult to achieve, and secondly because not all dyestuff in substrate may be reduced, causing visible specks of dyestuff particles to remain in the substrate [13].

In some techniques, vat acids or the ester derivatives of leuco compounds of vat dyes are added to the spinning dope [15, 16]. However, the leuco compounds are highly susceptible to oxidation, which may result in the formation of coarse dyestuff particles in dope thereby affecting the subsequent regeneration step [11].

#### ***Dissolved Colorants***

Some of the proposed mass coloration techniques involve adding to spinning dopes colorants dis-

solved in polar water-miscible solvents, or dissolving colorants directly in the spinning dope [17-24]. The colorants used in these methods are selected dyes, dye derivatives, or pigments. The choice of dyestuffs available for this technique is limited by the fact that not all dyestuffs can withstand the strong alkaline conditions present in the spinning dope, or the strong acid treatments imparted to substrates during regeneration [15]. Moreover, the use of water soluble dyestuffs in mass coloration of regenerated cellulose has been observed to result in poor water fastness of the formed products [13].

#### ***Dispersed Colorants***

The dispersion of finely milled organic or inorganic pigments in spinning dopes has been suggested as a possible route for mass coloration [25-33], with additives being recommended in some cases to improve pigment dispersability [28-30, 34]. The process of milling pigments to obtain a suitable particle size is time intensive, and is accompanied by the risks of recrystallization and/or regrouping of dyestuff particles [35]. The possibility of poor pigment dispersion in spinning dope is an inherent risk in this technique, which may lead to problems both in the regeneration process and with the uniformity of color in formed substrates [28, 30]. The dispersing agents added to pigment formulations sometimes cause undesirable foaming in the spinning mass [32]. The colored substrates tend to be opaque [13], exhibit dull shades [9], and may also exhibit dichroism [29]. This technique of mass coloration may also exert a deleterious effect on substrate strength [22].

#### ***Other Methods***

Other proposed techniques include the suspension of sulfur dye intermediates in spinning dopes [36], or utilizing waste cotton textiles dyed with reactive dyes by mixing them with fresh cellulose, subjecting the mixture to xanthation, and spinning colored filaments there from [37]. In what may be categorized as a quasi mass coloration method, it is proposed that naphthol dye grounders be dissolved or mixed in the alkaline spinning dope [38]. The color could then be developed by treating the fibers with coupling com-

ponents, even when the fibers have been incorporated into yarns or fabrics.

### Mass Coloration of Lyocell

Lyocell fibers are relatively new in comparison to the other regenerated cellulose fibers, with the first commercial samples being available in the mid-1980s and full-scale commercial production beginning in the early 1990s [6]. Hence, there are only a few methods reported for the mass coloration of lyocell.

In one of the first techniques reported [39], it is proposed that selected inorganic pigments, which contain small amounts of heavy metals and do not significantly decrease the decomposition temperature of the spinning mass, be mixed with the cellulose solution prior to fiber spinning. It has also been proposed that colorant or colorant precursors be mixed with the cellulose solution [40], with the caveat that the colorants be insoluble or sparingly soluble in amine oxide. In the most recent method reported [41], it has been suggested that cellulose pulp be dyed with a vat dye; and the dyed pulp optionally mixed with undyed pulp be used to spin lyocell fibers.

### Summary

Like many other processes, every method for the mass coloration of regenerated cellulose fibers has its advantages and limitations. Mass coloration processes in general offer the advantages of high color fastness in products and a high degree of colorant utilization which make the process more eco-friendly; but are usually cost efficient only in large-scale production [42]. There exist niche markets for such products, and mass colored regenerated cellulose fibers are commonly used in technical textiles such as in medical applications, and outdoor textiles.

### Acknowledgements

The authors gratefully acknowledge the financial support of the Christian Doppler Research Society (Vienna, Austria).

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