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ORIGINAL CONTRIBUTION

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Adsorption of whitening agents on cellulose fibers – monitored by streaming potential measurements, calorimetry and fluorescence

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Abstract Fluorescent whitening agents (FWA) are used to improve the whiteness of cellulose fabrics. It is well known but not completely understood that the fluorescence decreases (chemical and physical mechanisms of distinguishing) above a certain FWA concentration c_{crit}. This reduction of fluorescence correlates very well with the alteration of the adsorption process studied by calorimetry and zeta potential measurements. The results obtained by these methods indicate that the adsorption mechanism is different at concentrations below and above c_{crit}. The reduction of the intensity of fluorescence, the degree of whiteness and the zeta potential are caused by the adsorption of a second layer of fluorescent whitening agents. This second layer reduces the zeta potential due to a shielding effect and reduces the whiteness and fluorescence by a bathochromic shift of the reflection curves. The final effect is a reduction of the total reflection.

Key words Cotton fibers – dye – adsorption – calorimetry – zeta potential – fluorescence – degree of whiteness

Introduction

Textile materials in the loom state, whether from natural or synthetic fibers, are never as white as necessary; they have a more or less pronounced yellowish tinge which must be removed by bleaching if the material shall be used in pastel shades or white fabrics. Chemical bleaches break down most of the coloring components in the fiber, but do not by any means give a perfect white color. To get the necessary whiteness the material must be dyed with "colorless dyes" – so called Fluorescent Whitening Agents (FWA).

FWA absorb light in the near ultraviolet (UV) region of the spectrum, below about 400 nm, and reemit the light, as fluorescence, in the violet–blue visible region (Fig. 1. curve 1). Polymeric substrates of preponderant white color, e.g., bleached material (curve 2), possess an yellowness caused by absorption in the blue region.

When FWA is applied, the blue fluorescence complements the yellowness and adds a blueish hue to the substrate, which is appreciated by the eye as a brilliant white. The whiteness thus obtained is much superior to that achieved by chemical bleaching, even if the latter is carried out to the limit where the material is weakened by chemical degradation, or if chemical bleaching is supplemented by blue tinting (curve 3). However fluorescent whitening complements chemical bleaching and cannot replace it.

Fluorescence-concentration relationship

When cotton fabrics are treated under technological operating conditions with excessive concentrations of fluorescent whitening agents [2], a reduction of the degree of whiteness may occur. The fluorescence vanishes at FWA concentrations [3] above c_{crit}. The dependency of the degree of whiteness and fluorescence on the concentration

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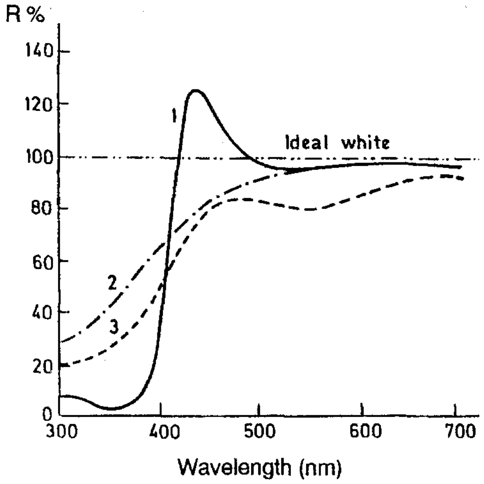


Fig. 1 Reflectance and fluorescence of chemically bleached material treated with FWA (curve 1). Reflectance of chemically bleached (curve 2) and chemically bleached and blue-tinted material (curve 3)

can be expressed by means of the Stern–Volmer equation

$$\frac{Q_m}{Q_0} = + \beta^*(c - c_0) , \qquad (1)$$

where Q_m is the maximal fluorescence intensity, Q_0 the fluorescence intensity, c the FWA concentration, c_0 the FWA concentration at which the extinction of fluorescence appears. A bathochromic shift of the remission curves takes place and the total remission is reduced.

Physical adsorption of FWA on cellulose fibers

FWAs used in textiles can be classified into three groups:

- those which have sulfonic acid groups, similar to direct dyes,
- those which are cationic and behave like basic dyes, and
- those which have no solubilizing groups and are similar to disperse dyes.

The application of substances from the first group, with one of the chemical constitutions shown in Fig. 2, to cellulose textile materials was studied.

They are anionic stilbene derivatives and, due to the anionic structure of both components, i.e., FWA and cellulose material, the adsorption process is caused by hydrogen bonding, van der Waals forces and hydophobic interactions.

Determination of FWA physical adsorption process

The adsorption process of anionic fluorescence agents and the changes of electrokinetic properties which appear during the process at the interface of the cellulose fibers and the aqueous phase were investigated using two methods:

- the adsorption process at different concentration of FWA was monitored *calorimetrically*,
- the electrokinetic properties, i.e., changes in the zeta potential of anionic fibers during the adsorption process were determined measuring the *streaming potential.*

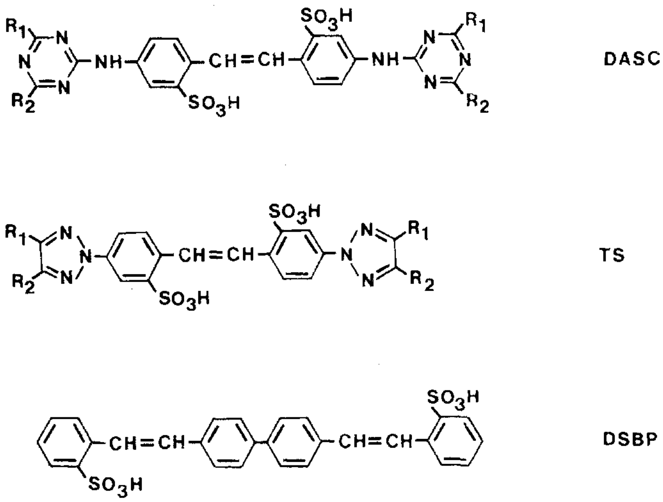


Fig. 2 Fluorescence whitening agents for cotton DAST = Diaminostilbenedisulfonic acidtriazinyl derivatives; 4,4'-Bis[(1,3,5-triazin-1-yl) amino]-stilbene-2,2'-disulfonic acid; TS = 4,4'-Bis(1,2,3-triazin-2-yl) stilbene-2,2'-disulfonic acid; DSBP = Distyrylbiphenyl; 4,4'-bis (styryl) biphenyl

Material and methods

The material used for analysis was 100% pure cotton.

Preparation Methods – Fluorescent whitening

Chemically bleached cotton material has been whitened by different concentrations of anionic FWA (Hostalux CBA, Hoechst AG concentration: 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 5.0%, relative to the weight of cellulose material).

After each treatment the fibers were washed in distilled water until a conductivity less than 3 μs/m was measured.

Analytical methods

Determination of the zeta potential of fibers

Electrokinetic surface properties of materials are generated by the electrochemical double layer described by Guy, Chapman, Stern and Graham [6] which exists at phase boundaries between solids and electrolyte solutions. The streaming potential method was used, as it has been shown to be the most appropriate electrokinetic technique [7] to study the zeta potential (ZP) of fiber systems. The ZP was calculated from streaming potential (Us) data by the Smoluchowski equation:

$$\xi = \frac{U}{\Delta P} \cdot \frac{\eta}{\varepsilon_0} \frac{L}{Q \cdot R} \, . \qquad (2)$$

In order to determine the ZP of films and fibers correctly, it is necessary to measure the streaming current/streaming potential as a function of the pressure difference (*dp*) in the electrolyte solution between the cell inlet and outlet [8]. The term *dUs*/*dp* represents the slope of the line if *Us* is plotted vs *dp*. The offset describes the asymmetric potential of the electrodes and does not influence the results. The most common method to determine the geometrical term *L*/*Q* (length over cross-section of the capillary system in the fiber plug) was developed by Fairbrother and Mastin [9], describing the channels in the fiber plug in the same way as a conductivity cell.

$$\frac{L}{Q} = \frac{\omega}{R} \, . \qquad (3)$$

The streaming potential was measured as a function of the pH in 0.001 N KCl, the surface conductivity was not taken into account.

The here mentioned ZP values are always those obtained at the constant part of the ZP-pH function in the alkaline region at pH = 9.

Instrument: Electrokinetic Analyzer EKA, A. Paar KG, fiber and flat plate cell.

Determination of the heat of adsorption by calorimetry

A parameter characterizing the adsorption process is the heat of absorption ΔH_{ads}. The calorimetric data were obtained using a heat-conducting calorimeter at semi-isothermal conditions.

The experiments were performed with 0.1 g fabric in 1.5 ml solvent in the calorimeter cell. The sample was placed along the walls of the measuring cell in such a way that stirring of the liquid phase was possible. The FWA solution was added stepwise from a stock solution so that the final concentration in the solution was the same as that applied in the fluorescence and zetapotential experiments. The heat of adsorption was measured after each addition of FWA solution to the liquid phase and calculated from the heat burst which occurred [10]. The heat is expressed as energy per added quantity of FWA. The heat of dilution was also measured and taken into account. The results are shown as heat of adsorption vs concentration of FWA in the liquid phase.

Instrument: Thermo Metric LKB 2277 thermal activity monitor.

Micro reaction system with titration cylindrical cell, 4 ml volume.

Numerical determination of whiteness and surface fluorescence intensity

The whiteness (W CIE) was determined according to the CIE equation:

$$W = Y + 800(x_n - x) + 1700(y_n - y) \, . \qquad (4)$$

Instrument: ACS Spectro Senzor SS-II, measuring geometry *d*/8, 400–700 nm, halogen light, CIE light source D 65.

The intensity of fluorescence (*Q*) was measured relative to the standard (Whatman Filterpaper Nr. 1 optical whitened by fluorescent whitening agent Blankophor B; $c = 1\%$).

Instrument: Reflectant light fluorimeter.

Results

The ZP as a function of the pH at different concentrations of FWA is shown in Fig. 3. An increase of the ZP with increasing FWA concentration is observed until a maximum at a FWA concentration of 0.8% is reached. Above that concentration the ZP decreases with increasing FWA concentration. This is in good agreement with the observed

Fig. 3 ZP-pH isoterms of cotton fibers as a function of FWA (Hostalux CBA) concentration (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 5.0% FWA)

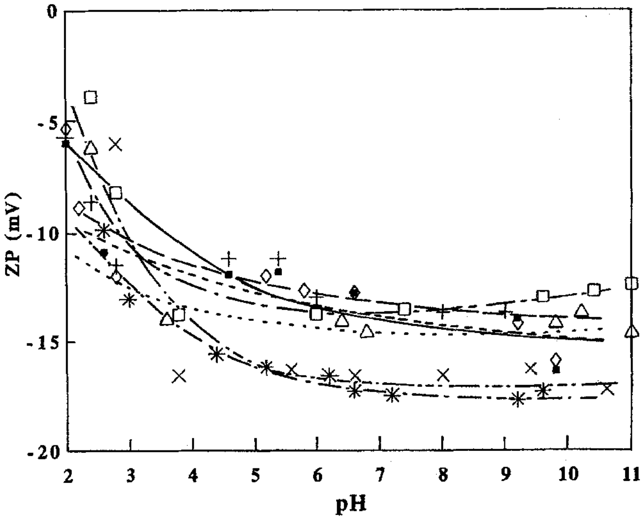
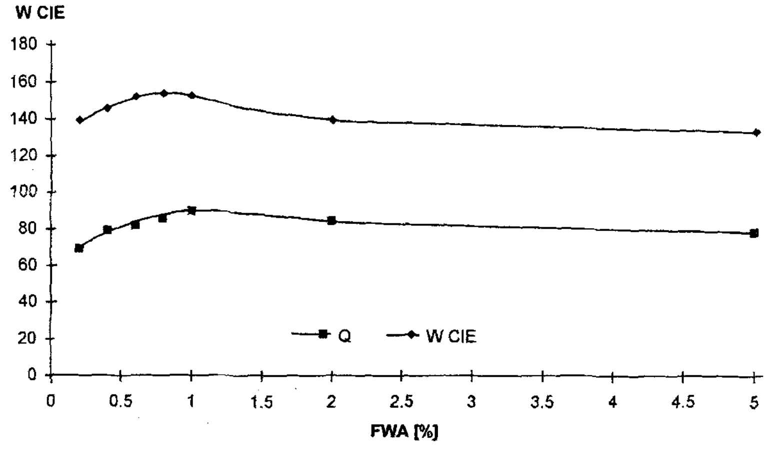


Fig. 4 Whiteness and intensity of fluorescence of cotton fibers as a function of whitener concentration (■ Intensity of fluorescence, ◆ degree of whiteness)



adsorption of anionic surfactants on negative charged surfaces [8] which causes the same effect due to an enlargement of the electrochemical double layer caused by the high amount of adsorbed surfactant.

A similar effect is observed regarding the intensity of fluorescence and the degree of whiteness (Fig. 4). Both parameters increase with increasing FWA concentration. The observed intensity remains constant, the calculated degree of whiteness decreases above the critical concentration of 0.8 to 1.0%.

The results obtained by calorimetric investigations are shown in Fig. 5. Two different types of exothermic adsorption processes are observed. One below the critical concentration of 0.8% shown at the left part of the figure which needs approximately 20 min to obtain a thermal equilibrium. The time constant of this process is independent of the actual concentration of FWA as long as it is below the critical concentration.

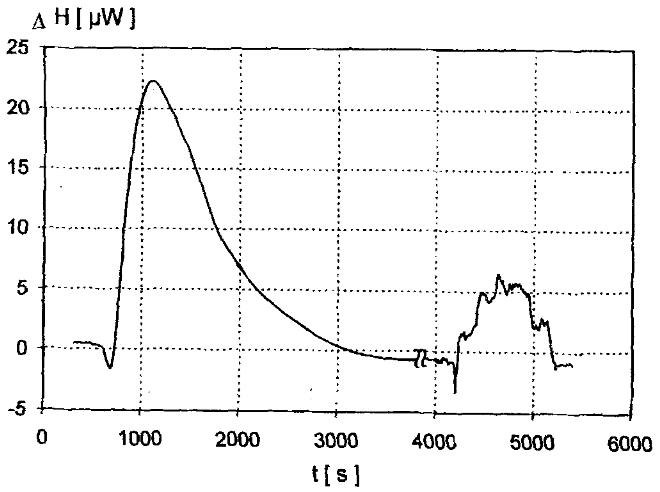
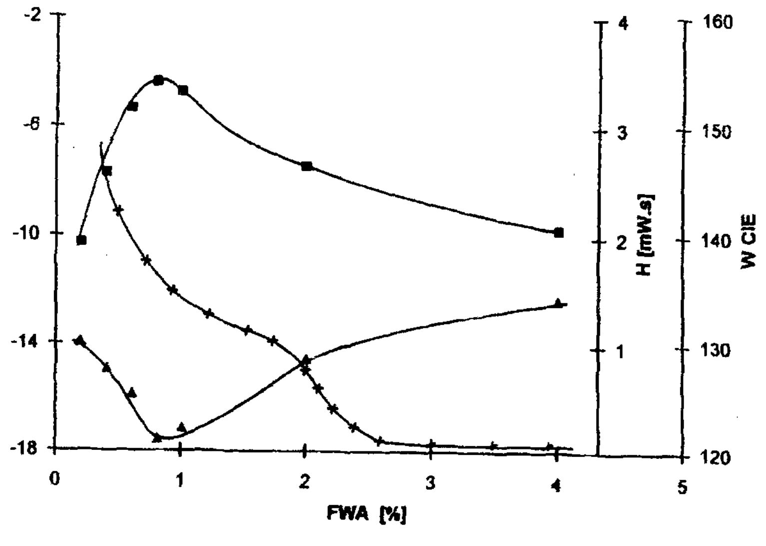


Fig. 5 *Heat bursts at the low (below 1% FWA-left part of the figure) and at the high concentration range (above 1,2% FWA-right part of the figure)*

Fig. 6 ZP, H_{ads} and W CIE of cotton fibers as a function of whitener (Hostalux CBA) concentration (▲ Zeta potential, ■ Degree of whiteness, × H_{ads})



At FWA concentrations above 0.8% a weaker adsorption process is observed reaching the temperature equilibrium after approximately 15 min, but exhibiting lower ΔH_{ads}. The time constant of this adsorption process is also independent of the actual FWA concentration if it is above 1 and below 2%. The slopes of the bursts at both adsorption mechanism are always the same, indicating that the amount of FWA adsorbed per unit time is constant.

The contribution of the heat of dilution can be seen as a small endothermic burst at the start of each adsorption peak. It is approximately 0.4 mW.s/0.1 mg FWA.

The heat of adsorption as a function of FWA concentration is shown in Fig. 6. At a FWA concentration below 0.8% the heat of adsorption decreases very strongly with increasing FWA concentration. ΔH_{ads} of 3 to 1.5 mW/0.2 mg FWA are measured for this process. Above 0.8% FWA the adsorption mechanism changes, the adsorption enthalpy remains approximately constant at 1.3 to 1 mW/0.2 mg added FWA and decreases again very pronounced at FWA concentrations above 2% until the H_{ads} is zero at concentrations above 2.5%. No adsorption takes place if the FWA concentration exceeds 2.5%.

Discussion

The comparison of results obtained by three independent methods shows (Fig. 6.) distinct changes in the physicochemical properties of cotton fibers at a critical FWA concentration- c_{crit} of approximately 0.8–1% of anionic whitener.

The intensity of fluorescence as well as the degree of whiteness exhibit a maximum at this c_{crit}. The observed phenomenon of the diminishing degree of whiteness and the intensity of fluorescence at FWA concentrations above c_{crit} is well known. The reason is a bathochromic shift of the emitted light and the so-called reabsorption of the emitted (reflected) photons in the second layer of adsorbed FWA molecules.

These observations agree very well with the results obtained by calorimetry and streaming potential experiments.

The negative zeta potential is not a linear function of the FWA concentration, it shows a maximum at c_{crit}. The adsorption of FWA molecules on the negative charged fiber surface causes an increase of the negative zeta potential until c_{crit}. Above that concentration the ZP is reduced again. This can be explained by an alteration of the thickness of the electrochemical double layer which may be due to the adsorption of a second layer of FWA.

The H_{ads} vs. c function shows also an alteration of the FWA adsorption process at c_{crit}. A primary adsorption takes place at concentrations below c_{crit}. Above c_{crit} an energetically less preferred adsorption process is observed. This can also be explained by the adsorption of a second layer of FWA molecules or by adsorption on less preferred adsorption places. Adsorption at concentrations above 2.5% does not occur.

The phenomenon of FWA adsorption and, finally, satisfaction of the fiber surface is observed in good agreement by these three methods and can be explained by a primary mechanism of strong adsorption at concentrations below 1% FWA and a weaker adsorption in the range of 1 to 2.5% FWA which causes the reduction of whiteness.

These results indicate the very important influence of textile cellulose fibers' electrokinetic properties on other textile finishing processes where components of the liquid phase are adsorbed on the fiber, i.e., dyeing with direct dyes (12).

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