

PHOTOFADING OF WOOL COLORED BY TRYPTOPHAN COLOR REACTIONS

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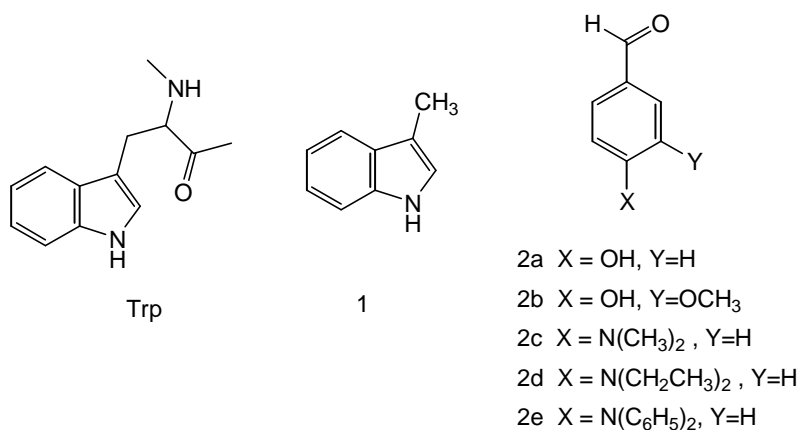
Abstract

Treatment of wool fabric with aromatic aldehydes followed by oxidation with hydrogen peroxide gave rise to coloring reaction. The colored fabric was bleached by reduction and recovered the color by oxidation. The oxidation in ethanol solution gave higher k/s values than that in aqueous solution. Photo-stability of the colored fabric was improved by treating with nickel sulfate.

1. Introduction

Dyeing industries face increasing demands for environmental protection. Recently Donowaki has developed a new method of coloring wool and silk by treating them with an acetic acid solution of trifluoroacetic acid in the presence of aromatic aldehyde derivatives and proposed a mechanism involving reactions at the tryptophan units (**Trp**) of the polypeptides [1]

In this work we examined the coloring reaction of wool using aromatic aldehydes and investigated their photofading reactions.



2. Experimental

Indol (**1**) was used as model compound of **Trp**. Aromatic aldehydes used were *p*-hydroxybenzaldehyde (**2a**), vaniline (**2b**), *N,N*-dimethyl-*p*-aminobenzaldehyde (**2c**), *N,N*-diethyl-*p*-aminobenzaldehyde (**2d**) and *N,N*-diphenyl-*p*-aminobenzaldehyde (**2e**). Fabrics of wool were treated with ethanol solutions or aqueous solutions of 3.0 % hydrogen chloride containing 0.5 wt% of aldehydes in liquor ratios of 1:50 at 60 °C for 12 h. After washed with water and then with ethanol, the fabrics were subjected to an oxidation process by

treating them with an ethanol solution or an aqueous solution of 3.0 wt% hydrogen chloride containing 0.25 wt% hydrogen peroxide in liquor ratio of 1:50 at 60 °C for 1 h.

The colored fabrics were exposed to a 366 nm irradiation of mercury lamp equipped with a filter. Reflectance at the absorption maxima of the fabric gave k/s value of Kubelka-Munk equation. Photofading of colored wool fabrics treated with 10 wt% nickel sulfate solution were also examined.

3. Results and discussion

As shown by Fig. 1, the fabric colored by **2a** was bleached on treatment with an aqueous solution of sodium dithionite. The fabrics recovered the color on treatment with aqueous solution of hydrogen peroxide.

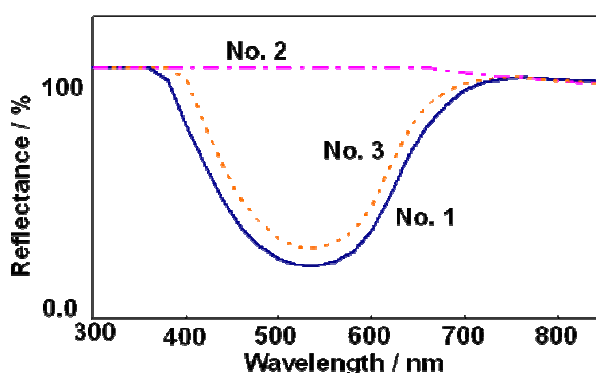


Fig. 1 Reflectance spectra of wool fabric colored with **2a**. No. 1, 2 and 3 are oxidized, reduced and reoxidized fabric, respectively.

To investigate the reaction mechanism with model reaction indol (**1**) was treated with *p*-hydroxybenzaldehyde (**2a**) in an acidic solution, yielding 4-bis-(2-methyl-1-indolyl)methylphenol (**3**). On oxidation **3** gave a reddish compound (**4**), which was reduced to **3** by sodium borohydride. Similar coupling reaction is considered to occur at the Trp unit of wool to cause the coloring reaction on oxidation.

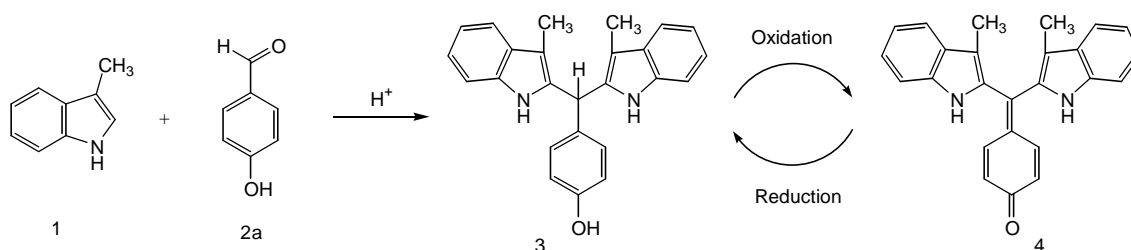


Table 1 shows k/s values of colored fabrics. As to the wool treated with **2a**, **2c** and **2e**, oxidation in ethanol solution gave k/s values about 4.3, 5.4 and 20 times higher than those in aqueous solution, respectively.

The colored fabrics were exposed to ultraviolet irradiation for 24h. Table 1 summarizes the

Table1 Condition of coloring of wool, k/s and relative k/s after irradiated for 24 h.

Aldehyde	Treatment ^{a)}		k/s (0h)	Relative k/s (24h)
	I	II		
2a	A	A	0.19	0.60
2a	A	B	0.59	0.64
2a	B	A	0.19	0.65
2a	B	B	0.82	0.66
2c	A	A	0.54	0.54
2c	A	B	2.8	0.52
2c	B	A	0.30	-
2c	B	B	2.9	0.67
2e	B	A	0.095	1.1
2e	B	B	1.9	0.59

a) I: Aldehyde treatment; II: Oxidation.

A: in aqueous solution; B: in ethanol solution.

relative k/s obtained as a ratio of k/s of the exposed fabric against the value at the initial stage of the reaction. The **1a**- as well as **1b**-colored fabrics that were treated with hydrogen peroxide in ethanol solutions showed little differences in photo-stability from those in the aqueous solution. The wool fabrics treated with **1c** increased k/s value on irradiation,

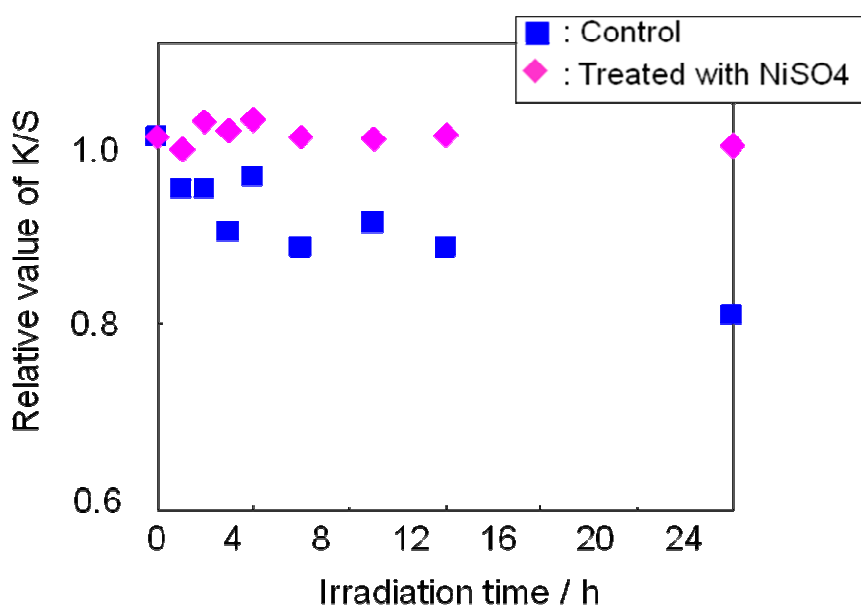


Fig. 2 Rate of photofading of wool colored with **2a**

implying photo-oxidation of the color precursor which survived oxidation with H₂O₂ in aqueous solution.

In many cases photofading of dyestuff had been found to involve oxidation by singlet oxygen generated by photochemical sensitization of the oxygen in ground state by dyestuff itself [2]. Nickel complexes are known to quench singlet oxygen [3]. The effect of nickel ion was examined for the photofading of the present colored fabric. Treatment with a nickel sulfate solution improved the photo-stability of **2a**-colored wool, implying a mechanism of photoreaction involving singlet oxygen intermediate. Little effect of nickel ion was observed for the photofading of wool colored by **2c** and **2e**. The benzaldehydes having amino functions are considered to give rise to color centers with positive charges, which prevent approach of nickel ion, reducing the quenching effect.

In general humidity accelerates the photofading reaction of polymers dyed with dyestuffs. Photo-stability of the present fabric colored by **2a** was decreased by 60 % in an atmosphere of high humidity.

4. Conclusion

The coloring of wool caused by the treatment of aromatic aldehydes in acidic media is considered to involve coupling reaction of the aldehyde at the tryptophan unit of the wool peptide followed by oxidation. The oxidation in ethanol solution gave higher k/s value than in aqueous solution. The photofading mechanism of the colored fabric is considered to involve singlet oxygen intermediate.

5. References

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