

# Utilization of Lignin *p*-Aminophenyl Carbamate as a Coupler for Dyeing Wool and Nylon\*

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## Synopsis

Lignin carbamate was prepared as a good blocking for the phenolic hydroxyl group of lignin. To reduce its color, the following was accomplished: first, condensation of lignin carbamate with *p*-nitroaniline to fulfill complete blocking; second, reduction of this compound with thiourea dioxide to give a new compound; and third, diazotization of this new compound with different phenolic compounds to give highly reactive dispersed dyes that have very attractive colors. Lightfastness and washing perspiration fastness were studied, and the relationship between spectral analyses and the fastness was also considered.

## INTRODUCTION

Lignin in wood is almost colorless. Lignin isolation procedures and pulping processes invariably introduce a variety of chromophores into the structure and render the isolated lignins strongly colored. Industrial lignins (such as sulfonated alkali lignins from the kraft and soda pulping processes and lignosulfonates from the sulfite pulping process) are colored to different degrees depending on the pulping conditions and the type of pulping process employed for delignification. The drastic conditions of a pulping process, e.g., use of high temperature and a strong caustic in combination with atmospheric oxygen, produce lignin so intensively darkened that their uses in many applications become objectionable because of the color.

The cause of the dark brown color of lignins and the mechanisms for the formation of chromophores during the pulping processes are not completely known, although numerous suggestions have been made previously. Gierer<sup>1</sup> proposed *o,p'*-stilbenequinone; *p,p'*-stilbenequinone; 1,4-bis-(*p*-hydroxyphenyl)-buta-1,3-diene; *o*-benzequinone; and methylene quinone as possible chromophoric structures. Imsgard et al.<sup>2</sup> estimated the amount of *o*-quinonoid structures in spruce milled-wood lignin to be about 0.7% and stated that the amount of quinonoid structures can account for as much as 35–60% of the light absorption of the lignin at 457 nm. The majority of chromophoric structures in alkali lignins and lignosulfonates appear to be some sort of conjugated system involving quinonoid and side-chain double bonds.

In our previous work, lignin carbamates<sup>3</sup> were prepared by treating alkali lignins with blocking agents to achieve at least a degree of blocking of 90%.

\* Patent in ARE 17268 (1984).



Lightfastness was carried out in accordance with *The Standard Methods for Determination of Colour Fastness of Textiles*.<sup>5</sup> Washing and perspiration fastness were determined according to the published method.<sup>6</sup>

## RESULTS AND DISCUSSION

### Effect of Substitution on Lightfastness

It is clear from Tables I and II that these dispersed dyes possess a higher light, washing, and perspiration fastness than do lignin dyes. It is also clear that lightfastness on wool is, in general, the same as on nylon. Compounds 1, 2, and 3 possess lightfastness 6–7. Introduction of Cl atom compound (4) and SO<sub>3</sub>H group compound (5) causes a drop of lightfastness to 5, a marked drop.

The electron-donating group could be expected to cause an increase in the bond order, and electron accepting could be expected to cause a decrease. This assumption is generally in agreement with our results that the  $-I$  effect of the Cl atom, especially in the O position in compound 4 and the  $-I$  effect of SO<sub>3</sub>H compound 5 caused a marked drop in lightfastness whereas the  $+I$  effect of the CH<sub>3</sub> group increases the lightfastness of compound I.

### Infrared Spectra

Figure 1 clearly shows the difference between lignin carbamate and lignin *p*-aminophenyl carbamate. Figures 2 and 3 show that all compounds possess bands at 1400–1440 cm<sup>-1</sup>. According to Bellamy,<sup>8</sup> not much is known about the IR absorption band arising from the  $-N=N-$  linkage. Such a band might be expected to be weak unless conjugated and may be absent in symmetrical structure. The position of the N=N band is not defined with certainty because of confusion with the skeletal vibration and strong vibration in the intensity. Since the N=N group is situated at the center of the molecule, the position of the band due to the stretching vibration might be better traced in molecules with poor symmetry character.

The  $-N=N-$  band was shown by Lefevre and others<sup>9</sup> to be located near 1400–1580 cm<sup>-1</sup>; it is therefore possible to assign the 1400–1440 cm<sup>-1</sup> band to the symmetric  $-N=N-$  stretching vibration. The other band lies within the region due to the C–N in the aromatic system. The position of both bands is influenced by the nature of substituents.

The position of the bands assigned to the C–N and symmetric N=N–stretch, namely, the 1210–1280 cm<sup>-1</sup> and the 1400–1440 cm<sup>-1</sup>, can be arranged in the following decreasing order: methylresorcinol > resorcinol > B-naphthol *o*-chlorophenol > 1-amino-2-naphtholsulphonic acid.

These values indicate that the force constant of the N=N decrease in the same order. This behavior can be explained by the assumption that the  $-I$  effect of the SO<sub>3</sub>H and Cl atoms cause a decrease in the charge density of the azo group. The electron withdrawing effect of these groups affects the resonance of the C–N bond with the phenyl ring, thus causing a lowering of the bond order in comparison with the parent compound. The lower bond order of the

TABLE I  
Dyeing of Wool with Substituted Modified-Lignin Dyes and Their Characteristic Properties

Compound	Color	Lightfastness	Washing fastness			Perspiration fastness acid and alkali			N=N	C-N
			Change in color	Staining		Change in color	Staining			
				Cotton	Polyester		Cotton	Polyester		
1-3-Methyl-resorcinol	Dark brown	7	5	5	5	5	5	5	1480	1212
2-Resorcinol	Black	6	4	4	5	5	4	4	1430	1250
3-B-naphthol	Greenish brown	6	4	4	5	5	4	4	1410	1260
4-o-chlorophenol	Reddish brown	5	3	3	4	4	3	3	1440	1210
5-Amino-2-naphthol-sulphonic acid	Brown	5	3	3	4	4	3	3	1420	1240

TABLE II  
Dyeing of Nylon with Substituted Modified Lignin Dyes and Their Characteristic Properties

Compound	Color	Lightfastness	Washing fastness			Perspiration fastness acid and alkali		
			Change in color	Cotton	Polyester	Change in color	Cotton	Polyester
1-3-Methylresorcinol	Orange	7	5	5	5	5	5	5
2-Resorcinol	Reddish brown	6	4	4	5	4	5	5
3-B-naphthol	Reddish brown	6	4	4	5	4	5	5
4- <i>o</i> -chlorophenol	Greenish yellow	5	3	3	4	3	4	4
5-1-Amino-2-naphthol-sulphonic acid	Brown	5	3	3	4	3	3-4	3-4

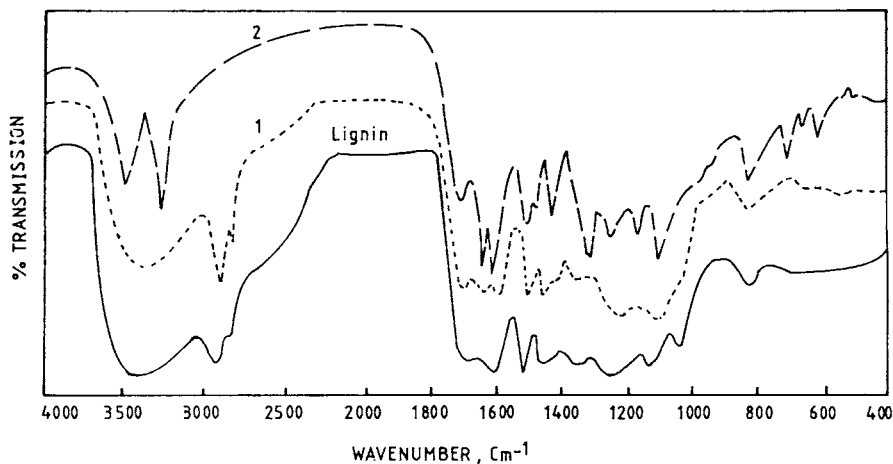


Fig. 1. IR spectra of alkali lignin: (1) IR spectra of lignin carbamate; (2) IR spectra of lignin-*p*-aminophenyl carbamate.

C-N and N=N groups decrease the stability of  $-\text{N}=\text{N}-$  as well as its bonding of the aromatic system.

On the other hand, the +I effect of the  $\text{CH}_3$  group presumably disturbs the resonance of the azo group with the phenyl ring, causing a stabilization of  $-\text{N}=\text{N}-$  bond. The inhibition of resonance would be decreased in the partial

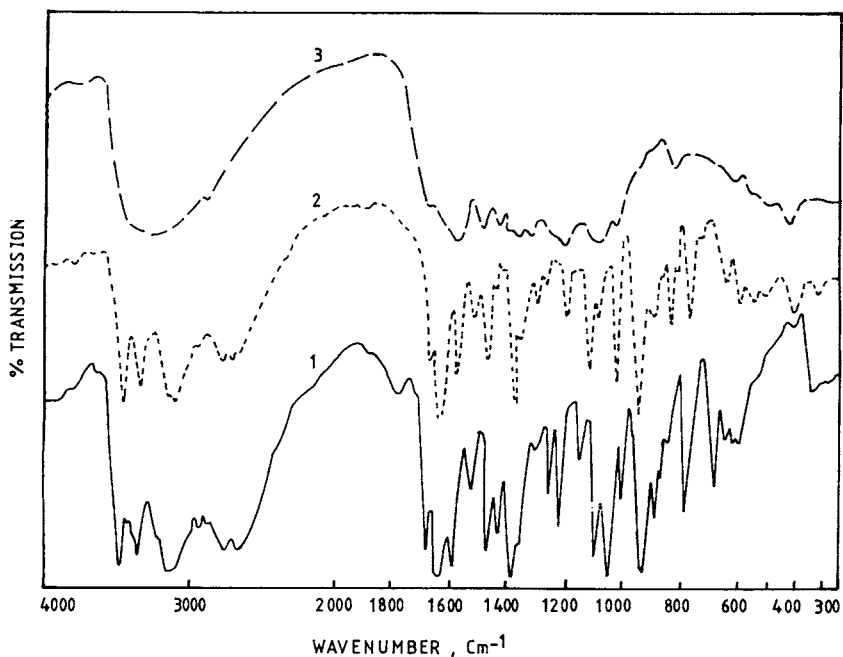


Fig. 2. IR spectra of substituted modified lignin dyes: (1) resorcinol; (2)  $\text{CH}_3$  resorcinol; (3) *o*-chlorophenol.

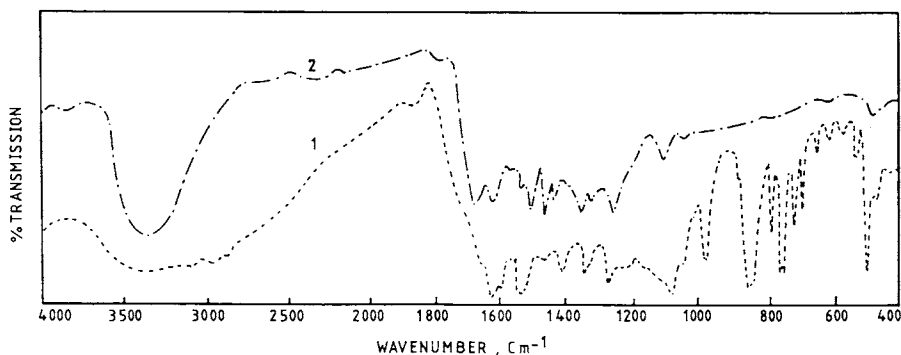


Fig. 3. IR spectra of substituted modified lignin dyes: (1) B-naphthol; (2) 1-amino-2-naphtholsulfonic acid.

double-bond character of the C—N bond; hence, the band due to the C—N linkages shifts to lower values than in the original compound. The decrease of the bond order to C—N linkage in the *o*-chloro compound 4 is explained by the lower charge migration from the ring than from the azo group. Thus, there should be a relation between the ease of the destruction of the —N=N— center and the strength of the C—N bond: The higher the bond order of C—N, and alternatively, the C—N frequency, the more stable the compound would be. This assumption is in harmony with the fact that the lightfastness of compound I with the +I effect of the CH<sub>3</sub> group is higher than it is with the compound-containing groups that have the —I effect compounds 3 and 4 (Tables I and II) in which the C—N bond order is lowered.

## CONCLUSION

- (1) Lignin carbamate condenses with *p*-nitroaniline to form *p*-aminophenyl carbamate as a coupler.
- (2) After reduction with thiourea dioxide, this new compound diazotized with phenolic compounds to give highly reactive dispersed dyes rather than dispersed lignin dyes.
- (3) Lightfastness on wool is nearly the same as on nylon.
- (4) The —I effect of the Cl atom in *o*-chlorophenol and SO<sub>3</sub>H in 1-amino-2-naphtholsulphonic acid has a pronounced effect on the decrease in lightfastness, whereas the +I effect in CH<sub>3</sub> resorcinol causes an increase in lightfastness rather than resorcinol itself.
- (5) From IR spectra, the position of the bands assigned to the C—N and symmetric N=N stretch, namely, the 1270–1280 cm<sup>-1</sup> and 1400–1440 cm<sup>-1</sup>, can be arranged in the following decreasing order 3-methylresorcinol > resorcinol > B-naphthol *o*-chlorophenol > 1 amino-2-naphtholsulphonic acid. It is clear that the —I effect of SO<sub>3</sub>H and Cl atoms decreases in the charge density of the azo group and also affect the resonance of the C—N bond with a phenyl ring, thus causing a lowering of the band order of C—N and the azo groups. This effect leads to a

decrease in lightfastness, whereas  $\text{CH}_3$  resorcinol due to the +I effect of the  $\text{CH}_3$  group enhances the lightfastness due to increasing the bond order of the C-N and N=N groups.

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Received November 20, 1989

Accepted January 20, 1990