

Preparation of Chemically Modified Cotton Via Introduction of Aromatic Amino Groups

Chemical modification of cotton via introduction of aromatic amino groups may be regarded as one of the most important processes used for preparation of chemically modified cotton.¹ This is due to a variety of reasons. First, the amino groups could be diazotized, and further Sandmeyer reaction would introduce sulfocyanide, hydrosulfide, sulfo, and other groups. Secondly, subsequent reactions leading to formation of azo compounds would give colored products. Third, the formation of cellulose macroradicals during diazotization and separation of diazo groups could be utilized to initiate vinyl graft copolymerization without simultaneous homopolymer formation. However, methods used in the preparation of cotton bearing aromatic amino groups are either tedious or do not give satisfactory results. Furthermore, it has not been possible up to now to prepare modified cellulose containing aromatic amino groups by nucleophilic substitution reaction.

The present work describes a novel method for the preparation of cellulose bearing aromatic amino groups by reacting cotton cellulose with 2,4-dichloro-6-(*p*-nitroanilino)-*s*-triazine in the presence of alkali and subsequent reduction of nitro groups to amino groups:

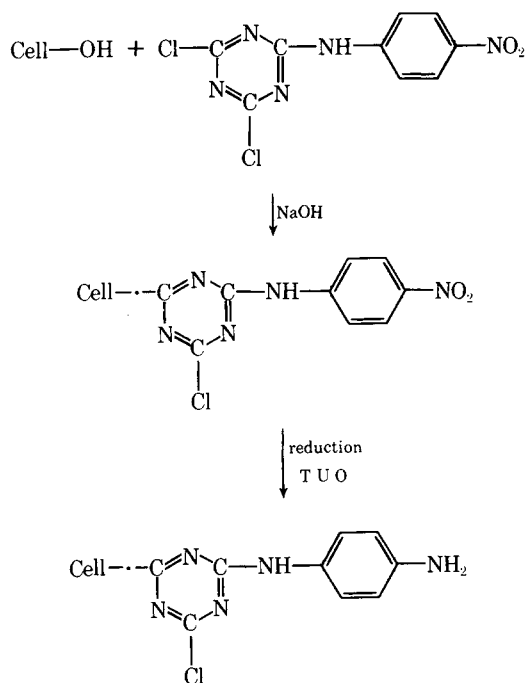


Figure 1 shows the extent of the reaction, expressed as percent nitrogen, versus alkali concentration. As can be seen, increasing the alkali concentration to 2% is accompanied by a significant enhancement in the extent of reaction. Beyond this concentration, the extent of the reaction falls substantially, indicating partial splitting off of the aromatic amino groups under the influence of both heat and the relatively high alkali concentration, similar to reactive dyes.²

Figure 2 shows variation of the extent of the reaction with duration of heating at 90°C, whereas Figure 3 shows the same relation except that no heating was involved, i.e., the fabric was merely stored at room temperature for varying lengths of time. Both figures reveal one common feature, i.e., the

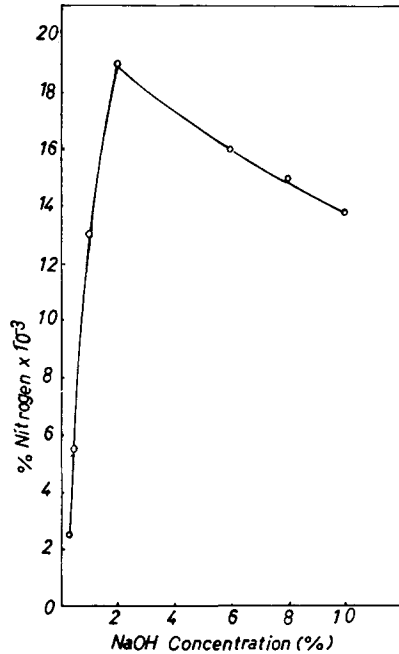


Fig. 1. Effect of sodium hydroxide concentration on the extent of reaction (expressed as percent nitrogen). Concentration of compound I, 1% in acetone; temperature, 90°C, time, 5 min.

extent of reaction increases considerably as the reaction time increases. Nevertheless, the extent of reaction is much greater, and the time required to attain a certain extent of reaction is much shorter at 90°C than at room temperature.

Figure 4 shows that the extent of reaction increases considerably by raising the reaction temperature to 90°C. Thereafter, increasing the reaction temperature has no significant effect on the extent of the reaction.

The reaction medium does also affect the extent of reaction. This may be realized from Table I, in which it is seen that for a given alkali concentration, tetrachloroethylene constitutes the most favorable medium, whereas water plus emulsifying agent constitute the least. On the other hand, acetone and acetone-water mixture stand in a midway position.

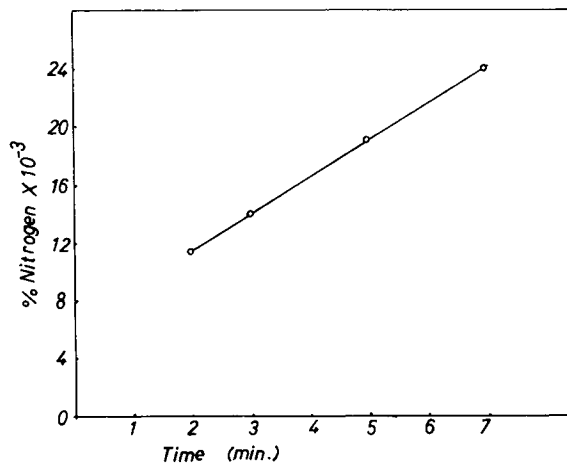


Fig. 2. Effect of duration of heating at 90°C on the extent of reaction (expressed as percent nitrogen). Concentration of I, 1% in acetone; sodium hydroxide concentration, 2%.

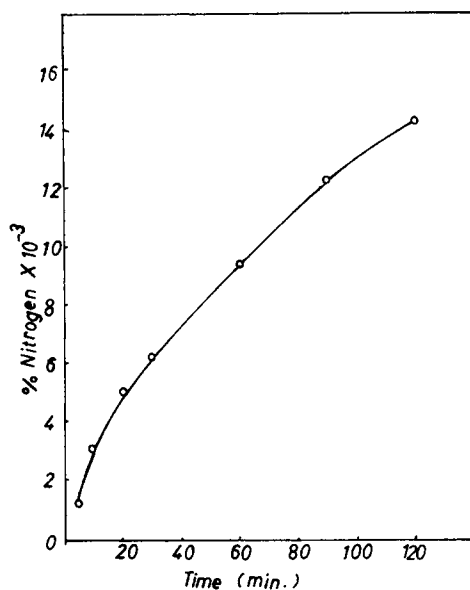


Fig. 3. Effect of storing time at room temperature on the extent of reaction (expressed as percent nitrogen). Concentration of I, 1% in acetone; sodium hydroxide concentration, 2%.

EXPERIMENTAL

Mill-scoured and bleached cotton fabric (Poplin, Misr Company for Spinning and Weaving, Me-halla El-Kobra) was used throughout this investigation.

2,4-Dichloro-6-(*p*-nitroanilino)-*s*-triazine was prepared as follows³: Cyanuric chloride (18.4 g) was dissolved in acetone (60 ml) and cooled down to 0°–5°C. To this, cold water (40 ml) was added under vigorous stirring. *p*-Nitroaniline (13.8 g) was dissolved in the least amount of acetone, cooled, and placed in a separating funnel to allow dropwise addition to the cyanuric chloride solution. This addition was performed under continuous stirring and at a temperature that never exceeded 5°C. The reaction mixture was then kept for 1 hr at room temperature. Following this, the calculated amount of aqueous solution of sodium carbonate (9%) was added, and a precipitate was formed. The latter was separated through filtration, then washed successively with cold hydrochloric acid (1%)

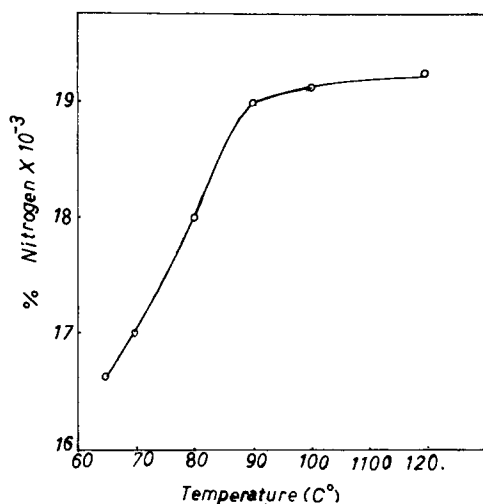


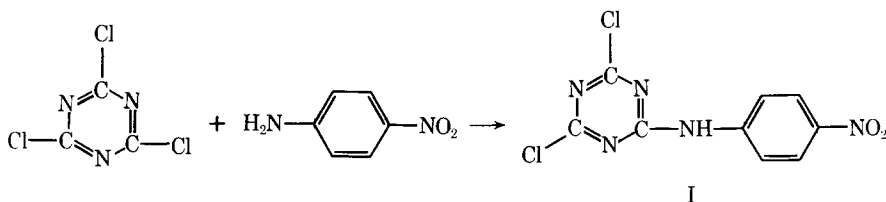
Fig. 4. Effect of heating temperature on the extent of reaction (expressed as percent nitrogen). Concentration of I, 1% in acetone; sodium hydroxide concentration, 2%; time, 5 min.

TABLE I
Effect of Reaction Medium on Extent of Reaction (Expressed as Percent Nitrogen)^a

Reaction medium	% Nitrogen $\times 10^{-2}$			
	0.025% NaOH	0.50% NaOH	1.0% NaOH	2.0% NaOH
Acetone	2.5	5.5	13.1	19.0
Tetrachloroethylene	4.4	22.1	35.0	70.0
Acetone-water mixture (50:50)	3.0	6.0	15.0	19.0
Water plus emulsifying agent	1.3	2.0	3.8	5.6

^a Concentration of I, 1%. Temperature, 90°C; time, 5 min.

and water. After being dried, the precipitate was crystallized from benzene to give yellow crystals having a melting point of 155°C. This is indeed the melting point reported³ for 2,4-dichloro-6-(*p*-nitroanilino)-*s*-triazine (I):



Thiourea dioxide (TUO) was prepared according to a method described elsewhere.⁴

Unless otherwise, the technical procedure adopted was as follows: The cotton fabric was padded with two dips and two nips in an acetone solution containing 1% of compound I and 2% sodium hydroxide to a wet pickup of ca. 80%. The fabric was then fixed in a frame and heated for 5 min at 90°C in an oven. The fabric was then thoroughly washed with water, treated with dilute acetic acid (1%), rinsed with water, and dried at ambient conditions. Subsequent reduction of the aromatic nitro groups to amino groups was carried out by impregnating the fabric at room temperature in a solution of 5% TUO at pH 8. Temperature was then raised to 80°C, and the treatment was continued at this temperature for 5 min. The fabric was then thoroughly washed, dried at ambient conditions, and analyzed for nitrogen. Nitrogen was determined according to a reported method.⁵

References

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