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Optimum Conditions for the Synthesis of Dimethylol Urea Textile Fixer

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Abstract: Being a major textile exporting country, Pakistan exports textile products and earns a lot of money. On the other hand it spends huge amounts of foreign exchange on importing textile auxiliaries like dye intermediates, dye fixing agents, fluorescent brighteners etc. Formaldehyde precondensates with amino compounds and this forms an important class of polymers like Phenol-formaldehyde, Melamine-formaldehyde etc. used largely and effectively in textile industry as dye fixing agents. At present Dimethylol Urea (DMU) is one of the main chemical is being imported from Germany and United States of America. Present project is an attempt to synthesize DMU locally on laboratory scale. Results revealed that formalin on treatment with urea at pH 7.5 synthesized low molecular weight precondensate (DMU) that was miscible with water. Optimum time period for the completion of reaction was found to be 2 hrs. Moreover it was determined that one mole of urea required 1.5 to 1.6 moles of formalin (formaldehyde) to react completely. The results revealed that DMU precodensate is the better for rayon as compared to cotton.

Key Words: Formalin, Urea, Dimethylol Urea (DMU) and Pakistan

Introduction

"Fixers are low molecular weight film-forming agents produced by the polymerization of simple intermediates in a homogenous dissolved or dispersed state."

Direct dyes and some of the reactive dyes have poor washing fastness on cotton and rayon fabric both in dyeing and printing. By mild soaping treatment some amounts of the dye bleeds into the soaping bath and then stains the white portions of the printed cloth. In order to overcome this problem various steps can be taken, Dye fixing agents or fixers are one of them being successfully used.

Fixing Mechanism: The reaction between fixer and dye or cellulose may be represented as

$$\text{FIXER--}CH_2\text{--OR+HO--Cell.} \overset{140\text{-}150^0C,\ pH\ (3\text{-}5)}{\rightleftharpoons} \text{FIXER--}CH_2\text{--O--Cell. +ROH}$$

Where 'R' is methyl or hydrogen. This is a reversible reaction and removal of methanol or water favors the forward reaction. This is also the reason that why during printing with an emulsion, an acid donor such as $(NH_4)_2HPO_4$,NH_4Cl and $MgCl_2$ should be added to the print paste to ensure these acidic conditions during fixation. In order to guarantee the fixation with dye or cellulose of high quality, it is necessary to use fixers which meet certain requirements such as:

i. Able to form a very soft film.
ii. It should be clear, colorless, odourless and transparent.
iii. Should have good stability for light, ageing and dry cleaning and adhere firmly to fibers and have abrasion resistance.
iv. It should have good ability to offer resistance to chemicals.
v. Water soluble and after curing should be water repellent.

Fixers used in textile industry most commonly and effectively are of urea-and melamine-formaldehyde. They are of outstanding importance in textile industry as they are not only used as fixers but also as crease resisting agents, binders and for improving the wash fastness of pigments. The urea-and melamine-formaldehyde condensates belongs to the class of synthetic polymers, that are colorless, transparent, sticky viscous liquids and resistant to chemical.

By the mid-1990,s world production of aminoplastics was estimated at about 6000,000 t.p.a. of which more than 5000,000 t.p.a were UF resins. The bulk of the rest were MF. Such bald statistics, however, disguise the fact that a considerable amounts of aminoplastics used are actually co-condensates of urea, melamine and formaldehyde.(Brydson, 2000).

In this paper, we report the optimum condition for the synthesis of DMU textile fixer and its comparative study based on the applications on cotton and rayon.

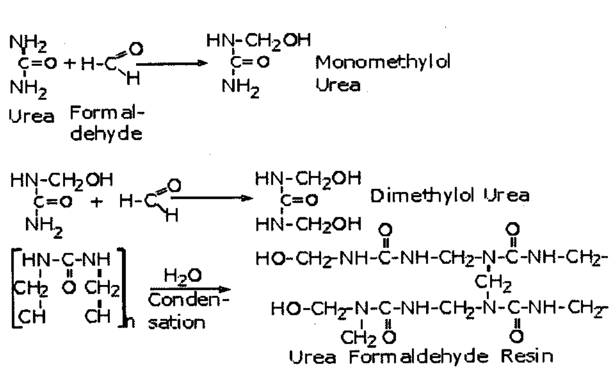
Materials and Methods

Dimethylol urea (DMU) was synthesized in the laboratory of Department of Chemistry, University of Agriculture, Faisalabad and application of DMU precondensate was conducted in the laboratory of Department of Textile Chemistry, National Textile University, Faisalabad.

Chemicals: All the chemicals used were of Analytical Grade (E-Merk).

Mechanism Involved in the Formation of DMU

Polymerization and Condensation from Urea and Formaldehyde Towards a Resin



The method was followed as described by Earland and Raven (1971); Gait and Hancock (1973) Stoichiometrically balanced amounts of formalin(17ml) and methanol (9ml) having pH 7.5 was taken in a three neck round bottom flask fitted on a hot plate with magnetic stirrer. Mixer was heated up to 70°C by using water condenser. 6.006 gm of urea was added into it and temperature of reaction mixture was maintained at 75°C. The pH of the media was checked from time to time. Within 2 hours the reaction was completed when clear, transparent, sticky and viscous liquid was appeared. Flask was cooled immediately and then was neutralized. Liquor was stored at 4°C and solvent was evaporated using Thin Layer Evaporator (at 30°C) to get pure samples of DMU.

Free formaldehyde and urea was estimated as described by Kappelmeier. The physical parameters (Refractive Index, Viscosity etc.) were measured by method as given by Bikales (1971).

The process of dyeing and application of fixer on cotton and rayon were followed as described by Shenai (1993), Speel and Schwarz (1995) and Shenai (1993). The rubbing and washing fastness of the samples were analyzed as described by (Anonymous 2001).

Results and Discussion

This is an A-stage synthesis, DMU was synthesized by the reaction of formaldehyde and urea at fixed molar ratio. The most important reaction conditions which were studied included pH, time period and temperature.

Optimum PH: A series of experiments were conducted keeping different pH conditions and its effect on end product was noted. The observations are recorded in Table 1.

Table 1: Reaction Behaviour at Different PH Values

PH	Reaction progress
6	Insoluble white solid.
7	Slightly milky liquid.
7.3	Very slightly milky liquid which crosslinked within a month
7.5	Clear, transparent liquid which showed a shelf life of 6 month.
8	Hard insoluble and infusible white solid.

It is obvious from Table 1 that at acidic pH reaction is too rapid too difficult to control giving insoluble polymer. While at alkaline pH (8) crosslinking took place. The optimum pH for the synthesis of DMU was found to be 7.5.

Optimum Time Period: A series of experiments were conducted keeping different time periods and its effect on end product was also noted. The observations are recorded in Table 2.

Amount of urea left after polymer formation is an important indicator of efficiency of reaction and quality of product formed. The results shown in Table 2 clearly show 2 hours to be optimum for high quality DMU precondensates.

Table 2: Time Dependent Methylolation Reaction

Time	Urea Content (approximately)
30min.	3-4gm.
1hr.	2gm.
1.30 hr.	1gm.
2 hr.	No urea contents were observed.
2.30 hr.	Crosslinked resins (Solid)

Optimum Temperature: A series of experiments were conducted for different temperature ranges and quality of the product was noted. The observations are recorded in Table 3.

Table 3: Reaction Prayress at Different Temperatures

Temperature	Reaction Progress
50°C	Reaction time increases (up to 8-10 hr.) and un-reacted urea was observed.
60°C	Time (up to 5-6 hr.) and other observations are same as for 50°C
70°C	Unusable for fabric but have no such fixing properties. While time is 2.30-3 hrs.
75°C	Clear, transparent liquid showed a shelf life of 6 month.
80°C	Milky in color and Crosslinked resins (Solid).

The reaction between urea and formaldehyde is endothermic and during the addition of urea fall of temperature was observed (up to 7°C). Therefore, increase of temperature favors reaction to forward direction.

It was observed that if the temperature was not carefully controlled the hard and infusible products were formed. This might be due to the reason that reaction of urea is endothermic. Therefore, decrease in temperature may convert product back into reactants while increase in temperature convert the reactants completely into products. As long as stirring is considered was to be a critical factor in successful completion of reaction. It is observed that 1.6 mole (approximately) was consumed by 1 mole of urea.

The product obtained under optimum conditions was clear, transparent, viscous and sticky liquid. It was miscible with water and methanol. It was slightly alkaline (pH7.3). These characteristics were comparable with sample present commercially in market. Some other physical parameters were also noted in Table 4.

Table 4: Physical Properties of DMU Textile Fixer

Property/Parameter	Observed Values	Literature Values
Refractive Index at 25°C	1.533	1.54-1.56
Specific gravity (g/cm^3)	1.517	1.47-1.52
Viscosity $\eta_{rel.}$, C,Poise	8.000	7-10
Specific viscosity $\eta_{sp.}$	7.000	6-9
Kinematic viscosity, C.Poise $gm^{-1}\ cm^3$	5.273	Variable

Rubbing Fastness: After the application of fixers on the dyed cotton it was analyzed for its fixing properties. Both the wet and dry rubbing fastness were analyzed by crockmeter. The results obtained are given in Table 5.

Table 5: Rubbing Fastness (Wet and Dry) of Unfixed and samples

S.No.	Dry fastness to rubbing	Wet fastness to rubbing
Unfixed (Cotton)	3	2
Unfixed (Rayon)	2-3	2
Fixed (Cotton)	4	3-4
Fixed (Rayon)	5	5

It is obvious that the fixing properties for rayon of DMU precondensate is the best while unfixed sample showed very poor fixing capacity.

Color Fastness to Washing: As for as color fastness to washing is concerned, the unfixed sample gave very poor washing fastness but fixed samples gave better results. Rayon showed the better fixing capacity as compared to cotton for washing fastness.

Table 6: Washing Fastness of Unfixed and Fixed Samples

S.No.	Change in color (G.S.)	Staining to fabric
Unfixed (Cotton)	3	2
Unfixed (Rayon)	3	2-3
Fixed (Cotton)	4	3-4
Fixed (Rayon)	5	5

From the results given in Table 5 and Table 6 it could be concluded that DMU precondensate is the best for rayon as compared to the cotton. DMU precondensates have the best fixing capacity for rayon and not chlorine retention was observed.

References

Anonymous, 2001. AATCC Technical Manual, Vol. 76. American Association of Textile Chemists and colorists, USA. 17-19, 88-92

Bikales , N. M., 1971. Characterization of Polymers. John Wiley and Sons. Inc, New York: 4-5,12-13,99,106.

Brydson, J. A., 2000. Plastics Materials. 7th Edition.Butterworth Heinemann, New Delhi, India. Page: 669.

Earland, C. and D. J. Raven, 1971. Experiments in Textile and Fibre Chemistry. Butterworth and Co. Ltd. London. 153-155

Gait, A..J. and E. G. Hancock, 1973. Plastics and Synthetic Rubbers. Pergamon Press, New York. 86-93.

Kappelmeier, C. P. A., 1959. Chemical Analysis of Resin-based coating materials. Interscience Publishers, INC., New York. 166-173

Shenai, V. A., 1993. Chemistry of dyes and principles of dyeing. Vol. II. Sevak Publications, Bombay (India). : 70,175-186,251-252,618

Shenai, V. A. and N. M. Saraf, 1995. Chemistry of Organic Textile Chemicals. (Vol. 5 and 7) Sevak Publications, Bombay (India). 356-359

Speel, H. C. and E.W.K Schwarz, 1995. Textile Chemicals and Auxiliaries 2nd Edition. Reinhold Publishing Corporation, New York. 137-138,158-159,411-413