Synthesis of Formaldehyde Based Textile Fixers

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Summary: The synthesis of a series of fixers by the reaction of formaldehyde with various molar ratios of melamine/ urea is described which belong to the class of thermosetting resins. All the products were clear, transparent, viscous and miscible with water. The dyed (C.I. Direct Red 2) cotton and rayon specimens were impregnated with fixers and cured at 150°C for 3 minutes using CH_3COOH (curing catalyst). The performance of all the fixers evaluated using rubbing and washing fastness tests. The rubbing fastness to crocking and color fastness to washing is reported and found to be dependent on the fixing efficiency of fixer to dye. Fixer based on 50:50 % molar ratio of melamine-urea-formaldehyde showed the excellent fixing efficacy.

Introduction

Fixers are precondensates or partially methylolated (low-molecular-weight, M. wt. 800-1500) film forming agents produced by the polymerization of simple monomers in a homogeneous dissolved or dispersed phase.

Direct dyes and some of the reactive dyes have poor rubbing and washing fastness on cotton and rayon both after dyeing and printing. By mild soaping treatment some amount of dye bleeds into the soaping bath and then stains the white portion of the cloth. In the beginning, dye-fixing agents (cationic or anionic) were used in large quantity but had some drawbacks. These dye-fixing agents (cationic or anionic) are sensitive to alkalies and acids, and also get hydrolyzed after 4-5 washings. By the developments of new dyes (color fast) and fixers with better fastness properties, the use of dye-fixing agents (cationic or anionic) has been reduced [1].

The ability of formaldehyde to form resinous substances had been observed by chemists in the 2nd half of 19th century. In 1859 Butlerov described formaldehyde-based polymers while in 1872 Adolf Bayer reported that phenols and aldehydes react to give resinous substances. In 1918 Hans John prepared resins by reacting urea with formaldehyde. The reaction was studied more carefully by Pollak and Ripper in an unsuccessful attempt to produce an organic glass during the period 1920-1924. Melamine-formaldehyde resins were discovered in Germany in the early thirties but there was no commercial development. In 1935, Henkel patented the production of resins based on melamine-formaldehyde [2].

Various steps were taken in order to solve the above-mentioned problems. The most suitable and widely used solution is the application of precondensates or fixers for fixation of water-soluble dyes (direct/ reactive). The treatment of the textile materials with low molecular weight amino formaldehyde condensation products has led to spectacular successes during the last decades. Besides crease proofing and shrinkage control, make a multitude of effects and finishes such as permanent water repellency, mildew proofing, chintz effect, stiffening, fixing of the pigments and dyes. It helped to produce "wash-and-wear" fabrics "no iron" and "drip dry" cotton, and helped to control drapability and good hand. Among the formaldehyde based textile fixers melamine-formaldehyde (MF) and urea-formaldehyde (UF) have outstanding importance in textile industry because both are colorless, odorless, non toxic, water soluble, more rapidly curable and after curing able to form very soft film in low concentration. These are stable for light, ageing, dry cleaning and other chemicals. While phenol-formaldehyde is amber in color and leave toxic effect on human health. Currently restrictions have been imposed on the use of formaldehyde, to result these restrictions fixers with low formaldehyde or formaldehyde free have been developed [3].

Golob and coworkers illustrated an ecological and colorimetric analysis of reactant-fixable direct

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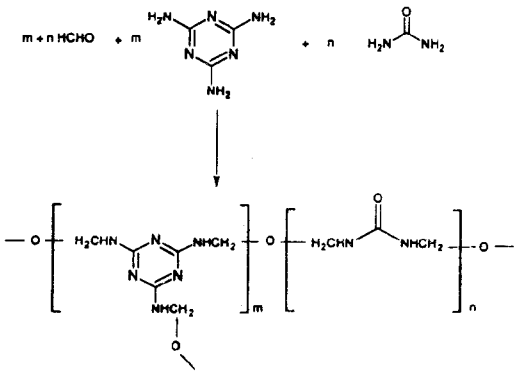
dye after treatments. Viscose fabric was dyed with direct dyes and aftertreated with mono-, di- and trifunctional fixatives. The after treatment baths were ecologically analyzed using COD and BOD methods. The effect of various fixing agents on wet fastness and on shade changes was assessed colorimetrically [4].

Many authors had conducted a lot of work on the synthesis of melamine-urea-formaldehyde condensates for particleboards. But the chemistry of these types of fixers has not discussed in detail. In present research work studies are made on certain fixers in which formaldehyde was reacted with melamine/ urea in various molar ratios (0: 100, 10: 90, 20: 80 .... 80: 20, 90: 10, 100: 0) respectively. The purpose of this work is to predict or sort out that molar ratio of melamine/urea-formaldehyde precondensate, which has the best pick up or fixing affinity for dye as well as economically feasible. The work depicted in this study describes the synthesis of eleven fixers of general structure (Scheme 1-b) and of molar ratios (Scheme 1-a) as:

Product Code	Molar Ratios of U : M	Mole %
KPB-01	0.00:0.10.10	m=100%, n=0%
KPB-02	0.01:0.09	m=90%, n=10%
KPB-03	0.02:0.08	m=80%, n=20%
KPB-04	0.03:0.07	m=70%, n=30%
KPB-05	0.04:0.06	m=60%, n=40%
KPB-06	0.05:0.05	m=50%, n=50%
KPB-07	0.06:0.04	m=40%, n=60%
KPB-08	0.07:0.03	m=30%, n=70%
KPB-09	0.08:0.02	m=20%, n=80%
KPB-10	0.09:0.01	m=10%, n=90%
KPB-11	0.10:0.00	m=0%, n=100%

Scheme 1-a.



Scheme 1-b.

Results and Discussion

This is an A-stage synthesis in which formaldehyde based textile fixers were synthesized with sequence of molar ratios of melamine and urea as (0: 100, 10: 90, 20: 80 .... 80: 20, 90: 10, 100: 0) respectively. The most important reaction conditions were pH, reaction temperature, reaction time and stirring rate. It has been observed that during the reaction, small change in pH showed large effect on reaction progress. As the pH increases from 7.5, the rate of reaction increases vigorously. At acidic *p*H the reaction was too vigorous difficult to control and drastically infusible white solid mass was appeared. At pH 7.5 low molecular weight precondensates were obtained. These were transparent, clear, water soluble and viscous liquids. At the start of reaction (1st 30 minutes), the temperature was maintained at 70°C. It has been observed that if the temperature was not carefully controlled the hard and infusible cross-linked resins (plastic) were appeared. Therefore, after first 30 minutes the temperature was lowered slowly to 65°C. It is expected that this temperature (65°C) shifts the reaction to forward direction *(addition reaction)* while increase in temperature convert the reactant to cross-linked *(elimination reaction)* resin. As long as stirring is concerned it has been noted to be a critical factor in successful completion of reaction. It has been observed that efficient stirring kept the reaction mixture homogenous and prevented cross-linking. It is expected that the most important factor to achieve the desired goal (stage) is the time period. Usually there are three reaction stages in synthesis.

The recommended names for these products are A-stage, B-stage and C-stage condensates. A-stage condensates are water-soluble after this time period B-stage condensates were obtained that were alcohol-water soluble and the last one is the higher polymer [3]. A-stage or precondensates were obtained within *105 minutes* and further time lead to alcohol-water soluble condensates that are useless for fabric treatment. The role of methanol is as a telomer i.e. a chemical compound capable of forming the terminal part of the polymer (a sort of end capping). These telomeres do not participate in the polymer growth but they do terminate it. It has been reported that etherified methylolated products have greater shelf life as compared to un-etherified. Etherification with water-soluble alcohol, usually methanol, is the

Table-1: Curing range of fixers at pH 5

Catalysts	Curing time at 150°C 1 min W. F.		2 min W. F.		3 min W. F.		4 min W. F.		5 min W. F.	
	C. C.	S. F	C. C.	S. F	C. C.	S. F	C. C.	S. F	C. C.	S. F
$(NH_4)_2HPO_4$	2	2-3	3	3	faded	faded	faded	faded	faded	faded
$NH_4H_2PO_4$	2	2-3	3	3	faded	faded	faded	faded	faded	faded
Na_2HPO_4	2	3	3	3-4	S.C.	S.C.	cracked	cracked	cracked	cracked
CH_3COOH	3	3	3	3-4	4-5	5	3-4	3-4	S.cracked	S.cracked

W. F.*= Washing fastness, C. C.*= Change in color, S. F.*= Staining to fabric, S.cracked*= Slightly cracked

usual procedure for imparting a high degree of water solubility and stability to the precondensates.

Physical Properties

All the precondensates were transparent, clear, viscous and sticky liquids. These were miscible with water and slightly alkaline (pH 7.2) in nature. When stored at pH 7, the shelf life is more than six months. Even after this time no sign of cross-linking was observed.

Curing Properties

The 100% cotton and rayon knitted fabric were dyed with direct dye. The optimum time period was also determined for different curing catalysts under different conditions. The data is presented in Table-1, as indicated in table three minutes was the optimum time period for fixation, CH_3COOH was the best curing catalyst for these fixers. The function of Catalyst is to promote the reaction between dye and methoxy group of fixer. It has been observed that $NH_4H_2PO_4$ or $(NH_4)_2HPO_4$ has drawback that during curing evolution of NH_3 takes place, that faded the fabric color and cannot be used for cotton and rayon. Na_2HPO_4 is not recommended because phosphate damaged the sensitive film of precondensate. For shorter curing time (1 and 2 minutes) some amount of precondensate deposited (uncured) and showed poor rubbing and washing results. While for 4 and 5 minutes, the film became brittle and cracking of film was occurred. After the optimization of conditions, all the study was made with CH_3COOH as catalyst and curing time for three minutes 150 °C.

Fastness Properties

Rubbing Fastness

After fixation, the fixing properties are evaluated and all the fixers exhibited very good level of fixing on cotton and rayon. Table-2, describes the rubbing fastness properties of fixers and it shows that

Table-2: Rubbing Fastness (Wet & Dry) of Samples

Sample Code	Molar Ratios of Urea: Melamine	Fastness to Dry rubbing		Fastness to Wet rubbing	
		Cotton	Rayon	Cotton	Rayon
KPB-00	Unfixed sample	4	4	2	2
KPB-01	0:100	4-5	4-5	3	3-4
KPB-02	10:90	4-5	4-5	3-4	3-4
KPB-03	20:80	4-5	4-5	3-4	3-4
KPB-04	30:70	4-5	4-5	4	3-4
KPB-05	40:60	4-5	4-5	4	3-4
KPB-06	50:50	5	5	4-5	4-5
KPB-07	60:40	4-5	4-5	4	3-4
KPB-08	70:30	4-5	4-5	4	3-4
KPB-09	80:20	4-5	4-5	4	3-4
KPB-10	90:10	4-5	4	4	3-4
KPB-11	100:0	4	4	3-4	3-4

all the fixers have good improvement in fastness properties. But the fixer based on 50:50 % molar ratio of melamine/ urea-formaldehyde showed the excellent properties of rubbing and rating is 5 and 4-5 (dry and wet respectively). This might be due to the excellent affinity of fixer for dye.

Color Fastness to Washing

The washing fastness properties are the ultimate confirmatory proof for the quality of fixation. The results of washing fastness of treated and untreated samples are presented in Table-3. All the fixers impart very good fastness to washing while unfixed (untreated) samples showed very poor fastness rating 1 and 1-2. The values for loss in color due to staining on white specimen were also determined for fixed and untreated samples after washing fastness test; the results are summarized in Table-3. The sample having 50:50 % molar ratio of melamine/ urea-formaldehyde showed the excellent fixing capability for dye. The reason can be attributed to the largest molecular size of fixer as compared to the others and also have larger number of substituents capable of bond formation and therefore, the lower in the magnitude of dye removal under the influence of washing solution. All the fixers used are neutral (neither cationic nor anionic) in nature and it is postulated that this improved wash fastness could be attributed to: The formation of a 'thin film' of the polymeric agents at the periphery of the dyed fiber

Table-3: Washing Fastness of Fixed and Unfixed (untreated) Samples

Sample Code	Molar Ratios of Urea: Melamine	Change in color (Gray Scale) or G.S.		Staining to white fabric	
		Cotton	Rayon	Cotton	Rayon
KPB-00	Unfixed sample	1	1-2	1-2	1-2
KPB-01	0:100	3- 4	4	3	3-4
KPB-02	10:90	3-4	3-4	3-4	3-4
KPB-03	20:80	3-4	3-4	3-4	3
KPB-04	30:70	3-4	3-4	4	3-4
KPB-05	40:60	4-5	4-5	4	4
KPB-06	50:50	5	5	5	5
KPB-07	60:40	4-5	4-5	4	4
KPB-08	70:30	3-4	3-4	3-4	3-4
KPB-09	80:20	3-4	3-4	3-4	3-4
KPB-10	90:10	3-4	3-4	3	3
KPB-11	100:0	3	3	3-4	3

which reduces aqueous solubility within the fiber after curing reaction. Such a mechanism would serve to lower the rate at which the dye diffused out of the dyed substrate during washing and thus improve wash fastness. In addition to this physical encapsulation of dye molecules with fixers enhanced chemical bonding of dye with cellulose –OH is also observed (A).

Fixing Mechanisms

There are two mechanisms, internal finishes and external finishes. The first one is the cellulose fixing mechanism and second is the dye fixing mechanism. But we discussed here more sophisticated mechanism:

Dye Fixing Mechanism (A)

$$\text{Cell.-OH---D-NH}_2\text{+RO-CH}_2\text{-FIXER} \xrightarrow{p\text{H-5 (150}^{\circ}\text{C)}} \text{FIXER-CH}_2\text{-Cell.-O-H---D-NH-CH}_2\text{-FIXER + ROH}$$

Where Cell= cellulose, D= dye part, Fixer= fixer part and R= $-CH_3$ or -H.

Most direct dyes have most likely to interact via hydrogen bonds with hydroxyl groups are placed at intervals corresponding approximately to the hydroxyl group spacing in cellulose. The fixer forms the encapsulation of dye as well as cellulose; hence make the diffusion of dye impossible.

Experimental

Instruments

The pH meter (Hanna) was used for *p*H adjustment of the media. Thin Layer Evaporator (Gucci) was used for the evaporation of methanol and water. High pressure Jigger (Warner Mathis AG, Switzerland) was used for dying and Padder (Tsuji Dyeing Machine Mfg. Co. Japan) was used for padding of fixer solution on fabric. Stenter machine (Tsuji Dyeing Machine Mfg. Co. Japan) was used for fixation. Crock meter (Shirley Development) was used for rubbing fastness and Launder meter (Tsuji Dyeing Machine Mfg. Co. Japan) was used for washing fastness.

Synthesis of Fixers

All the fixers were synthesized in the laboratory of Department of Chemistry, University of Agriculture, Faisalabad and applied processes were conducted in the laboratory of Department of Textile Chemistry, National Textile University, Faisalabad-Pakistan.

The method was followed as described by [5-8]. Stoichiometrically balanced amounts of formalin and methanol adjusting pH 7.5 were taken in a three neck round bottom flask (1L, Pyrex, Quick fit) fitted in an oil bath on a hot plate with magnetic stirrer. Mixer was heated up to 70 °C using water condenser on a three neck round bottom flask. Stoichiometrically balanced amounts of melamine/urea was added and refluxed at 70 °C for 30 minutes. After 30 minutes temperature was gradually decreased to 65 °C. The pH of the media was checked from time to time. Within 105 minutes the reaction was completed i.e. clear, transparent, sticky and viscous liquid was appeared. The reaction flask was cooled and neutralized with 0.1 M NaOH/HCOOH solutions. Liquor was stored at 0-4 °C and solvent was evaporated using Thin Layer Evaporator until all the free formaldehyde was removed. Total of eleven sets of experiments were conducted for synthesis of eleven samples based on various molar ratios of

melamine/ urea (0: 100, 10: 90, 20: 80, ... 80: 20, 90: 10, 100: 0) respectively.

Impregnation of Dyed Samples

All the samples were dyed with Direct Red 4B C. I. Direct Red 2, C. I. # 23500 (2 % shade) as described by [9]. Conditions were optimized for different curing times and catalysts by applying fixers on the dyed samples for 1, 2, 3, 4 and 5 minutes with different catalysts i.e. $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, Na_2HPO_4 and CH_3COOH. The pH of solution was maintained at 5, samples were impregnated as described [8, 10]. The dyed samples (2 x 5 inch) were dipped in 100 ml fixer solution for 10 minutes, then samples were passed through the rollers of Padder. Fixation was carried out at 150 °C on Stenter, then for the confirmation of fixation each sample analyzed by rubbing and washing fastness. After the optimization, all the experimental work was conducted with CH_3COOH as catalyst, curing time for three minutes and other conditions as such.

Rubbing Fastness (Color fastness to Crocking) Method

The fastness to rubbing of cotton and rayon samples was carried out by ISO 105-X12 standard method [11]. Placed the test specimen on the base of the crock meter resting plate on the abrasive cloth with its warp dimension in the direction of rubbing and was placed specimen holder over specimen as an added means to prevent slippage, then was mounted a white test cloth square, the weave parallel with the direction of rubbing, over the end of the finger which projects downward from weighted sliding arm. Lowered the covered finger onto the test specimen and was cranked the meter handle for 10 complete turns at the rate of one turn per second to slide the covered finger back and forth 20 times. This method was applied for both wet &dry specimens, and was evaluated the rubbing fastness by means of Chromatic Transfer Scale or Gray scale for staining. The results were coded in Table-2.

Color Fastness to washing

The color fastness to washing of various specimens was carried out by ISO 105-CO6-3A standard method [11]. Prepared the samples (2x6 inch) for Test No. 3A and was adjusted the temperature 71 °C of Launder meter.

100 stainless steel balls and 50 ml of 1500 ppm detergent solution were added in each canister. Then was entered well-crumpled test in each canister and clamped the covers on the canisters. Set up the laundering machine for 45 minutes, after 45 minutes, was rinsed the each sample for three times and then dried in an air circulating oven, temperature should not be exceeded 71 °C and assessment were made with Gray Scale. The results were coded in Table-3.

Conclusions

On the basis of these experiments it can be concluded that both rubbing and washing fastness properties of the dyed samples are improved after the application of fixer. But the intensity of improvement depends on the amount and nature of fixer. The results clearly indicate that as we go towards 50: 50 molar ratios of urea and melamine the improvement in fastness properties is observed. The difference in behavior is due to the differences in natures of urea and melamine moieties in the fixed precondensate. Urea is quite hydrophilic but have higher tendency for hydrogen bonding with cellulosic substrates while precondensates based on melamine show opposite behavior.

Note

Nitrogenous bases (nucleophile) should not be used for adjustment of pH of media because formaldehyde can also react with it and chances of side products increases. The pH and temperature of the reaction should be carefully controlled because slight fluctuation of pH or temperature may lead to undesired results. Free formaldehyde should be carefully removed due to its hazardness effects (carcinogenic) on human health, and also because of color fading properties.

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