SYNTHESIS AND APPLICATION OF MELAMINE UREA BASED PRECONDENSATES

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Abstract:

Formaldehyde based low molecular weight precondensates (fixers) are always have very important role in processing of woven fabrics. Two important applications of these chemicals are in fixing of dyes and improvement of crease resistant behavior of fabrics. The synthesis of a series of precondensates by the reaction of formaldehyde with various percent mole ratios of melamine/urea is described which belong to the class of thermosetting resins. The dyed cotton specimens were impregnated with fixers and cured at 150 °C for 3 minutes using acetic acid curing catalyst. The rubbing fastness to crocking, color fastness to washing and light fastness is reported and found to be dependent on the fixing efficiency of precondensate to dye. Precondensate based on 50:50% mole ratio of melamine-urea-formaldehyde showed the excellent fixing efficacy. The fastness to light is found to be dependent on the aromatic character of melamine ring which obviously is due to the preferably absorption in the UV region. The fabrics with an intense color and good characteristics were obtained thus presenting a possibility for extension of the applied in practice textile precondensates.

Key words:

Melamine, urea, formaldehyde, reactive dyes, dye fixing agent, curing, cotton, fastness properties

Introduction

Dye fixation has always been remained a serious matter in dyeing industry. There are many dyes which give very good tinctorial strength, but their poor fixation does not allow their use on commercial scale. Different techniques are used for the improvement of washing fastness of reactive dyes, use of cationic surfactants and metal treatment decrease the solubility of these dyes under washing conditions but their effect is not permanent. On the other hand, organic fixing agents give more pronounced and permanent effect in improving the fixation of these dyes. 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.

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[1].

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 fixing of the pigments and dyes, make a multitude of effects and finishes such as permanent water repellency, mildew proofing, chintz effect, stiffening, crease proofing and shrinkage control. 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 are able to form very soft film in low concentration. These are stable for light, ageing, dry cleaning and other chemicals. Currently restrictions have been imposed on the use of formaldehyde, to result these restrictions fixers with low formaldehyde or formaldehyde free have been developed [2].

In present research work our emphasis on the application of these synthesized precondensates and point out the fixer ratio that having the novel characteristics to textile application viewpoint. By varying the mole ratio of urea and melamine eleven different samples were prepared. The mole ratios of

Table 1. Percent mole ratio of the urea and melamine in different precondensates.

Product Code	Mole % of U:M	
MUF-01	m=100%,	n=0%
MUF-02	m=90%,	n=10%
MUF-03	m=80%,	n=20%
MUF-04	m=70%,	n=30%
MUF-05	m=60%,	n=40%
MUF-06	m=50%,	n=50%
MUF-07	m=40%,	n=60%
MUF-08	m=30%,	n=70%
MUF-09	m=20%,	n=80%
MUF-10	m=10%,	n=90%
MUF-11	m=0%,	n=100%

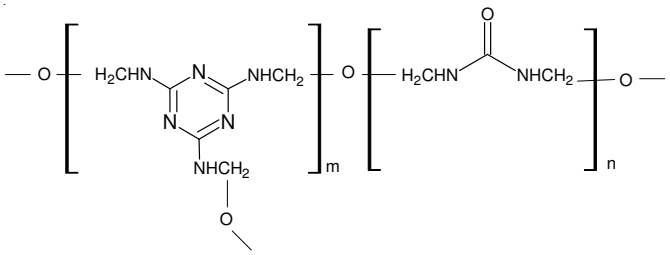

Figure 1. General structure of the dye fixer.

urea and melamine are given in Table-1, and with general structure of precondensates given in Figure-1.

Experimental

Instruments

The pH meter (Hanna) was used for pH 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. Light fastness meter was locally equipped with 500 watts mercury lamp.

Synthesis of precondensates

Many authors had been conducted a lot of work on the synthesis of melamine-urea-formaldehyde condensates used for particleboards. But the chemistry of these types has not been discussed in detail in textile application view point so far. Here in this study we developed the low molecular weight and partially methylolated precondensates for the improvement of reactive dye fixation quality.

Stoichiometrically balanced amounts of formalin and methanol 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 while maintaining the pH 7.5. Mixer was heated up to 70°C using water condenser on a three neck round bottom flask. Stoichiometrically balanced amount of melamine/urea was added, 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. In 105 minutes the reaction was completed i.e. clear, transparent, sticky and viscous liquid was appeared. The reaction flask was cooled and neutralized pH of liquor by 0.01M NaOH/HCOOH solutions. Liquor was kept at 0-4°C and solvent was evaporated using Thin Layer Evaporator until all the free formaldehyde was removed. The separated product was washed with HPLC grade chloroform repeatedly for the ultra purification of the product. For the confirmation of formaldehyde free product, free formaldehyde was estimated as described by Kappelmeier [3]. Total of eleven sets of experiments were conducted for synthesis of eleven precondensates based on various mole 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. # 23500(1% o.w.f., shade) as described [4-6]. Conditions were optimized for different curing times and catalysts by applying precondensates on the dyed samples for 1, 2, 3, 4 & 5 minutes using 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[7]. The dyed cotton specimens (2x5inch) were dipped in 100 ml precondensate solution for 10 minutes, and then samples were passed through the rollers of Padder. Fixation was carried out at 150oC on Stenter using CH_3COOH as catalyst keeping curing time 3 minutes and pH 5, then for the confirmation of fixation each sample was analyzed to rubbing, light and washing fastnesses.

Rubbing fastness (Color fastness to crocking)

The fastness to rubbing of cotton specimens was carried out by following ISO 105-X12 standard method[8]. The test specimen was placed 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. The covered finger was lowered 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 dry & wet specimens, and the rubbing fastness was evaluated by means of Chromatic Transfer Scale or Grey Scale for staining. The results are presented in Table 2.

Color fastness to washing

The color fastness to washing was carried out by following ISO 105-CO6-3A standard method [8]. The samples (2x6inch) were prepared for Test No.3A keeping 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. The laundering machine was set for 45 minutes, after 45 minutes, each sample was rinsed for three times and then dried in an air circulating oven keeping temperature 71oC and assessment was made with Grey Scale. The results are given in Table 3.

Color fastness to light

The light fastness of the dyed samples after application of the precondensates was evaluated according to ISO 105-B05 [9]. In this study, Mercury Lamp was used instead of Xenon Arc Lamp but the time was extended to 48 hours instead of 16 hours. The light fastness of sample without fixer and samples after application of the fixer was studied and the results are summarized in Table 4.

Results and Discussion

This is an A-stage synthesis in which formaldehyde based precondensates were synthesized with sequence of %mole ratios of melamine and urea (0:100, 10:90, 20:80, ... 80:20, 90:10, 100:0), respectively. The most important reaction conditions were pH, stirring rate, temperature and reaction time. It was observed that during the reaction, small fluctuation in pH significantly affects reaction progress. As for as the pH increases from 7.5, rate of reaction increased vigorously while at acidic pH the reaction was too vigorous difficult to handle and drastically infusible white solid mass was appeared. At pH 7.5 partially methylolated low molecular weight

Table 2. Rubbing Fastness of Cotton Samples (dry & wet)

Product Code	Mole % of U:M	Rubbing Fastness (Dry)	Rubbing Fastness (Wet)
MUF-00	Unfixed sample	4	2
MUF-01	0:100	4-5	3
MUF-02	10:90	4-5	3-4
MUF-03	20:80	4-5	3-4
MUF-04	30:70	4-5	4
MUF-05	40:60	4-5	4
MUF-06	50:50	5	4-5
MUF-07	60:40	4-5	4
MUF-08	70:30	4-5	4
MUF-09	80:20	4-5	4
MUF-10	90:10	4-5	4
MUF-11	100:0	4	3-4

Table 3. Washing fastness of cotton samples (treated and untreated)

Product Code	Mole % of U:M	Change in color (Grey Scale) or G.S.	Staining to white fabric
MUF-00	Unfixed sample	1	1-2
MUF-01	0:100	3-4	3
MUF-02	10:90	3-4	3-4
MUF-03	20:80	3-4	3-4
MUF-04	30:70	3-4	4
MUF-05	40:60	4-5	4
MUF-06	50:50	5	5
MUF-07	60:40	4-5	4
MUF-08	70:30	3-4	3-4
MUF-09	80:20	3-4	3-4
MUF-10	90:10	3-4	3
MUF-11	100:0	3	3-4

Table 4. Light fastness of cotton samples (treated and untreated).

Product Code	Mole % of U:M	Grey scale value of light fastness (max. 7)
MUF-00	Unfixed sample	4
MUF-01	0:100	4
MUF-02	10:90	4
MUF-03	20:80	4-5
MUF-04	30:70	6
MUF-05	40:60	6-7
MUF-06	50:50	6-7
MUF-07	60:40	6
MUF-08	70:30	5
MUF-09	80:20	3-4
MUF-10	90:10	3-4
MUF-11	100:0	3

precondensates were obtained. It was 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 from 70 °C to 65°C. It is expected that this (at 65°C) shifts the reaction to forward direction (addition reaction) while increases in temperature switched reactant to cross-linked (elimination reaction) resin. The reaction time is also considered an important factor for the success of desired stage of product. Usually, there are three reaction stages in synthesis i.e. 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 usually[10]. The desired formaldehyde free products were obtained in 105 minutes and further time leaded to alcohol-water soluble condensates that are useless for fabric treatment.

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. All these syntheses were carried out in methanol and it also worked as an end capping or etherifying reagent which obviously improve the shelf life of product by minimizing chances of self cross-linking against the environment. The precondensates when stored at pH 7, the observed shelf life were more than six months. Even after this time no sign of cross-linking was observed. The curing properties of these precondensates were studied and described in our previous work [11]. The fixation of these precondensates was made with CH_3COOH as catalyst and curing time 3 minutes at 150°C, and keeping the pH 5 through out the experiments of fixation.

Rubbing fastness

The fixing properties were evaluated and all the precondensates exhibited good level of fixing on cotton. Table-2 describes the rubbing fastness properties of precondensates and it shows that all of them have good improvement in fastness properties. But the precondensate based on 50:50% mole ratio of melamine/urea-formaldehyde showed the excellent properties of rubbing, and rating is 5 and 4-5 (dry & wet), respectively. This might be due to the excellent affinity of precondensate for dye.

Color fastness to washing

The washing fastness properties are the ultimate confirmation test for assessment of quality of fixation. The results of washing fastness of treated and untreated samples are presented in Table-3. All the precondensates imparted good fastness to washing while unfixed (untreated) sample 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 treated and untreated samples after washing fastness test; the results are summarized in Table 3. The sample having 50:50% mole ratio of melamine/urea-formaldehyde showed the excellent fixing potential for dye. The reason can be attributed to the largest molecular size of precondensate 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 precondensates used were 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 which reduces aqueous solubility within the fiber after curing reaction. Such a mechanism would serve to lower the rate at which dye diffused out of the dyed substrate during washing and thus,

improved 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).

Dye Fixing Mechanism (A)

Cell.-OH—D-NH_2+RO-CH_2-**FIXER** $\rightarrow$

FIXER-CH_2-**Cell.**-OH—D-NH-CH_2-**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 placing at intervals corresponding approximately to the hydroxyl group spacing in cellulose. The fixer forms encapsulation of dye as well as cellulose hence, made the diffusion of dye impossible.

Color fastness to light

Although in this study mercury lamp was used instead of Xenon Arc Lamp, but the data obtained was reliable enough for getting the performance comparison of all the samples prepared. The grey scale values of light fastness of these precondensates applied cotton samples are summarized in Table 4. The performance of these samples improved with increasing in melamine structural units and excellent performance was observed in samples MUF 5 and MUF 6. On further increased in melamine ratio in synthesis recipe, showed a slight declined in light fastness behavior. It is well understood that the near UV region (350 nm to 380 nm) is the main cause of the fading of color. The aromatic compounds absorb this region efficiently and hence, any increase in the melamine, an aromatic structural component, in precondensate structure enhances the performance of the dyes. The maximum performance was observed when there was a balance between aromatic moieties and the more hydrophilic urea groups in the precondensate structure. This group retains moisture and supports the interaction of fixer with dye molecules and cellulosic rings of the cotton fiber. Any further increase in melamine ratio significantly affect on the fixer-dye and fixer-cellulose interaction. Hence, this change showed negative effect on the performance.

Conclusion

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 precondensate. But the intensity of improvement depends on the amount and nature of precondensate. The results clearly advocate that as we go towards 50:50 mole ratios of urea and melamine, the improvement in fastness properties was noted. The difference in behavior is due to the differences in nature of urea and melamine moieties in the precondensate. Urea is quite hydrophilic but have higher tendency for hydrogen bonding with cellulosic substrates while precondensates based on melamine show opposite behavior. The fabrics with an intense color and good characteristics were obtained, thus presenting a possibility for extension of the applied in practice textile precondensates.

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