

**Research Article**

# The Effect of N,N-dimethylamylamine on the Properties of Reactive Dye Fixing Agent

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**Abstract**

Diallyl dimethyl ammonium chloride (DMDAAC) is very popular cationic monomer that is used to synthesize color-fixing agent. But this kind of fixing agent has some drawbacks. This paper reports to minimize those drawbacks by co-polymerizing with N,N-dimethylamylamine (DMAA). The effect was studied by varying the amount of DMAA with respect to main monomer DMDAAC. Also the effect of APS was observed on the polymer properties. The best polymer was found with DMDAAC and DMAA 61% and 1% respectively where the amount of APS was 0.5%. The synthesized agents were applied according to the industrial procedure on cotton woven fabric dyed with reactive dye. Color fastness to wash, color fastness to dry & wet rub, change in K/S, lightness DE and overall color differences DE were observed to evaluate the synthesized agents.

**Keywords:** Cationic color fixing agent; DMDAAC; N,N-dimethylamylamine; Reactive dye fixing agent; Synthesis of color fixing agent

**Academic Editor:** Taihong Shi, PhD, Sun Yat-sen University, China

**Received:** August 9, 2015; **Accepted:** October 27, 2015; **Published:** December 2, 2015

**Competing Interests:** The authors have declared that no competing interests exist.

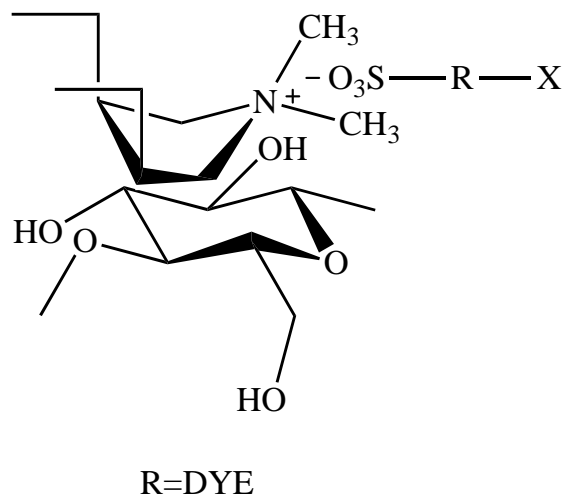
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## 1. Introduction

It is well known that, reactive dyes are very popular in textile industry for its excellent fastness properties and diversity of shades[1, 2]. Reactive dyes are the newest class of dyes for cellulose fibers that contain chromophore combined with one or more anchors groups, which can react with cellulose via covalent bond between dye and fiber[3]. Cellulose fibers are dyed in presence of excessive amount of salt and fixed under alkali condition[4]. Although many researchers are still trying to improve dye fixation by modifying cellulose structure but, still there are some disadvantages like lower lighting fastness, lower washing fastness significant change in hue and problems in further processing[4-7]. Dye fixation for cotton can be increased by (1) modifying the substrate, (2) modifying the dye, (3) by adding a crosslinking agent and (4) Cationic group combine with anionic group. In recent years development of reactive dyes has been done to improve dyeing as well as performance such as colorfastness to wash, light, perspiration etc. Physical & chemical properties of dyes depend on different functional groups and also one functional group can affect on the functions of another functional group. That's why it is also difficult to get all the features in a single dye. The different classes and types vary in terms of factors such as their cost, ease of application, fastness properties, etc. However, although reactive dyes are widely used for the exhaustion dyeing of cotton and other cellulosic fibers, the dyes suffer the disadvantage that the dye-fiber reaction is less than 100% efficient [8]. For improving the fastness to washing and to light of dyes on textile fibers, chemical after treatment are available over the last 100 including metal salts, tanning agents and cationic 'fixing' agents[9]. Cationic polymers are introduced from the late of 1960s to increase the electrostatic forces between the dyes and the basic cationic groups in the polymer[10]. Poly (dimethyldiallylammonium chloride) (PDMDAAC) dye-fixative would be one of the most optimum polycationic fixatives, which is the polymer of monomer dimethyldiallylammonium chloride (DMDAAC) and has the similar structure (Figure 1) of cellulose[11]. In 1981, Nippon Senka Kogyo company used 0.1% (o.w.f) PDMDAAC to treat cotton fabric dyed with Remazol Black B, the results showed that wash fastness was improved from 1-2 grade when untreated to 4-5, development of this kind of fixing agents occurs rapidly. In 2008 Wang synthesized a fixing agent by co-polymerization of DMDAAC and allylamine that also increase the chloride fastness 1 grade [10]. Another great problem of Reactive dyed fabric is resistance to acid hydrolysis. Due to the influence of acidic substance or the like this covalent bonds between dyes and cellulose may be broken, that causes color fading. Polycationic dye fixative can solve this problem but hue of the dyed product changes and its fastness to light and chlorine decreases upon the treatment with this type of dye fixative. It has been discovered that the above-mentioned problem can be solved by a copolymer of monoallylamine and or a diallylamine derivative[12]. Poly diallylamine film is very thin and their surface molecules that are able to react through their  $\text{NH}_2$  functions[13]. Another great feature of allylamine ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_2$ ) can partially penetrates the cellulose crystal lattice and effects only partial transformation to the cellulose-amine complex; due to this the negligible or no color change is occurred upon applied on reactive dyed fabric[14].



**Figure 1** Fixing mechanism of PDMDAAC dye-fixative on cotton fabric

## 2. Experimental

### 2.1 Materials & Instruments

Diallyl dimethyl ammonium chloride (DMDAAC), N,N-dimethylamylamine (DMAA), Acetic Acid & APS  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  were collected from Zhejiang Runhe Auxiliaries Ltd., China. All the above materials were used without any further preparation. Commercial grade of 100% cotton reactive dyed woven fabric was collected from Hebei Huafang Printing And Dyeing Co., Ltd., China. A double-necked flask with a mechanical stirrer, thermometer and a heater was used as a reactor to prepare the fixing agent.

### 2.2 Methods

#### 2.2.1. Synthesis of polymer

DMAA, DMDAAC & water were taken in a double necked flask at room temperature. Afterward temperature was increased gradually at 80 °C for 30 min. Medium stirring speed was maintained. APS dropping was started when the temperature was exactly at 80 °C and continuously dropped for 90 min. After finish APS dosing the stirring was continuing for 15-20 min & then temperature was raised up at 85 °C for 30 min. After 30 min temperature was reduced at 40 °C-50 °C & pH 6 was adjusted by Acetic Acid.

#### 2.2.2. Determination of Solid Content

Approximately 3 g of the sample was taken and weighed it accurately in a glass dish. Placed it in the oven for 4 hours at 110 °C. After cooled in the desiccator, weighed the dish accurately and solid content was measured by using the following equation-

$$\text{Percentage Solid content} = \frac{\text{Dry weight}}{\text{Actual weight}} \times 100.$$

#### 2.2.3. Application of Method of Fixing Agent

0.15 g/L fixing agent was applied while the M:L was maintained 1:20. The bath was run for 20 min at 40 °C, then after rinsed it was dried at 105 °C in woven.

### 2.2.4 Test of Color Fastness to Wash

Dyed sample was prepared with a size 10 x 4 cm and was sandwiched between two adjacent fabrics and stitched. The sample and the adjacent fabric were washed together. The washing solution was preheated to the required temperature of washing. The liquor ratio was 1:50. After soaping, the specimen was removed from adjacent fabric, rinsed twice in cold water. Squeezed and dried in air at a temperature not exceeding 60 °C. The color change was evaluated with the help of grey scale.

### 2.2.5 Test of Color fastness to Dry & Wet Rubbing

According to AATCC 116 -1995 methods by using standard crock meter cloth, maintain uniform pressure for applying rubbing strokes and number of strokes. Degree of staining and color changing are assessed by Grey scale.

In the case of wet rubbing, % moisture on the crock cloth has to be kept to uniform level and rubbing cloth that has been wetted with water, has to be squeezed to contain its own weight of water. Wet pick up is to be maintained between 65 ±5% by squeezing the wet crock meter cloth using a AATCC blotting paper.

### 2.2.6 Measurement of K/S value & Color difference

By using Datacolor 400 <sup>TM</sup> spectrophotometer the K/S value of color in fabric and color differences were measured before and after application of fixing agent.

## 3. Result and discussion

### 3.1 Effect of APS on Fixing Agent

To initiate the polymerization reaction must required minimum amount of initiator like 0.1%-0.3%. APS has significant effect on synthesized polymer so, primarily the effect of APS was observed by changing the amount from 0.3%-0.6%. While the amount of DMAA, DMDAAC and water were 2 g, 62 g & 38 mL respectively. Then the amount of solid content was measured for all samples, as well as other application performances are also tested to determine the precise amount of APS on dyed sample. The solid content of the commercial sample was also measured in same method.

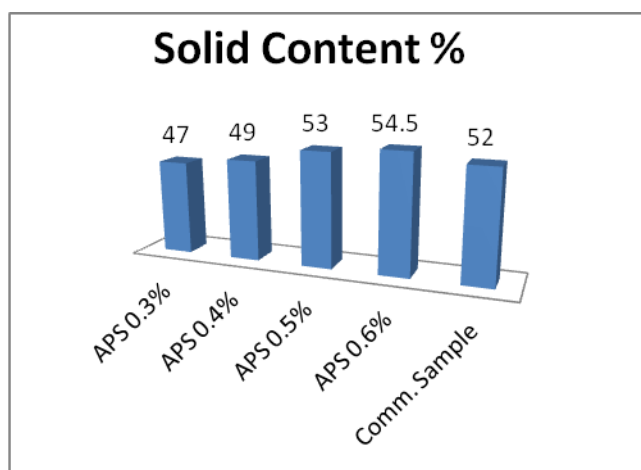


Figure 2 Effect of APS on Solid content and Performance of Fixing agent

The **Figure 2** shows that for the when the APS amount 0.5% the solid content was 53% that was very near to the commercial sample. When APS dosing is more than 0.5% then solid content is going high. And from **Table 1** it is also clear that color fastness to wash was 4, color fastness to dry rub was 3-4 & wet rub was 3-4 while the APS was used 0.5%, that is superior to others result shown in the table. The test results were also same for APS 0.6%. If the APS amount increased, the reaction rate will be increased. As a result some amount of the monomers can be unreacted and solid content amount become increased, that is shown in **Figure 2**. In the other hand for the APS amount 0.3% & 0.4% the result changes were unsatisfactory. Due to more APS the particle size will be small and small particle size makes the fixing agent penetrate inside the fibre and increase proper bonding. As a result fastness increases.

**Table 1** The effect of APS amount on fixing agent performances

Sample Reference	DMAA:DMAAC (g)	Water (mL)	APS (%)	Before Application			After Application		
				C.F to Wash	C.F to Rubbing		C.F to Wash	C.F to Rubbing	
					Dry	Wet		Dry	Wet
					Rub	Rub		Rub	Rub
	2:62	38	0.3	2-3	3	2-3	3	3-4	2-3
RA005	2:62	38	0.4	2-3	3	2-3	3	3-4	2-3
	2:62	38	0.5	2-3	3	2-3	4	3-4	3-4
	2:62	38	0.6	2-3	3	2-3	4	3-4	3-4

### 3.2 Effect of DMAA on solid content

As the DMAA is cross-linking monomer that's why in the first prepared sample RA001 (Table 2) the amount of that was taken 0; i.e. the synthesised fixing agent has no cross-linking effect. From sample RA002 to RA006 the amount of DMAA was increased by 0.5 g and synthesised five more samples. While in the first sample the main monomer was 62 g and was gradually decreased by 0.5 g up to the sample RA006 (Table 2).

**Table 2** The amount of DMAA, DMAAC, water and APS in prepared sample

Sample Reference	DMAA (g)	DMAAC (g)	Water (mL)	APS (%)	Total
RA001	0	62.0	38	0.5	100
RA002	0.5	61.5	38	0.5	100
RA003	1.0	61.0	38	0.5	100
RA004	1.5	60.5	38	0.5	100
RA005	2.0	60.0	38	0.5	100
RA006	2.5	59.5	38	0.5	100

Then the amounts of solid content were measured with the help of above described equation and compared with the commercial samples. The results are shown in below Figure 3. In all cases the amount of APS was constant; 0.5%. It is perceived that, the solid content of sample RA001 was very high (55.20%) and then for sample RA006 was in second highest position (55%). The solid content were closer to the commercial sample while the amounts of DMAA were 0.5-1.5 g (Sample RA002-RA005).

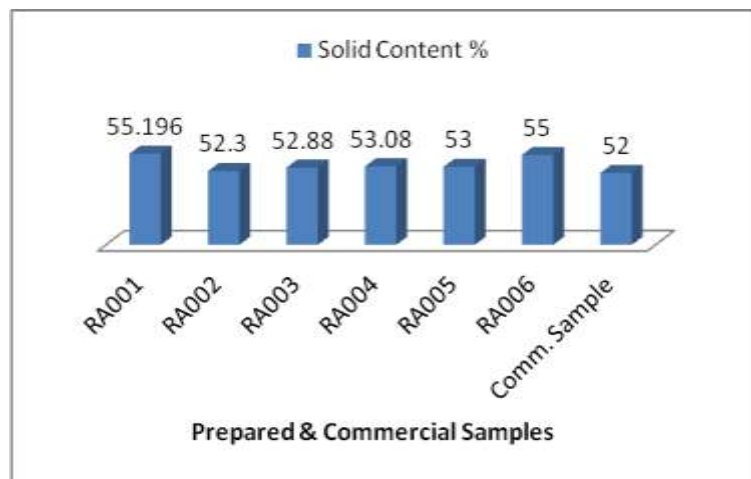


Figure 3 Effect of DMAA on Solid Contents

### 3.3 Effect of DMAA on Color fastness to wash

Prepared fixing agent samples were applied on cotton fabric and their wash fastness were estimated. Figure 4 shows the effect of DMAA on color fastness to wash; before and after application of fixing agents.

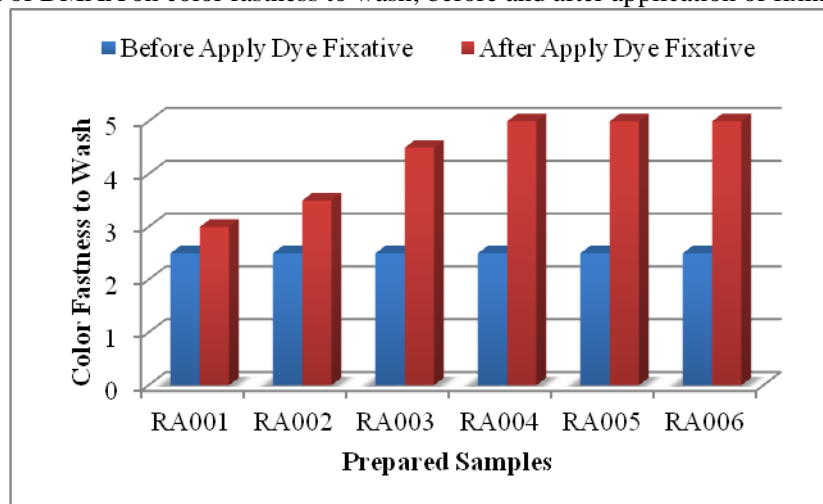


Figure 4 Color fastness to wash fastness before & after application

Here after using fixing agent the color fastness to wash became increase significantly except for the sample RA001 where, DMAA was absent. Due to increasing the DMAA the colorfastness to wash was also increased and found satisfactory result as for sample RA003 to RA006. It can be stated that, the more amount of DMAA means more number of cation and stronger covalent bonds between dye and fixing agent.

### 3.4 Effect of DMAA on Color fastness to dry rubbing & wet rubbing

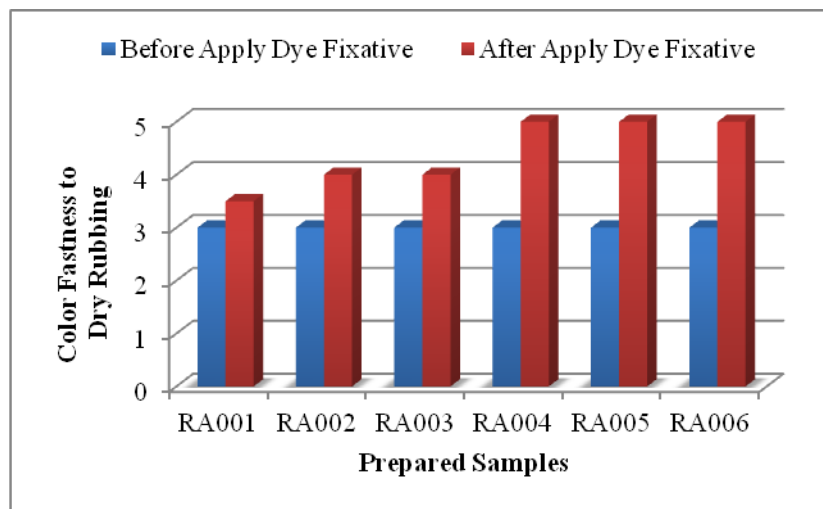


Figure 5 Color fastness to dry rubbing

Like colourfastness to wash amount of DMAA shows the same result for color fastness to dry rub (Figure 5). For sample RA004 to RA006 the results were superior to others. But in case of sample RA003 the result improved up to satisfactory level.

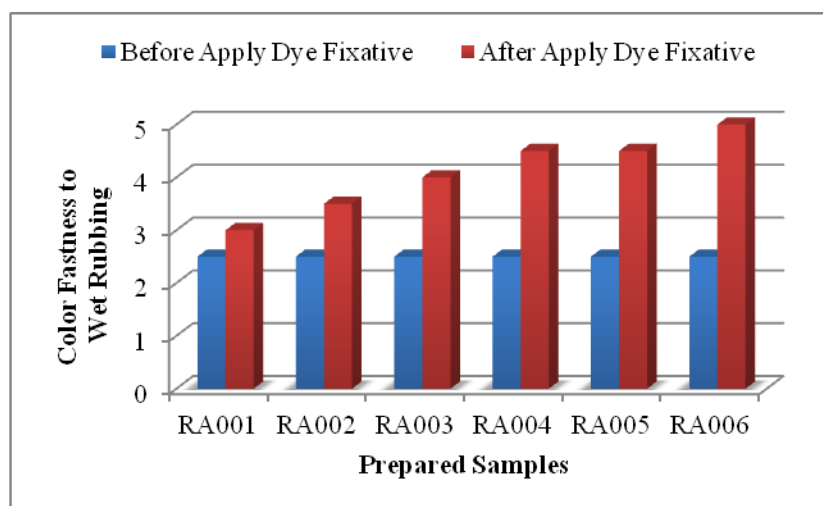


Figure 6 Colorfastness to wet rubbing before and after application

It is also noticed that the color fastness to wet rub increased with the increasing amount to DMAA (Figure 6). Above figure shows the result was best while the amount of DMAA was 2.5 g. And for the sample RA003 to RA005 the result decreased from the colorfastness to dry rub. It may happen due break some covalent bond between dye and cellulose due to water as the crocking cloths were moistened. But still it has improved the results up to satisfactory level.

### 3.5 Effect of DMAA on K/S

The K/S value before fixative treatment of the dyed fabric was measured using spectrophotometer and K/S was found 22.598 at wavelength 580-630 nm.

Table 3 shows that the DMAA has effect on K/S value. For the sample RA003 the K/S change was negligible.

**Table 3** K/S Value of the dyed samples after apply the prepared fixing agent

Prepared Fixing Agents	K/S After Fixative Treatment
RA001	24.504
RA002	24.812
RA003	22.784
RA004	24.067
RA005	24.342
RA006	23.551

### 3.6 Effect of DMAA on DL & DE

**Table 4** Color differences; DL & DE values of the samples

Prepared Fixing Agents	CIE DL	CIE DE
RA001	-0.93	0.95
RA002	-1.15	1.19
RA003	-0.07	0.17
RA004	-0.79	0.81
RA005	-0.96	1.03
RA006	-0.55	0.56

Color differences are observed after apply the fixing agents with the standard sample (untreated fabric). Table 4 shows the DL & DE values. If the DL value is positive, it means colour of the sample is lighter than colour of the standard, if the value is negative then it means the sample is darker than the standard. DE value however shows the magnitude of total colour difference. From the above table it is clear that for fixing agent RA003 the DL & DE were the best comparative to the other prepared fixing agents. And it is clear that DMAA has effect on DL & DE and best result was found the the amount of DMAA is 1.0 g.

## 4. Conclusion

The application demonstrated that, by changing DMAA [N, N-Dimethylallylamine] & APS during synthesis we had obtained a good fastness properties. The result showed that, DMAA had a remarkable effect on the fastness properties of fixing agent. On the contrary, the properties of the fixing agent are almost not affected by DMDAAC [Diallyl Dimethyl Ammonium Chloride]. Reactive dye fixing agent is most essential auxiliaries of dyeing industry. To meet the targeted dyeing quality industries want a very good solution. The application result of the synthesized agent showed the similar results. Also the raw materials as well as the fixing agent are free from all hazardous chemical according to OEKO-Tex standard. The production method was very simple and required less time than other conventional preparation method. The fixing agent was easy applicable, no yellowing & color changing properties and eco-friendly; that is the pre-requirements of a color fixing agent. Although the results were satisfactory but further study is required for the industrial production and application.



## 5. Acknowledgement

I would like to express deep appreciation to my supervisor Prof. Quan Heng, Vice Dean, Department of Chemistry & Chemical Engineering, Wuhan Textile University, China for his inspiring guidance, encouraging attitude and valuable suggestions throughout my research work. I also express sincere appreciation to Dr. Li Cui Professor, Department of Chemistry & Chemical Engineering, Wuhan Textile University, China for her guidance and suggestions throughout the research work. I would like to express my sincere thanks to the Zhejiang Runhe Auxiliaries Ltd. for providing the raw materials for this project.

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