



Improved Fastness Properties of some Novel Triarylmethane Dyes on Acrylic Fibres

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ABSTRACT

In this research, several series of triarylmethane dyes containing one or more terminal methoxy substituents with a variable tertiary amino groups have been used. These dyes have been applied to different substrates by using various methods including transfer printing and then their fastness properties were measured. These dyes shows exceptionally high light fastness (6-7) on acid modified polyacrylonitrile fibres. Prog. Color Colorants Coat. 2(2009), 123-130. © Institute for Color Science and Technology.

1. Introduction

A great disadvantage of using triarylmethane dyes, especially triphenylmethane (TPM) type, is their low fastness properties on various fibres. Bathochromic shifts and increasing molar extinction coefficients reported previously [1] shown by these dyes are commercially important from the economic view point since smaller amount of these dyes are required to give the same depth of color as the parent systems. Most of the triphenylmethane dyes listed in the Color Index have low light fastness properties on wool. Several workers have been investigated to improve the light fastnesses properties of triphenylmethane basic dyes on acrylic fibres, such as Acrilan and Orlon [2, 3]. For example, Wegman observed [2] that a relationship exists between the light fastness on Orlon and the basicity of the dye

cation; the more basic the cation, the lower the light fastness properties of the dyed fibre.

Basic dyes have regained same importance since the introduction of acrylic fibres. These dyes and also novel cationic dyes can readily be applied to modified polyacrylonitrile and bright dyed fibre with good light fastness properties is obtained. Unlike natural fibres which have to be mordanted before dyeing with basic dyes, polyacrylonitrile fibres are hydrophobic in nature and the dyed site in the fibre is not easily accessible to moisture and oxygen. This property is generally supposed to be responsible for the improved light fastness properties of basic dyes on acrylic fibres [4]. The dyeing mechanism effectively consists of absorption of the cation dye on the surface of the fibre, thus neutralizing the negative fibre potential, and at high

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temperature the dye molecules penetrate into the fibre and react within, forming a heteropolar combination. The exhaustion of basic dyes on acrylic fibres are low at below 80 °C, but it increases rapidly above that temperature and it will be maximum at 100 °C [5].

Psaar, Hubertus (Bayer Aktiengesellschaft) [6] has claimed that certain analogues of Malachite Green containing only one basic nitrogen atom provided intense color ranging from red to bluish-red with good light fastness properties on acrylic fibres.

A preliminary investigation by Gandhi [7] confirmed that triarylmethane dyes containing one terminal nitrogen atom and one or more terminal oxygen atoms show good light fastness properties on acrylic fibres. In previous works the synthesis of several diarylmethane dyes containing one or more terminal methoxy substituents together with a variable tertiary amino groups were described. [8] The spectroscopic studies of dyes containing different terminal bridging groups were also reported [1]. Several methods in particular the phenyl lithium directly and transmetallation techniques with butyl lithium have been used for synthesizing the required triarylmethane dye bases. However, the initial aim of this paper is the application of these novel

triarylmethane dyes (I-IV) (Figure 1) for dyeing purposes and investigation of their fastness properties.

Acrylic fibres are effectively in two main types:

- Straight acrylic fibres contain at least 85% polyacrylonitrile, the remainder including units possessing acidic groups to confer substantivity for basic dyes. Examples of this kind include Courtelle, Orlon 42 and Acrilan 16.
- Modified acrylic or modacrylic fibres, such as Dynel, contain 35-85% acrylonitrile units together with basic section which enable dyeing to take place with acid dyes.

The fibre manufacturers have progressively modified their products to increase the number of acidic sites in the fibre and thereby the uptake of dye at saturation. Acrilan 16 has 31 strongly acid groups and 21 weakly acid groups, on the other hand Courtelle has 154 weakly acidic groups with no strongly acidic groups and. Consequently this could be related to their different dyeing properties.

The novel dyes [1] have been applied to acrylic fibres by two methods

- (a) Dyeing in acid dye bath
- (b) Transfer printing technique.

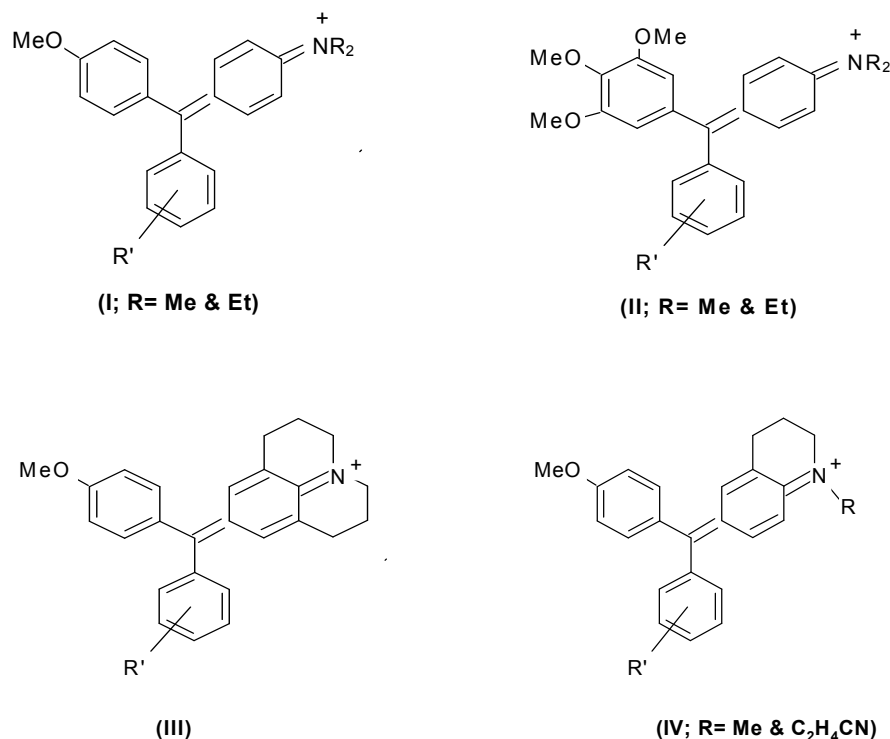


Figure 1: The structure of triarylmethane dyes (I-IV).

It was observed that the most satisfactory dyeing was obtained on Acrilan, possessing strongly acidic groups, rather than Courttelle.

The amount of dye adsorbed at saturation is determined by the total number of acidic groups present on the fibre. However, change in dye adsorption by changing of pH in the dye bath depends upon the number and strength (pK value) of the weakly acidic groups present on the fibre. Therefore the adsorption of basic dyes by this type of fibre is so pH sensitive [1].

Transfer Printing

This method generally involves the heat transfer of a dye from one surface to another, usually from a printed paper to a textile material. Three commercial methods of transfer printing may be carried out in this regard as:

Physical or melt transfer: in this method the dye and binder print to the paper, then a layer from the paper transfer on to the textile substrate by pressure and heat.

Migration printing: in which water soluble dyes are printed on paper with appropriate chemicals (to give fixation) and applied as above.

Vapor phase printing: which is usually used for the application of disperse dyes at a temperature between 180-220 °C for 30 sec.

In general, the color which is obtained on acrylic substrate by transfer printing is weaker than which is obtained on the other substrates such as polyester. This finding is primarily due to the relatively low temperature application which must be employed during the transfer printing process on acrylic fibre. Some acrylic fibres produce a strong yellow discoloration when transfer printing is carried out at 200 °C. This is the case with ordinary (standard) courttelle fibre when a longer dwell time is used [10]. Basic dyes, owing to low volatility, generally show poor heat transfer printing properties. However, these methods have been developed by using additive including oxidizing agents to improve the transfer properties [9].

By alternative approach [11] an anhydrous printing ink containing dye base is used; this method has been employed in the present work. The relevant printing pastes contain customary binders and thickeners as well as suitable stable solvent devoid of anionic groups.

2. Experimental

Dyeing Procedure

Dyeing of acrylic and wool fibres was carried out with

the appropriate dye (2% w/w) using two different dyeing assistants as follows:

Formic acid (1%): In each case, a dyebath was prepared with 20 mg of dye base dissolved in a solution of 1% formic acid (100 ml). After heating to 80 °C, the material was entered into the dyebath. Then the temperature was raised slowly to 95 °C, agitating the sample frequently. For this purpose a rotary dyeing machine (Rotating –Tube type, Linitest, Hanau, UK) was used and the dyeing process was carried out for 60-90 min, keeping the temperature at 95 °C. The dyebath was then cooled and the substrate was rinsed thoroughly with hot water and then with cold water before drying.

Acetic acid (1%) and crystalline sodium acetate (2%): The dyebath was prepared by using 20 mg of dye base; then the fabric was added to the dyebath at the boiling temperature and dyeing was continued at that temperature for at least 2 h. There were not many differences between the two methods.

Transfer printing procedure

For each dye base, 6 mg of dye was added to a solution consisting of ethylene glycol (10 mg), ethanol (82 mg), ethyl cellulose (4 mg) and sodium methylate (4 mg). The mixture was then homogenized or brought into solution in a ball mill. The resulting ink was then applied to transfer printing paper or aluminum foil with a coating knife and then allowed to dry. The pasted strip was put on top of the textile to be printed and was then placed between the two plates of Badische hot press. In order to simulate commercial conditions, the heat transfer printing was performed at 200 °C for 30 sec.

Fastness to light

The light fastness was tested according to ISO 105-B02 method. The dyed samples were exposed to xenon arc lamp using a Xenotest-ISO, Suntest (Hanau, UK) at standard testing conditions along with the Blue Scale standards. The fastness properties of samples were then assessed by comparing the change in color of them with those of the dyed wool standards.

Fastness to Washing

The wash fastness was also measured according to ISO 105-C03 [9]. In this method, a specimen of the dyed textile in contact with the adjacent fibres in specified conditions of time and temperature in a solution of soap and sodium carbonate have been applied, then rinsed and

dried. The change in color of the sample and the staining of the adjacent fibres are evaluated with the gray scales.

3. Results and discussion

Washing Fastness

The washing fastness of the dyes on Acrilan 16 was measured and the results are summarized in Tables 1 to 4. The washing fastness of each group of dyes effectively increases with the size of terminal nitrogen substituent which coincides with the increasing conjugative ability of the group. The staining test in each case is marginally better than the change in color rating. The dye with an *o*-trifluoromethyl group in the phenyl ring shows better

washing fastness properties compared with the analogous derivative of Malachite Green. Steric hindrance in the case of *ortho* substituents has virtually no effect on washing fastness properties. The two cyanoethyl derivatives (Table 4) have higher washing fastness properties than the other trifluoromethyl compounds and this may be associated with the polar nature and high molecular mass of the cyano group.

It is also noticeable that, by increasing the number of methoxy groups in dyebase [12] the ability of such dyes to form hydrogen bonds with the water and the surfactants present in the washing liquor increase so that they are more easily washed off.

Table 1: Washing fastness ratings of dyes I (R= Me, Et) on acrilan 16.

R'	(R= Me)		(R=Et)	
	C*	S**	C	S
H	3-4	4-5	3-4	4-5
2-Me	4	4	-	-
3-Me	4	4-5	3-4	4-5
4-Me	3-4	4-5	4	4-5
2-OMe	3	3-4	3	4
4-OMe	3	3-4	3	4
2-CF ₃	2	3	-	-
3-CF ₃	3	3	2	3
M.G.***	1	2	-	-

C*: Change in color S**: Staining M.G***: Malachite Green

Table 2: Washing fastness results of dyes II (R= Me, Et) on acrilan 16.

R'	(R= Me)		(R=Et)	
	C	S	C	S
H	3	4	3	4
3-Me	3	3	3-4	4
4-Me	3	3-4	3-4	4-5
2-OMe	3	3	3	3
3-OMe	3	3	3	3
4-OMe	2-3	3	3	3-4
3-CF ₃	2	3	2	2-3
4-CF ₃	2	3	2	2-3

Table 3: Washing fastness ratings of dyes III on acrilan 16.

R'	C	S
H	4-5	4
2-Me	4	4
3-Me	4-5	4
4-Me	4	4
2-OMe	3-4	3-4
3-OMe	4	3
4-OMe	4	3-4
3-CF ₃	3	3

Table 4: Washing fastness results of dyes IV (R= Me, C₂H₄CN) on acrilan 16.

R'	(R= Me)		(R= C ₂ H ₄ CN)	
	C	S	C	S
H	4	4-5	-	-
3-Me	4	4	-	-
4-Me	4-5	4	-	-
4-OMe	3-4	4	-	-
3- CF ₃	-	-	4	4
4-CF ₃	-	-	4	4-5

Light Fastness

Good light fastness is one of the most important properties; of a dyed substrate. Light fastness rating of the dyes on various fibres is given in Tables 5 to 8.

The light fastness properties of a dyed substrate depends on many factors, with the most important factor is being the inherent photostability of the dye chromophore and the way in which this stability is effected by the chemical nature of the substrate. The other factors which lead to changes in the hue or depth of color observed up on exposure of a dyed fibre can be summarized as follow [13]:

- the dye concentration,
- the wavelength distribution of the incident radiation,
- the nature of the fibre.
- the composition of the atmosphere.

In the case of triphenylmethane dyes, apart from variations in the substrate, external agent such as oxygen and water has a marked effect on the rate of fading of the dyes. The autoxidation of the dye or oxidation by hydrogen peroxide formed by photochemical oxidation of traces of water in the fibre are main causes of fading.

The vast majority of basic TPM dyes show very poor light fastness properties on wool, silk or cotton [14]. Interest in this class of dyes increased due to moderately high light fastness observed on polyacrylonitrile fibres. Investigations have been carried out by several workers [1, 2, 15]. In particular, it was found [1] that a relationship exists between light fastness of TPM dyes on acrylic fibres (especially on Orlon) and the basicity of the cation dye, the more basic the cation, the lower the light fastness of the dyed fibre.

Table 5: Light fastness ratings of dyes I (R= Me, Et) on acrilan 16 and courtelle.

R'	(R= Me)			(R=Et)		
	A*	C**	W***	A	C	W
H	7	5-6		7	4-5	1-2
2-Me	7	5		-	-	
3-Me	7	5		7	5	
4-Me	7	5-6		7	5-6	
2-OMe	7-8	5-6		7-8	5-6	
4-OMe	7-8	5	1-2	7-8	5	
2-CF ₃	6	4-5		-	-	
3-CF ₃	5-6	4-5		6	4	
M.G.***	2-3	1-2		-	-	

A*: Acrilan 16 C**: Courtelle W***: Wool

Table 6: Light fastness results of dyes II (R= Me, Et) on acrilan 16 and courtelle.

R'	(R= Me)		(R=Et)	
	A	C	A	C
H	7	5	7	4-5
3-Me	7	4-5	6-7	5
4-Me	7	4-5	7	5
2-OMe	7	5-6	7	5
3-OMe	7-8	5	6	5
4-OMe	7	5	7	5-6
3-CF ₃	5-6	4	5-6	4-5
4-CF ₃	5-6	4-5	5-6	4-5

Table 7: Light fastness ratings of dyes III on acrilan 16 and courtelle.

R'	A	C
H	6	4
2-Me	6-7	4
3-Me	6-7	4-5
4-Me	6-7	4-5
2-OMe	7	5
3-OMe	7	5
4-OMe	7	4-5
3-CF ₃	6	4

Table 8: Light fastness results of dyes IV (R= Me, C₂H₄CN) on acrilan 16 and courtelle.

R'	(R= Me)		(R= C ₂ H ₄ CN)	
	A	C	A	C
H	7	5-6	5-6	5-6
3-Me	7	5	3	3
4-Me	7	5-6	5-6	5
4-OMe	7-8	6	3-4	4
3- CF ₃	-	-	5-6	4-5
4-CF ₃	-	-	5-6	4-5

The light fastness properties of all the dyes is considerably better on acrilan 16 than on courtelle and much better than on wool. The acid modified acrilan 16 has 31 units of strongly acid groups while courtelle has none; acrilan contains 21 weak acidic groups whereas courtelle has 154 such groups. As well as the better light fastness on acrilan, this substrate is more effectively dyed than courtelle and is suitable for transfer printing using the parent dye bases which are readily converted to the corresponding dyes by interaction with the strongly acidic groups present in the fibre.

The relatively low fastness results (light and wash fastness) show by the dyes derived from the cyano ethyl ketones [16] are probably associated with impurities present in the dye bases as well as with the structural features of the system.

The highest fastness ratings on acrilan belongs to dyes possessing two p-methoxy groups in the molecule and the various methoxy substituted dyes tend to show better light fastness than the corresponding methyl analogous and the parent dyes. In contrast, the electron withdrawing trifluoro methyl group's produce relatively low fastness ratings. It has been pointed out [17] that although the presence of CF₃ groups is sometimes associated with improvements in light fastness, these substituents can equally give rise to reduction in light fastness.

The differences in the conjugative ability of the terminal nitrogen atoms do not appear to have any marked effect on light fastness although the Julolidine contain dyes have marginally lower ratings than the Karoline analogues. Since it is established that the

conjugation of the nitrogen lone pair with the aromatic system is maximized in Julolidine derivatives [18], the decrease in fastness can probably be associated with build up of electron density at the central carbon atom. It is noteworthy that the 3-trifluoromethyl derivative has a higher light fastness than in the other series so that the inductive withdrawal of electron density by the CF₃ group to some extent affects the build up at the central atom.

It is interesting that the differences between acrilan and courtelle are least marked in the case of the dyes possessing a cyano ethyl group (Table 8). The cyano ethyl group reduces the electron donating ability of the terminal nitrogen atom and therefore its basicity and it seems likely that the interaction between the dye base and the acrilan fibres is less efficient in this case. The cyano ethyl derivatives clearly have lower light fastness ratings than the corresponding kairiline analogues, and this finding contrasts with the relative effects of these terminal groups in mono azo dyes [19]; the cyano ethyl compounds have marginally better light fastness on nylon and polyester.

The presence of a crowding substituents at the 2-position of the phenyl ring does not lead to any variation in light fastness.

4. Conclusions

Triarylmethane dyes containing one or more terminal methoxy substituents together with variable amino groups are suitable for transfer printing and show improved fastness properties on acid modified acrylic

fibres compared with common TPM dyes such as Malachite Green, Crystal Violet and Brilliant Green (Table 1). Light fastness ratings of the most dyes are significantly better than their washing fastness properties (Tables 1-8). The dyeing and fastness properties of dyes

are showing much improvement on Acrilan 16 comparing with Courtelle (Tables 4-8). However, the dyeing and fastness properties of the dyes are good enough to permit their use as commercial products.

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