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**Continuous Dyeing Using Radio
Frequency Energy**

**Part IV: The Fixation of Disperse Dyes on Pre-
Dried Polyester**

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CONTINUOUS DYEING USING RADIO FREQUENCY ENERGY PART IV: THE FIXATION OF DISPERSE DYES ON PRE-DRIED POLYESTER

by E. GARNER

ABSTRACT

When polyester was padded with a number of disperse dyes, dried and then subjected to radio frequency energy, no dye fixation was obtained. When, however, certain chemical substances such as urea and glycerol were present on the dried fibre, higher dye fixation was obtained particularly for dyes of high dipole moment. Fixation obtained after conventional heating was independent of dye polarity and was shown to be responsible for considerably lower dye fixation than that achieved by direct RF absorption.

INTRODUCTION

In a previous publication¹ the results were reported of a study into the radio frequency (RF) fixation of disperse dyes on polyester tow. The results indicated that the fixation of disperse dyes on polyester depended not only on the heat and steam produced by the water present, but also on a direct interaction between polar dye molecules (polarity being expressed in terms of dipole moment) and RF energy. In that investigation it was not possible to separate completely the effects of this interaction from those of steam. Nevertheless, it was possible to show that the relationship between dye fixation and dipole moment improved when moisture was removed from the system. It was therefore considered of value to attempt RF dyeing under conditions in which the effect of steam on dye fixation was further reduced.

As well as the effects of steaming on dye fixation, during wet RF dyeing, it is also possible for dyeing to occur by a purely heat energy (thermofixation) route. Unlike steaming, thermofixation can still take place in the absence of moisture. Previous results¹ had strongly indicated that dyes of high dipole moment would be more capable of fixation in a RF field than would those of low polarity. There was, however, no evidence to suggest (or reason to believe) that dye dipole moment should influence heat absorption. It was also decided to include in the investigation a study of the effects of dye dipole moment on thermofixation.

In the drying or dyeing of textiles using RF or microwave energy, the substance which absorbs the energy is usually considered to be liquid or gaseous

water. Relatively little attention has been paid to the dielectric relaxation* of other compounds in the system such as the dyes, auxiliary products and the fibre itself. A survey of the literature outside the textile field, however, revealed that a large number of investigations have been carried out on the dielectric properties of materials in the solid state. As would be expected for solids, relaxation is generally considered to be less than that of the corresponding liquids. For example, ice is almost "lossless" in the microwave region, whereas microwave cooking primarily involves energy absorption by free water². It is, however, not possible to generalise regarding solid/liquid phase relaxation behaviour. The action of solid materials in RF and microwave fields is complex and is dependent upon the substance being considered.

Smyth³ has pointed out that the dielectric relaxation of polar solids will depend upon the freedom of molecules or their polar parts to alter in orientation when placed in an electric field. If the molecules are without a dipole moment, the dielectric constant will be small for both the solid and the liquid phases. The dielectric constant of liquid molecules possessing dipole moments, is considerably larger than those of non-polar liquids and dielectric absorption occurs in a frequency region which is dependent upon the size and shape of the molecule, the viscosity of the liquid and the temperature. Upon solidification of the polar liquid, the normal behaviour for many compounds is a fixing of the molecules in a space lattice preventing molecular orientation and reducing the dielectric constant to that of a non-polar substance.

Pauling⁴ in contrast to the above view has shown by means of quantum mechanical calculations and specific heat data that rotation within the space lattice is possible for a number of molecules with small moments of inertia such as hydrogen halides. He also found⁴ that the aliphatic carbon chains in mono-alkyl substituted ammonium halides displayed symmetry when examined by X-rays, arising from rotation of the molecule or group within the space lattice. Even a zig-zag carbon chain has a low moment of inertia around its long axis.

Smyth and Hitchcock⁵ have also reported that methanol showed dipole rotation between -114°C and its melting point. Further measurements⁶ indicated this to be due to rotation of the entire molecule. Methanol, of course, will have an extremely small moment of inertia around an axis through the C and O nuclei.

In general, molecular rotation in a solid has been considered⁷ to be unlikely unless the moment of inertia of the molecule concerned is small and the internal field weak. A number of moderately large polar organic molecules have, however, shown evidence of molecular rotation in the solid state⁸, viz.

*Dielectric relaxation is the process responsible for dielectric heating. It is conveniently thought of as the return to random order by polar molecules on withdrawal of an electric field.

cyclohexanol, camphor, borneol, etc. It seems probable, therefore, that supplying a polar substance with thermal energy and that loosening of the molecular lattice as the melting point is approached, gives sufficient freedom to an occasional polar molecule to overcome the effect of its moment of inertia and permits its orientation in the externally applied field⁸. The dipole moments of camphor and water are 3,10 D and 1,84 D, respectively⁹.

There is some evidence therefore, for molecular freedom of movement and dielectric relaxation of polar organic solids and one might expect the absorption of RF energy by solid phase dye molecules also to be possible under favourable conditions. It was therefore decided to study the RF fixation of disperse dyes on polyester after drying.

EXPERIMENTAL

Material

Both polyester sliver and knitted fabric were used. The sliver material was ®Trevira type 820 with a linear density of 18 ktex, fibre 16,7 dtex and mean staple length 150 mm. The fabric was knitted from textured polyester yarn, 34 dtex and had a mass of 228 g/m².

Dyestuff and Auxiliaries

These were all of commercial quality. Samples were padded to a 100% wet pick-up in a ®Benz laboratory padder with a padder liquor containing:

15 g/l Dyestuff

20 g/l ®Matexil WA — HS (wetting agent)

10 g/l ®Invalon TA — ZA (carrier)

10 g/l ®Manutex F (thickener)

Acetic Acid to pH 4,5

In some cases other substances were substituted for the carrier. The relevant details are discussed in the text. These chemicals were of laboratory reagent quality.

Radio Frequency Treatment

Padded, dried polyester sliver was treated in a ®Fastran RF continuous top dyeing machine. The generator current was set at a standing value of 150

mA. The radiation frequency was 27,12 MHz.

To avoid the presence of steam during dyeing, it was necessary to change the dyeing procedure which had previously been used^{10,11}. Polyester slivers, 6 m in length, were padded as before and then dried thoroughly for 16 hours at 50°C, after which the mass loss at 105°C was less than 5%. They were then folded into plugs *ca.* 30 cm x 15 cm in size, and placed manually in the RF machine tube between the electrodes. Radiation treatment times of 10 min and 60 min were used.

Polyester knitted fabric was also subjected to RF treatment after padding with dye liquor solution and drying. The machine used for this work was a®Pye RF Generator Type 1,5/13 operating at a field frequency of 13,56 MHz and with a power output of 1,6 kW. In this machine the fabric is placed between two electrodes 4 cm apart and made up of sets of staggered aluminium panels which are open to the atmosphere. Treatments were of 30 s duration.

Temperature Measurements

Maximum dyeing temperatures obtained in the®Fastran machine were measured using®IBV thermal test papers located within the sliver plugs.

Thermofixation

Polyester sliver was padded with dye liquor, dried and then thermofixed in a laboratory fan-circulation oven. Baking temperatures used were 127°C and 180°C. The treatments were carried out for 10 min.

Determination of Dye Fixation

This was carried out by means of acetone extraction and measurement of the solution absorbance as described previously¹.

RESULTS AND DISCUSSION

The Effect of Dipole Moment on Dye Fixation

Four commercially available disperse dyes of known dipole moments^{12,13,14}, were selected for study and are shown in Table 1.

Each of these dyes was treated for 60 min in the®Fastran RF dyeing machine. These attempts were totally unsuccessful — resulting in zero dye fixation, even for the dyes of high dipole moment.

It was then decided to investigate the possibility of including some auxiliary chemical in the padding composition which could absorb RF energy,

TABLE 1
DISPERSE DYES USED

Commercial Name	CI Disperse	Measured Dipole Moment D
®Celliton Yellow G	Yellow 3	3,6 ¹²
®Celliton Pink FF3B	Red 11	4,7 ¹³
®Celliton Scarlet B	Red 1	8,1 ¹³
®Celliton Rubine B	Red 13	8,2 ¹⁴

even in the solid state after drying. Urea was chosen for the following reasons:

- It has a dipole moment of 4,56D¹⁵. (This compares favourably with 1,84 D for water).
- It is a relatively small molecule with the same high symmetry as that of the water molecule (C_{2v} point group).
- It is a cheap textile processing auxiliary often used in dyeing applications.

In a further attempt to obtain RF dye fixation on pre-dried polyester, therefore, the same four disperse dyes were padded in liquors containing 5% urea as well as the other dyeing auxiliaries. After drying as before to a moisture content of less than 5%, they were treated for 1 hour in the ®Fastran RF dyeing machine. On this occasion there was considerable dye fixation for some of the disperse dyes. Fixation values, as determined by acetone extraction, are shown in Table 2:

TABLE 2
RF FIXATION OF DISPERSE DYES ON DRY POLYESTER IN THE PRESENCE OF 5% UREA

Dye CI Disperse No.	Dipole Moment (D)	% Dyestuff fixation
Yellow 3	3,6	9
Red 11	4,7	73
Red 1	8,1	91
Red 13	8,2	82

Possible Mechanisms of Dye Fixation in the Presence of Urea

As can be seen, dye fixations were, in general, highest for dyes of high dipole moment. One interpretation of these results is that, on the addition of urea, the dielectric constant of the dye system is simply raised to a level which permits the necessary absorption of RF energy required for dye fixation. Another possible interpretation is that bulky dye molecules in pre-dried polyester are too movement-restricted to absorb RF energy. Further, the other components of the dyeing system lack the requisite polarity to respond to the RF field. Urea molecules, however, are small, symmetrical and polar enough to transform the RF energy into thermal and kinetic effects. These effects are sufficiently large to permit, in turn, energy absorption by the dye molecules. Whatever the underlying mechanism, however, it is clear that the fixation of disperse dyes on polyester in the solid state and in the absence of some assisting chemical species (e.g. water or urea) is extremely limited. This applies to dyes of both low and high polarity.

Effects of the Heat Produced During RF Treatment

Three interesting observations were made during the RF treatment of the dry polyester containing the dyestuffs and urea:

- A small current change of ca. 10 mA in excess of the normal 150 mA standing current, was noted.
- There was a smell of ammonia gas (presumably from urea breakdown).
- In the case of the higher dipole moment dyes, the centres of the polyester samples were extremely hot after dyeing.

These observations indicated that RF energy was being absorbed and that heat was being generated. Temperature measurements were therefore made during RF treatment. These showed that the maximum temperatures reached at the polyester plug centres were 127°C for CI Disperse Yellow 3 and 171°C for CI Disperse Red 1. This indicated that energy absorption was greatest for the dye with the high dipole moment. RF treatment of dry polyester tow padded with 5% urea alone, also showed energy absorption with a maximum temperature of 121°C being recorded.

The function of the urea may be simply that proposed by Püschner¹⁷ for microwave heating of water, namely absorption of dielectric energy thereby producing heat for dye fixation. Evans and Skelly¹⁸ have suggested, however, that one function of moisture in the microwave dyeing process is to facilitate dye diffusion through the fibre. It may be considered possible that water and urea

may both assume this role in RF dyeing also — allowing RF energy absorption *and* providing a medium through which dye molecules can vibrate and migrate into the fibre structure.

Previous measurements made in the ®Fastran machine during wet continuous dyeing had suggested a maximum operating temperature of *ca.* 115°C. This, of course, is a result of limitations imposed by the use of water as the energy absorbing medium (i.e. steam pressure loss from the RF field during dyeing). The melting point of urea is 132°C and would not normally, therefore, be able to provide the liquid environment necessary for dye migration under these temperature conditions. It has been reported, however¹⁹, that urea is capable of forming eutectic mixtures with small quantities of water and, indeed, with some disperse dyes. The melting point of the eutectic melt is considerably lower than that of pure urea. The maximum temperatures attained during dry RF dyeing could therefore allow urea to fuse and thereby assist dye diffusion. This would apply in the case of dyes of both high and low polarity.

To establish the effect of heat only (no RF energy) on dye fixation, samples of the dried slivers were thermofixed under two sets of conditions. Table 3 shows the dye fixation values obtained.

TABLE 3

DRY HEAT DYE FIXATION IN THE PRESENCE OF 5% UREA

Dye CI Disperse No.	% Dyestuff fixation after heating at	
	180°C for 1 min	180°C for 10 min
Yellow 3	33	92
Red 11	36	90
Red 1	30	90
Red 13	40	88

The lack of variation between dyes for each set of thermofixation conditions contrasts markedly with the RF fixation values shown in Table 2. It is clear that RF dye fixation is much more sensitive to dye dipole moment than is thermofixation.

Comparison of the Dye Fixations Due to Thermal and RF Energy

Until now, the time used for RF treatments had been 1 hour. In a further experiment, dried polyester sliver containing CI Disperse Red 1 and 5% urea was

treated for 10 min. in the RF machine. This corresponds to the time the fibres normally spend between the electrodes during continuous processing. The maximum package temperature recorded was 127°C and the dye fixation was 65%. To determine the effect of the heat only on dye fixation, a sample of the dried sliver containing the dye and urea was heated for 10 mins. at 127°C. Under these conditions the dye fixation was only 13%. Since 127°C was the maximum temperature reached during the RF treatment, it can be concluded that the quantity of dyestuff which was fixed by heat only, during the RF dyeing process, was 13% at most.

Comparison of Urea and Carrier in RF Dyeing of Pre-dried Polyester

In a previous report¹¹, attention was drawn to problems regarding the build-up of some disperse dyes on polyester when dyed on a ®Fastran RF dyeing machine. This work had been carried out following the conventional RF dyeing procedure involving treatment of wet fibres and the use of carrier in the padding recipe. Carriers are commonly used to improve the fixation of disperse dyes on polyester by a number of processes. In the light of the fact that urea increased dye fixation, it was decided to carry out a direct comparison between the fixation of dyes on dried polyester in a RF field and in the presence of either carrier or urea. Three commercial disperse dyes which had previously been found to give unsatisfactory fixation by conventional RF dyeing, were applied to polyester knitted piece fabric in pad liquors containing the conventional ingredients (including carrier) or with the carrier replaced by 10% urea. After drying to a residual moisture content of less than 10%, all the samples were treated on a ®Pye RF Generator. Dye fixations after 30 s treatment are shown in Table 4.

TABLE 4

COMPARISON OF DRY FIXATIONS OF CERTAIN DYES USING CARRIER AND UREA

CI Disperse	% Dye Fixation with Pad Liquors Containing	
	Carrier	Urea
Yellow 114	12	47
Red 184	20	53
Blue 165	16	48

As can be seen, the formulations containing urea resulted in dye fixation of around 50%, whereas the conventional formulations produced very low dye fixation. It is clear that, even in the case of dyes which are difficult to fix by the conventional RF process, the presence of urea results in sufficient RF energy absorption and heat generation to give good dye fixation, even in the presence of relatively small amounts of water.

Alternative Dyeing Assistants

Glycerol was also examined as an auxiliary for the dry RF dyeing process. It has a dipole moment of 2,56D¹⁹ and is, like urea, also widely used in textile dyeing and printing as a dye solubilizing agent²⁰. It was found that glycerol also facilitated dye fixation in a manner similar to that of urea. Glycerol appeared not to be as effective however, 20% glycerol being required to achieve the same dye fixation obtained with 10% urea.

NOTE: Since the completion of the work, a high frequency process has been published²¹ in which various glycols and other polyhydric alcohols of high dielectric loss are used to fix disperse dyes on polyester. Glycerol itself is not included.

SUMMARY AND CONCLUSIONS

In order that the mechanism of fixation of disperse dyes on pre-dried polyester using RF energy might be studied, four disperse dyes varying in dipole moment from 3,6 D to 8,2 D were examined. Polyester was padded with conventional quantities of dye, wetting agent, carrier, thickener and acid and then dried before being subjected to a RF field. It was found that no dye fixation took place, no matter how polar the dye molecule. In further studies it was found that the addition of certain chemical substances to the padding liquor facilitated dye fixation.

Urea and glycerol were two such compounds and, in their presence, very high dye fixation was obtained for polar disperse dyes. In general, fixation of dyes in a RF field and on pre-dried polyester seemed to correlate with dye dipole moment.

Temperature measurements indicated that RF energy was being absorbed by both the urea itself and by the formulations containing dye and urea, and converted into thermal energy. Dyes with high dipole moment resulted in temperatures higher than those of low polarity. Temperatures of greater than 170°C were possible for highly polar disperse dyes in the presence of urea.

It was concluded that urea and glycerol in some way were modifying the dielectric properties of the solid system. There are various possible explanations

for this phenomenon and further research is under way to establish the exact mechanism(s) by which urea and glycerol function.

With dyes which gave poor fixations by conventional (wet) RF treatment, fixation on dried polyester was shown to be increased by as much as 300% by replacing conventional carrier with urea.

Thermofixation of disperse dyes on dried polyester appeared to be insensitive to dye polarity. When dried polyester containing a highly polar dye was heated for the same time and at the same temperature as that observed during RF treatment, dye fixation was only 13%. This compared with 65% when RF energy was used.

It is not yet clear whether the initial energy absorber during dry RF dyeing of polyester is unrestrained dyestuff, urea or glycerol, trace quantities of water (occluded by urea or associated with glycerol) or another dyebath auxiliary, such as acetic acid. The evidence from the work reported, however, does indicate a direct interaction between RF energy and polar dye molecules, in the presence of urea or glycerol.

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USE OF PROPRIETARY NAMES

®Denotes registered trade marks. The fact that products with proprietary names have been used in this investigation does not imply that SAWTRI recommends them or that there are not substitutes as good or better.

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