

STUDIES ON THE BEHAVIOUR OF DISPERSE DYES INCORPORATING N-SUBSTITUTED CARBAMATE GROUP UNDER HEAT TRANSFER-PRINTING CONDITIONS

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Mass spectra studies of dyes incorporating N-substituted carbamate group have shown that these dyes generate free isocyanate group under transfer-printing conditions. This has been confirmed further by the presence of substituted ureas as unfixed species in the transfer-prints obtained from these dyes as indicated by the mass spectra of the unfixed dyes extracted from the prints.

INTRODUCTION

Heat transfer-printing is a recent innovation in textile printing in which multicoloured designs printed on paper are transferred in vapour phase to a suitable fabric kept in contact with the paper at 150-220° in a press or a continuous callender. This new technique has the technical advantage of reproduction of intricate designs and patterns with outstanding definition.

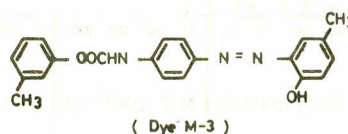
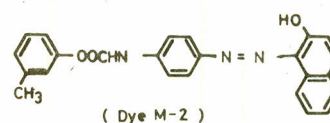
Transfer-printing has been applied mainly to polyester. Natural fibres like wool and cotton present difficulties as they have little or no affinity for disperse dyes used in transfer-printing.

One of the various suggested solutions [1-4] to the problem is the use of volatile or sublimable reactive disperse dyes. There are, however, some difficulties in this approach as well, e.g., (i) as a result of the introduction of the reactive group in the dye molecule its molecular weight is increased and consequently its volatility is decreased. (ii) the reactive group may decompose at transfer-printing temperature; and (iii) there also arises the question of the extent of reactions between the dye and the substrate.

To overcome these difficulties disperse dyes incorporating "masked" isocyanates in the form of N-substituted carbamate have been synthesised. The present paper deals with the results of studies carried out to ascertain the generation of isocyanate group containing dyes from the carbamate dyes under the conditions of transfer-printing.

Although the literature [5] describes the generation of isocyanates from the corresponding N-substituted carbamates either under the action of heat alone (150-500°C) or in the presence of P₂O₅, yet there is no mention of

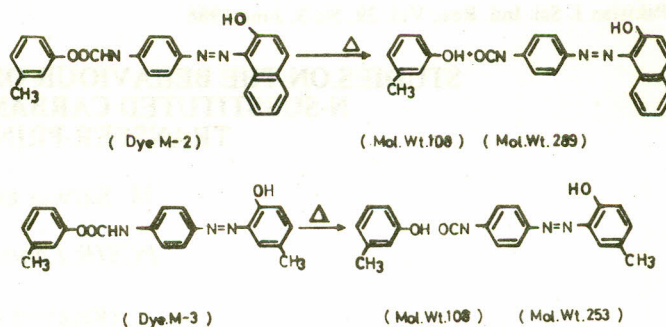
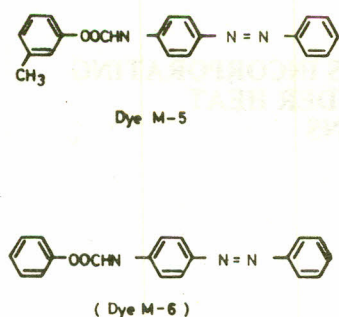
whether relatively high molecular weight compounds like dyes containing isocyanate groups can also be generated from the carbamates. Moreover, the use of P₂O₅ and temperature above 210° are not desirable in transfer-printing natural fibres. Therefore, in order to determine whether carbamate dyes do regenerate the corresponding isocyanate dyes under transfer-printing conditions dyes M-2 and M-3 with the following structures were studied.



In both of these dyes m-cresol has been used to mask the isocyanate group in the form of N-substituted carbamate group.

Thermal decomposition products of carbamate dyes.
The regeneration of free isocyanate group containing dyes from the carbamate dyes by simply heating to melt was indicated by the following observation. Thin layer chromatography (TLC) of the dyes under investigation after heating to melt gave two coloured spots each. One of the spots was due to the original carbamate dye in each case, while the second spot was due to the corresponding free isocyanate group containing dye. This was confirmed in the case of dyes M-5 and M-6 with the following structures.

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In both of these cases the R_f value of the second spot was found to correspond to that of pure 4-(phenylazo)-phenyl isocyanate.

Mass spectrometry of dyes. A more convincing proof regarding the regeneration of free isocyanate dyes from the carbamate dyes was however provided by the mass spectra of these dyes. When dyes M-2 and M-3 were subjected to mass spectrometry under chemical ionisation (using methane as a reagent gas) as well as electron ionisation conditions, it was observed that molecular ions or parent ions had m/e values of 289 and 253 respectively (Fig. 1 and 2). Now 289 is the molecular weight of the free

The molecular ion of parent ion is produced by the removal of a single electron from the molecule and is the simplest event that occurs when a compound is subjected to mass-spectrometry and at this stage there is no fragmentation of the molecule under investigation. The presence of molecular ions or parent ions with m/e 289 and 253 in the mass spectra of dyes M-2 and M-3 respectively therefore indicated that the dyes under investigation regenerated the corresponding isocyanate dyes on simple heating and thereby produced the parent ions by the removal of an electron each from their molecules.



(Free isocyanate dye from Dye M-2)



(Free isocyanate dye from Dye M-3)

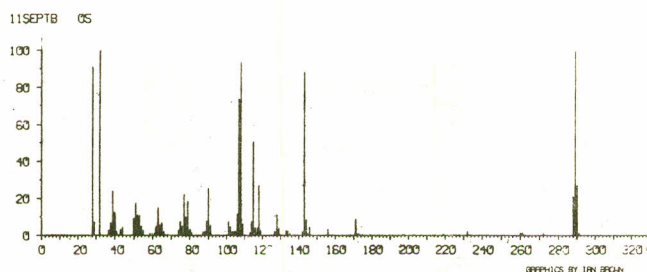


Fig. 1. Masked isocyanate dye M-2. 200°C electron ionization.

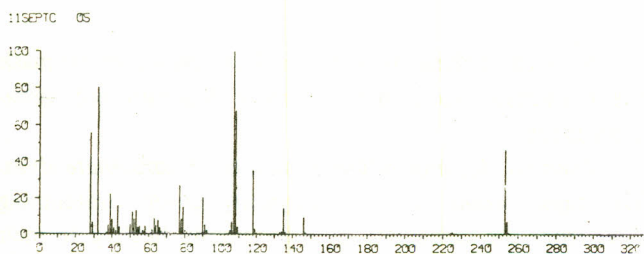


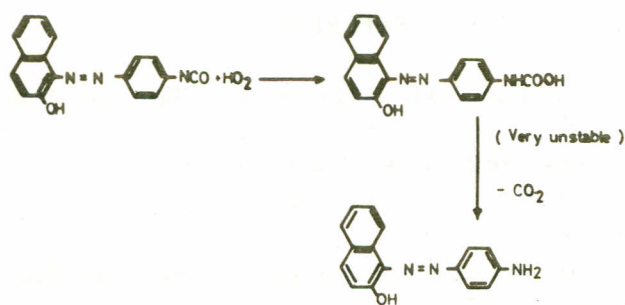
Fig. 2. Masked isocyanate dye. M-3. 200°C electron ionization

isocyanate group containing a dye corresponding to the dye M-2 and 253 is the molecular weight of the isocyanate dye from the dye M-3; thus:

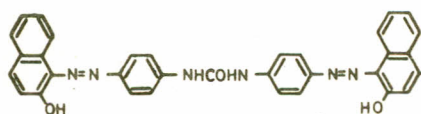
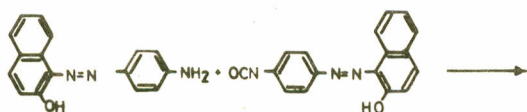
A major peak with m/e 108 which corresponds to *m*-cresol was also present in the mass-spectra in both cases.

Mass spectrometry of hydrolysed products from dyes M-2 and M-3. The regeneration of isocyanate dyes from the carbamate dyes under transfer-printing conditions was supported further by mass-spectra studies of hydrolysed products obtained during transfer-printing of dyes M-2 and M-3. These products obtained by solvent extraction of prints transfer-printed with dyes M-2 and M-3 were purified by preparative TLC.

Studies of the mass-spectra of the hydrolysed product from the dye M-2 showed in addition to a peak with m/e 289 due to the corresponding isocyanate group containing dye, other peaks due to fragments of m/e 389, 410 and 268. These fragments can be explained by taking into consideration the reaction of the isocyanate group containing dye with moisture:



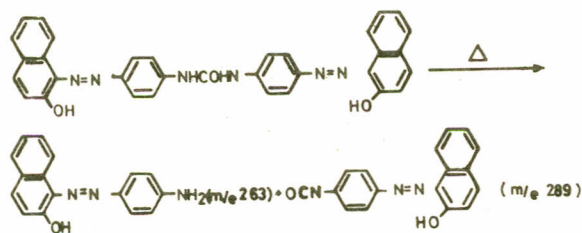
Followed by



During transfer-printing some of the regenerated isocyanate dye reacts with moisture, present in the fibre to give the carbamic acid group in place of isocyanate.

The carbamic acid group, being, very unstable, readily loses CO₂ to give a primary amino group. The amino group thus produced will react further with the isocyanate dye to give substituted urea.

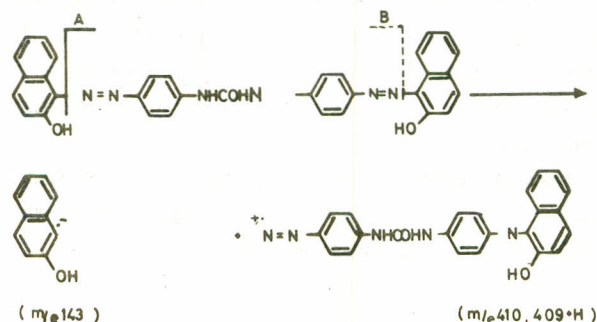
That the hydrolysed product under examination is a substituted urea is supported by the presence of fragments with m/e 289 and 263 in the mass spectra. These fragments are produced from the substituted urea:



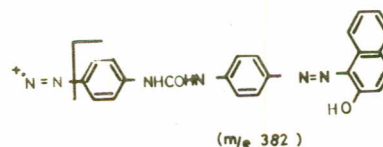
That ureas also decompose under the action of heat to give parent isocyanate is a known fact.

The presence of a fragment with m/e 410 in the mass spectra of the hydrolysed product from dye M-2 also supports the above. The formation of this fragment can be

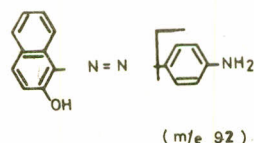
explained as due to the fragmentation of the substituted urea molecule at A or B:



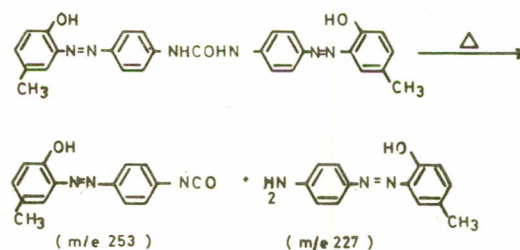
The fragment with m/e 143 which is due to the β -naphthol ion is present in the mass-spectra. Further breaking of the fragment with m/e 410 gives an ion with m/e 382 which is also present in the mass-spectra:



The fragment with m/e 92 may be explained as being due to breaking of fragment with m/e 263 to produce an aniline ion C₆H₆N⁺:



Mass spectra of the hydrolysed product from the dye M-3 showed major peaks at the high mass end of the scale with m/e 227 and 253 which may also be attributed to the decomposition of the corresponding substituted urea:



It is, therefore, obvious that substituted ureas are also produced during transfer-printing using N-substituted carbamate dyes. The formation of ureas is only possible through the regeneration of isocyanate dyes from carbamate dyes.

CONCLUSION

Dyes incorporating N-substituted carbamate groups generate free isocyanate group on heating. These dyes, therefore, behave like reactive dyes containing a free isocyanate group when employed for transfer-printing of natural fibres.

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