Beyond the Black-Novel High Waterfast Dyes for Colour Ink Jet Printing

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Introduction

Colour printing in the office environment is now becoming a major growth area and it is envisaged that ink jet, due to its relatively low cost compared to other non-impact methods, will become the dominant technology. However, at the present time, deficiencies still exist with colour ink jet printing, one of the main problems being poor waterfastness of the prints when using plain papers. This can cause the print to smudge or smear when handling with moist fingers or by contact with water. The poor waterfastness is due to the types of dyes currently in use. These are normally commercially available products such as acid dyes and direct dyes, normally used for textile outlets, that have been purified, desalinated and filtered for use in ink jet.

Examples of dyes currently in use are CI Direct Yellow 86, CI Direct Yellow 132, CI Acid Yellow 23, CI Acid Red 52, CI Acid Red 249, CI Direct Blue l99 and CI Acid Blue 9. The dyes were all selected because of their hue (colour) reliability in use, good solubility in the aqueous ink media (they all contain an abundance of water solubilising sulphonic acid (SO_3H) groups) and good thermal stability leading to good kogation when used in bubble jet or thermal ink jet systems. However, these desirable ink properties lead to the poor waterfastness of the print, the dye forming the image still being a water soluble dye.

Until recently this situation also existed in the black shade area with low waterfast commercially available dyes such as CI Food Black 2 and CI Direct Black 168

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being commonly used. Research carried out and presented at previous IS&T Conferences[1,2] has led to black dyes having high waterfastness on plain papers now being commercially available. These products were specifically designed for use in ink jet. It was shown that by removing some or all of the water solubilising sulphonic acid groups present in conventional black ink jet dyes and replacing them by less acidic carboxylic acid (CO_2H) groups, waterfastness could be greatly enhanced, whilst still maintaining good solubility in the aqueous ink media.

This same principal has now been extended to colour ink jet dyes in the yellow, magenta and cyan shade areas.

Results

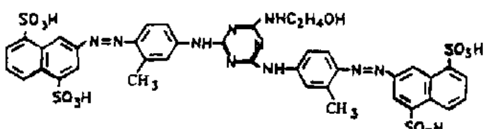
Two approaches to producing water soluble dyes containing carboxylic acid groups have been evaluated.

(1) Water insoluble disperse dyes, solvent dyes or pigments have been modified to include carboxylic acid groups.

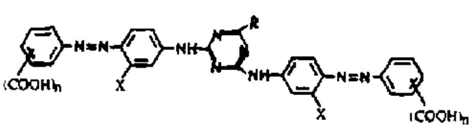
(2) Some or all of the sulphonic acid groups present in water soluble dyes have been replaced by carboxylic acid groups.

Generally, the second approach was more successful.

Yellow Shade Area

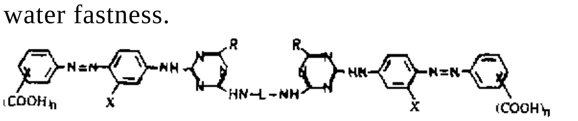


CI Direct yellow 86



(1)

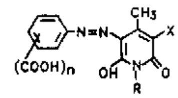
The water solubilising sulphonic acid groups present in CI Direct Yellow 86 are all situated in the diazo component. Replacing this diazo component by one containing carboxylic acid groups results in dyes of structure (1) having very high levels of water fastness[3]. By varying the groups X and Y the shade can be varied from greenish yellow to reddish yellow. Variations in the group R also allows other properties such as solubility to be altered. Unsymmetrical dyes where X and Y are different can also be synthesized and this permits even greater flexibility to obtain the required shade, solubility and water fastness.



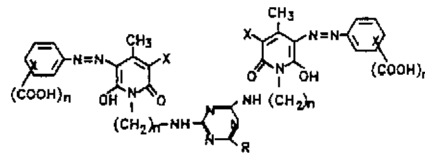
(2)

The related dyes (2), prepared by reaction of two molecules of the chlorotriazinyl-mono-azo dye with a diamine, also produce very high waterfast prints. The linking group can be aliphatic, aromatic or heterocyclic in character.

Bright yellow disperse dyes, solvent dyes and reactive dyes based on the azo-pyridone structure are commercially available. By introducing carboxylic acid groups into this type of molecule ink jet dyes (3) can be synthesised. However, the waterfastness of these monoazo dyes is still poor. Linking two molecules through a triazine ring to give dyes of structure (4) leads to much enhanced waterfastness. The light fastness of dyes (3) and (4) tends to be lower than those of dyes (1) and (2).



(3)

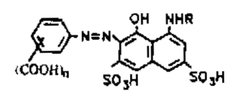


(4)

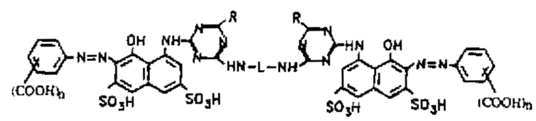
Molecular size and shape is therefore also an important factor in producing high waterfastness.

Magenta Shade Area

Carboxy containing mono azo magenta dyes of structure (5) based on derivatives of 1-amino-8-naphthol-3,6-disulphonic acid (H Acid) do not give particularly high waterfastness. However, by linking two chlorotriazinyl mono azo dyes of this type through a diamine to give (6) much higher waterfastness is observed[4]. The diamine can again be aliphatic, aromatic or heterocyclic.



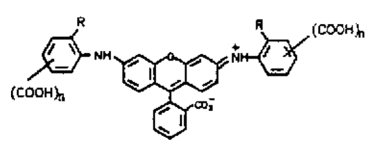
(5)



(6)

By choice of the linking diamine, the number of carboxylic acid groups in the molecule and the nature of R, magenta dyes can be obtained having high waterfastness, good solubility and moderate-good light fastness.

If very bright magenta shades are required then xanthene dyes related to CI Acid Red 52 but containing carboxylic acid groups can be used.



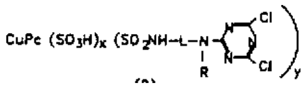
(7)

The lightfastness of these very bright bluish magentas is, however, still poor, being similar to CI Acid Red 52.

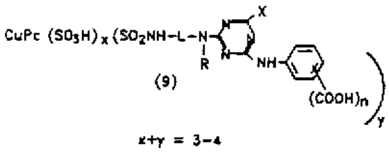
Cyan Shade Area

There are a number of commercially available bright turquoise reactive dyes based on the copper phthalocyanine structure (8). These are prepared by chloro sulphonation of copper phthalocyanine followed by reaction with a diamine. The reactive dichlorotriazinyl group can then be introduced.

Further reaction of these compounds with amines substituted with one or more carboxylic acid group gives ink jet dyes of type (9).



(8)



(9)

By varying the ratio of x:y and hence the number of sulphonic acid groups: carboxylic acid groups in the molecule and by varying the nature of R, X and L, high waterfast cyan dyes can be synthesised with very good light fastness[5].

Conclusions

It has been shown that yellow, magenta and cyan ink jet dyes containing carboxylic acid group can be synthesised and these dyes show high waterfastness when printed on a variety of plain papers. In certain cases these dyes are sufficiently soluble in the ink media and show good thermal stability to be of value in bubble jet or thermal ink jet printers.

ZENECA Specialties will be launching in 1994 a high waterfast trichromat PROJET Fast Yellow 2, PROJET Fast Magenta 2 and PROJET Fast Cyan 2 based on this carboxy dye approach.

References

1. S. Hindagolla, D. Greenwood and N. Hughes, Waterfast Dye Development for Ink Jet Printing, *Sixth International Congress on Advances in Non-Impact Printing*, p. 181, Orlando, 1990.
2. P. Gregory, J. S. Campbell and P. Mistry, Novel Waterfast Black Dyes for Ink Jet Printing, *Seventh International Congress on Advances in Non-Impact Printing Technologies*, p. 142, Portland, 1991.
3. European Patent 468647 ICI.
4. European Patent 468648 ICI.
5. European Patent 468649 ICI.