

Magenta Dyes for Ink Jet Applications

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Abstract

Within the competing non-impact printing technologies, ink jet has emerged as one of the leading digital printing technologies due to its capability to print black and color on many surfaces.

Significant improvements have been achieved in this field including the development of dye and pigment based inks. For recent multicolor industrial ink jet applications such as near-photographic color printing and wide format color graphics, there is a growing demand for light fast and water fast dyes.

Developing water soluble magenta dyes showing the desired brightness and hue combined with good fading and water resistance has proved a difficult target.

In this paper, a survey of known magenta dyes is presented including spectroscopic features, aggregation behaviour and fastness properties. In addition, novel polycyclic metal-free magenta dyes are presented which are derived from pigments, vat dyes and solvent dyes.

Optical and light stability characteristics of the novel dyes are compared with commonly used magenta dyes.

Introduction

In contrast to electrophotography (laser printing, photocopying) and thermography, ink jet printing is a true primary non-impact process. Liquid ink droplets passing through fine nozzles are electronically directed to surfaces including paper, plastics, metals, ceramics and textiles.^{1,2}

Due to considerable progress in hardware and ink technology, ink jet has proven to be the first technology that achieved a high level of color quality at a reasonable price.

There are two basic forms of ink jet systems, continuous and drop-on-demand, which can be subdivided further. Classical ink jet applications are monochrome and color office printers, and industrial printers for marking, addressing and coding. Recently, attractive multicolor industrial ink jet applications have appeared including wide format printing, color graphics, color proofing³ and photographic imaging.⁴

Within the different components—hardware, substrate, ink—comprising a reliable ink jet system, inks play a decisive role. Basically there are three types of inks—aqueous, solvent and hot melt-suited for the different printing technologies. Solvent dyes are mainly used in inks for continuous printers and phase-change devices whereas the most common inks for drop-on-demand office printers, both piezo and thermal, are aqueous based. Consequently, colorants for aqueous ink jet inks are water soluble dyes selected from food, acid, direct and reactive dyes.

Dyes versus Pigments

The innovations which are necessary to meet the specific requirements for colorants in ink jet systems are reflected by a high level of patent applications. The main topic has been directed toward tailoring water soluble dyes for ink jet applications⁵ and ink formulations to improve print quality, for example less feathering and reduced black-color and color-color bleeding. Recently, pigment dispersions exhibiting increased stability due to specific resin additives have been claimed and carbon black based inks have been introduced into commercial printers² showing advantages in water and light fastness as compared to water soluble black food, acid or direct dyes.⁶

However, considerable progress has been achieved in developing water soluble dyes with improved water fastness due to differential solubility.^{1,7,8} Recently, the use of dyes versus pigments has been reviewed for various ink jet applications.^{9,10}

Accordingly, the choice of dye or pigment depends on how dye properties such as color gamut, transparency, color strength and ease of use are ranked against pigment attributes like light fastness, insolubility and crystallinity. So far, only carbon black based inks have appeared on the printer market but no trichromat based on color pigments. Obviously, the development of pigmented ink formulations with stable particle sizes < 100 nm to prevent light scattering has been a difficult target.

Significant parameters for the primary colors yellow, magenta and cyan used in the subtractive color system are peak wavelength, narrow and symmetrical absorption curves and the absence of secondary absorptions.¹¹

Dyes being present in the monomolecular state satisfy these requirements best. However, many dyes show anomalous spectroscopic behaviour at higher concentrations and do not appear to obey Beer's law. This effect is ascribed to the formation of dimers, trimers and higher aggregates of dye molecules. In most cases aggregation results in broader absorption curves and in a decrease of brightness. The purity of the reflected light is reduced which is also true for scattering of light from pigment particles.

Useful relationships between light fastness of colored substrates and the physical and chemical structures of colorants are well established.¹² Accordingly, besides the inherent photostability of the colorant, the degree of aggregation of the dye on the substrate belongs to the most important factors.¹³

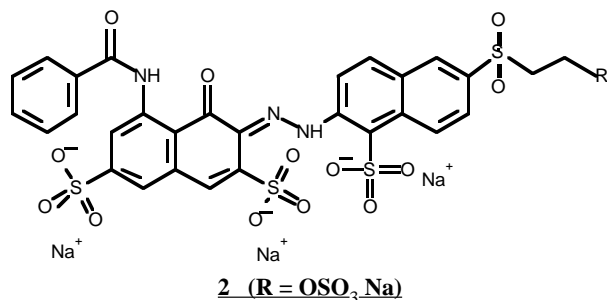
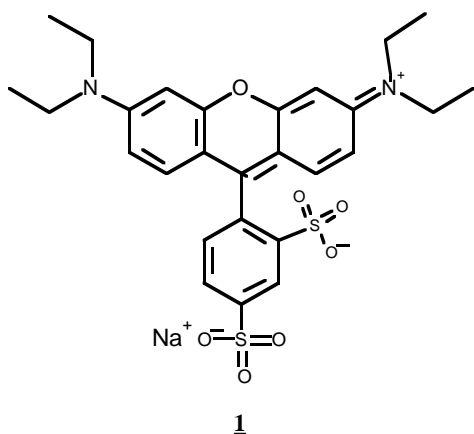
Clear electron micrographs of aggregates of direct dyes in cellulose films have been obtained showing a direct relationship between light fastness and aggregation. Dyes of low light fastness did not reveal any particles in the fibre while those with high light stability formed clearly detectable particles up to 1 μm . Correspondingly, the light

fastness of most pigments is related to the particle size because the surface area decreases as its particle size increases.¹²

Magenta Dyes, State of the Art

Magenta dyes exhibiting a combination of optimal brightness and hue, high light fastness, high water and rub fastness and good solubility are proving extremely difficult to develop.^{1,5}

Using xanthenes dyes such as CI Acid Red 52 **1**, ink jet prints are obtained showing excellent brightness in accordance with narrow absorption curves. However, **1** exhibits very poor light fastness, rated 2 according to the blue wool scale (1 to 8), and low water fastness.



The water fastness of **1** can be improved by introducing carboxyl groups, however the light fastness remains poor.⁷

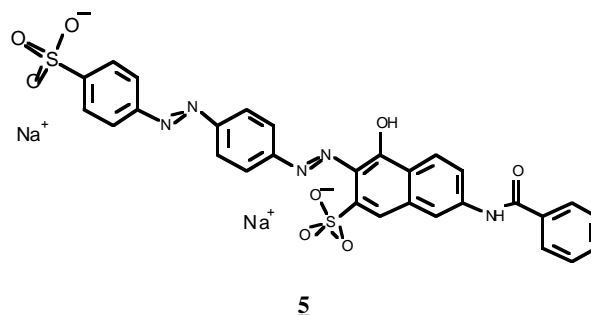
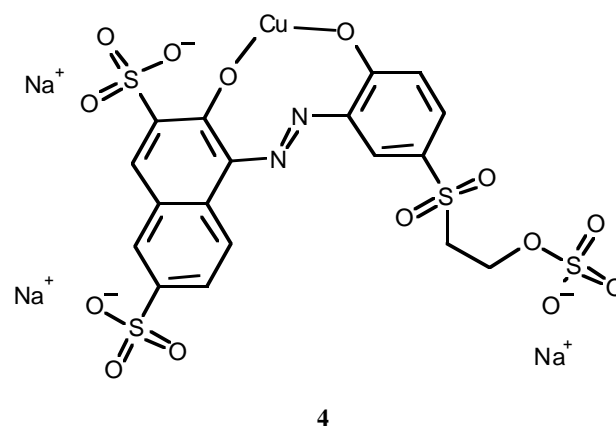
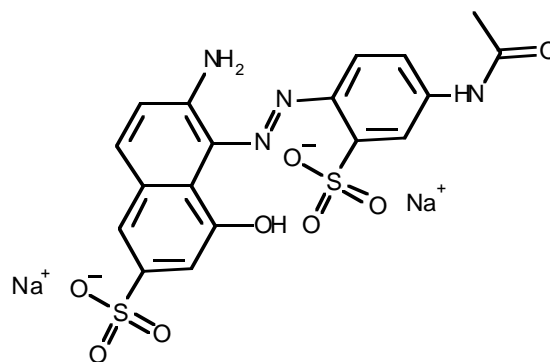
Monoazo dyes derived from H - Acid of the type CI Acid Red 249 or CI Reactive Red 180 **2** are used commercially exhibiting enhanced light fastness and a combination of high brightness and moderate water fastness.⁵

Dyes of type **2** mainly exist in the hydrazone form which has been related to moderate light fastness.¹⁴

In contrast to **2**, monoazo dyes of the type CI Acid Red 37 **3** exist exclusively in the azo form **14** and show increased light fastness as compared to hydrazone dyes **2**, however at the expense of brightness.

Light fastness is further improved in copper complex dyes such as CI Reactive Red 23 **4**.

A color change is observed towards duller shades which has been explained by the formation of sheet like aggregates.¹⁴



In addition to numerous patent applications directed to magenta ink jet dyes, mainly by modifying dyes of type **2**, **3** and **4**, magenta disazo dyes based on J-Acid derivatives have been proposed for ink jet printing.¹⁵

Disazo dyes like CI Direct Red 81 **5** are not suited as primary colors for ink jet printing due to secondary absorptions.⁵

In Table 1 spectroscopic properties and light and water fastness characteristics of dyes **1** to **4** are summarized.

Table 1. Properties of Magenta Dyes 1 to 4

Dye	λ_{max} (nm) (ϵ) ¹	light fastness ²	water fastness ³	dE ⁴
<u>1</u>	565 (89300)	2	30%	44.3
<u>2</u>	544 (31300) 520 (30500)	4	65%	10.7
<u>3</u>	513 (23500)	5	70%	8.1
<u>4</u>	524 (20000)	6	50%	4.8

1) 10^{-5} moles/l in water (pH 11.5)

2) blue wool scale; 2.5% ink in water/ diethyleneglycol

3) 1 min water immersion fastness

4) 96 h xenon test

Results and Discussion

Dye Aggregation

According to Figure 1, CI Acid Red 52 1 shows a sharp absorption band centered at 565 nm ($\epsilon = 90000$) at low concentration of 10^{-6} to 10^{-5} moles/l with a shoulder at 531 nm. By stepwise increasing the dye concentration to 3×10^{-4} moles/l the appearance of a definite absorption band at 531 nm ($\epsilon = 40000$) is observed, accompanied by a decrease of the molar extinction coefficient of the main band from 90000 to 80000. Obviously, aggregation to higher aggregates, probably dimers, occurs.

Disazo dye CI Direct Red 81 5 is extensively used for textile and paper applications due to good light fastness and high affinity to cellulose fibres.⁵ According to Figure 2, a marked secondary absorption at 395 nm can be detected at low concentrations of 10^{-5} moles/l. An increase in concentration results in a change in the absorption characteristics; the peak at 395 nm increases at the expense of the main absorption band.

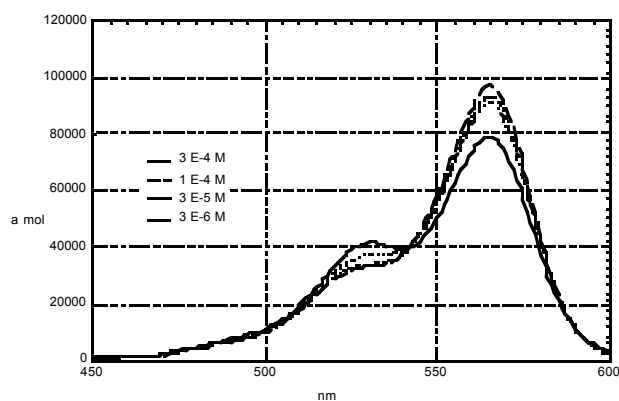


Figure 1. Variation of absorption spectrum of CI Acid Red 52 with concentration

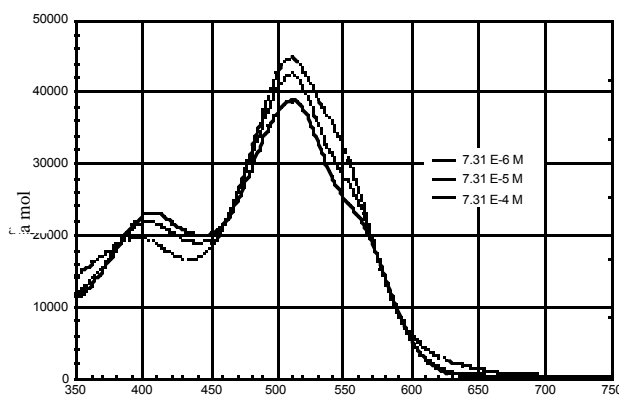


Figure 2. Variation of absorption spectrum of CI Direct Red 81 with concentration

Apparently, in planar dyes with extended conjugation, dye aggregation already occurs at low concentrations.

Self-association of CI Reactive Red 180 has been monitored spectrophotometrically at dye concentrations of 10^{-3} to 10^{-5} moles/l. The longer wavelength at 544 nm, most marked in dilute solutions, is typical of the monomer, while the band at 520 nm corresponds to the dimer.¹⁶ At higher concentrations further self-association can occur. However, rather than progressive association into trimers and tetramers, clustering to form larger aggregates usually occurs. This phenomenon is comparable with the self-association of surfactants into micelles above the critical micellar concentration (CMC) which can be determined by surface tension measurements.

An access to brilliant magenta dyes exhibiting enhanced water fastness is achieved by displacing the sulfate group in CI Reactive Red 180 2 with aliphatic amines to give dyes 6 to 9.^{5,17}

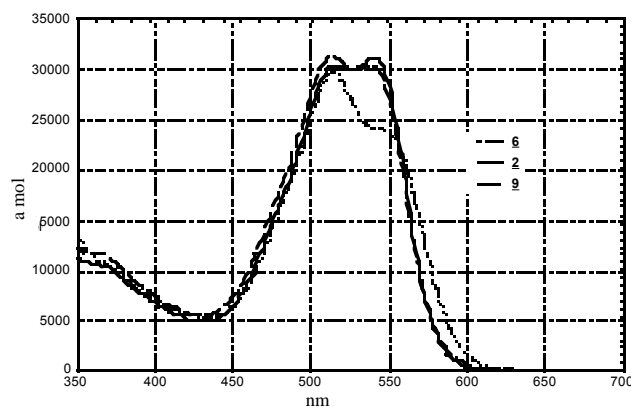


Figure 3. Absorption spectra of dyes based on CI Reactive Red 180 (10^{-5} molar in water)

In dyes 6 to 8 water fastness is improved without affecting the brightness of ink jet prints. Obviously, the improvement in water fastness is mainly due to hydrogen bonding between the amine group containing dye and the hydroxyl groups of the cellulose fibre and not to aggregation which normally leads to duller shades..

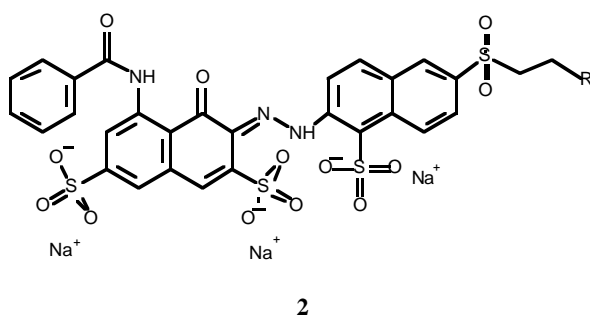


Table 2. Side Chain Modification of CI Reactive Red 180

Dye	substituent R	water fastness
2	OSO ₃ Na	66%
6	NH(CH ₂) ₃ N(CH ₃) ₂	80%
7	NHCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂	80%
8	NH(CH ₂ CH ₂ NH) ₂ CH ₂ CH ₂ NH ₂	80%
9	NH(CH ₂ CH ₂ NH) _n CH ₂ CH ₂ NH	90%

Table 3. Variation of Absorption Characteristics of Monoazo Dyes 3 and 4 with Concentration

Dye	concentration (moles/l, aq. buffer, pH 11.5)	λ_{\max} (nm) (ϵ)
3	10 ⁻⁵	513 (23500)
	10 ⁻⁴	508 (22800)
	10 ⁻³	503 (21900)
4	10 ⁻⁵	524 (20000)
	10 ⁻⁴	523 (19500)
	10 ⁻³	519 (16900)

Dyes 7 and 8 exhibit properties similar to 6. By fixing CI Reactive Red 180 to polyethylene imine, further improvement in water fastness is observed, however paired with a duller shade on paper probably due to self-association. The absorption spectra of dyes 7, 8 and 9 at dye concentrations of 10⁻³ to 10⁻⁵ moles/l indicate the predominant presence of dimers. A decrease of molar extinction coefficients at higher concentrations indicates an increase in dimer formation.

By varying the dye concentrations of monoazo dyes 3 and 4 between 10⁻⁵ and 10⁻³ moles/l no secondary absorption band is observed. However, as shown in Table 3, the absorption maximum is shifted to shorter wavelengths, accompanied by peak broadening and a decrease in molar extinction coefficients, which again can be ascribed to aggregate formation

Novel Water Soluble Polycyclic Magenta Dyes

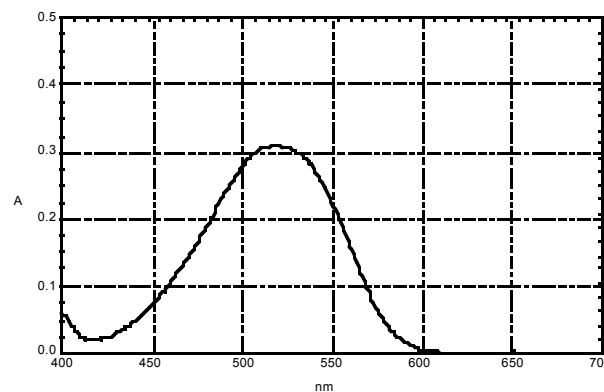
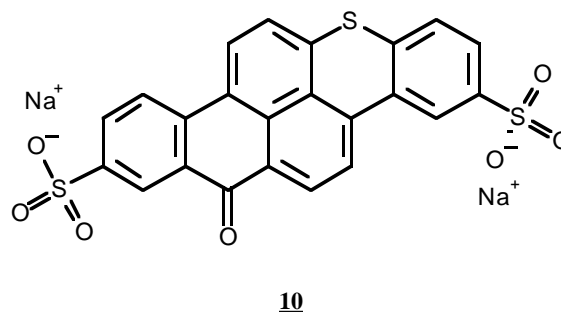
Sulfonated derivatives of copper phthalocyanine like CI Direct Blue 86 and CI Direct Blue 199 exhibiting high brightness, color strength and superior light fastness represent the industry standard of water soluble cyan ink jet dyes, both for piezo and thermal applications.¹ These cyan dyes are manufactured by sulfonation and sulfochlorination reactions of copper phthalocyanine.

Modifying magenta colorants of the solvent dyes, vat dyes and pigments range, novel water soluble polycyclic metal-free magenta dyes have been obtained whose potential for ink jet applications has been determined.

Solvent Dye Based

Sulfochlorination of CI Solvent Orange 63, subsequent hydrolysis of the initially formed sulfonylchloride and neutralization with sodium hydroxide results in the formation of water soluble polycyclic dye 10 in its form of the disulfonic acid, disodium salt 10¹⁸ exhibiting a bright magenta hue and fluorescence at 595 nm.

The absorption spectrum of 10 shows a narrow symmetrical absorption curve centered at 519 nm with no secondary absorptions.

Figure 4. Absorption spectrum of 10 ($\lambda_{\max} = 519$ nm, $\epsilon = 17500$)

Spectroscopic measurements of salt-free 10 in water at higher concentrations reveal an anomalous behaviour: the molar extinction coefficient decreases and the absorption maximum is shifted to shorter wavelengths.

As shown in Figure 5, the surface tension decreases as the dye concentration is raised and then remains nearly con-

Table 4. Variation of absorption maxima of 10 with concentration

concentration of <u>10</u> in water (moles/l)	λ_{\max} (nm) (ϵ)
10^{-5}	519 (17500)
10^{-4}	515 (16200)
10^{-3}	511 (14600)

stant. This is similar to the behaviour of classical surfactants, in which large aggregates are formed above the CMC.

Light fading of 10 is accompanied by an undesirable hue shift (dC: - 15,6; dH: - 2,4; dE: 16,0 after 96 hours xenon light exposure) probably due to oxidative fading. Control experiments show that the absorption maximum of 10 is shifted to shorter wavelengths upon oxidation with hydrogen peroxide in aqueous solution.

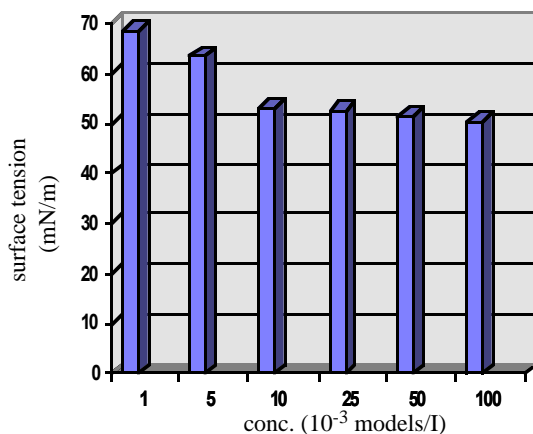


Figure 5. Variation of surface tension with concentration of 10 in aqueous solution.

Vat Dye Based

Thioindigo dyes 11 are used commercially as brilliant vat dyes for textile applications.¹⁹

Sulfochlorination of thioindigo derivatives 11 CI Vat Red 41 (R₁, R₂ = H) and CI Vat Red 1 (R₁ = CH₃, R₂ = Cl) at 100°C, followed by hydrolysis and neutralisation with lithium hydroxide results in the formation of thioindigo sulfonic acid lithium salts 12 A and 12 B.

Water soluble thioindigo dyes 12 A and 12 B exhibit symmetrical absorption curves centered at 545 nm and 537 nm, respectively, but low molar extinction coefficients as compared with xanthenes or azo dyes.

Ink jet prints on plain paper show a marked hue shift to dull, violet shades indicating aggregate formation on the fibre. Obviously, thioindigo dyes 12 show a similar behaviour as indigo. Here a drastic bathochromic shift and broadening of the absorption curve in the solid state have been observed as compared to monomer solutions of indigo.²⁰

Table 5. Absorption characteristics and fastness properties of thioindigo dyes 12

Dye	R ¹	R ²	λ_{\max} (nm) (ϵ)	light fastness	water fastness
<u>12 A</u>	H	H	545 (11500)	5	80
<u>12 B</u>	CH ₃	Cl	537 (9600)	5	80

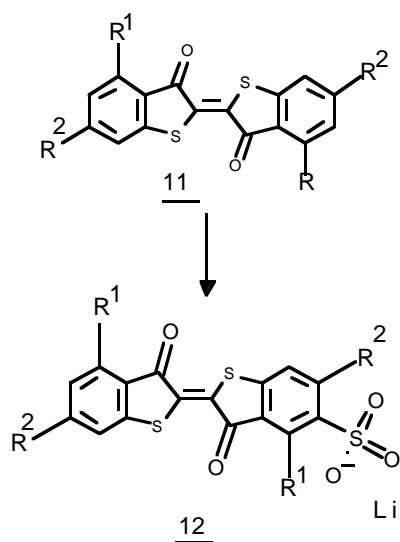
Pigment Based

By sulfonating CI Pigment Red 88 (tetrachloro thioindigo) sparingly water soluble products have been obtained probably due to increased association.

Quinacridones CI Pigment Violet 19 and CI Pigment Red 122 can be converted to water soluble disulfonic acid derivatives 13 A (R = H) and 13 B (R = CH₃) by sulfochlorination with chlorosulfonic acid at temperatures of 100 to 120°C followed by hydrolysis of the corresponding sulfonyl chlorides and neutralization with ammonia.

According to Table 6, dyes 13 A and 13 B exhibit broad absorption curves in the visible region and low molar extinction coefficients. Consequently, water soluble quinacridone derivatives are not suited for ink jet applications due to low color strength and dull hues.

However, the use of quinacridone based pigment dispersions exhibiting bright shades and high light fastness²¹ might be of interest if the development of stable inks with low particle size distribution succeeds.



Perylene dyes and pigments 14 are of industrial importance,^{21,22} also for electrophotography,²³ because of unique properties like high light fastness as well as superior thermal stability and chemical inertness.

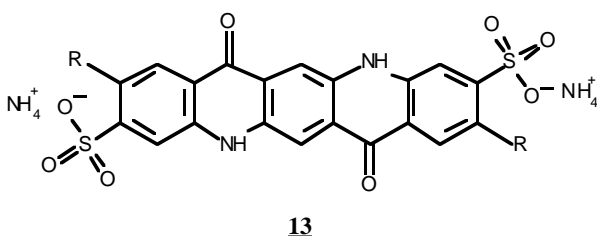
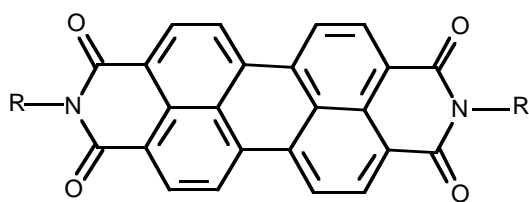
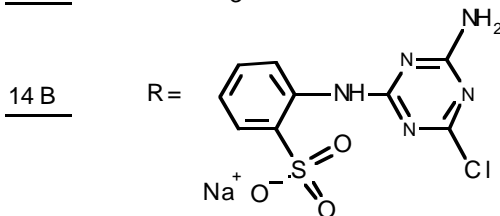


Table 6. Absorption Maxima of Water Soluble Quinacridone Dyes 13

Dye	R	λ_{\max} (nm) (ϵ)
<u>13 A</u>	H	299 (104000) 488 (5400) 526 (6200)
<u>13 B</u>	CH ₃	296 (87000) 532 (7400) 510 (6000)



14 A R = CH₃



UV/VIS-spectra of perylene dyes are only slightly influenced by substituents R or by solvents and show molar extinction coefficients of about 90000.²²

No water soluble products are formed by sulfochlorination of CI Pigment Red 179 14 A with chloro sulfonic acid in the temperature range of 100 to 120°C followed by hydrolysis and neutralization.

Biscondensation products of perylene tetra carboxylic acid with 1,4 diaminobenzene-2-sulfonic acid have been treated with cyanuric chloride and subsequently with ammonia to yield water soluble perylene dye 14 B.²⁴

However, magenta dye 14 B is not well suited as a primary color for ink jet printing due to secondary absorptions.

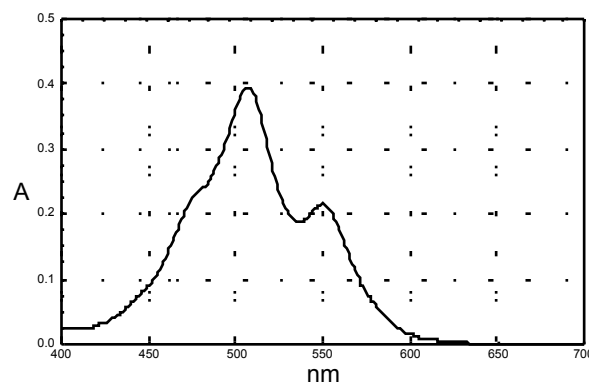


Figure 6. Absorption spectrum of perylene dye 14 B ($\lambda_{\max} = 507$ nm; $\epsilon = 30600$, 549 nm; $\epsilon = 16000$)

Conclusion

For near photographic color printing and wide format color graphics, dyes with narrow, symmetrical absorption bands are preferred; these display the highest chroma. This is true for the monomolecular state. Dye aggregation on the substrate results in higher light fastness but also influences the purity of the reflected light due to broadening of the absorption curves.

Novel water soluble magenta polycyclic dyes based on CI Solvent Orange 63, CI Vat Red 1, CI Vat Red 41, CI Pigment Violet 19, CI Pigment Red 122 and perylene dyes do not offer advantages in brightness of shade, color strength and light fastness as compared to known magenta dyes.

Xanthene dyes like CI Acid Red 52 show the desired brightness, however paired with low light and water fastness. Mono azo dyes of the type CI Reactive Red 180 exhibit a combination of acceptable brightness, light fastness and water fastness. Light fastness is further improved in dyes of the structure CI Acid Red 37 and copper complex dyes of the type CI Reactive Red 23, however at some expense of brightness.

The water fastness of reactive dyes can be conveniently improved by displacing reactive groups by amine substituents.

Despite many efforts to develop novel magenta dyes combining superior light stability, water fastness and optimal coloristic properties, all targets have not yet been reached.

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