

Novel Black Colorants for Ink Jet Applications

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Abstract

Within the competing non-impact printing systems, ink jet printing has achieved a dominant position due to considerable advances in printer and colorant technology, and its capability of printing black and color on many surfaces at low cost. The continuing innovations in the field of dyes, pigments and inks for this true primary printing process are reflected by an increase to more than 640 patent applications in 1995. For recent industrial ink jet applications such as near-photographic, wide format and bar-code printing there is a growing demand for light fast colorants.

In this paper, novel black disazo and tetrazo copper-complex dyes are presented exhibiting improvements in light stability as compared to metal-free black azo dyes. The improved light fading resistance can be explained by enhanced dye aggregation. Furthermore, novel heavy metal-free black polyazo and polycyclic dyes for industrial ink jet applications have been developed on a pilot scale showing superior light fastness and bar code readability using infrared lasers. Optical as well as light and water fastness characteristics of the novel dyes are compared with commonly used heavy metal-free colorants.

Introduction

In addition to desktop printing, new applications such as wide format color graphics, photographic imaging, and multifunction, color office and industrial printing are providing optimistic marketing opportunities for ink jet printing devices [1].

Within the different components comprising a reliable ink jet system, inks play a decisive role. Depending on the specific ink jet technology, three different types of inks are used: aqueous, solvent and hot melt. Solvent dyes are mainly used for continuous industrial and hot melt printers; for drop-on-demand printers, both office and thermal, aqueous inks are preferred. Consequently, colorants for aqueous based inks are water soluble dyes selected from Food, Acid, Direct, Reactive and Sulfur Dyes. Additionally, carbon black - based dispersions with increased stability due to specific resins have been introduced to commercial printers [2].

The subjects of the continuing high level of patent applications are mainly directed toward ink formulations, tailoring of dyes to meet specific ink jet requirements [3] and improved pigment dispersions.

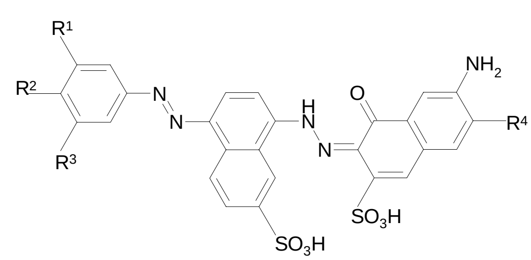
Considerable progress has been achieved by developing water soluble dyes with good water fastness on plain paper due to pH dependent differential solubility [2] and pigment-like light fading resistance.[4] Useful relationships between fading resistance and the chemical structure of colorants are well established [5]. Besides the inherent photostability, the degree of aggregation on the substrate belongs to the most important criteria. Dyes of low light stability do not reveal a significant aggregation whereas with dyes of high light fastness, particles up to 1 micron are formed on the substrate which are clearly detectable by electron microscopy [6].

This is the point where dyes meet pigments. The light fastness of most organic pigments is related to their particle size. Once they are fine enough to pass the nozzles of modern print heads and match the color space of dyes they partly lose their inherently better light stability because of the larger accessible surface area [5]. In addition, the light permanence of printed images is strongly influenced by the image receiving layer [7].

Black Colorants, State of the Art

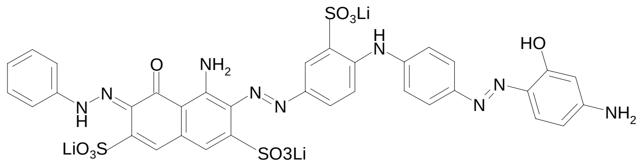
Considerable research effort has been invested in developing black dyes for ink jet applications [2,3].

By replacing sulfonic acid groups in C.I. Food Black 2 (1 A) with less acidic carboxylic acid groups, bluish-black dyes of the type (1 B) have been introduced to the market exhibiting high water fastness due to differential solubility [8].



1 A (R^1, R^3 = H; R^2, R^4 = SO_3H)
1 B (R^2, R^4 = H; R^1, R^3 = COOH)

As a result of developing safe replacements for black benzidine based dyes, C.I. Direct Black 168, lithium salt (2) has been successfully introduced to the ink jet market [9].



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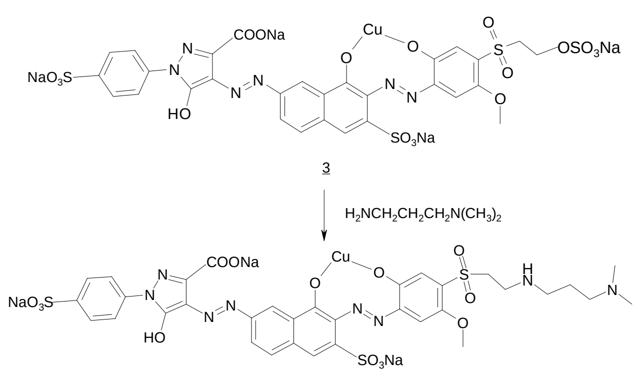
Key advantages of C.I. Direct Black 168, lithium salt include high print optical density, neutral black shade, good solubility, good water and light fastness on different media and thermal stability for bubble jet applications.

Other black dyes that have been used for ink jet printing include the trisazo dyes C.I. Direct Black 154, C.I. Direct Black 171, tetrakis azo dye C. I. Direct Black 19 and C.I. Solubilized Sulfur Black 1 [2].

Results and Discussion

A recent trend in ink jet technologies is toward smaller nozzle diameters for high resolutions and a higher number of jets for print speed. To prevent nozzle clogging, dyes are preferred for many applications even though pigment dispersion chemistry has improved in the past few years [10].

For newly emerging markets such as wide format printing and photographic imaging, there is a growing demand for light fast dyes. It is well established that fading stability is considerably improved in copper complex dyes which has been explained by the formation of sheet-like aggregates on the substrate [5].



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Scheme 1: Modification of C.I. Reactive Black 31

The properties of disazo copper complex dyes of the type C.I. Reactive Black 31 (3) can be adjusted to specific ink jet requirements[11]. According to *Scheme 1*, Reactive Dye 3 is converted to dye 4 by adding 3-dimethylamino propylamine. As expected, light fastness, hue and absorption characteristics of 3 and 4 are comparable. However, by introducing external amino groups, water fastness of ink jet prints is improved, especially on acidic ink jet papers. This effect can be explained by the formation of sparely soluble betaine structures formed by protonation of the external amino group.

Table 1 summarizes the properties of metal-free and copper complex disazo dyes.

Table 1: Properties of metal-free and copper complex disazo dyes 1A, 1B, 3, 4

Dye	Light Fastness [a,c]	Water Fastness [b)] Inkjet Paper [c)]	Plain Paper [d)]
1 A	2	62 %	31 %
1 B	1-2	98 %	95 %
3	4	82 %	30 %
4	4	98 %	33 %

a) Blue Wool Scale; ink jet prints containing 4 % dye
b) 1 min water immersion test
c) HP Premium Inkjet Paper (HP 51634Z)
d) Plain Paper Kompass Data Copy, No. 2228010001

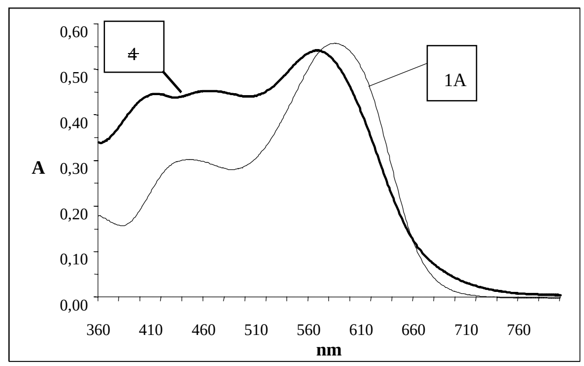
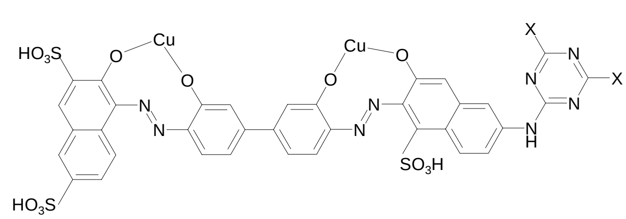


Figure 1: Absorption spectra of
1 A (λ_{max}^{1}=447 nm,ε=18520;λ_{max}^{2}=586 nm,ε =34170)
4 (λ_{max}^{1} =414 nm, ε =21300; λmax^{2}=569 nm,ε=21300)

As compared to metal-free bluish-black dyes 1A and 1B, copper complex dye 4 offers both a neutral black shade and higher light stability.

Disazo copper complex reactive dyes of the type 5A (X = Cl) have also been modified by replacing the chlorine atoms in the cyanuric moiety. With amines, e.g. taurine, dye 5B (X = $NHCH_2CH_2SO_3Na$) is formed which shows improved solubility and stability of inks [12]. Similar to copper complex dye 4, a high light fastness is observed with dye 5. However, dyes of the type 5 exhibit dark blue shades (absorption spectrum see Fig. 3).

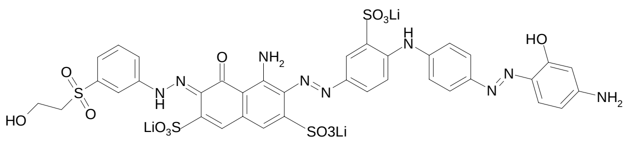


5

To obtain neutral black shades, these dyes have to be combined with light fast yellow and red dyes, respectively.

Another approach has been to covalently link a navy blue disazo copper complex dye with an orange dye, using a chlorotriazine as the linking group [13].

In trisazo dye 6 which is formed by introducing hydroxyethyl sulfonyl groups into C.I. Direct Black 168 (2) , both solubility, water fastness and light fastness are improved as compared to the parent dye [14] .



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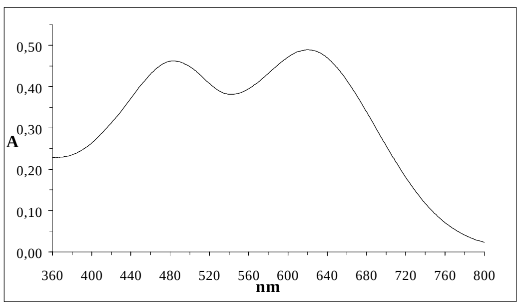
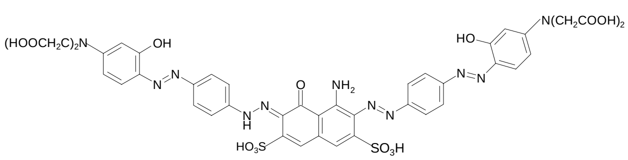


Figure 2: Absorption spectrum of 6
(λ_{max}^{1} = 483 nm*; ε = 34130; λ_{max}^{2}: = 619* nm*; ε = 36100)*

Neutral black prints exhibiting high optical density are obtained with dye 6 covering the whole visible region as indicated in *Figure 2.*

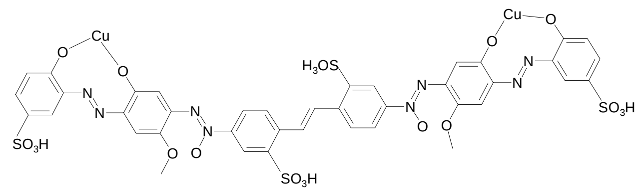


7

Tetrakis azo dye C.I. Direct Black 19 has been modified by selectively introducing carboxylic acid groups; as expected, dye 7 exhibits improved water solubility and high optical density.[15]

As shown in the absorption spectrum of tetrakis azo copper complex dye 8, the whole range of the visible spectrum is covered .

This dye exhibits a neutral black shade combined with a high fading resistance. However, the solubility of the common sodium dye 8A is poor and has to be adjusted to ink jet requirements. As shown in *Table 2*, this can be achieved by conversion to its lithium or triethanolammonium salt 8B or 8C , respectively [16].



8

Table 2 : Properties of black tetrakisazo stilbene copper complex dyes 8A, 8B, 8 C

Dye	Cation	Solubility [a)]	Light Fastness [b)]
8A	Na^+	3 %	5-6
8B	Li^+	7 %	5-6
8C	$HN^+(CH_2CH_2OH)_3$	10 %	5-6

a) H_2O, 25 °C
b) Blue Wool Scale ; ink jet prints with inks containing 4 % dye

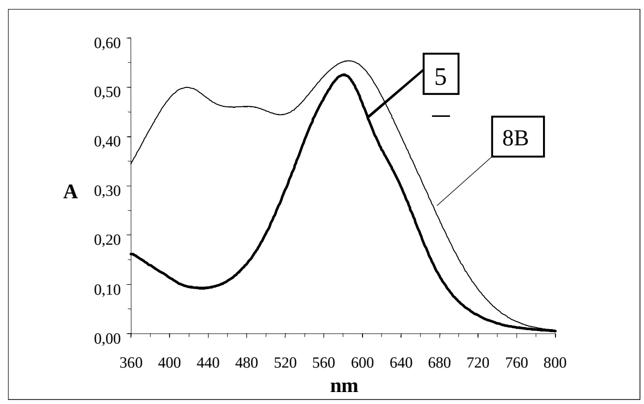


Figure 3 : Absorption spectra of copper complex dyes
5B (λ_{max} = 580 nm ; ε = 46790)
8B (λ_{max}^{1}=417 nm,ε =23620; λ_{max}^{2}=585 nm,ε=29060)

For ecological and toxicological reasons novel chromium-free dyes with good solubility in alcoholic solvents have been developed on a pilot scale.

The novel polycyclic dyes are obtained by the oxidation of C.I. Solubilized Sulfur Black 1 and subsequent cation exchange with specific long chain alkyl ammonium salts like 2-ethylhexyl ammonium chloride [17].

Table 3 shows that the tailor-made product surpasses the chromium complex dye C.I Solvent Black 27 with respect to light fastness and solubility in ethanol.

As depicted in Figure 4, the absorption spectrum of C.I. Solubilized Sulfur Black 1, 2-ethyl hexylammonium salt exhibits absorption bands in the near infrared region thus proving bar code readability using infrared lasers or light emitting diodes (LEDs).

Table 3: Properties of oxidized C.I. Sulfur Black 1

Dye	Cation	Solubility [a)] H_2O Ethanol	Light Fastness [b]
C.I. Sol.Sulfur Black 1	Na^+	15 % < 1 %	7-8
Oxidized C.I. Sulfur Black 1	Na^+	15 % < 1 %	7-8
Oxidized C.I. Sulfur Black 1	$H_3N^+C_8H_{17}$	< 1 % 15 %	7-8
C.I. Solvent Black 27		< 1 % 4 %	6

a) 25 °C
b) Blue Wool Scale

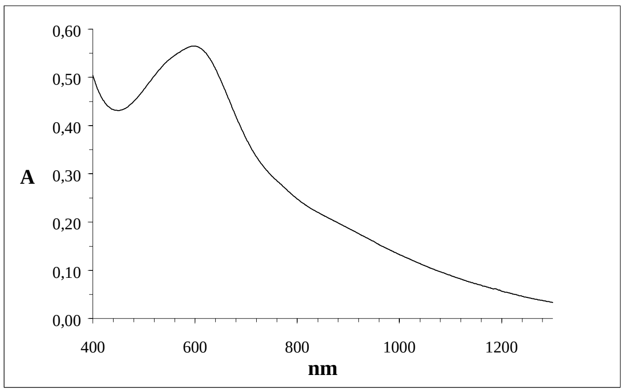


Figure 4: Absorption spectrum of oxidized C.I. Solubilized Sulfur Black 1, 2-ethyl hexylammonium salt in ethanol (54,7 mg/l)

Conclusion

For wide format printing, photographic imaging and industrial applications light fast colorants are required.

By selecting copper complex azo dyes, polyazo and polycyclic dyes and tailoring them for ink jet applications, novel black dyes exhibiting high light fading resistance have been developed.

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Biography

Wolfgang Bauer received his Ph. D. in Chemistry at the Technical University of Darmstadt, Germany, in 1968. Subsequently, he was granted postdoctoral fellowships in the USA at Yale University, New Haven, and IBM Research Laboratories, San Jose, California.

Dr. Bauer joined Cassella AG, a member of the Hoechst group of companies, in 1973 and is now with Clariant GmbH, Works Cassella-Offenbach, Frankfurt, where he is a member of the Product Management of New Systems/ NIP within the Division Pigments & Additives.

His current interests are focused on dyes and pigments for ink jet applications.