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The Role of Organic Molecules in Colour Hard Copy

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ABSTRACT

The differences between a dye and a pigment and the advantages and disadvantages of each are described. The three main hi-tech processes for producing colour hard copy, namely thermal, ink-jet and electrophotographic, are explained and the different requirements of colourants for each technology emphasised. In addition to providing the final print image, coloured molecules are also employed as key components in producing this image in electrophotography because of their electrical and photoelectrical properties. These are also discussed.

INTRODUCTION

Many papers deal with the technology of colour hard copy but very little has been presented about the raw materials, i.e. the chemicals which are essential for the technologies to work. An attempt is made in this paper to remedy this situation by explaining the role of organic molecules, particularly coloured organic molecules, in producing colour hard copy.

The paper concentrates on the three most important technologies, namely thermal, ink-jet and electrophotography. The conventional technologies of silver halide photography and impact printing are not discussed. It also provides an insight into how a raw materials supplier views and approaches the colour hard copy area.

ORGANIC MOLECULES

As shown in Fig. 1, the organic molecules used for producing colour hard copy can be either coloured or non-coloured. The coloured organic

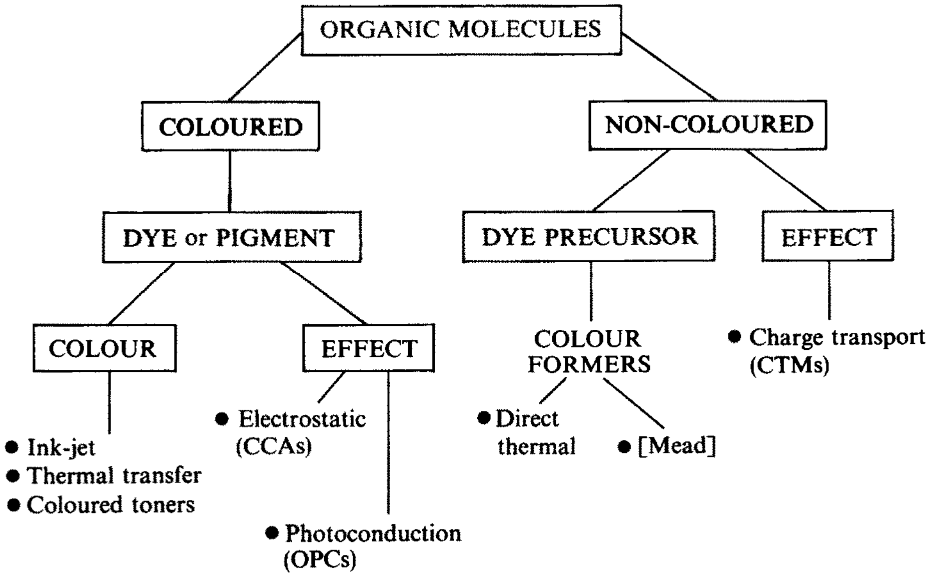


Fig. 1. Organic molecules used for producing colour hard copy.

molecules can be divided into two types: dyes and pigments. These can be used for their colour itself, as in ink-jet dyes, thermal transfer dyes and pigments, and in coloured toners. Alternatively, coloured molecules can be used for some other effect apart from their colour, for example electrostatic effects, as in charge control agents for toners, and photoconductive effects, as in organic photoconductors.

The non-coloured molecules can be similarly divided into two types: those which function as colour precursors and those which are used for a special effect. Colour formers are an example of dye precursors. These are used in direct thermal printing and in the related full colour process developed by the Mead Corporation. Charge transport materials are an example whereby colourless molecules are used for a specific effect, in this case the transport of electric charge.

Coloured organic molecules—dyes and pigments

As already stated, the coloured organic molecules can be classified into dyes and pigments. What is the difference between a dye and a pigment? And what are their advantages and disadvantages? The classical definition of the difference between a dye and a pigment is that a dye, at some stage during its application process to a substrate, passes through a *solution* phase. A pigment, on the other hand, remains completely *insoluble*. Therefore, in simple terms, a dye may be considered as a soluble coloured material (either in water or organic solvents) whereas a pigment is a coloured material which is insoluble in both water and organic solvents. As seen from Fig. 2, the advantages of dyes are that they are bright, tinctorially strong, transparent and cover a larger colour gamut owing to the much greater availability of dyes relative to pigments. The main deficiency of dyes is their lower fastness to various agents such as light, heat and solvents. In contrast, the main advantage of pigments is their high fastness to these same agents. They can also exhibit high crystallinity, a feature which is very useful in certain applications. The disadvantages of pigments are that they are duller, weaker and have some degree of opacity.

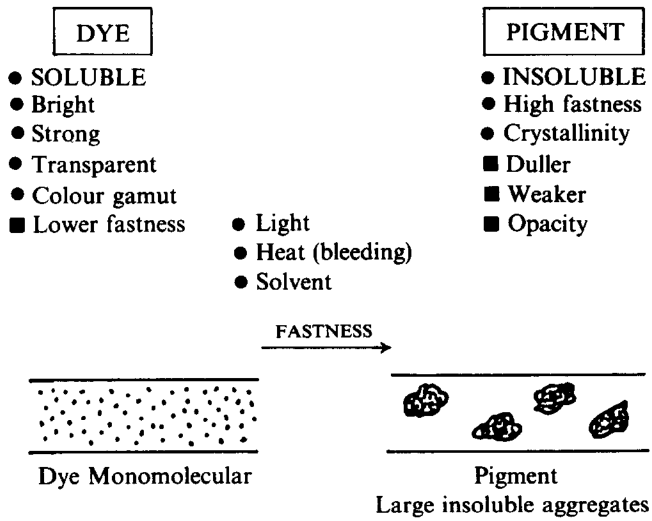


Fig. 2. The advantages and disadvantages between dyes and pigments.

The explanation for some of these properties is shown in Fig. 2. A dye, being soluble, is generally present in the monomolecular state. This accounts for the transparency and high strength of dyes. However, it also presents a large surface area for attack by light and solvents and this accounts for the lower fastness properties of dyes. In contrast, pigments are present as large, insoluble aggregates comprising many individual molecules. This explains their high fastness to water and solvents, and to heat and light since the surface area available to attack is very small. It also explains their opacity and lower tinctorial strength since only the molecules near the surface absorb the light.

The choice of either dye or pigment depends upon the effect required and the intended application.

- Potential market (colour hard copy)
- Strategy

Two approaches

1. Existing materials (modified)
2. Novel materials

Option 1—adopted if possible

- Availability
- Cost effective

Option 2—expensive/delay

- Research
- Development
- Tox (mfr / use)

£80 000 • Registration • Europe • USA • Japan

Large market / High quality ⟶ Option 2

Fig. 3. The colour manufacturer's strategy.

COLOUR MANUFACTURER'S STRATEGY

Having identified the colour hard copy area as a potential market, what strategy does the colour manufacturer apply to supply that market? There are two approaches. The first is to use existing materials, modified or purified if necessary, and this approach is adopted if at all possible because of the ready availability of the materials and the cost saving. The second approach is to invent a completely new material. This is an expensive option since it not only involves the research and development costs but also the toxicology testing and registration costs (see Fig. 3). These factors also mean a time delay of several years before a novel material reaches the marketplace.

MAJOR TECHNOLOGIES

As seen from Fig. 4, the three major technologies for producing colour hard copy are thermal, ink-jet and electrophotography. These may be subdivided further. The types of organic molecules used in these technologies will now be considered, beginning with the thermal technologies.

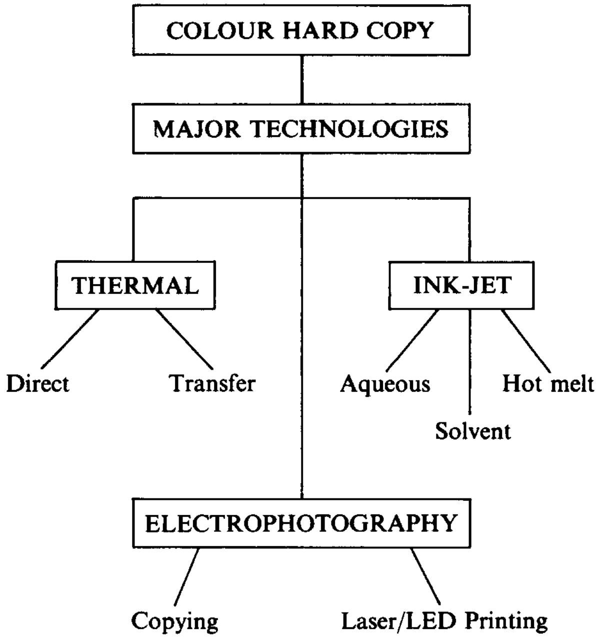


Fig. 4. The major technologies for producing colour hard copy.

Direct thermal printing

Direct thermal printing is exemplified by thermal paper, which is white paper that produces colour when written on with a heated element (stylus or thermal head). The colour is monochrome, mainly black but also blue.

The molecules used are colourless ones that can generate colour, i.e. colour precursors or colour formers. The thermal paper contains a coating of dispersed colour former and a solid acidic resin. The application of heat melts the acidic resin which in turn contacts the colour former and generates the (black) dye. The structures of a typical black colour former and the resultant black dye are shown in Fig. 5.

Both the print quality and fastness, particularly lightfastness, of direct thermal prints are poor.

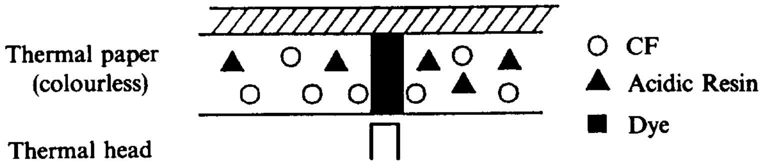
Recently, the Mead Corporation have produced full colour prints using colour formers. In this case, yellow, magenta and cyan colour formers are used and the process is pressure-sensitive rather than thermally sensitive.

There are two types of thermal transfer: wax transfer and dye diffusion thermal transfer (D2T2).

Thermal wax transfer

In thermal wax transfer the colour sheet or ribbon consists of a very thin

- Process



Monochrome: Black or Blue

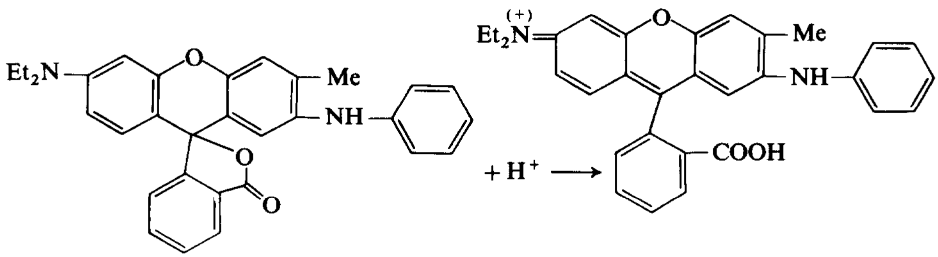
- Properties

Colourless molecule ⟶ Coloured molecule (Dye)

Colour precursor

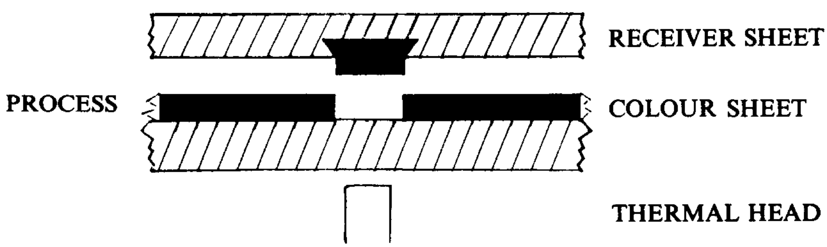
COLOUR FORMER

- Chemistry ○ + ▲ → ■



- Quality/Fastness—poor

Fig. 5. Direct thermal printing.



PROPERTIES REQUIRED

- FASTNESS
  - heat (non-bleeding)
  - light
- COMPATIBILITY
  - dispersibility

PIGMENTS

Y Azo
M Quinacridone/azo/xanthene
C Phthalocyanine
B Carbon black

EXISTING PIGMENTS

Fig. 6. Thermal wax transfer.

(*c.* 6 μm) plastic film coated on one side with a dispersion of a colourant in a solid low-melting-point wax. Application of heat from a thermal head from the reverse side melts the wax and the molten wax plus colourant is transferred to the receiving substrate, usually paper or an overhead slide. Two points to note are (a) that it is generally a total transfer process and (b) that the majority of transferred wax plus colourant resides on the surface and is thus prone to smearing. As seen from Fig. 6, the properties required of the colourant are fastness, especially to heat treatments (non-bleeding and non-sublimable) and to light. Furthermore, the colourant must be compatible with the wax, giving a homogeneous dispersion. Pigments fit these requirements best and it is no surprise that most commercial wax transfer systems are based upon pigments. Typically, the yellows are azos; the magentas, either quinacridone, azo or xanthenes; the cyans, phthalocyanines; and the blacks, carbon black.

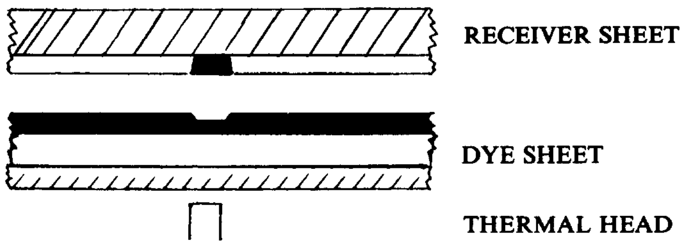
The market is relatively small, the technology does not produce high-quality prints and in keeping with the guidelines offered earlier (Fig. 3) it is existing pigments that are generally used in thermal wax transfer.

Dye diffusion thermal transfer (*D2T2*)

The more recent thermal transfer technology is Dye Diffusion Thermal Transfer or D2T2 for short. The dyesheet again comprises a thin plastic film, usually 6 μm polyester, coated on one side with a heat-resistant 'backcoat' and on the other side with a colour coat. This consists of an intimate mixture of colourant and binder (to 'glue' the colourant to the substrate). The receiver sheet is normally a white plastic sheet containing a thin film of a clear (co)polyester receiving layer (see Fig. 7). Heat supplied from the thermal heads, usually at high temperature (up to 400°C) for short times (milliseconds) transfers the colourant from the dyesheet into the receiver sheet. Points to note are that the colourant actually dissolves in the receiver sheet (i.e. does not sit on the surface; cf. thermal wax transfer) and that the amount of dye transferred is proportional to the quantity of heat supplied so that true grey scales are achieved.

The properties of thermal transferability and solubility mean that dyes rather than pigments are used as colourants in D2T2. As seen from Fig. 7, the dyes have to satisfy a number of demanding criteria and it has been found that existing dyes generally do not fulfil all these criteria. The ability of D2T2 to produce grey scales and to attain high optical densities ($>2{\cdot}0$) means that high-quality prints can be produced to rival those of conventional silver halide photography. Thus, the two factors of an enormous market and a high-quality product both apply and it is therefore not surprising that there is intensive research to find novel dyes for D2T2.

● PROCESS



● PROPERTIES REQUIRED ● THERMAL TRANSFERABILITY
● SOLUBILITY (IN RS)

DYES

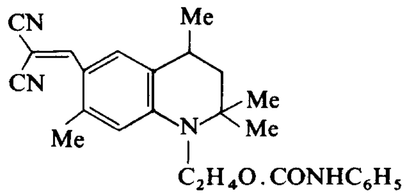
- Colour — YMC [B]
- Strength — OD
- Solubility
- Thermal stability (up to 400°C)
- Fastness
  - LF } Image stability
  - HF } Image stability
  - DS stability
- Toxicology — Ames-ve

● GREY SCALE
● HIGH ODs (>2·0) ⟶ HIGH QUALITY Ag Hal PHOTOGRAPHIC MARKET

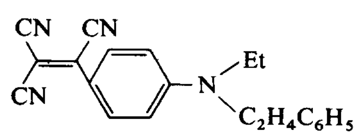
NOVEL DYES

Fig. 7. Dye diffusion thermal transfer (D2T2).

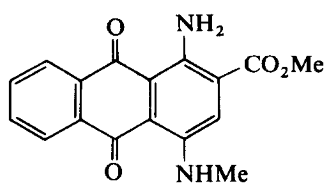
Y Azo
Hydrazone
Quinophthalone
METHINE



M Azo
Anthraquinone
TRICYANOVINYL



C Azo
Indoaniline
ANTHRAQUINONE



● Small molecules
● Solvent or disperse

Fig. 8. D2T2 dyes.

D2T2 dyes. Figure 8 shows the major classes of dyes evaluated in the three shade areas of yellow, magenta and cyan. Typical structures are shown. Points to note are that the molecules are small (to allow thermal transfer and subsequent diffusion into the receiver sheet) and that they belong to the solvent or disperse dye classes.

Laser thermal transfer

The thermal technologies, unlike the ink-jet and electrophotographic technologies, can undergo a step change by switching from thermal heads to lasers as the energy source. As seen from Fig. 9, lasers offer many benefits.

STEP CHANGE

THERMAL HEADS ⟶	LASERS
• Slow	• Fast
• High power usage	• Low power usage
• Limited resolution	• High resolution
	• Non-contact

Fig. 9. Advantages of lasers over thermal heads for thermal transfer.

Ink jet

The colour manufacturer is not really concerned about the various aspects of ink-jet technology such as continuous, drop-on-demand, piezo, etc.; in fact, all he needs to know are the answers to two basic questions:

(1) What is the solvent?
(2) Is it thermal ink-jet?

Ink-jet dyes

Knowing these answers, he can then produce the appropriate colourant.

The main properties required for an ink-jet colourant are high solubility in the appropriate solvent, good fastness properties and highly pure dyes. These apply to any ink-jet colourant. In addition, high thermal stability is required of a colourant for a thermal ink-jet system. Solubility is a prime requirement so obviously dyes rather than pigments are the colourants for ink-jet systems.

Dyes for aqueous-based ink-jet systems belong to the acid, food and especially the direct types and are typically azos or phthalocyanines. C.I. Direct Yellow 86 and C.I. Direct Blue 199 are representative dyes (see Fig. 10). The group conferring water solubility is the sulphonic acid group

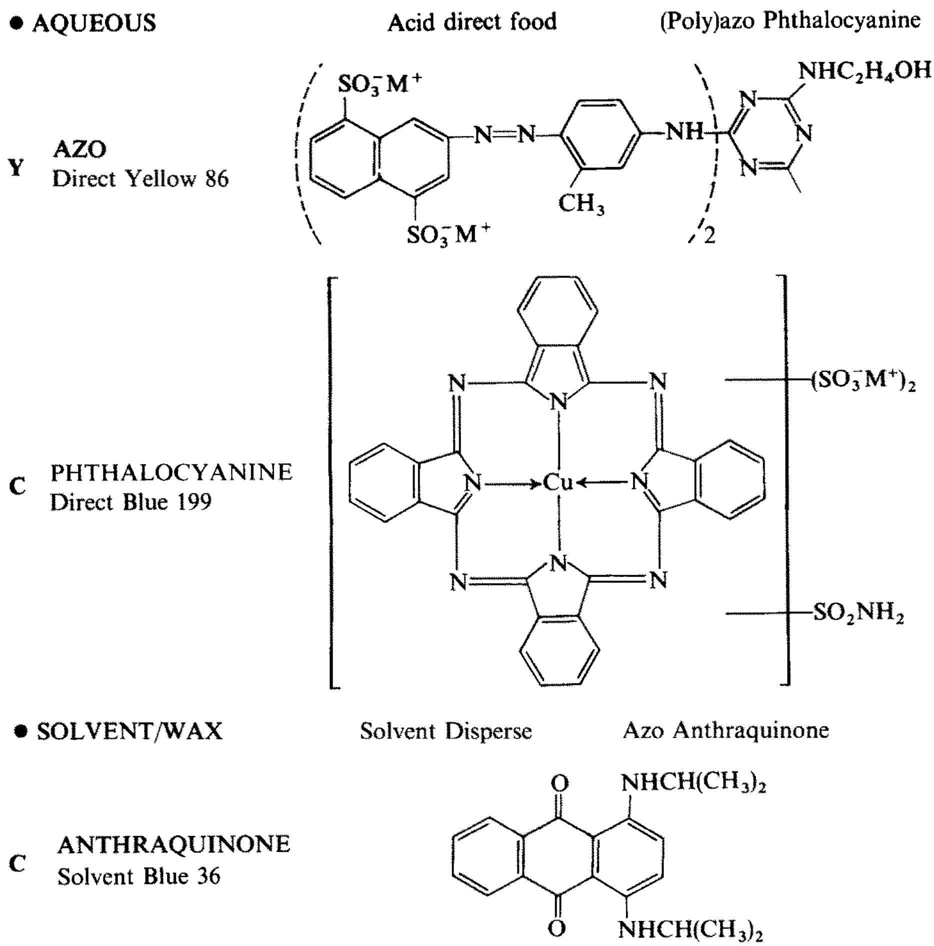


Fig. 10. Dyes for aqueous-based and solvent-based ink-jet systems.

($SO_3^-M^+$). The metal cation (M^+) affects the solubility: lithium is particularly useful for providing high aqueous solubility.

Ink-jet dyes for solvent- or wax-based systems are normally of the solvent or disperse type and are typically azos or anthraquinones. Obviously, they are devoid of polar, water-solubilising groups such as sulphonic acid; instead, they contain solvent-promoting groups such as alkyl. C.I. Solvent Blue 36 is a representative dye (see Fig. 10).

Electrophotography

This is by far the biggest of the reprographic technologies but it has yet to make a real impact in full colour printing (>99% is monochrome, i.e. black).

The basic process, whether it is photocopying or laser/LED printing, can be described by the five basic steps shown in Fig. 11. In the first step, the photoconductor drum or belt is given a uniform electrostatic charge of several hundred volts. As the name implies, a photoconductor is a conductor of electricity in the presence of light. Therefore, in the second step, the imaging step, the laser or LED writes on the photoconductor and dissipates the electrostatic charge. This produces a latent electrostatic image on the photoconductor of a charged background area and an uncharged image area. The third step, the development step, consists of rendering this latent image visible by treating with a toner. The toner particles have the same charge as the background and are repelled into the uncharged imaged areas. The fourth and fifth steps simply involve the transfer and thermal fixation of the toner to plain paper. This is the reason why copies emerge hot from a photocopier or printer!

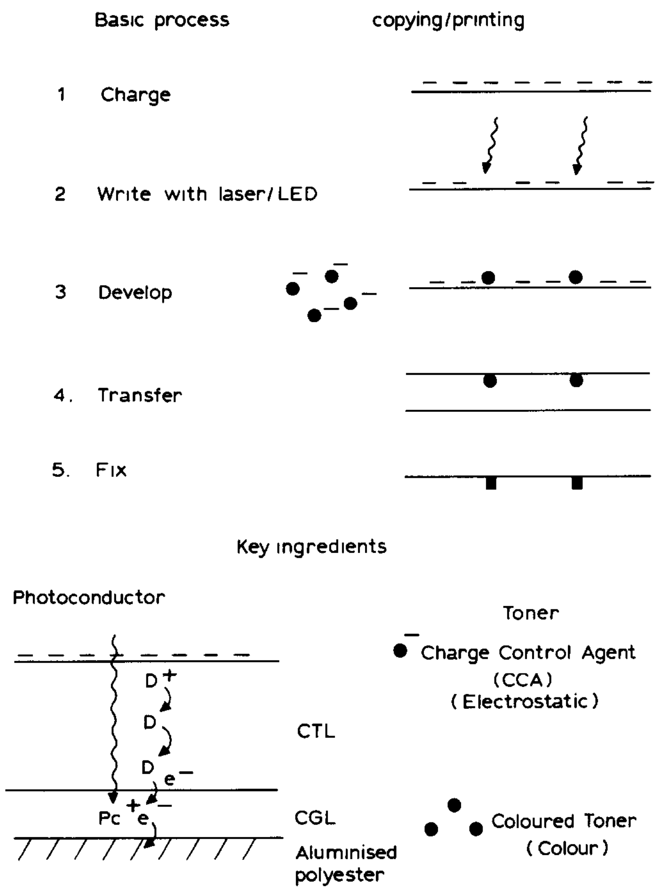


Fig. 11. The basic processes in electrophotography.

The key ingredients are the photoconductor, and this is now mainly an organic photoconductor, and the toner. Organic photoconductors are dual-layer devices, comprising a thin charge generation layer (CGL) on top of which is a thicker charge transport layer (CTL). Light passes through the transparent CTL and upon striking the CGL, which usually contains a pigment, forms an ion-pair complex. The electron passes to earth leaving a positive hole which is transported to the interface—hence the need for pigments of high crystallinity in the CGL to avoid crystal defects which can trap the positive holes and hinder their transport to the interface. The CTL contains highly electron-rich compounds which readily donate an electron to the positive hole, forming a positive hole in the CTL: this is transported to the surface by a hopping mechanism where it then neutralises the negative charge. Thus, the key chemicals in OPCs are the charge generation materials (CGMs) in the CGL and the charge transport materials (CTMs) in the CTL.

There are two types of coloured molecules that are used in the toner, namely the charge control agent (CCA) and the colourant. The CCA is used to impart and control the triboelectric charge on the toner particles (negative in Fig. 11) whereas the colourant is used for its colour. This is normally black but can be yellow, magenta or cyan in coloured toners.

Charge generation materials (CGMs)

These are coloured molecules which are used not for their colour but for a special effect, namely photoconduction. The first property of a CGM is that it has to be compatible with the light source. This is white light (*c.* 400–700 nm) for copiers and red (~630 nm) and near-infrared (~800 nm) for LED/laser printers respectively (see Fig. 12). The other properties which a CGM has to fulfil are shown in Fig. 12: it is apparent that pigments are more appropriate than dyes.

The structure of a typical red pigment, dibromoanthanthrone, for white light copiers and a blue pigment, x-form metal-free phthalocyanine, for laser/LED printers are shown.

Charge transport materials (CTMs)

These are colourless molecules which are used for an effect, namely charge transport, rather than as colour precursors.

As seen from Fig. 13 they are electron-rich conjugated molecules with low ionisation potentials and are easily oxidised; in other words, they readily donate an electron. They also have to be very pure, solvent-soluble and non-toxic, particularly Ames-negative. CTMs fall into a relatively small number of chemical types of which the most important are oxadiazoles, pyrazolines, amines and especially leucotriphenylmethanes and hydrazones. Common

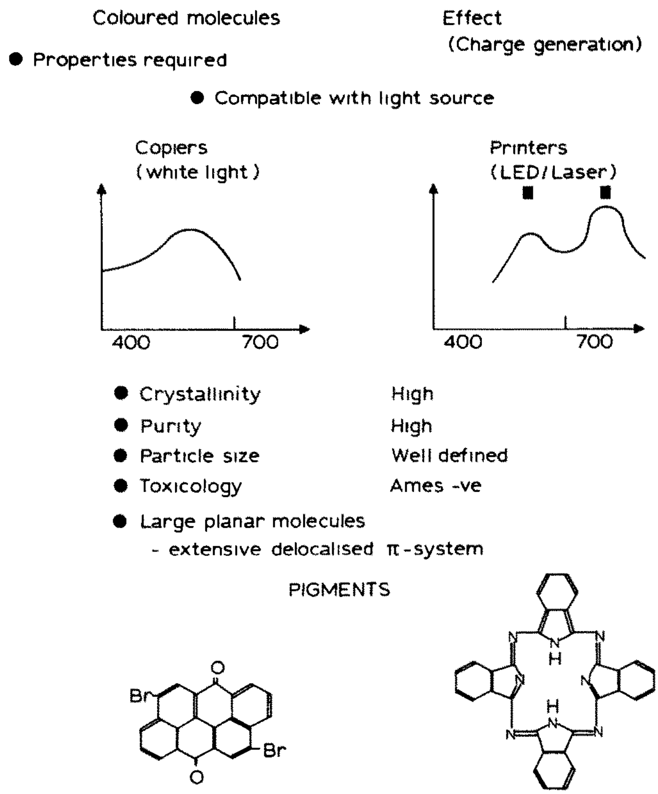


Fig. 12. Charge generation materials (CGMs).

structural features are a number of benzene rings and powerful electron donor groups such as diethylamino (Fig. 13).

Specific combinations of CGMs and CTMs often function the best.

Both CGMs and CTMs tend to be a mixture of both existing materials, usually highly purified, and novel materials.

Toners—charge control agents

Charge control agents (CCAs) can be coloured or non-coloured molecules which are used for a special effect, namely imparting electrostatic charge to toner particles. There are two basic types of toners: those with a negative charge and those with a positive charge. The former require negative CCAs and the latter positive CCAs.

The properties required of a CCA are shown in Fig. 14; both dyes and pigments can be used. These tend to be existing materials, slightly modified and purified.

Negative CCAs. These tend to be organic molecules carrying an inherent

Colourless molecules — Effect (Charge transport)

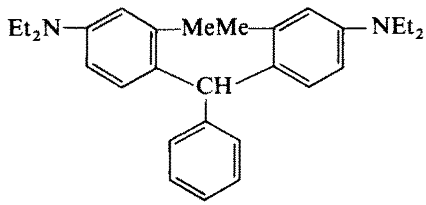
- Properties required
- Electron-rich, conjugated molecules, low IP
- Purity — Very high
- Solubility — Solvents
- Toxicology — Ames-ve

OXADIAZOLES

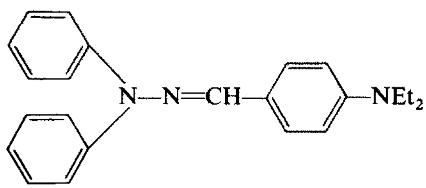
PYRAZOLINES

AMINES

Leuco TRIPHENYLMETHANE



HYDRAZONES



CGMs + CTMs: Mixture EXISTING and NOVEL materials

Fig. 13. Charge transport materials (CTMs).

Coloured or non-coloured molecules — Effect (Electrostatic charge)

Colour irrelevant (undesirable)

(−ve) TONERS (+ve)

−ve CCAs — +ve CCAs

- Properties required
- Effective CCA
- Cost effective
- Purity (H_2O: Electrolytes)
- Toxicology (Ames −ve)
- Thermal stability (Processing conditions)
- Dispersibility (in toner resin)

DYES and PIGMENTS

Existing dyes—purified

Fig. 14. Charge control agents (CCAs).

negative charge. The two common groups carrying a negative charge are sulphonic acid and carboxylic acid but organic sulphonates ($R—SO_3^-$) and carboxylates ($R—CO_2^-$) have found only limited use as CCAs. The best CCAs are 2:1 Cr^{III} or Co^{III} complexes of azo dyes. These coloured CCAs are typified by CCA 7 (ICI) (see Fig. 15). The feature to note is that the negative charge is delocalised over an extensive π-system rather than being localised on a small number of atoms as is the case with carboxylates and sulphonates. Because these delocalised CCAs are intensely coloured (dull violet in the case of CCA 7), they can only be used in black toners where the colour of the carbon black completely masks the colour of the CCA.

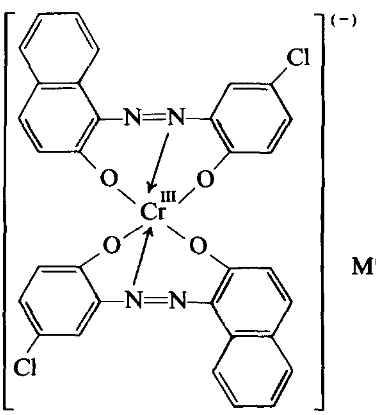
In contrast, colourless CCAs are required for coloured toners so that the CCA does not affect the colour of the yellow, magenta and cyan colourants. Again, these tend to be 2:1 Cr^{III} complexes, but this time not of coloured azo dyes but of colourless salicylate compounds. Bontron E81 (Orient Chemical Industries) is a typical structure (Fig. 15). These are less stable, have less delocalisation and are less effective CCAs than the coloured types.

Organic molecules with a negative charge

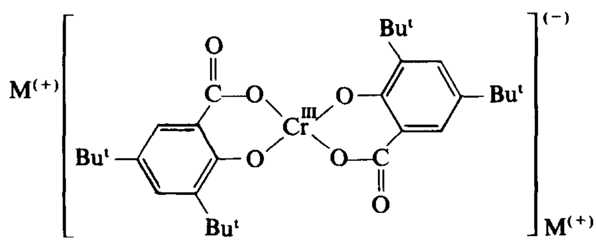
2:1 Cr^{III} or Co^{III} COMPLEXES

COLOURED
(Dull Violet)
AZO DYES

NON-COLOURED
(SALICYLATES)



CCA 7
(ICI)
Black toners



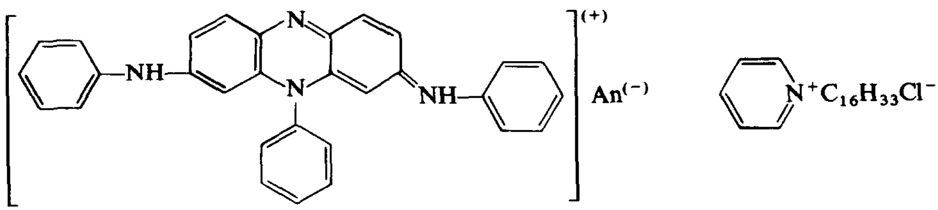
BONTRON E81
(ORIENT)
Coloured toners

- Less stable
- Less delocalisation
- Less effective

Fig. 15. Negative CCAs (from Ref. 1).

Organic molecules with a positive charge

COLOURED (Black)	NON-COLOURED
NIGROSINES (Mixtures)	QUATERNARIES



BONTRON N SERIES (ORIENT) Black toners	CETYLPYRIDINIUM CHLORIDE (XEROX) Coloured (and black) toners (YMC)

Fig. 16. Positive CCAs.

Positive CCAs. These are organic molecules with a positive charge.

Coloured positive CCAs tend to be nigrosines, which are a mixture of compounds of which highly arylated phenazines are the major component (see Fig. 16). As in the case of the coloured negative CCAs, the charge is delocalised over an extensive π-system. The Bontron N series (Orient

Coloured molecules—colour

- Full colour copying/printing
- Highlighting

PIGMENTS	DYES
● Fastness (non-bleeding)	● Bright
■ Opacity	● Strong
■ Tribo charge control [CCA Class]	● Transparent
	■ Fastness (bleed)

Y AZO

M QUINACRIDONE/XANTHENE

C PHTHALOCYANINE

PROBLEM: Small market size

Fig. 17. Coloured toners.

Chemical Industries) typify coloured positive CCAs. These black-coloured CCAs can obviously only be used in black toners.

Colourless positive CCAs tend to contain a quaternised nitrogen atom and cetylpyridinium chloride (Xerox) is one of the most widely used. As was the case for the colourless negative CCAs, the colourless positive CCAs are less effective than the coloured nigrosine type. They can be used in either coloured (YMC) or black toners.

Most of the CCAs, both positive and negative, tend to be existing materials.

Coloured toners

Coloured toners can be used either for full colour copying or printing, or for highlighting. In theory, pigments or dyes can be used as the colourants. The main advantage of pigments is their high fastness properties, especially to heat, so that they do not bleed and lose resolution during the final fixation stage of the process. However, they have some degree of opacity (a consequence of their larger particle size), an undesirable feature for full colour copying, and control of the triboelectric charge is difficult. This is because the yellow, magenta and cyan pigments belong to different chemical classes (see Fig. 17), each with its own inherent charging characteristics. Thus, the less effective colourless CCAs have to override these effects and adjust the triboelectric charge to a similar value for each of the three colourants, by no means an easy task. On the other hand, dyes are bright, strong and completely transparent but have fastness problems, especially heatfastness. They tend to bleed during the heat fixation stage with consequent loss in resolution.

As far as the colour manufacturer is concerned, the major problem is the small market size and low growth of colour copying/printing. This has precluded significant research on novel colourants.

SUMMARY

The following effectively summarises the role of organic molecules in colour hard copy.

- Three major technologies: thermal, ink-jet and toners.
- Dyes/pigments/colourless.
- Colourants used for their colour: ink-jet dyes, thermal transfer and coloured toners.
- Colourants used for other effects: electrostatic (CCAs) and photoconduction (OPCs).

- Colourless organic molecules: colour precursors (CFs) and electrical (CTMs and CCAs).
- Choice—depends on effect/application.
- Use existing molecules (purified).
- Scope for improved molecules.

REFERENCE

1. Birkett, K. L. & Gregory, P., *Dyes and Pigments*, **7** (1986) 341.