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Metal Complex Dyes as Charge Control Agents

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SUMMARY

Certain dyes and pigments possess highly desirable properties apart from being coloured. These properties are being utilised in the multi-billion pound high technology industries such as electronics and reprographics. One such application is the use of dyes as charge control agents (CCAs) for toners in electro-photography (photocopying). Certain 2:1 chromium(III) or cobalt(III) complex azo dyes have been found to be the best negative CCAs. Performance is dependent on several parameters, especially dye structure.

INTRODUCTION

The traditional use of dyes and pigments is to impart colour to a substrate, such as textiles, paper, leather and plastics. Indeed, this is still the major application for dyes and pigments today. However, it is being discovered that certain dyes and pigments possess other highly desirable and, in some cases, unique properties apart from being coloured. The properties are being utilised in the multi-billion pound high technology industries such as electronics and reprographics (Fig. 1). For example, three specific uses of dyes in electronics are in liquid crystal displays, lasers and as infrared absorbers. Although there are many other uses for dyes and pigments in the electronics industry, it is their use in the less familiar reprographics industry with which this paper is concerned.

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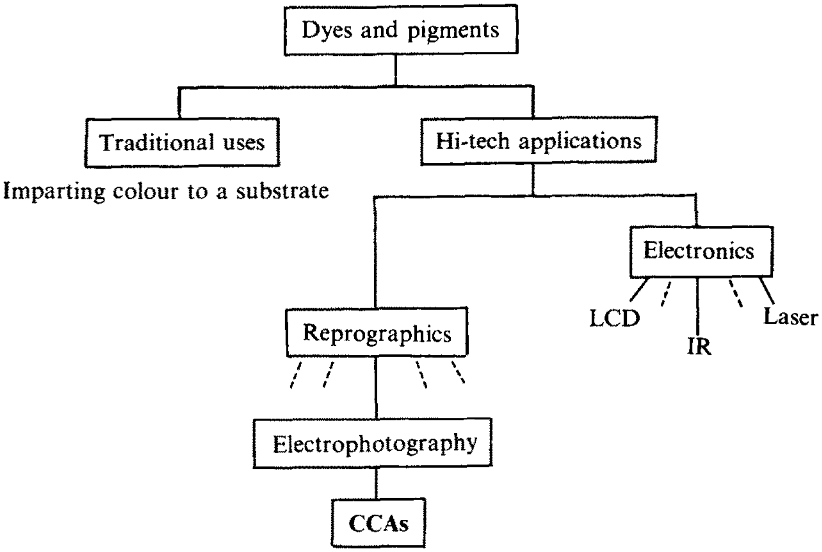


Fig. 1. Metal complex azo dyes as charge control agents.

Reprographics embraces several technologies. Electrophotography, perhaps more familiar as photocopying, is by far the most important technology and it is in this field that charge control agents (CCAs) are used (Fig. 1).

THE PHOTOCOPYING PROCESS

Before discussing charge control agents it is essential to have a basic understanding of the photocopying process. Only the most important photocopying process, the dry two-component process using selenium-based photoconductors, will be discussed.

As the name implies, electrophotography involves the interaction of light energy with (static) electricity to produce an image. The process is best described in five steps (Fig. 2):

(1) The photoconductive surface, usually a drum or a belt, is given a uniform electrostatic charge.
(2) The plate is exposed to the subject using light to produce a latent electrostatic image on the photoconductor.
(3) The latent electrostatic image is developed by oppositely charged toner particles.

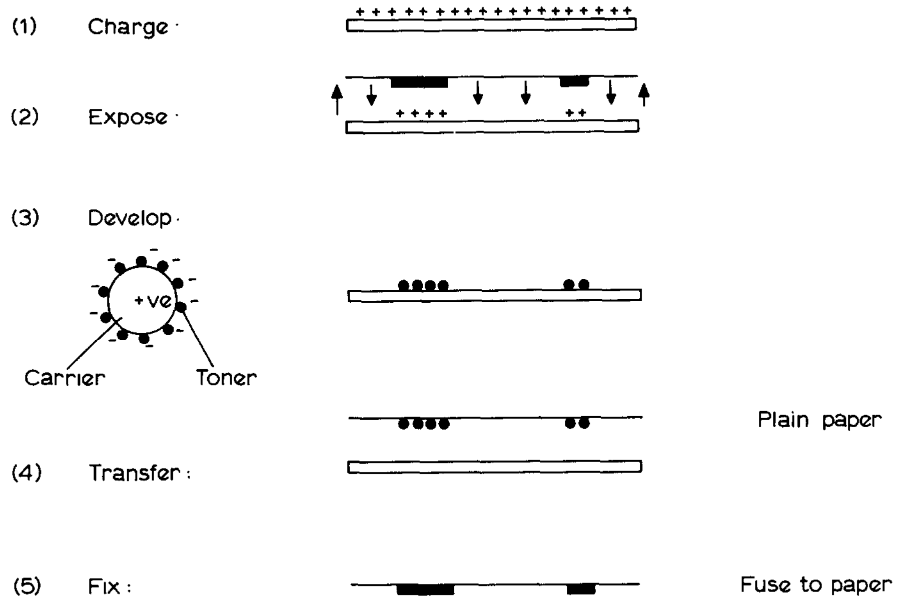


Fig. 2. Steps in electrophotography.

(4) The developed image is transferred to a substrate, usually paper.
(5) The image is fixed by heat.

The photoconductor is normally charged to a voltage of 500–800V using a corona discharge. Selenium photoconductors are charged positively since they function more efficiently with a positive charge.

As the name suggests, a photoconductor is a conductor of electricity in the presence of light: in the dark it is an insulator. In the imaging step, the document to be copied is illuminated with light: where there is no print, the light is reflected on to the photoconductor and causes the electrostatic charge to be dissipated. In contrast, where there is print (usually black), the light is absorbed and little or none of it reaches the photoconductor. Hence, the electrostatic charge remains intact. Thus, after step (2) there is a latent electrostatic image of the document on the photoconductor.

This latent image is rendered visible by development, most commonly with a dry two-component developer which consists of carrier particles and smaller toner particles. These are agitated in the machine so that they develop triboelectric (static) charges. For selenium-based copiers the toner particles develop a negative charge and are held to the surface of the carrier, which develops a positive charge, by a weak electrostatic attraction. The developer is then brushed or cascaded over the surface of the photoconductor: in areas where an electrostatic charge remains, the toner particles are plucked from the carrier surface because the attraction between the positively charged photoconductor and the toner is greater than the weak attraction between the toner particles and the carrier. At this point, there is a visible toned image of the original document on the photoconductor (step (3)).

The fourth step simply involves transferring this image from the photoconductor to the substrate, usually plain paper. This is normally done by applying an electrical potential to the paper of opposite sign to the toner particles (this potential would be positive in the case of selenium based copiers).

The final step is that of fixing the image to the paper, which is achieved by a heat treatment which melts the toner resin (see later) and fuses it to the paper. It is also the reason why copies emerge hot from a photocopier! This, then, is the basic photocopying process.

It is the third stage, the development step, with which we are concerned. As just mentioned, the developer consists of a carrier and a toner. The most commonly used materials for the carrier are iron, steel and ferrite, although silica and glass are also employed. Toner particles are composed mainly of resin: the other three ingredients are the pigment, which is invariably carbon black, an anti-offset wax and the charge control agent (Fig. 3). The resins need to have low melting points (typically 60–70 °C) in order to facilitate the final fusion step to the paper, and to be good insulators to allow them to accommodate an electrostatic charge. Styrene–acrylic copolymers, such as styrene-*co*-*n*-butyl methacrylate, are by far the most important, accounting for about 80 % of the toner resins used. Polyesters are the other important resins.

Toners are prepared by a hot melt kneading process. Briefly, the ingredients are premixed and then hot melt kneaded at ~ 150 °C for up to several hours. The melt is cooled, crushed and ground and toner particles of the desired particle size, namely 5–15 μm, obtained by classifying. The toner is then made into a developer by adding a carrier and the suitability of the toner is assessed by measuring its triboelectric charge using the so-called Blow-Off test. The triboelectric charge is expressed as micro-coloumbs per gram ($\mu C\,g^{-1}$): typical values are ± 10–$50\,\mu C\,g^{-1}$.

If the triboelectric charge is satisfactory, then the ultimate test is to use the toner in a machine to produce copies: this can involve running as many as 100 000 copies continuously.

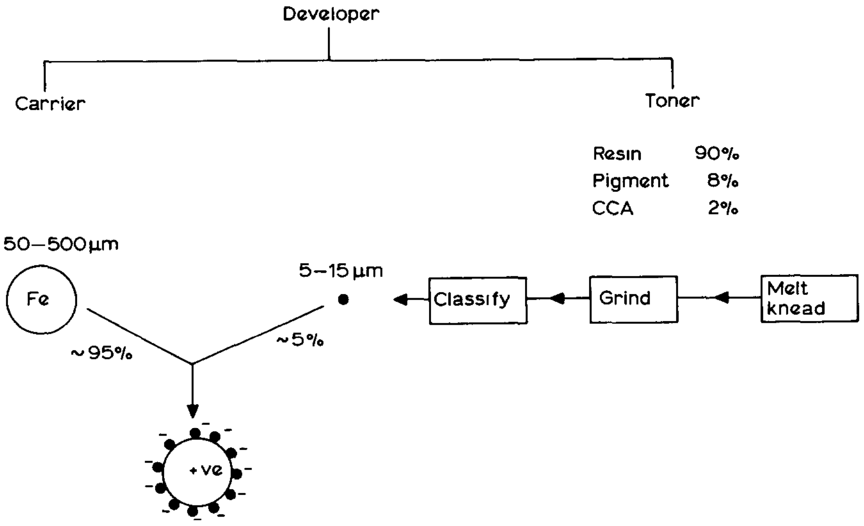


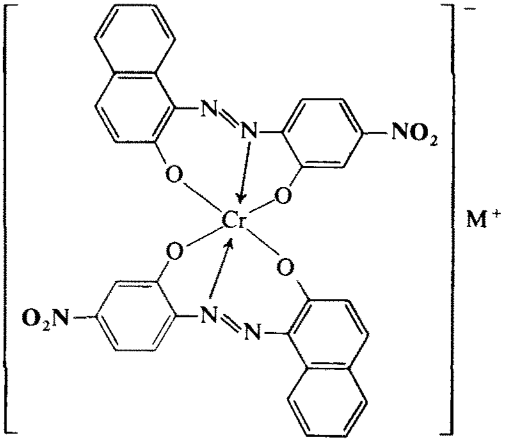
Fig. 3. Step 3: Development.

The CCA is a key ingredient. It ensures that the toner particles acquire the correct level of triboelectric (static) charge, i.e. neither too high nor too low, and keeps it constant over long periods of time. This produces high-quality copies: visually, very sharp, distinct black images on a pure white background. Without a charge control agent poor quality copies result, with less distinct black images on a fogged (grey) background.

NEGATIVE CHARGE CONTROL AGENTS

The two common groups in organic chemistry which carry an inherent negative charge are the sulphonic acid group and the carboxylic acid group. Therefore, it is hardly surprising that many organic molecules containing either sulphonic acid or carboxylic acid groups, or derivatives of these groups, have been evaluated as negative charge control agents. Generally, however, they are unsatisfactory. This is probably because the negative charge is localised on oxygen atoms which results in an ionic group in the molecule; this hinders dispersibility in the toner resin. In contrast, 2:1 chromium complex azo dyes, devoid of sulphonic acid or carboxylic acid groups, have been found to be excellent negative charge control agents. Here, the molecule contains a unit negative charge which is delocalised throughout the π-electron system of the whole molecule.

Such dyes exhibit good compatibility with the toner resin. Apparently, this discovery was made by accident. A black metal complex dye was incorporated into a toner containing carbon black in an attempt to modify the shade. Instead, the quality of the copies produced by that toner were so superior to those to which no dye had been added that it was obvious that some unique effect had been discovered!



I. CI Acid Black 63 (Bontron S31).

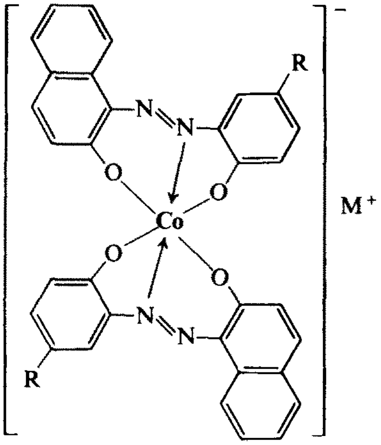
CI Acid Black 63 (**I**), which is marketed by Orient Chemical Industries as Bontron S31, is typical of the early 2:1 chromium complex azo dyes which function as negative charge control agents. However, CCAs must be able to withstand the processing involved in the preparation of toner particles, in particular the hot melt kneading at temperatures of 150–200 °C for several hours, and CI Acid Black 63 has only borderline thermal stability. Detailed thermochemical experiments using Differential Scanning Calorimetry showed the nitro group in CI Acid Black 63 to be a major cause of its low thermal stability.

In order to design and synthesise charge control agents superior to Bontron S31, four objectives need to be met:

(1) Optimum performance;
(2) Non-toxicity;
(3) Good thermal stability;
(4) Easy synthesis.

The first step was to remove the nitro group to improve the thermal stability of the 2:1 chromium complex azo dyes. Also, 2:1 cobalt(III) azo dye complexes were evaluated since, by ligand field theory, these should also have good stability. Furthermore, they are generally easier to synthesise than the chromium(III) complexes.

Combination of all this information led to the synthesis of 2:1 cobalt(III) complex azo dyes which performed well as CCAs. The best dyes were those containing sulphonamide groups (CI Acid Red 277, **II**) and chlorine atoms (ECCA 9, **III**).

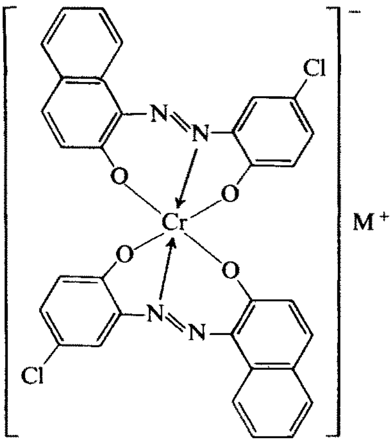


II. R$=$SO$_2$NH$_2$ (CI Acid Red 277)
III. R$=$Cl (ECCA 9)

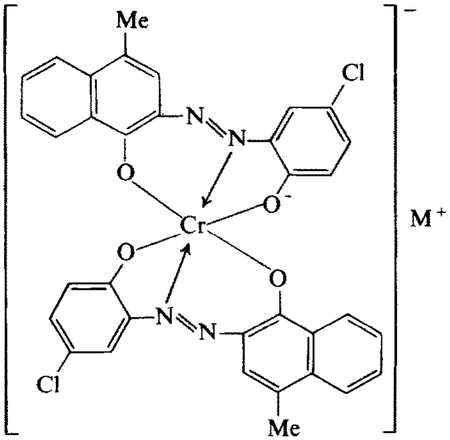
Only a few dyes are good CCAs. From the many types examined, the best negative CCAs are the 2:1 chromium(III) or cobalt(III) complexes of 1-phenylazo-2-naphthols, **IV**, devoid of ionisable groups. Even analogous dyes from the isomeric 2-phenylazo-1-naphthol system, **V**, perform poorly as CCAs.

Although the structure of the dye is the single most important parameter affecting its performance as a CCA, other parameters are also important (Table 1). These include the properties of the counter-ion. In conventional textile dyes, this is normally the sodium ion (Na$^+$) but the best counter-ion for CCA performance has been found to be the hydrogen ion (H$^+$). This is because it enhances the compatibility of the dye with the resin but primarily because it is small and highly mobile (see later).

The thermal stability of the dye needs to be high and its solubility in the toner resin needs to be low. These two parameters obviously depend directly upon the dye structure. Further, the dyes need to have low levels of inorganic ion, such as sodium and chloride, and water. Particle size and



IV. 1-Phenylazo-2-naphthol (good)



V. 2-Phenylazo-1-naphthol (poor)

morphology are also important: small amorphous particles are preferable.

It is not really known how CCAs work. Indeed, the subject is treated as a 'black art'. However, the following tentative ideas may have some relevance. Triboelectric effects are a surface phenomenon. The charging process of the developer probably involves transfer of the CCA counter-ion at the surface of the toner to the surface of the carrier during contact between the particles (Fig. 4a). The toner particles would then become

TABLE 1

Important Parameters Affecting CCA Performance

Parameter	*Requirement*
Dye structure	$[\text{Dye}]^- \text{M}^+$
Counter-ion properties	High mobility/compatibility enhancement
Thermal stability	High, for processing at 150–200 °C
Solubility (in toner resin)	Low
Inorganics (Na^+, Cl^-, ...)	Low
Water	Low
Particle size	Small
Morphology	Amorphous

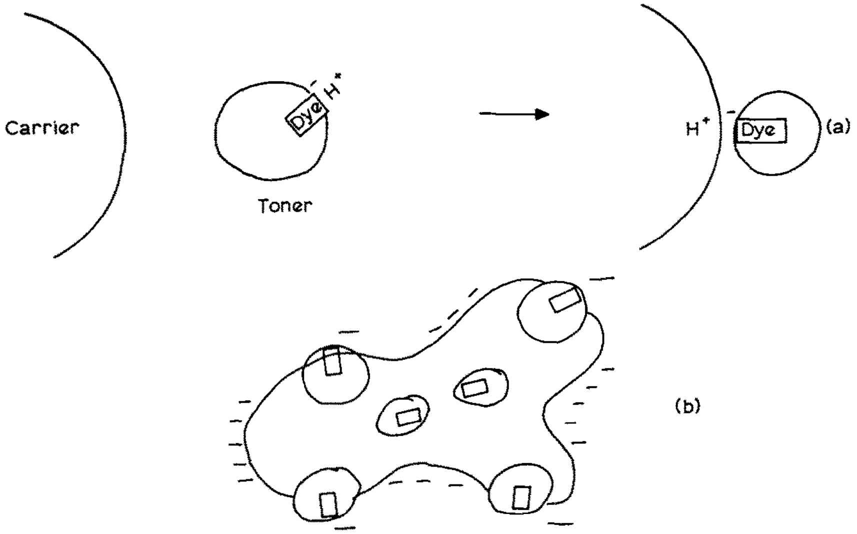


Fig. 4. Mode of action of CCAs. (a) Charging process; (b) toner action.

negatively charged because of the CCA anions and the carrier positively charged because of the protons. This mechanism also explains why certain 2:1 chromium(III) or cobalt(III) complex azo dyes having a proton as the counter-ion are particularly effective CCAs:

(1) because a proton, being the smallest counter-ion, is highly mobile, and
(2) the single negative charge in the dye anion is delocalised over an extremely large π-system resulting in an easy removal of the proton. In contrast, removal of a proton attached to an atom containing an essentially localised negative charge, as in carboxylic and sulphonic acids, will be more difficult.

The presence of aggregates of the CCA at the surface of the toner (probably associated with the carbon black) means that the toner will always have a certain minimum level of negative charge. Repeated contact of the toner and carrier particles will cause further negative charge build-up at the surface of the toner devoid of CCA (it should be remembered that the resins used are chosen because they charge triboelectrically) but this will be limited by the centres of negative charge due to the CCA (repulsion of like charges). CCA not at the surface of the toner would have no effect (Fig. 4b).

This simple picture does explain how a CCA could prevent the charge on a toner particle from being too low or too high. Some proof that this may be the case is that removal of the CCA from the surface of the toner (by leaching with brine containing a dispersing agent) causes a dramatic drop in the triboelectric charge of the toner.