Dyes Versus Pigments: The Truth

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Introduction

Colorants may be divided into dyes and pigments. There are a number of commonly held perceptions about dyes and pigments. Some of these perceptions are true whilst others are false. These perceptions are presented and their validity questioned. The theoretical basis behind the effects is discussed later.

Lightfastness

The common perception is that pigments have excellent lightfastness whilst dyes have poor lightfastness. The truth is that lightfastness is variable for both dyes and pigments. For example, there are dyes and pigments that have poor lightfastness and dyes and pigments that have excellent lightfastness. In general, if extremely high lightfastness is required, as is the case for automotive paints for cars, then pigments are the colorants to use. However, the lightfastness of a colorant only needs to be sufficient for its intended use. In office ink jet printing, a moderate lightfastness of 3 on the blue wool scale (1 = poor; 8 = excellent) is generally sufficient since this represents a lifetime of 25-50 years in the home or office[1].

Cost

Pigments are cheaper than dyes is a perception held by many people. Overall, this is probably correct. The whole truth, however, is that dyes are generally more cost effective than pigments because of their greater colouring power. For example, 1% of a yellow dye based ink can produce the same print optical density in ink jet printing as 8% of a yellow pigment based ink. Therefore, unless the pigment is less than 8 times the cost of the dye, the dye is more cost effective.

Ease of Use

The perception is that dyes are easier to use than pigments. This is true. Stable homogeneous solutions are more easy to handle than metastable heterogeneous dispersions.

Transparency

The perception that dyes are more transparent than pigments is also true. Transparency is important for overhead projector slides in order that bright true colours are projected.

Colour Gamut

The perception is that dyes are brighter than pigments and therefore give a bigger colour gamut. This is true. Comparison of the colours produced from ink jet, electrophotography and thermal transfer show dye based systems produce a wider range of colours than pigment based systems.

Choice

The perception that pigment choice is limited whereas dye choice is enormous is true. There are > 5000 commercially available dyes but < 400 commercially available pigments. More importantly, the synthetic flexibility of dyes is infinite. This results in major advances at frequent intervals for dyes and allows dyes to be designed for a specific application. In contrast, advances in pigments are rare. The number of new commercial dyes per decade (>> 100) versus the number of new* pigments (< 10) reflects these facts.

Waterfastness

The perception is that pigments have excellent waterfastness and that dyes have poor waterfastness. Pigments do indeed have excellent waterfastness. Dyes have variable waterfastness. Some are poor (e.g. CI Food Black 2) but some are excellent and equal the waterfastness of pigments.

Rationale

The theory behind the above effects is discussed in this section.

Colorants are intensely coloured materials which can be applied to a substrate and are durable once on the substrate. Dyes are *soluble* organic colorants whereas pigments are *insoluble* organic (or inorganic) colorants.

Both dyes and pigments have an extensive delocalized pi-electron system which is usually conjugated to a 2pz orbital—this is normally provided by hydroxy (-OH) or amino ($-NR_2$) substituents. These interact to form a charge transfer (CT) band in the visible portion of the electromagnetic spectrum. Beyond this point the similarities end. Pigments are essentially planar molecules and usually contain strong hydrogen-bonding groups such as amide (-CONHR) and carbonyl (C=0). These molecular features facilitate strong intermolecular attrac-

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tive forces leading to stable crystals having high lattice energies which are difficult to disrupt by solvents. Thus, pigments are insoluble. In contrast, dyes are non-planar molecules which may also contain solubilising groups, for example sulphonic acid or carboxylic acid. The intermolecular forces are weaker than in pigments with the result that the crystals are less stable and are easily broken up by solvents to give solutions—Figure 1.

Colorants

Pigments	Dyes
- Planar	- Non planar
- H-bonding groups	- Solubilizing groups
Stable crystals (high lattice energies)	*Unstable* crystals (low lattice energies)
Solvent	**Solvent**
Insoluble	Soluble

The features described above for typical pigments and dyes are illustrated by the phthalocyanines (1) and (2) and the azos (3) and (4).

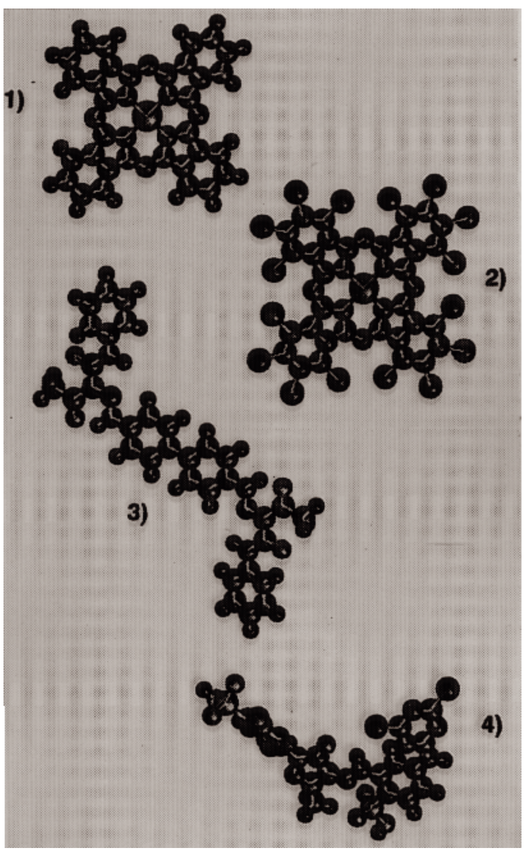

Figure 1. Dye and Pigment Features

Dyes exist in a monomolecular state. In contrast, pigments exist as particles, typically ranging in size from 0.1 to 1.0 micron. Each pigment particle contains a large number of molecules. Figure 2 shows that each 0.1 micron particle of beta-copper phthalocyanine contains ~1.5 million molecules.[2] Of these, -10% occupy surface sites.

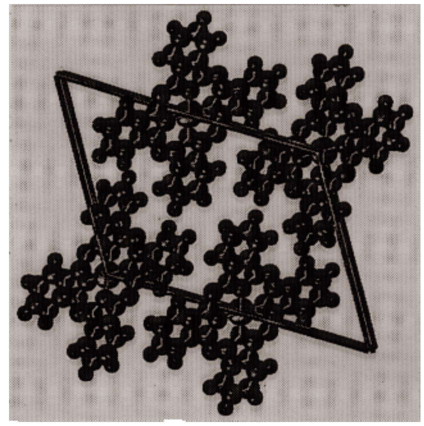

Figure 2. Estimation of number of molecules in a pigment particle of beta-copper phthalocyanine

Application of the above information regarding the molecular structure of dyes and pigments enables the different properties exhibited by these classes of colorants to be rationalized theoretically.

The relative surface areas of dyes versus pigments is responsible for several effects. Dyes, being present in a monomolecular state, have a vastly larger surface area than pigments. Thus, attack by photofading agents such as singlet oxygen ($^{1}0_{2}$) and ultraviolet radiation is greatly facilitated. In contrast, only those molecules at the surface of a pigment particle (10% of the total) readily absorb photons. The large crystalline particle facilitates the dissipation of the energy of the photoexcited molecules. Even if these surface molecules photofade, they present a barrier to help retard the photofading of the molecules within the pigment particle.

The lower surface area of pigments compared to dyes, whilst advantageous as regards lightfastness, is a major drawback when it comes to colouring power and cost effectiveness. Each dye molecule, being in a monomolecular state, absorbs a photon and thereby contributes to the colouring power. In a pigment, only those molecules either at or near the surface absorb a photon: the majority of molecules therefore are redundant and don't contribute to the colouring power. Therefore, pigments are tinctorially much weaker than dyes which severely impairs their cost effectiveness.

Because individual dye molecules are so much smaller than the wavelength of light, no scattering is possible. In contrast, pigment particles in the range of 0.2 to 1.0 microns are of the right size to scatter white light (0.4 to 0.7 microns wavelength). This m makes pigments less transparent than dyes.

Colour gamut depends upon chroma (brightness) and chroma depends upon the purity of the reflected light. Colorants with a narrow, symmetrical absorption band display the highest chroma. Being present in a monomolecular state, dyes satisfy this requirement best. Aggregation of molecules results in broader absorption curves which is manifested as dullness. The scattering of light by pigments also reduces the purity of the reflected light from pigments.

Technology	Dye	Pigment
Ink jet		
- Aqueous	√	
- Phase change	√	√
EP - OPCs		√
- Colorants		√
- CCAs	√	
Thermal -Wax		√
- D2T2	√	

Figure 3. Current usage of dyes and pigments in non-impact printing

The ease of use and wetfastness of dyes vs. pigments has already been explained.

Whether a dye or pigment is chosen for a particular application depends on how properties such as colour gamut, transparency, colouring power, choice/synthetic flexibility and ease of use are ranked against excellent lightfastness, insolubility and crystallinity. Figure 3 shows the current usage of dyes and pigments in non-impact printing.

Conclusion

The colorant of choice depends on the properties required. Generally, dyes not only equal the properties of pigments but also offer many additional benefits.

References

* New refers to new molecules, not new formulations of existing molecules.

1. S. I. Anderson, G. W. Lawson, 2nd Int. Meeting on "Stability and Preservation of Photographic Images", Ottowa, 25-28th October 1985.
2. R. Docherty, unpublished results.