Recent Trends in Organic Color Pigments

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Abstract

Full-color copiers, laser printers and short-run digital printing devices have become popular. For the colorants in use, three major tendencies can be observed: tailored technical improvements, fulfillment of modern eco-tox demands, and compliance with an increasing number of chemical laws and government regulations.

Technical tailoring: To optimize the properties of organic pigments, various approaches can be taken, either by changing the chemical constitution, by using selected combinations (e. g. mixed coupling or solid solutions), or by tailoring the solid state properties like particle size and shape, or the crystal structure and the degree of crystallinity.

For toner applications an additional demand is towards electrostatically neutral pigments, which allow combinations with all common toner resins and CCAs (Charge Control Agents).

The paper will also give a selected focus on eco-tox demands and certain aspects of world-wide registration according to the existing national regulations. It is well-understood that for modern color pigments these aspects have to be covered in a proactive way.

Introduction

As we reported recently,[1] there exists a wide choice of organic color pigments for yellow, cyan and magenta toners. Color toners typically consist of 90-95% resin (polyester, styrene acrylic copolymers etc.), 3-5% colorant, 1-3% charge control agent (CCA), and other additives like waxes. Since the colorants have to meet many different demands, the number of pigments actually in use for full-color copying and printing is much smaller.

Figure 1 gives an overview of how the color gamut is covered by the various chemical pigment classes, and which pigments are typically used in toner systems.

In the following it is described by the example of some magenta and yellow pigments, that in the future the toner industry can increasingly count on tailored “tonergrade” pigments.

Experimental

Test toners were prepared by dispersing the pigment (5%), into a toner resin (polyester and/or styrene acrylate). All pigment parameters, and the test toner charge were measured according to the literature.[3]

Results and Discussion

Pigment Tailoring

Various approaches have been made to tailor pigments according to the needs of electrophotography.[4] Special efforts have been undertaken for the MAGENTA shade. For this hue the pigment with the highest fastness properties is

Pigment Red 122
(2,9-Dimethylquinacridone)

Two toner types were established for this pigment.[5] A more yellowish magenta, based on rod-like crystals with an anionic surface charge and a moderately negative electrostatic influence; and a more bluish type, with cubic crystals, having a cationic surface charge and a minor positive influence on the toner charge.

For the understanding of the electrostatic influence, the correlation between the pigment particle surface charge and the electrostatic influence is of significance:

anionic particle surface charge—negative tribo effect
cationic particle surface charge—positive tribo effect

For a series of charge control agents (CCA) it was shown by Zeta potential measurements, using organic solvents with different donor-acceptor properties,[6] that cationic surface charge (measured in aqueous suspension) runs parallel with distinct particle donor properties, and vice versa, anionic surface charge with distinct acceptor properties.

With the (pigment) particle surface charge, a material parameter is established with direct correlation to the electrostatic properties, which even can be traced to the final toner system.[6]

Table 1. Some properties of the new Pigment Red 57:1 type.

P.R. 57:1	Ratio* (average)	d_{50} (µm)	BET m^2/g	Shade	Transparency
New Type	2.5:1	120	90	more bluish	more transparent
Standard	2.9:1	160	35	compared to standard	

* length-to-width ratio   BET = specific particle surface

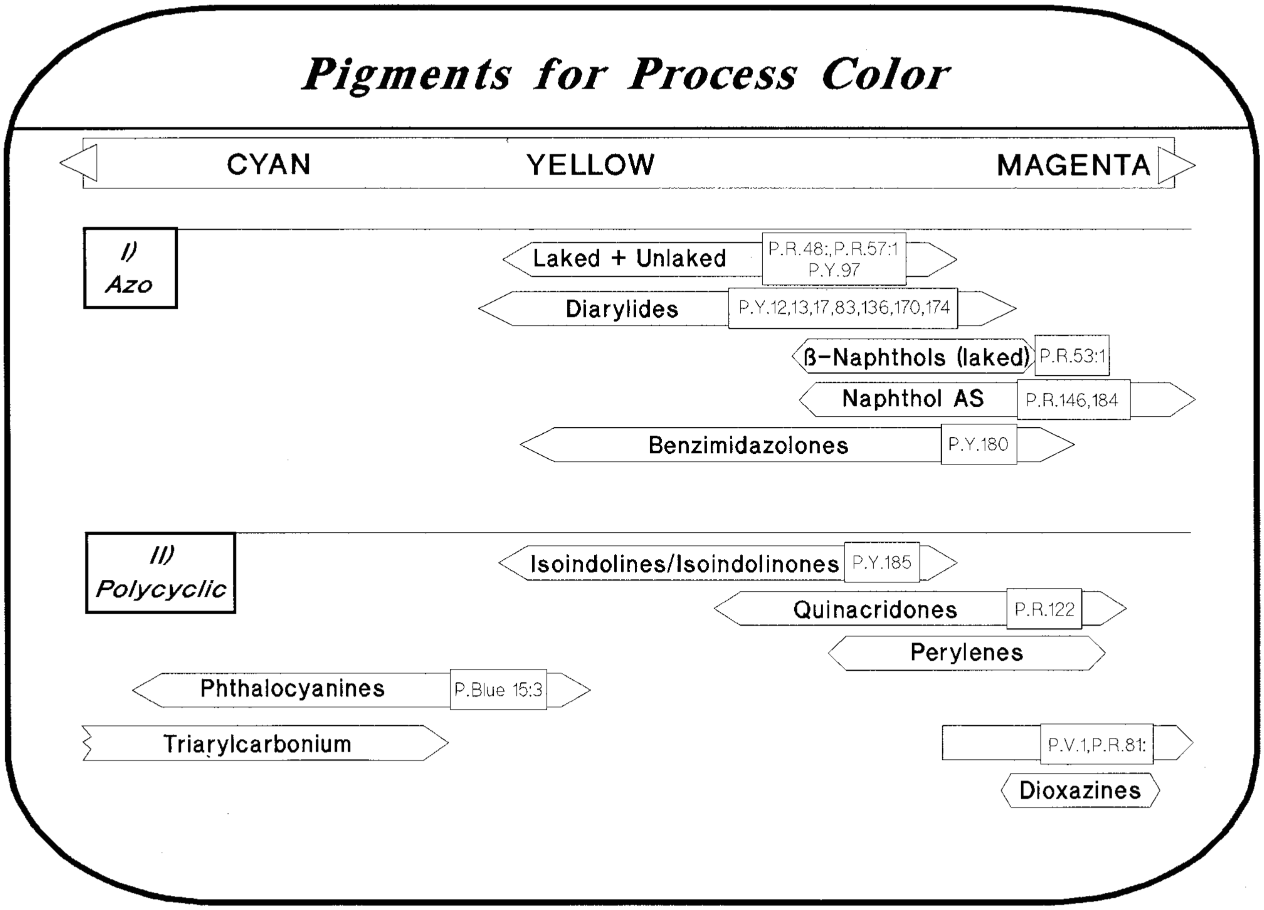

Figure 1. Pigments for full-color copying and printing. While for cyan almost exclusivley C. I. Pigment Blues 15[2] are in use, for yellow and magenta many different pigments or pigment combinations are available.

A further choice for magenta is

Pigment Red 184
(Naphthol type azo-pigment)

This pigment is a mixed-coupling product, based on Pigment Red 146 (naphthol type azo-pigment) and Pigment Red 147 (naphthol type azo-pigment).

Although it exhibits only moderate fastness properties,

Pigment Red 57:1
(Calcium-laked[7] azo-pigment)

has its place, since this pigment is the standard magenta in printing ink applications, and easy to disperse.

Recently a new grade was established, which is more transparent and more bluish, and therefore especially suitable for toner application. By shifting the pigment particle shape from needle towards more cubic type, a pigment with a "length-to-width" ratio of 2.5:1 on average could be obtained, with the advantages of being more transparent and more bluish.

On the YELLOW side various diarylide azo pigments are in use. As an alternative a benzimidazolone tonergrade pigment was recently introduced (P.Y. 180), which is electrostatically neutral and highly transparent due to its solid state properties.[1]

For the CYAN shade almost always phthalocyanines are used (Pigment Blue 15:3). The phthalocyanine-based Pigment Green 7 is available for shading.

Eco-tox Aspects

It is well known that environmental and toxicological aspects are becoming increasingly important. On the pigment side this leads to the demand for highly thermostable pigments,[8] which should not be based on hazardous heavy metals and should be free of nitro groups and organic chlorine, for example.

The various environmental and toxicological regulations, and how they are met by the pigment suppliers is described in the brochure "Safe Handling of Pigments".[9]

Besides government regulations, environmental labels also become important.[10,11] They can be applied voluntarily, and are used to ensure in a proactive way the eco-tox friendliness of the product to the consumer.

World-Wide Chemical Laws

From the above one could conclude that R&D targets for pigment suppliers are easy to define: develop new products which fulfill in an ideal way the technical and eco-tox demands. Here a big obstacle is the various existing chemical laws, which for each new chemical, demand very intensive and time-consuming investigation.

Table 2 gives an overview of countries in which chemical laws exist; many other countries have begun the pro-

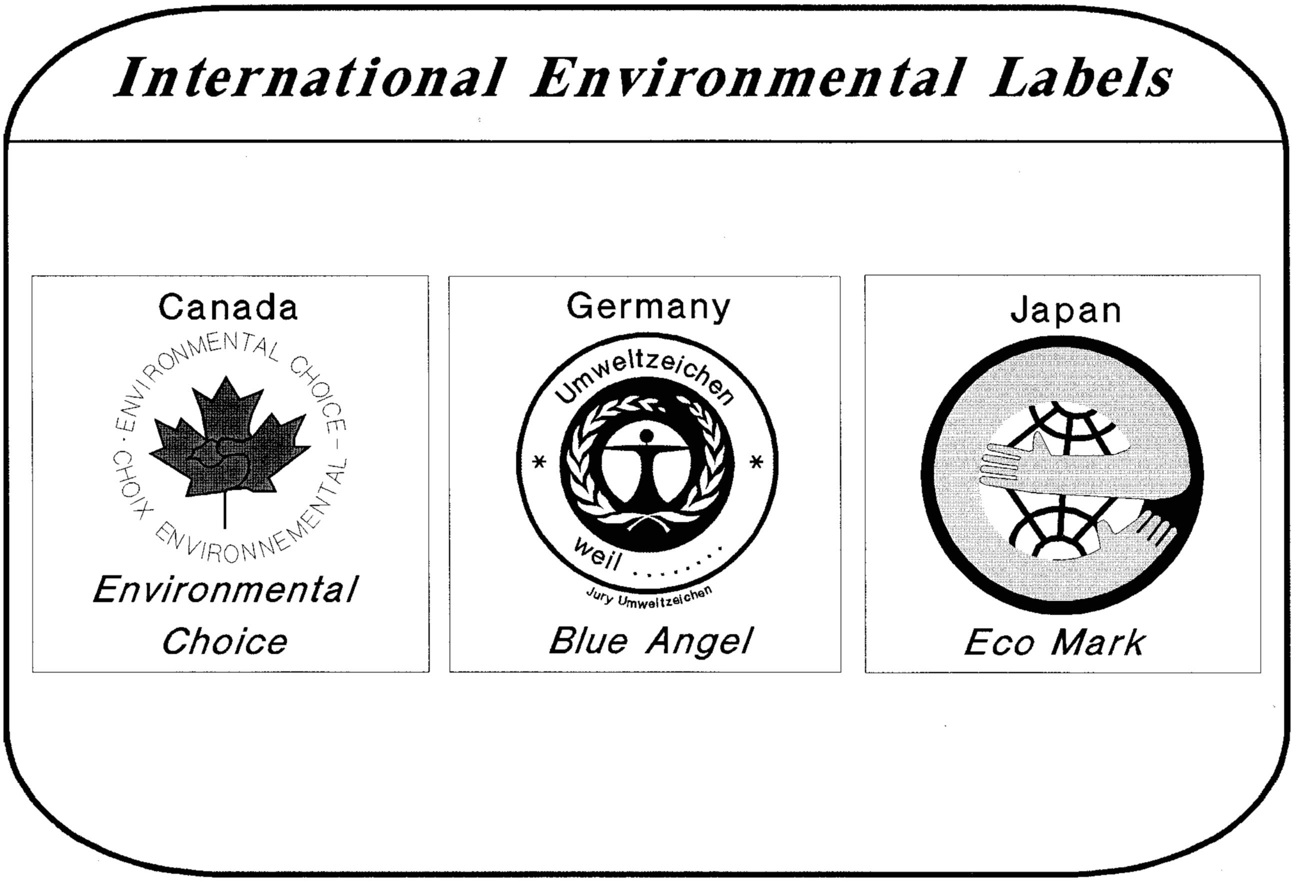

Figure 2. Some typical environmental labels

cess to establish chemical inventories. Unfortunately each country has its specific requirements, and the tendency is that the chemical laws become even more diverse from country to country.

So to a certain extent these laws which were meant to protect the environment, all of a sudden, due to their multitude and non-uniformity, turn out to be a barrier for the development of innovative products. One concludes that only a world-wide registration would allow the global commercial use of a particular pigment.

Table 2. A schematic overveiw of where chemical laws exist. Only a world-wide registration allows the global commercialization of a product.

Some countries with existing chemical laws

Europe	North America	Asia/Pacific
European Community (EC)	Canada*	Australia
Switzerland	USA	Japan
Hungary*	Mexico	South Korea
		Peoples Republic of China*
		Phillippines*

* Inventory under discussion/to be established.

Conclusions

It was shown that the profile of colorants "suitable for the 21st century" is shaped by technical improvements, increasing eco-tox demands, and the boundaries of world-wide chemical legislation. Nevertheless there is plenty of opportunity for further developments, and since the principles for the triboelectric influence of pigments are not well understood, it is also a promising field for basic research.

References

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2. *Colour Index*, 3rd Issue, The Society of Dyes and Colourists, Bradford/UK, 1982. The Colour Index describes and lists the different individual pigments in terms of running numbers and combines these numbers with CAS-No and chemical constitution information.
   For instance: Pigment Yellow 180 = P.Y. 180, CAS No. 77804-81-0; benzimidazolone
   Pigment Red 122 = P.R. 122, CAS No. 980-26-7; quinacridone
   Pigment Blue 15 = P.B. 15, CAS No 147-14-8;Cu-phthalocyanine
3. R. Baur, H.-T. Macholdt, "Charge Control Agents For Tri-

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5. H.-T. Macholdt, "The Various Aspects of Organic Pigments by the Example of Magenta", *American Ink Maker* **79** (10), pp. 60-64, 1992.
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7. The term "laked" describes a salt or complex formation of the chormophore with a specific metal-ion.
8. R. Az, B. Dewald and D. Schnaitmann, "Pigment Decomposition in Polymers in Applications at Elevated Temperatures", *Dyes and Pigments* **15** (1991) pp. 1-14.
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