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Charging Effects of Organic Pigments in Electrophotographic Toners

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SUMMARY

Electrophotographic copying and printing is becoming more extensively used world wide. The 'electronic printing ink' for electrophotography is called toner and until recently only black copies and prints were available. However, colour hard copy is now becoming increasingly attractive and organic pigments can be used to give colour to the toner. They do, however, also influence the toner chargeability.

For this reason we have investigated the influence of organic pigments on the electrostatic chargeability of xerographic toners. These charging effects were studied by measuring Q/M-values of test toners consisting only of toner resin and 5% pigment. By use of this method, a correlation between toner chargeability and the incorporated pigment is apparent.

1 INTRODUCTION

The inventions of the American lawyer Chester F. Carlson[1,2] gave birth to modern electrophotography in 1938. During the last two decades this method has gained enormous success, so that at present almost all types of office and high-performance copiers, as well as laser-printers (making up to 200 or more copies per minute), have become common all over the world.

To develop the 'latent electrostatic image' in copiers, laser-printers and similar devices, toners ('electronic printing inks') are used. Toner production worldwide is roughly estimated at 50 000 tons per year and the supply of toner to copiers and printers has developed into a specialised industry.

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The basic property of electrophotographic toners is the electrostatic chargeability of the toner-particles, which is either positive or negative depending on the type of copier or printer. As shown in Fig. 1, the photoconductor drum (or belt) is first electrostatically charged. The information is conveyed onto the photoconductor either by light reflected from the original, or by a modulated beam from a suitable light source, commonly a laser, where it forms a 'latent electrostatic image'.

The charged toner is then transferred onto the photoconductor to yield the visible image, which is in turn transferred to paper, cardboard, film, etc.

Because of the complexity of the toner formulations, more or less every copier or printer needs its own special toner. Toners for two-component developers are by far the most common. They consist typically of 85–95% nonconductive toner resin (mainly styrene–acrylic copolymer), 5–10% colourant (carbon black, colour pigment), 0·5–2% charge-controlling agent and 0·5–5% other constituents (e.g. flow auxiliaries, waxes).

The particle size of such toners is typically around 10 μm. The second component in the two-component developer is the carrier (e.g. iron, iron oxide, or glass particles) which transports the toner to the photoconductor and charges the toner electrostatically by triboelectric activation.

Apart from the resins and colourants, the charge-controlling agents play a key role, since they determine in particular the polarity of the charged toner. There has been much discussion in the literature about the mechanism of charging and the interaction of charge-controlling agents with the toner and

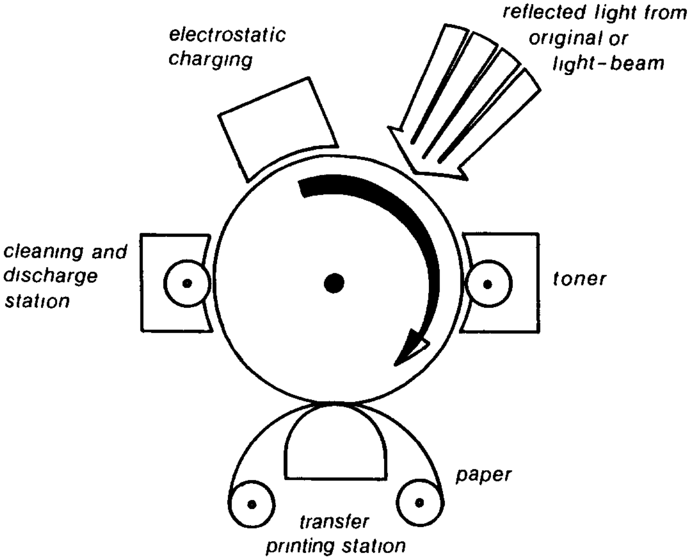


Fig. 1. The principle of electrophotographic copiers and printers.

the carrier.[3-5] The interpretation of these effects presents many difficulties, since the pertinent interactions which have to be considered are quite complex, e.g. different surface phenomena, semiconductor effects, etc.

Until recently only black toners were commercially available, but in the last few years coloured toners have become available and are becoming more important. Coloured toners are used for process colour (yellow, cyan, magenta), as well as for additional colours such as red, green, blue, etc. There is an increasing demand for toner-suitable colour pigments.

It is well known that dyes and pigments can have more or less significant charge-controlling properties. The intention of this present study was to investigate in which way the chemical constitution and solid-state parameters of organic pigments are responsible for the charge-controlling behaviour. For these investigations, test toners were prepared which consisted only of toner resin and 5% pigment, thus making it possible to show the charging effect of each pigment.

2 EXPERIMENTAL

2.1 Test toners

Test toners were prepared by dispersing 5% pigment in a styrene–methacrylic (60:40) copolymer toner resin. Great care was taken to reach optimum dispersion quality and toner homogeneity. After milling and classifying the toner, the 5–25 μm particle fraction was activated with a styrene–methacrylic copolymer-coated magnetite carrier.

Toner (3 parts) was roll-milled with carrier (97 parts) at 150 rev min^{-1} for 30 min. The toner charge was measured on a commercial Q/M-meter.[6] As is generally known, the Q/M values are relative ones and can shift due to the toner resin and the carrier material.

2.2 Pigments

In characterising pigments, the following parameters were evaluated:

(a) Particle size: the average particle size (d_{50}) was determined.
(b) Crystallinity: the full width at half intensity (FWHI) of the maximum reflection of the X-ray diagram was measured.
(c) Purity: the total content of electrolytes (salt and other impurities) was measured according to DIN-ISO 787.[7]
(d) Specific volume resistivity: the resistivity (ohm cm) was measured using thin tablets (diameter 4 cm, thickness *ca* 0·7 mm) which had deposited gold as electrodes on both faces.

(e) Surface type: with the Streaming Current Detector the surface character of the pigments was determined.[8,9] Anionic surface character leads to the conclusion of acidic groups on the pigment surface, and similarly, cationic character implies basic groups. The consumption (μl) of polyelectrolyte needed for neutralisation of the surface charge was measured and gave a guide as to the quantity/intensity of the charge.

3 RESULTS AND DISCUSSION

The large influence of the incorporated pigments on the toner chargeability is evident from the Q/M values which range from $-80\,\mu\mathrm{C\,g^{-1}}$ up to $+50\,\mu\mathrm{C\,g^{-1}}$.

3.1 Charging properties and chemical constitution

When plotting the toner charge versus the incorporated pigments, it is apparent that each pigment class has its typical range within the charging spectrum (Fig. 2). There are some exceptions which will be discussed later.

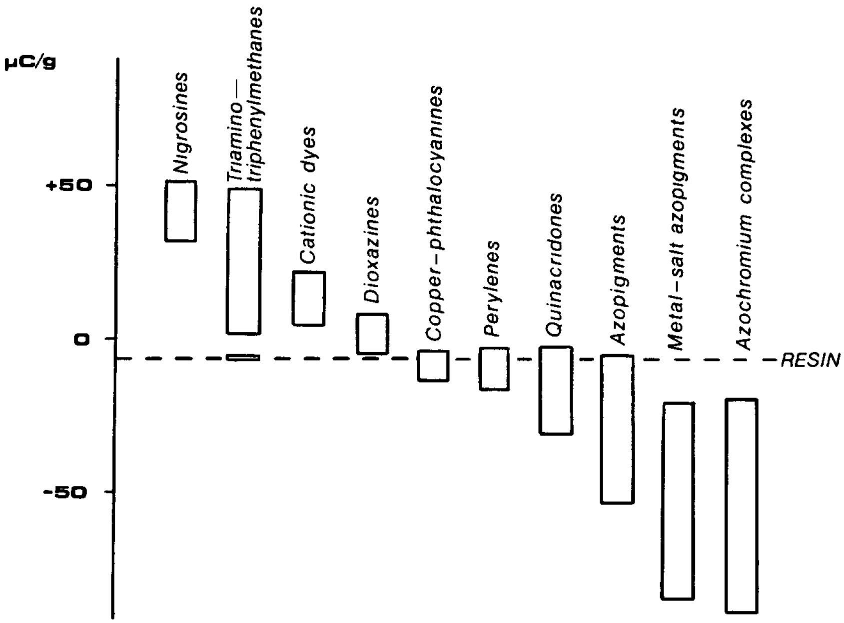


Fig. 2. Effect of the incorporated pigments on the triboelectric charge of the test toners. The broken line indicates the charge of the pure resin.

Nigrosines and triaminotriphenylmethanes, as well as some cationic dyes, give the toner a significant positive charge. Azochromium complexes and metal-salt azopigments are responsible for a highly negative toner charge.

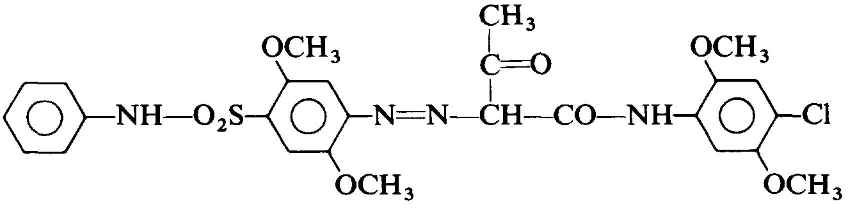
These results are in agreement with the expectation that substances with NR_3 and NR_4^+ groups are positive-charging and substances with COOH, $CONR_2$, SO_3, SO_2NR_2, etc., groups are negative-charging. Although triaminotriphenylmethanes usually charge positively, it is interesting that a derivative can be produced which is in the negative-charging region. In this case, the triaminotriphenylmethane is substituted with three SO_3 groups, the presence of which makes this particular derivative, although still a triaminotriphenylmethane, no longer positive-charging.

The influence of electron-accepting groups (shift to negative charge) and electron-donating groups (shift to positive charge) is well known and has been documented.[10,11] For example, a chromium complex has been described which has, by appropriate substitution, positive-charging properties.[12]

3.2 The influence of solid-state parameters

In addition to chemical constitution and effect of substituents, the influences of solid-state properties of the pigments on the toner chargeability were also investigated. Solid-state parameters can be modified either by special finishing procedures or by variation of the synthesis conditions. Because of the wide variety of pigment groups, only four characteristic types are discussed here in detail, namely monoazo- and disazo-pigments, quinacridones and perylenes.

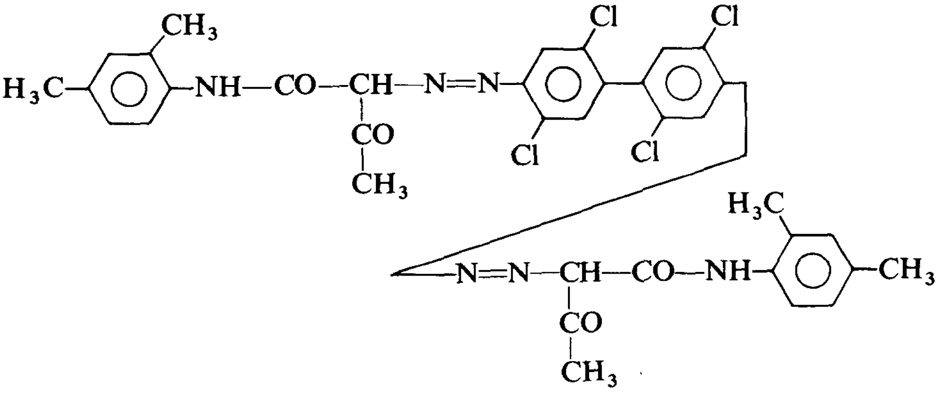
Examples of typical azopigments are Novoperm Yellow FGL (Pigment Yellow 97; CI 11767; **I**) and Novoperm Yellow H10G (Pigment Yellow 81;



I

CI 21127; **II**). A variation of the solid-state parameters in these pigments gives rise to a change in triboelectric charge, as shown in Tables 1 and 2. Abbreviations and a description of the parameters used in these Tables are given in Section 2.2.

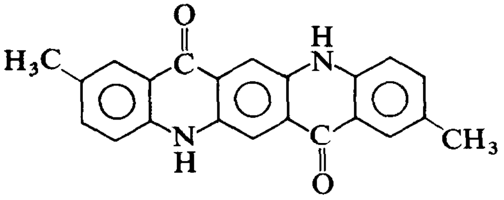
Tables 1 and 2 show that for these two azo-pigments there is a correlation



II

between higher charging effect and increasing volume resistivity of the pigments. Particle size, crystallinity and the content of electrolytes do not have a major influence on the charging properties, and it was surprising to observe that toner charge seems to be independent of the type of surface of the pigment.

In the case of the quinacridone pigment Hostaperm Pink E (Pigment Red 122; CI 73915; **III**), the charging effect increases with better crystallinity (Table 3). When comparing 2,9-dimethylquinacridone with a solid-solution



III

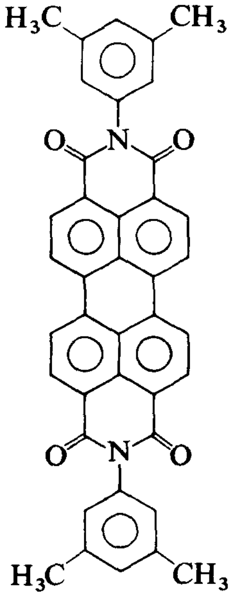


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TABLE 1

Novoperm Yellow FGL: Variation of Pigment Parameters in Relation to the Charging Effect

Pigment[a]	*Test toner charge* ($\mu C g^{-1}$)	*Pigment characteristics*					
		Particle size, d_{50} (*μm*)	*FWHI*[b] (*deg.*)	*Electrolytes*		*Surface type*	
				Conductance (*mS*)	*Specific volume resistivity* (*ohm cm*)	*Character*	*PC*[c] (*μl*)
1	−4·9	0·48	0·250	0·25	$1{\cdot}8 \times 10^{9}$	Anionic	43
2	−4·2	0·55	0·245	0·03	8×10^{10}	Neutral	
3	−9·6	1·0	0·220	0·03	$7{\cdot}2 \times 10^{12}$	Anionic	47
4	−11·4	1·01	0·215	0·06	$5{\cdot}9 \times 10^{16}$	Anionic	37
5	−12·7	0·58	0·24	0·05	$5{\cdot}8 \times 10^{16}$	Anionic	35
6	−19·2	0·21	0·365	0·02	$9{\cdot}9 \times 10^{15}$	Anionic	19

[a] Pigments: 1, commercial sample; 2, sample no. 1 with additional water treatment; 3, sample no. 2 with additional methylene chloride treatment; 4, synthesis with purified starting material; 5, synthesis with shorter coupling time than no. 1; 6, synthesis with longer stirring time after coupling than no. 1.

[b] At 2θ (CuKα) 25·4°.

[c] PC, polyelectrolyte consumption (see text).

of 2,9-dimethylquinacridone and unsubstituted quinacridone, an increase of the toner charge can be seen.

This observation also agrees with the experimental data observed (Table 4) for the perylene-based pigment PV Fast Red B (Pigment Red 149; CI 71137; **IV**). As was observed with the quinacridone pigments, the perylene pigments also show a solid-solution effect on the charging properties. In both cases, the second component of the pure solid solution on its own shows a similar low charging effect to the pure major component alone.

TABLE 2

Novoperm Yellow H10G: Variation of Pigment Parameters in Relation to the Charging Effect

Pigment[a]	*Test toner charge* ($\mu C g^{-1}$)	*Pigment characteristics*					
		Particle size, d_{50} (*μm*)	*FWHI*[b] (*deg*)	*Electrolytes*		*Surface type*	
				Conductance (*mS*)	*Specific volume resistivity* (*ohm cm*)	*Character*	*PC*[c] (*μl*)
1	−5·6	0·36	0·355	0·7	$2{\cdot}3 \times 10^{10}$	Anionic	20
2	−4·4	0·35	0·405	0·01	$6{\cdot}9 \times 10^{13}$	Anionic	5
3	−11·3	0·4	1·85	0·01	$> 10^{17}$	Anionic	20·5

[a] Pigments: 1, commercial sample; 2, sample no. 1 with additional water and methylene chloride treatment; 3, synthesis with longer stirring time after coupling than no. 1.

[b] At 2θ (CuKα) 25·4.

TABLE 3
Hostaperm Pink E: Variation of Pigment Parameters in Relation to the Charging Properties and Solid-Solution Effect

Pigment[a]	*Test toner charge* ($\mu C g^{-1}$)	*Pigment characteristics*					
		Particle size, d_{50} (μm)	*FWHI*[b] (*deg*)	*Electrolytes*		*Surface type*	
				Conductance (*mS*)	*Specific volume resistivity* (*ohm cm*)	*Character*	*PC*[c] (μl)
1	−2·5	6·9	1·6	0·02	2×10^{12}	Neutral	
2	−10·9	0·2	0·45	0·1	1×10^{13}	Anionic	55
3	−12·4	0·5	0·37	0·03	5×10^{12}	Anionic	31
4	−31·1	0·15	0·54	0·42	1×10^{10}	Anionic	37

[a] Pigments: 1, 2,9-dimethylquinacridone, crude without treatment; 2, Hostaperm Pink E, commercial sample; 3, 2,9-dimethylquinacridone, DMF treatment; 4, solid-solution of 2,9-dimethylquinacridone and unsubstituted quinacridone
[b] 2θ (CuKα) 5·4.

TABLE 4
Perylene Pigments: Pigment Parameters and Solid-Solution Effect

Pigment[a]	*Test toner charge* ($\mu C g^{-1}$)	*Pigment characteristics*					
		Particle size, d_{50} (μm)	*FWHI*[b] (*deg.*)	*Electrolytes*		*Surface type*	
				Conductance (*mS*)	*Specific volume resistivity* (*ohm cm*)	*Character*	*PC*[c] (μl)
1	−7·1	0·78	0·855	0·2	3×10^{12}	Anionic	50
2	−17·2	0·9	0·935	0·04	7×10^{14}	Anionic	14
3	−18·9	0·87	1·0	0·3	2×10^{14}	Anionic	37

[a] Pigments: 1, PV Fast Red B, commercial sample; 2, solid-solution of Pigment Red 149 with small content of a second component;[13] 3, solid-solution of Pigment Red 149 with higher content of a second component.[13]
[b] At 2θ (CuKα) 13·8

4 CONCLUSION

It has been shown that organic pigments can markedly influence the sign and magnitude of toner chargeability. Each chromophoric pigment class has its own typical range within the charging spectrum. Nigrosines and triaminotriphenylmethanes are typically positive-charging pigments; chromium complexes and metal-salt azo-pigments are typically negative-charging.

Substituents can modify the charging effect considerably and expand the values of Q/M beyond the 'normal' range of the pigment class.

Apart from chemical constitution, solid-state properties can also have an influence. For the pigments studied in this present work the experimental data show a correlation between volume resistivity or crystallinity and charging effect, whereas particle size and electrolyte content, for example, seem to have little or no influence.

Both the chemical constitution and solid-state parameters of a pigment determine the charging effect of the pigment in the toner. The solid-state parameters give the opportunity either to characterise the pigment in detail or, by variation of these parameters, to modify the charging effect.

Real toners are however much more complicated than our test toners, which consisted only of toner resin and pigment. For commercial toners, apart from the sign and magnitude of the charging effect, the influence of the pigment on the long-term stability of the toner charge is important. An additional report on the influence of different pigments and pigment parameters on the long-term charge stability is planned.

REFERENCES

1. Chester F. Carlson, US Patent 2221776 (1938).
2. Chester F. Carlson, US Patent 2297691 (1939).
3. D. Winkelmann, *J. Electrostatics*, **4**, 193 (1977/1978).
4. T. Shinbrot, *J. Electrostatics*, **17**, 113 (1985).
5. K. L. Birkett and P. Gregory, *Dyes and Pigments*, **7**, 341 (1986).
6. J. H. Dessauer and H. E. Clark, *Xerography and related processes*, New York, Focal Press (1965).
7. DIN-ISO 787, Part 9.
8. W. Schempp, P. Hess and Th. Krause, *Papier* (*Darmstadt*), **36** (10A), 41 (1982); *Chem. Abstr.*, **97**, 218287.
9. P. H. Cardwell, *J. Colloid Interface Sci.*, **22**, 430 (1966).
10. H. W. Gibson, *J. Amer. Chem. Soc.*, **97** (13), 3832 (1975).
11. *Proc. 2nd Toner and Developer Industry Conf.*, Imaging Materials Seminar Series, Diamond Research Corporation, Santa Barbara (1986).
12. Hodogaya Chem. Co. Ltd, European Patent Application 0141377 (1984).
13. Hoechst AG, European Patent Application 0176902 (1985).