

Charge Control in Colored Toners: Overcompensation versus Neutralisation

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Introduction

Direction and level of the triboelectric charge¹ of yellow, magenta and cyan toners have to be adjusted in colored toner manufacturing.

The addition of Charge Control Agents allows to overcompensate the polarity of the resin and to adapt it to the preferred position in the triboelectric series. Our concept and understanding of CCA performance will be discussed in part I of the report.

Colorants can also have a strong but more or less undesired impact on the triboelectric charge of the resin² which complicates the toner development. We elaborated methods to overcome this problem. Examples of triboelectrically neutral trichromatic sets of pigments and dyes will be given in part II and III of the report.

Experimental

Test toners were based on styrene acrylate or linear polyester resins containing 2 wt% colorless CCA or 4 wt% colorant. They were prepared in the sequence of melt kneading, pulverizing and classification. Triboelectric data were determined after activation of the developer for the time indicated. Measurements were carried out in a commercially available Q/m-meter^{3,4}. Developers consisted of steel or ferrite carrier⁵, test toner concentration in the developer was 3 wt%.

Results and Discussion

Part I: Positive and Negative Colorless CCA

Our development of colorless CCAs was based on the observation that molecular structures of ionic charge control agents show common features, literature known substances as well as commercially available products:

Positive CCAs like Nigrosine or Triphenylmethane dyes consist of bulky organic cations and small inorganic counterions of high charge density. Negative charge controlling agents are most often bulky anionic metal complexes with protons or metal ions as counterparts.

From this observation a working hypothesis was deduced for the mechanism of charge control agents⁶. Consequently the polarity of the activated toner should be predictable based on molecular features of the CCA.

According to our understanding of positive CCAs the stabilizing effect is caused by the anion which shows high charge density and high mobility. It is possible to adjust the triboelectrically induced positive charge in the resin. The

bulky immobilized cation does not play an active role in this particular process because broad delocalization of the positive charge should lower the charge density to a negligible value. If this is true the charge stabilization effect should also be a function of the size of the delocalized system.

The principle “small hard inorganic ion and large soft organic counterion” should vice versa also be valid for negative toners.

Benzimidazole derivatives⁷ were chosen as one of our basic structures for positive colorless CCAs. Chloride, Bromide and Tetrafluoroborate were found to be the most effective counterions (Figure 1).

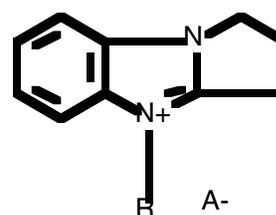


Figure 1. Benzimidazolium salt.

R determines the hydrophobic character of the CCA and its affinity to the resin. Consequently it is decisive for solubility, degree of dispersion and effectiveness of the CCA. An other explanation is an increased shielding of the positive charge by the group R. As a result the influence of cation on the resin is reduced. Figure 2 demonstrates how the charge level is rising depending on bulkiness and chain length of group R.

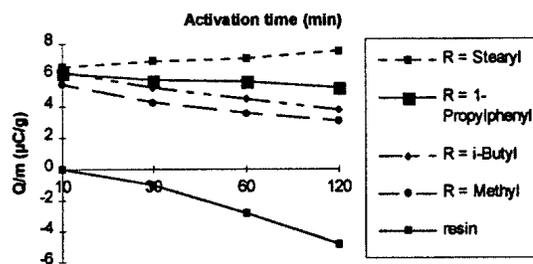


Figure 2. Triboelectric data of benzimidazolium salts in a styrene-acrylate resin vs. a steel carrier.

Realisation of colorless negative CCAs was achieved by using alkaline or earth alkaline salts of β -di- and tricarbonyl compounds⁸ (Figure 3).

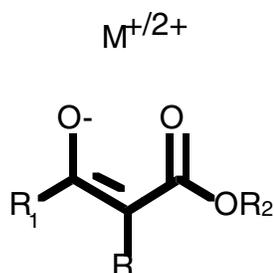


Figure 3. Colorless negative CCA.

Calcium salts of acetoacetic ester derivatives (Figure 3, dicarbonyl 1 and 2: R = H, R₁ = Methyl, M²⁺ = Ca²⁺, R₂ = Alkyl) were found to be less effective than the corresponding acylated products (tricarboxyl compound 1 and 2, Figure 3, R = Acetyl). This superiority of the tricarboxyl compounds supports the idea of the necessity of a widely delocalized anion.

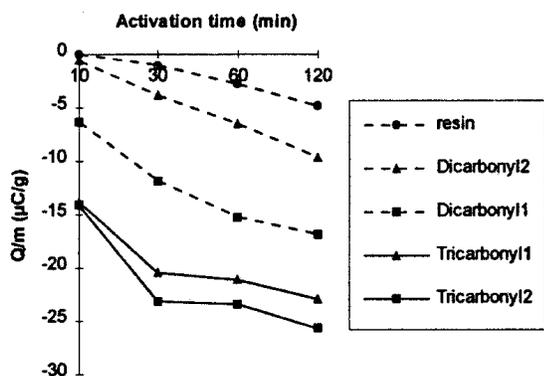


Figure 4. Triboelectric data of calcium salts of di- and tricarboxyl compounds in a styrene-acrylate resin vs. a steel carrier.

Part II: Triboelectrically Neutral Pigments

The influence of pigments with respect to magnitude and polarity of the toner charge is often discussed² in literature. Studies prove that, depending on chemical structure and solid-state parameters, colorants can shift the chargeability of toners in positive or negative direction. While copper phthalocyanines and perylenes exhibit less marked effects, azo pigments impart negative polarity.

By contrast we found that pigments can remain without any influence on the charge level of the resin, a result that strongly simplifies colored toner development. According to our understanding the effect is based on one simple principle: high degree of dispersion. The key to success was the development of a special pigment flushing process⁹ in order to prepare highly concentrated master batches. These so called Lupreton[®] brands can conveniently be used to manufacture colored toners.

A complete trichromatic set was built on Pigment Blue 15:3 (β-copper phthalocyanine), Pigment Yellow 185 (isoindolenine) and Pigment Red 57:1 (laked azo pigment).

Figure 5 shows the charging behaviour of badly dispersed pigments: While Pigment Yellow 185 and Pigment Blue 15:3 perform like positive stabilizers, Pigment 57:1 exhibit negative charge directing characteristics.

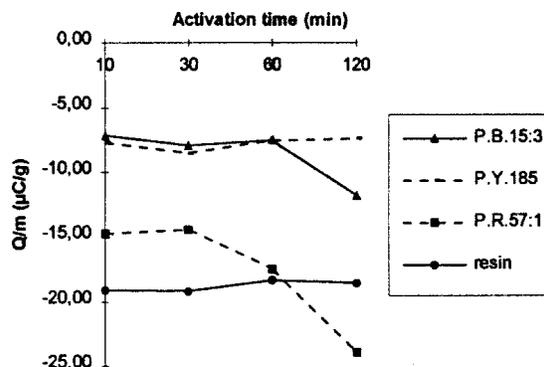


Figure 5. Tribo electric data of Pigment Blue 15:3, Pigment Yellow 185 and Pigment Red 57:1 dispersed in a linear polyester resin vs. a ferrite carrier. Low degree of dispersion.

On the contrary pigment particles which are homogeneously dispersed in the resin yield toners of nearly identical values (Figure 6).

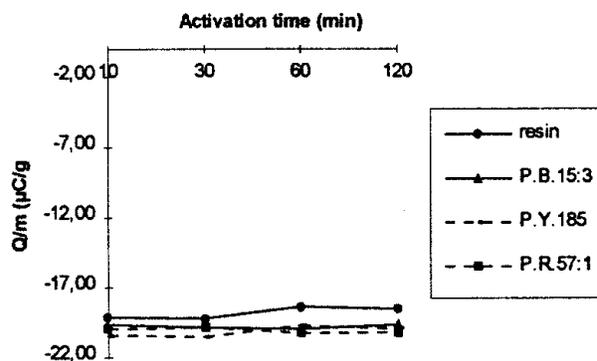


Figure 6. Tribo electric data of Pigment Blue 15:3, Pigment Yellow 185 and Pigment Red 57:1 dispersed in a linear polyester resin vs. a ferrite carrier. High degree of dispersion.

As could clearly be demonstrated by the variety of pigments used the observed effect is not related to certain chemical structures. According to our understanding solid-state parameters are mainly responsible for the charge directing impact of pigments. But solid-state effects are minimized or even "neutralized" during the dispersing process when pigment agglomerates are destroyed or even primary particles are affected resulting in unchanged charging characteristics of the resins.

This principle of high dispersion ceases to be valid if other molecular features of the colorant give an impact on the resin. An example therefore is Pigment Red 81:1. Due to its high brilliance and transparency Pigment Red 81:1 seemed to be suitable for the preparation of toners. Despite that, the amorphous, small sized particles proved to be easily dispersible but no stable charging behaviour of negative toners could be obtained. The long term stability was always more than unsatisfying. Figure 7 shows that P.R.81:1 has obviously positive charge directing but no stabilizing abilities.

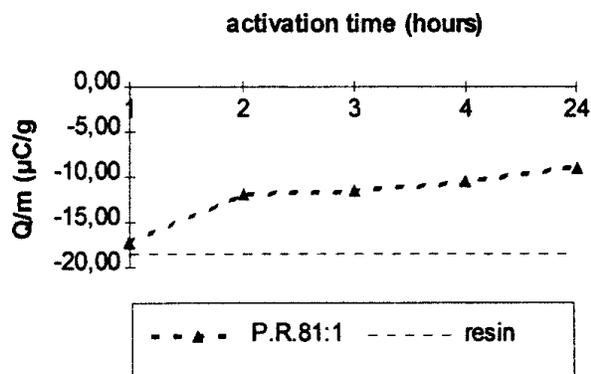


Figure 7. Triboelectric data of Pigment Red 81:1 in a linear polyester resin vs. a ferrite carrier. Data for resin extrapolated.

Our molecular approach for the mechanism of ionic CCA explained in part I gave us finally an idea how Pigment Red 81:1 influences the resin. Though it is a pigment the molecular structure seems to be decisive. Chemically, Pigment Red 81:1 is a rhodamine laked with molybdc silicic tungstic acid. But opposite to effective charge stabilizing agents, both organic cation and inorganic anion are large, bulky and of low charge density. The lacking dominance of the inorganic counterion gives rise only to a charge directing but no stabilizing effect.

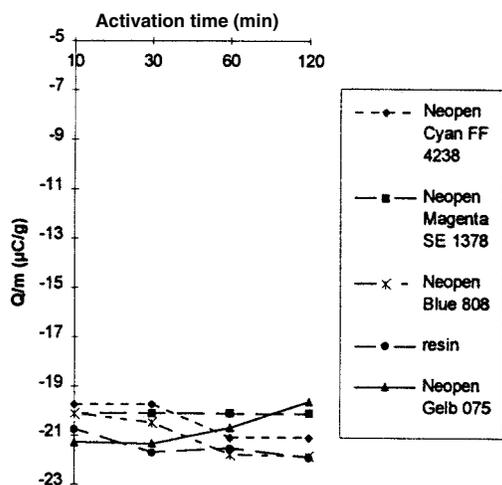


Figure 8. Triboelectric data of Neopen® dyes in a linear polyester resin vs. a ferrite carrier.

Part III: Triboelectrically Neutral Dyestuffs

Due to their compatibility to polar organic solvents nonionic Neopen® dyes were chosen as suitable candidates for colored toners. The colorants represent a wide variety of different chemical structures proving that structural param-

eters are not significant: Neopen Yellow 075 is a heterocyclic azo dye, Neopen Magenta SE 1378 and Neopen Cyan FF 4238 are methine dyes and Neopen Blue 808 is a copper phthalocyanine derivative. According to their nonionic structure no charge stabilizing or directing effects based on molecular features have to be expected. The compatibility of the dyes to the toner resin should allow easy preparation of toners exhibiting ultrafine distribution of colorant particles. Even dissolving colorants in the resin could be assumed. Consistently solid-state parameters should be minimized or excluded.

The performance of the Neopen dyes is shown in Figure 6. As supposed they do not influence the charging properties of the toner resin which supports our mechanistic considerations. It also allows us to present a trichromatic set of dyestuffs which is tailor made in terms of high brilliance, transparency and easy preparation.

Conclusion

As shown charge control in toner resins is affected by molecular and solid-state parameters:

1. Molecular features determine the charge controlling characteristics of ionic CCAs. Ionic CCAs consist of bulky ions and small counterions of high charge density. The small hard counterions are decisive for the charge stabilizing effect. CCAs stabilize and overcompensate the charge level of the resin. The prediction of the charge directing effect of ionic CCAs is possible. These molecular effects cannot be suppressed by dispersion.

2. Pigments and dyes can become triboelectrically neutral when they are compatible with the resin and perfectly dispersed in it. Prerequisite is that only solid-state parameters and no molecular features are determining their influence on the resin.

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