Charging Characteristics of Electron Donor-Acceptor Complexes formed by Combination of Positive and Negative Charge Control Agents

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Abstract

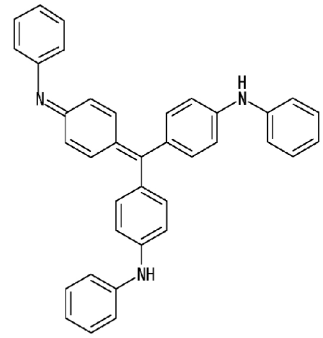
The charging characteristics of charge control agent (CCA)/ binder-resin matrix films containing a combination of a positive and a negative charge control agents were investigated by measuring the amount of tribo-charges. Tri-phenylated-para-rosaniline (TPPR) was used for the positive type CCA and 3,5-tert-butylsalicylate (TBS), 3,5-tert-bytylsalicylate zinc complex (SZC) and n-propyl gallate (PG) were used for the negative type CCA. The CCAs are dissolved in a styrene-acryl resin-binder solution and coated on a stainless steel plate to prepare the CCA/binder-resin matrix films. Ferrite powders were cascaded onto the matrix film surface and the generated cascade charge was measured.

The results show that TPPR (positive type CCA) forms an electron donor/acceptor complex with the negative type CCAs, and the amount of the positive charge increases by adding an increasing amount of negative type CCAs. The formation of the complex was confirmed by increasing light absorbance at 600 nm by adding an increasing amount of negative type CCAs to the resin-binder solution containing TPPR. The factors that affect the charge control capability of the CCA in determining the amount of the tribo-charge on toner particle are discussed from the viewpoint of electron donor/acceptor interactions between CCAs and other components in the toner formulation.

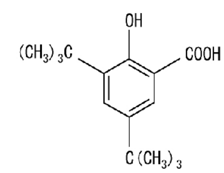
Introduction

For the toner in electrophotographic developer, the CCAs are indispensable components to obtain suitable charging characteristics. The CCA is considered to control the amount of tribo-charging of toner to a requested value even though other components such as pigments and resin binders are changed. Actually, however, some types of pigments and resin binders seriously affect the charge control capability of the CCA. These phenomena suggest that there must be some interactions between CCA particles or molecules and other components added to the toner.[1]

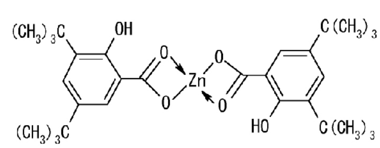
The acid/base or electron donor/acceptor interactions between CCA and toner components were observed as an effect weakening the charge control capability of the CCA.[2] In the case of the toner which contains a positive type CCA, for example, the positive charge imparting capability by addition of the positive type CCA is weakened by the acidic functional group in the binder-resin.2 In toner particles, the pigments and dyes having a strong electron accepting or donating functional group in its molecular structure also affect the charge control capability of the CCA. The effects are remarkable in the case that both the CCA and components are completely dissolved in the resin-binder to a molecular size. The interaction between negative type and positive type CCAs where both CCAs are dissolved in the resin binder to a molecular size would be an extreme case that affects charging capability of each CCA.



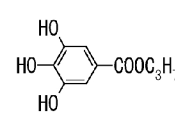
Tri-phenyl-Para-Rosaniline (TPPR) ; Positive



3,5-tert-Butyl-Salicylate (TBS) ; Negative



3,5-tert-Butyl-Salicylate Zinc complex (SZC) ; Negative



n-Propyl gallate (PG) ; Negative

Figure 1. Structural formulas of positive and negative type CCAs.

According to the above consideration, the effects of negative type CCA addition to the charge control capability of tri-phenylated-para-rosaniline (TPPR; positive type CCA) in toner-resin-binder were investigated by measuring the cascade-charge using CCA/ binder-resin matrix films. An unexpected result was obtained that the amount of positive charge was increased by adding an increasing amount of a negative CCA.

The details of the experiment are mentioned below.

Experimental

Preparation of CCA/Binder-Resin Matrix

Tri-phenyl-para-rosaniline (TPPR) was used as the positive type CCA.[3]

Either 3,5-tert-butyl-salicylate (TBS), 3,5-tert-bytylsalicylate zinc complex (SZC) or n-propyl gallate (PG) was used as the negative type CCA. The structural formulas of these CCAs are shown in Figure 1. A styrene-acryl copolymer (St-Ac, acid value: 0.3, bimodal molecular weight distribution, Mw/Mn: 85) was used as the binder-resin for the matrix film.

The St-Ac was dissolved in the toluene/2-butanone (1/1) mixed solvent to prepare a resin-binder solution (R solution). The concentration of St-Ac in the R solution was 5wt%. A prescribed amount of each CCA was added and dissolved in the R solution to prepare the M solution for the matrix film. All types of CCAs were completely dissolved into the R solution and no remaining CCA particles were detected under microscopic observation.

A stainless steel (SUS) plates was dipped into the M solution, pulled up, and dried in a 70 degree C oven for more than 1 hour to obtain a dry matrix film. The films were prepared by using the M solutions containing different types of CCAs of different concentrations.

Cascade Charge Measurement

Ferrite beads (diameter: 74–147 μm) were cascaded onto the matrix film coated on the SUS plate set on the inclined surface of a PTFE block. The inclination angle was 60 degrees. The charge generated on the film was measured with an electrometer connected to the SUS plate.

Results

Effects of SZC Particle Size on the Matrix Film Surface

The positive charge increase profile of the tri-phenyl-para-rosaniline (TPPR; positive type CCA) with the increasing amount of its addition in the matrix film is shown in Figure 2. The result shows that the TPPR can be regarded as an effective positive type CCA that gives a strong positive charge to the matrix film especially in the range of addition from 0 to 10wt%.

Figure 3 shows the charge increase profiles with the increasing amount of various negative type CCAs in the matrix film. The dotted lines show the negative charge increase profiles of the 3,5-tert-butyl-salicylate (TBS), 3,5-tert-bytylsalicylate zinc complex (SZC) and n-propyl gallate (PG) with the increasing amount of their addition to the matrix film, respectively. On the other hand, the solid lines show the positive charge increase profiles of these negative type CCAs with the increasing amount of their addition to matrix films containing 3wt% positive type CCA (TPPR), respectively. In this case, the positive charge increases with the increasing amount of negative type CCAs addition.

Figure 4 shows the positive charge increase. profiles with increasing molar fraction of negative type CCAs in the matrix film containing 3wt% TPPR (positive type CCA). Comparison with the positive charge increases profiles show by the solid lines in Figure 3 makes it clear that positive charge increasing effects by adding increasing amounts of negative type CCAs are more obvious. By increasing the molar fractions of the negative type CCAs, each positive charge reaches the maximum value at a certain molar fraction.

Discussion

Positive Charge Increase Profile by the Addition of Positive Type CCA (TPPR)

The positive charge increase profile of the TPPR with the increasing amount of its addition to the matrix film shown in Figure 2 can be divided into three regions.[4]

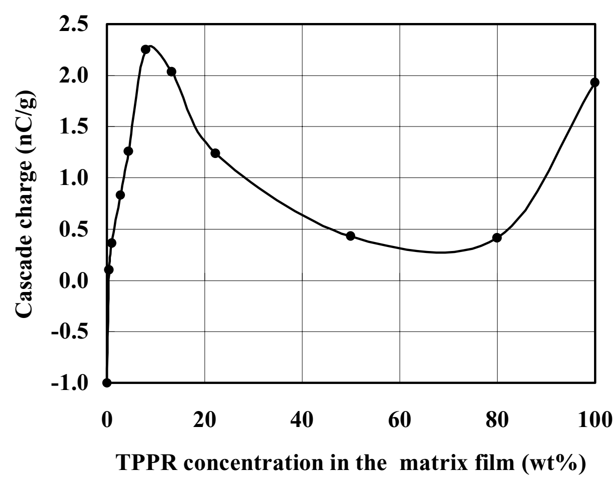


Figure 2. Relationship between the amount of cascade charge and TPPR concentration.

By increasing the amount of TPPR addition, the positive charge increases rapidly and reaches a saturation value (region I; 0-10wt%), then gradually decreases (region II; 10-80wt%), and finally increases again to attain the value corresponding to 100wt% TPPR (region III; 80-100%). In region I, the TPPR molecules deposited on the matrix film surface are oriented. The population of TPPR molecules increases as the amount of its addition to the matrix film increases and reaches the maximum value at about 10wt% TPPR concentration. The charge decrease in region II is attributed to a disorder caused by the excess amount of TPPR molecule deposition on the film surface. The ratio of the oriented molecules on the surface gradually recovers toward the film containing 100wt% TPPR. Suganami et al. observed the same charging profiles with a matrix film using SZC/resin solution.[5]

Negative Charge Increase by Addition of Negative Type CCA

The dotted lines in Figure 3 shows that the amount of the negative charge increases with the increasing amount of the negative type CCA. Among the three types of negative type CCAs, TBS shows the smallest or no negative charge imparting effect to the matrix film. SZC, which is the zinc complex of TBS, on the other hand, shows the largest negative charge imparting effect to the matrix film. It is interesting that, in the case of SZC, the negative charge imparting effect to the matrix film is enhanced by the combination of an electron accepting TBS^- anion and an electron donating Zn^{2+} cation. Hashimoto et al. confirmed the same effect by using a series of tetra-phenyl-borate (TBP) complexes which are the combinations of electron accepting TBP^- anions and electron donating metal cations (M^+).[6)]

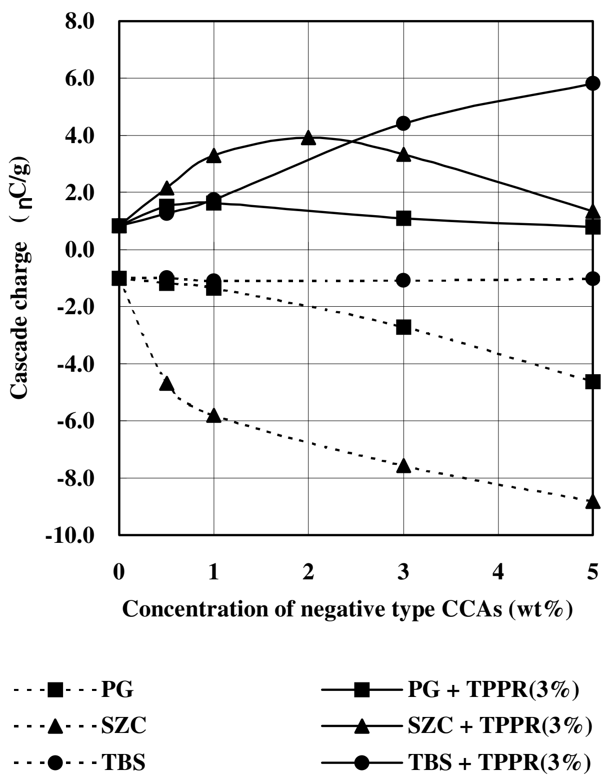


Figure 3. Relationship between the cascade charge and concentration of negative type CCAs.

The Positive Charge Increase by the Addition of Negative Type CCA

The positive charge increase by increasing the molar fraction of the negative type CCAs in Figure 4 suggests that each negative type CCA forms an electron donor/acceptor complex with TPPR and enhances its positive charge imparting capability to the matrix film. The formation of the complex was confirmed by the measurement of light absorbance spectrum of the M solution containing both TPPR and SZC. The results are shown in Figure 5. The light absorbance at 600 nm increases by increasing the amount of SZC addition to the M solution containing 3wt% TPPR.

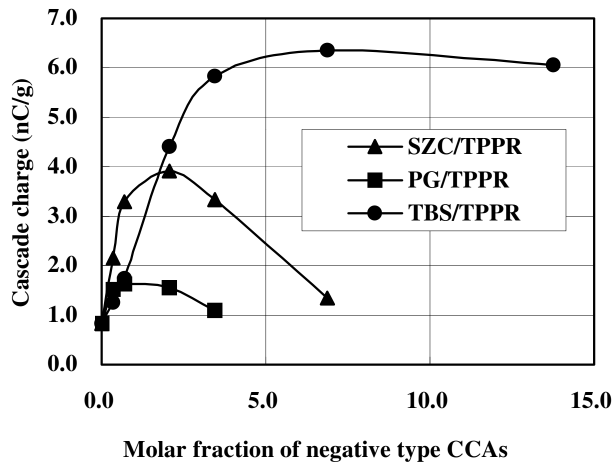


Figure 4. Relationship between the cascade charge and the molar fraction of negative type CCAs.

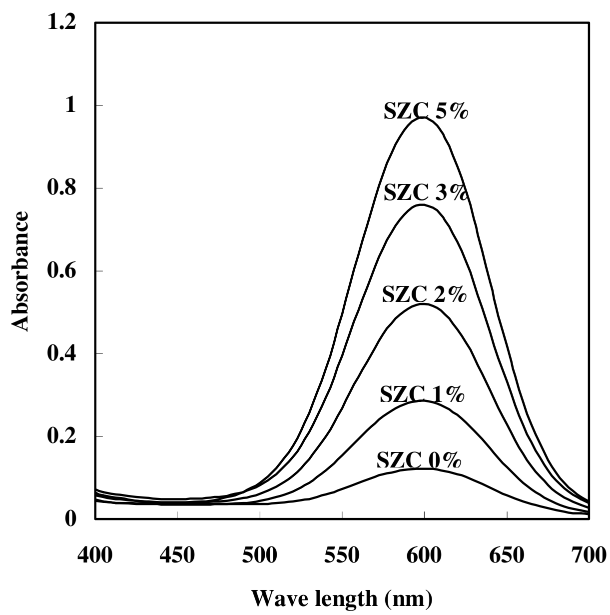


Figure 5. Increase of light absorbance with the increase of the amount of SZC addition.

It is known that the TPPR formed the complex with some anion (electron accepting compound) such as $-SO_3^{2-}$, $-NO_3^-$ and $-Cl^-$.[7] The light absorbance at 600 nm in these complexes increases in proportion to the amount of addition of these anions. The reason for the increase of the absorbance has been explained by the formation of a conjugated double bond through the phenyl ring in the tri-phenyl methane group in TPPR; by the complex formation, all the phenyl rings in the TPPR molecule change their configuration to form a planar structure.[8]

In the charge increase profiles in Figure 4, the maximum charge is attained at a certain molar fraction of the negative CCAs. The molar fraction at which the maximum charge is obtained is estimated to be an integer which is 2 in PG, 3 in SZC, and 6 in TBS per a unit mol of TPPR. The integer seems to relate to the coordinating number of the negative type CCA molecules to the TPPR molecule, but further analysis is needed to elucidate this behavior clearly.

The positive charge enhancing phenomena mentioned above are somewhat similar to that of the negative charge enhancing phenomena in the complex formation of TBS^{-} $/Zn^{2+}$ and TBP^{-}/M^{+}.

Role of CCA in Toner Charge Control

In the market, SZC is regarded as an excellent negative type CCA. The above experiment shows that SZC easily turns into a positive charge enhancing agent as the result of complex formation with TPPR (positive type CCA). In general, almost all components appearing in the toner formulation is regarded to have an electron donating or an electron accepting properties to form the charge transfer complex with CCA molecules in toner. That is why selection of suitable CCA is essential according to the toner formulation. The formation of the complex can be confirmed by the amount of increase of absorbance in spectral absorbance curves. Above all, the cascade charge can be regarded as an indicator for sensitively detecting the complex formation on the matrix film surface.

Conclusion

The charging characteristics of the CCA/binder-resin matrix film containing a combination of a positive and a negative charge control agents were investigated by measuring the amount of tribo-charge.

The positive type CCA forms the electron donor/acceptor complex with the negative type CCAs, and the amount of the positive charge increases by adding an increasing amount of negative type CCAs. The formation of the complex was confirmed by increasing light absorbance at 600 nm with the increasing amount of negative type CCA addition to the resin-binder solution containing TPPR. The factors that affect the charge control capability of the CCA were discussed from the viewpoint of electron donor/acceptor interaction between CCA and other components in the toner. The formation of the complex can be confirmed by the increase of light absorbance. Above all, the cascade charge can be regarded as an indicator for sensitively detecting the complex formation on the matrix film surface.

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Biography

Keiki Suganami obtained his B.S. in chemistry from Sophia University in 1982. Since that year, he has been working on research and development division at Morimura-Badische Co., Ltd. 1999, the company name was changed to Morimura-Chemicals Ltd. In last year, he entered a Ph D. course of Ibaraki University.