A study on the charge-control mechanism

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Abstract

A charge-control mechanism of CCA (Charge Control Agent) has been proposed in the present investigation that assumes an appreciable temperature increase at the "toner/carrier" interface due to the tribo-electrification. Further assumption is that CCA be present on the surface of both toner and carrier. Because of the present local heating, the electrical resistivity of CCA is remarkably decreased to give a conductive channel, through which the carrier-flow occurs effectively to charge up the toner. These two assumptions have experimentally been verified. Especially, the local heating up to around 100 °C has been confirmed by using a pigment-marker which changes its color from black to red. Around this temperature, the electrical resistivity of CCA is also found to be significantly lowered by three orders of magnitude as deduced from the temperature dependence of the electrical resistivity.

1. Introduction

Charge-control agents (CCAs) are widely used in electrophotography that create a desired charge level and polarity. A number of investigation have been carried out on the charge-control mechanism on the basis of the work function,[1] mass transfer[2] and charge transfer.[3] However, no clear-cut, consistent explanation has been established yet at the moment.

In the present paper, we propose a novel model that assumes an appreciable temperature increase at the "toner/carrier" interface due to the tribo-electrification.[4] Because of the present local heating, the electrical conductivity of CCA (which resides on the surface of both toner and carrier) is remarkably increased to give a conductive channel, through which the carrier-flow occurs effectively to charge up the toner.

2. Our proposed model on the charge-control mechanism

We assume in the first place that the toner charge arises from the difference in work function between toner and carrier and that CCA resides, though an extremely small quantity, on the surface of both toner and carrier. The existence of CCA has experimentally been verified by Nash et al.[1] and Oguchi et al.[2] We assume that the phenomenon of the tribo-electric charging between toner and carrier is similar to that of the charging at the interface between two different metals (say, A & B) in a thermocouple: *i.e.* $\Delta\phi = \phi_A - \phi_B$ where ϕ denotes the work function. In general, simple contact of two different metals fails to function as a thermocouple due to oxide barriers at the metal surface which disturbs the electron flow as induced by the difference in work function. Therefore, flame or electric welding is often used to contact two metals in the presence of a small amount of flux. Flux serves as a material to remove oxide layers as well as to increase the wetting properties. We assume that CCA plays a similar role in tribo-electrification to facilitate the charge flow.

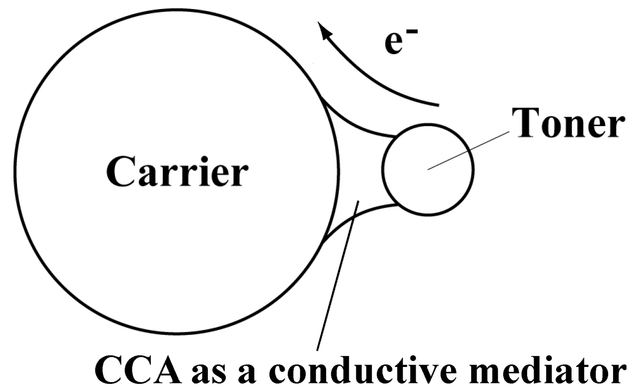
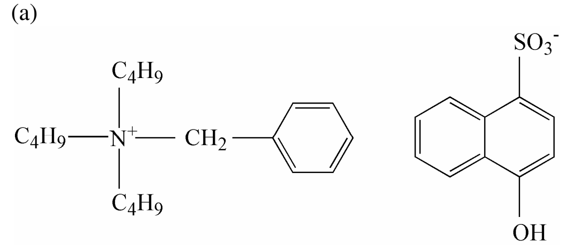


Fig. 1 *Charge transfer at the "toner/carrier" interface upon tribo-electrification.*

Fig. 1 shows the toner and the carrier which are bridged by a CCA (rather exaggerated picture !). Our model assumes that the temperature at the interface "toner/carrier" increases upon mutual collision during the tribo-electrifrication. That is, the kinetic energy of both toner and carrier can be converted into thermal energy upon instantaneous impact. Then, the CCA is immediately heated to a certain temperature, say 100 ºC. Since CCA is an organic semiconductor, its electrical conductivity increases exponentially to form conductive channels between toner and carrier. This ends up with a rapid charging and a saturated charging level. The saturation charge is primarily determined by the difference in work function of the polymers which cover the surface of toner and carrier and secondarily by the coverage of the CCA. Complete coverage of the toner or carrier surface with CCA leads to non-charging because no effective difference in work function exists between toner and carrier: $\Delta\phi \approx 0$ where ϕ denotes the work function.

In order to verify our proposed model, the following issues must be addressed in experiments: 1) local heating at the interface "toner/carrier" upon impact, 2) temperature dependence of the electrical conductivity of CCA, 3) carrier determination of CCA and 4) existence of CCA on the surface of toner and carrier.

(a)



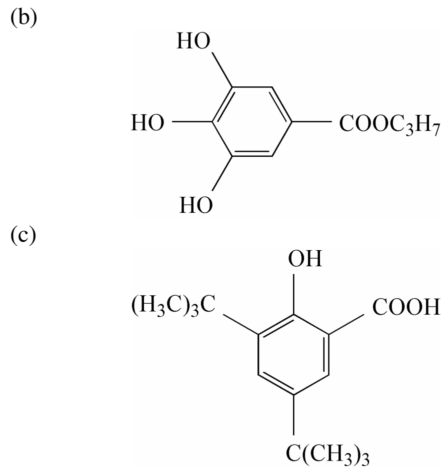


Fig. 2 *CCAs : (a) p-51 (b) PG and (c) TBS*

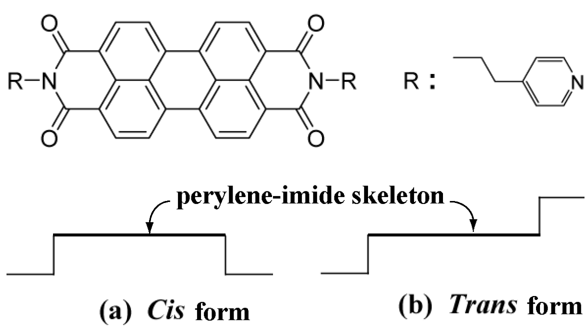


Fig. 3 *Molecular structure of 4-pyridylethylperylene-imide (PEP) : (a) cis form and (b) trans form.*

3. Materials

In the present experiment, pseudo toners made of a styrene-acryl polymer as well as teflon-coated carriers were used. Quaternary-ammonium salt (P-51 of the positive type from Orient Chemicals, *n*-propyl gallate (PG) and 3,5-*tert*-butylsalicylate (TBS) were used as CCAs because these possess melting points and thus easier to prepare reproducible samples (Fig. 2).

4. Results and Discussion

4.1 Local temperature at the interface "toner/carrier"

Ethylpyridyl-perylene-imide derivative (EPP) shown in Fig.3 is known to exist in either *cis* or *trans* isomers in the solid state, characterized by red and black colors, respectively.[5] In addition, the *trans* form can be transformed into the *cis* form when heated above 100 ºC. Therefore, EPP can serve as a sensitive marker to check the local temperature at the interface between toner and carrier upon impact.

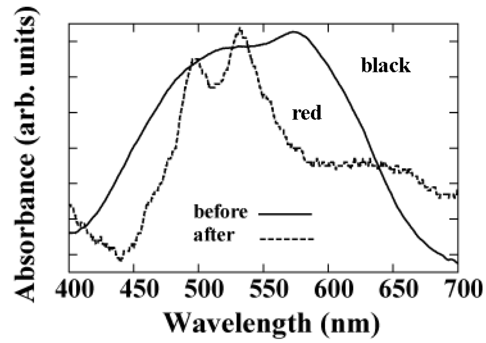


Fig. 4 *Diffuse reflectance spectra before and after shaking.*

1 g of pseude toner (8.5 ± 0.5 µm in diameter), 10 g of the teflon-coated carrier (70 µm in diameter) and 10 mg of PEP were charged in a bottle of 100 ml and then shook with a paint conditioner for 30 min. After that, diffuse reflectance spectra of the carrier were measured.

Fig. 4 shows the diffuse reflectance spectra before and after shaking. As evident from the spectra, the longest-wavelength band in the black spectrum disappears due to tribo-electrification, showing a color change from black to red. This indicates that the local temperature at the interface between toner and carrier rose up to, at least, about 100 °C as a result of collision between toner and carrier. Then, the CCA which resides between toner and carrier (see Fig. 1) can also be heated above 100 °C, leading to the formation of conductive channels between toner and carrier.

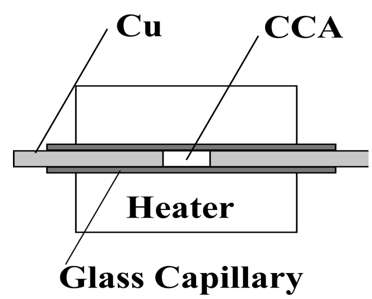


Fig. 5 *Experimental setup for measurements of the electric conductivity as a function of temperature.*

4.2 Temperature dependence of electrical conductivity of CCA

Electrical measurements in powdered form is widely known to lead to scattered results. Therefore, measurements were made on fused samples prepared in the following way. Powdered samples were charged in a capillary tube (Fig. 5) and then melted, followed by a gradual cooling. Great care was taken to keep the sample entirely transparent while cooling. Then, measurements were made in air in the temperature range between RT and 200 °C.

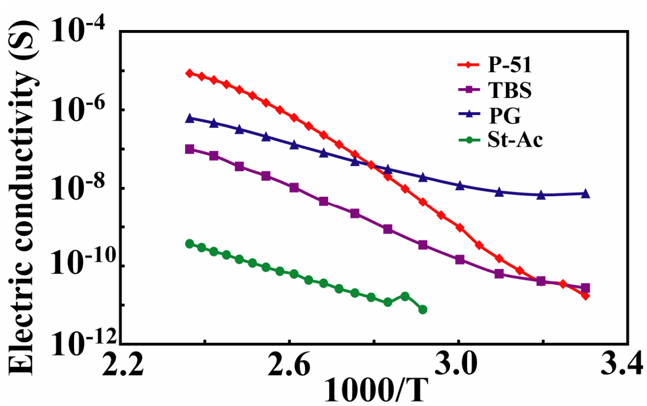


Fig. 6 *Arrhenius plot (logσ vs 1/T) for various CCAs and styrene-acryl polymer.*

Since CCAs are regarded as organic semiconductors, the temperature dependence of the electrical conductivity is expected to follow the Boltzmann distribution as given by the following equation:

$$n = n_0 \exp\left(-\frac{E_g}{2k_B T}\right)$$

where n, ΔE, T and k_B denote the number of carriers, activation energy, temperature and Boltzmann constant, respectively.[6)]

Fig. 6 shows the temperature dependence of the electrical conductivity (Arrehnius plot) for P-51, PG, TBS and styrene-acryl (St-Ac) resin that is the main constituent of toners. The conductivity increases linearly with temperature in these samples, showing a typical semiconductive behavior. The electrical conductivity of St-Ac polymer is lower than that of P-51 by two-three orders of magnitude. P-51 and TBS exhibit a similar temperature gradient, although the conductivity of the former is higher than that of the latter by two orders of magnitude. In both samples, the conductivity at about 100 °C is three orders of magnitude higher than that at RT. The temperature gradient of PG is smaller than that of P-51 and TBS. Nevertheless, the increase in conductivity amounts to two orders of magnitude. It is also to be noted that the conductivity of St-Ac is lower than that of P-51, PG and TBS by about two orders of magnitude.

The above results clearly indicate that the CCA between toner and carrier (see Fig. 1) which can be heated above 100 °C forms a conductive channel for the charge carrier. This accelerates the charging rate and thus supports directly our charge-control mechanism.

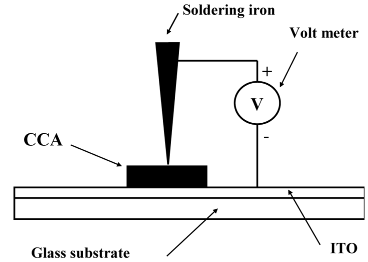


Fig. 7 *Experimental setup for measurements of the Seebeck effect.*

4.3 Determination of the charge carrier

The determination of the charge carrier provides us with valuable information on our charge-control model. It is however difficult in highly resistive materials to determine the carrier by means of the Hall effect. Instead, we employed the thermo-electric power method based upon the Seebeck effect.[7)] This method determines the sign of the potential which appears between hot and cold ends. If the potential is positive, then the charge carriers are electrons; whereas the hole conduction gives a negative potential.

Fig. 7 shows the experimental setup where the hot end is a soldering iron maintained at 100 °C while the cold end is ITO at RT. As a result, P-51 and PG gave positive potentials, indicating that the charge carriers are electrons. However, the Seebeck potential was too small in TBS to determine the charge carrier.

4.4 Verification of the existence of CCA on the surface of toner and carrier

As stated in Introduction, Nash and his coworkers[1)] as well as Oguchi et al.[2)] reported that a small portion of CCA resides on the surface of toner and carrier. We tried here to measure the work function of the carrier by means of UPS (Ultraviolet Photoelectron Spectroscopy) before and after mixing with CCA-embedded toners. The present measurements gave the values of 4.90 and 5.05 eV, respectively. The difference in work function suggests that the work function of the carrier has been modified by CCA.

4.5 Wetting properties of CCA

Based upon the preceding discussions, CCA works as a conductive mediator upon tribo-electrification to facilitate the charge transfer between toner and carrier. Another important function of CCA is the wetting effect of CCA to minimize the surface tension and to maximize the contact area of the "toner/carrier" interface. This is supposed to further accelerate the charge transfer efficiency. The present function or role is compared to that of flux used often in solid-state reactions or in "metal/metal" soldering.

5. Conclusions

We have presented a novel charge-control mechanism that assumes an appreciable temperature increase at the "toner/carrier" interface due to the tribo-electrification. We have rationalized the present model on the basis of the experimental results below.

1. The local temperature at the "toner/carrier" interface amounts to at least 100 °C.
2. The CCA sandwiched by toner and carrier is accordingly heated above 100 °C.
3. The electrical conductivity of CCA at about 100 °C is higher by two-three orders of magnitude as compared with that at room temperature. This indicates that the CCA forms a conductive channel, through which the carrier-flow occurs effectively to charge up the toner, ending up with a steady charge level.
4. The resistivity of St-Ac is two-three orders of magnitude higher than that of CCA.

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