Toner-Toner Interaction Force Between Opposite Polarity Toners

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Abstract

Although a lot of charging behavior for toner and carrier has been reported, little work on toner-toner interaction force has been done in two component development system. The purpose of the present research was to investigate the toner-toner interaction force with two kind of toners which had opposite polarity each other and equivalent charge-to-mass ratio against a certain carrier.

It was shown that by mixing the carrier and different mixing ratio of these two kinds of toners, the developer flow was affected by the mixing ratio. Additionally, these toners showed visible agglomerations by electrostatic attractive force when they mixed, and the interaction force was also investigated quantitatively as toner flow ability and cohesiveness by changing the ratio of the two toner mixes.

Charge distribution spectrographs of those developers were also measured with E-SPART analyzer, and as the results, such blending of positive and negative polarity toners in the ratio of one to one showed a single peak in the vicinity of zero charge instead of the bi-model charge distribution split into plus and negative region. Thus, charge distribution of those developers has been incorporated in toner-toner interaction.

Introduction

In the design of two component developer for stabilizing high quality image, tremendous efforts have been made to get a sharp charge distribution at optimum charge level. There are several interesting reports on the relation between background and charge distribution[1-3], but little work on effect of wrong-sign toner to the developer has been done in two component development system.

For example, Hays proposed a background mechanism based on an electric-field-dependent contact charge modification of toner caught between a carrier bead and image receiver, and for an increasing back bias voltage applied across the developer, the amount of low charge and wrong sign were increased[1]. It is important to confirm the effect of wrong-sign toner when it is accumulated during longevity usage, because most of the residual wrong-sign toners on the image receiver are removed and recycled in the developer by cleaning function of developer brush if it occurs as he proposed.

As Julian et al. proposed[4,5], toner-toner charge exchange process is of roughly equal importance with the toner-carrier process. Similarly, considering the probability of first collision toner and carrier, it depends specific surface area of existing toner and carrier in the developer, though this charge exchange process is a function of time.

Equation (1) gives total surface area S of spherical particle.

$$S = \frac{3m}{\rho r} \tag{1}$$

where, ρ, r and m mean a specific gravity, a radius as a sphere and a mass respectively. Simply, since the probability of particle collision is due to individual specific surface area of toner and carrier, as one typical example, in case of T/D = 5%, r of average carrier and toner are 100 and 10μm, and ρ of carrier and toner are 9 and 1.25g/cm³ respectively, the carrier and toner surface ratio is;

$$S_{carrier} / S_{toner} = \frac{m_{carrier}\, \rho_{toner}\, r_{toner}}{m_{toner}\, \rho_{carrier}\, r_{carrier}} = 0.26$$

Thus, the probability of toner-carrier contact is only one forth of toner-toner contact. It means it should not be discussed without effect of toner-toner interaction.

Especially in actual development, researchers have worked to minimize wrong sign toner by design of toner and carrier system so that they could improve the image quality. Thus sharp charge distribution is targeted, the amount of wrong-sign toner is too small to discuss the effect against the system. Our intention is to manipulate a lot of wrong-sign toner to observe the effects more significantly.

Additionally, there were several examples on dual peak in charge distribution split in low charge and high charge or wrong-sign and regular region[3,5,7]. Then another purpose is to clarify effect of wrong-sign toner in charge distribution spectra, and how wrong-sign would be change the distribution. We analyzed the charge distribution by varying the wrong sign toner ratio to regular toner.

Experimental

(a) Material

Carrier 1: Spherical copper/zinc ferrite powders of nominal 50µm diameter. The conductivity was 15 µA, resistivity value was 10.6 log Ω with c-meter (Epping GmbH) applying 10 volts with 9000pF of condenser and magnetic force at 572 gauss.

Polyester resin 1: Polyoxypropylene (2.2)-2,2'-bis (4-hydroxylphenyl) propane, Polyoxyethylene (2.2)-2,2'-bis (4-hydroxylphenyl) propane, trimelitic anhydride, octenyl succinic anhydride and telephtalic acid were allowed to react for condensation polymerization at 230 ºC with small amount of dibutyltin oxide in a glass flask, which was equipped with a thermometer, a stainless steel stirring rod, a reflux condenser and nitrogen inlet tube. The value of measured AV according to ASTM D1980-67 was 20 KOH mg/g. The degree of polymerization was monitored by softening point (Tsp) measured according to ASTM E28-67, then the reaction was terminated when the Tsp reached to 145 °C. The glass transition temperature (Tg) was 63ºC by DSC Model 200 manufactured by Seiko Instruments Inc., at a heating rate of 10 ºC/min.

Styrene Acrylic resin 1: Styrene, 2-ethylhexylacrylate and dimethylaminoethyl methacrylate were copolymerized in xylene with dicumyl peroxide as a initiator at 130 ºC, then up to 200 ºC followed by removal of xylene. The obtained resin showed 130 ºC of Tsp and 65 ºC of Tg. This resin gave positive charge when it was combined with Carrier 1.

Toner N-01: To 100 percent by weight (wt%) of Polyester resin 1, 2 wt % of Chrome azo-benzene complex and 1 wt % of nigrosine compound were used as CCA. 2 wt % of a polypropylene wax and 6 wt % of carbon black were added. They were compounded by a twin screw extruder, then they were micronized and size-classified to produce a volume median diameter of 11µm. The powder was externally treated with 0.3 % of hydrophobic silica to get efficient flow ability.

Toner P-01: To 100 percent by weight of Styrene Acrylic resin 1 which was positively chargeable, 2 wt % of a polypropylene wax and 7 wt % of CB were added. The toner sample was prepared as same as N-01.

(b) Measurement Procedures

Charge-to-mass ratio (Q/m): Each toner powder was combined Carrier-1 at 10 % of T/D, and mixed for appropriate time on a roll mill. 0.5 grams of the mixture was then transferred into a pre-weighted Faraday cage and the toner particles were blown off from the carrier by air jet (2 sec. at 1.5 kgf/cm^2) through a wire screen with 36µm opening and then the Q/m was calculated.

Toner falling rate: Toner flow tester: 300 gram of toner was put in a bottle and closed with a cap, then it was shaken 20 times by hand to have toner aerated. Then the cap was removed and the bottle was equipped to the Toner drop tester. The position of the bottle was changed upside-down that direction of the spout came to downwards. Toner weight in receipt cell under bottle was measured after 5 minutes rotation at 6 RPM and calculated the falling rate (gram/minute). The poor the flow ability of toner gets, the less the toner falling rate becomes.

Apparent density of Developer (AD): 20 grams of toner and 180 grams of Carrier-1 were weighed and put in 250 ml of polypropylene bottle and each of these are mixed on a roll mill at 250 RPM for 3, 10, 60 minutes respectively. Then, without additional mixing, 100 grams of developer was loaded the test specimen carefully into funnel of the Hall Flow meter (Alcan Powders and Pigments). When the powder completely fills and overflows the periphery of the density cup, with the blade held perpendicular to the top of the cup, level off the powder flush with the top of the density cup. By weighing it, the AD (gram/cm^3) was calculated. (according to ASTM B417, ISO No. 3923).

Developer Cohesiveness : 20 grams of toner and 180 grams of Carrier-1 were weighed and put in 250 ml of polypropylene bottle and mixed on a roll mill at 250 RPM for 3 minutes. Then, without additional mixing, 10 grams of mixed developer were put on stainless steal mesh which had 149 µm opening (100 Mesh) silently. After fixing the cell with spring to Micro-electromagnetic vibration Type M-100 (Tokyo Tsutsui rikakagaku instrument), this mesh was vibrated at Volume 1 for 10 seconds. The residual percentage of the developer was calculated by weighing the residual weight on the mesh. This measurement was repeated 2 times and taken the average as cohesiveness.

Toner Cohesiveness : 3 grams of toners were weighed and put in 50 ml of polypropylene bottle. Then it was mixed on a roll mill at 250 RPM for 15 seconds. Without additional mixing, 1 gram of mixed toner was put on the measurement cell which had stainless steal mesh of 105 µm opening (150Mesh) silently, and further procedures were followed measurement of Developer Cohesiveness.

Charge distribution : Charge distribution of 3,000 toner particles was measured by a laser Doppler method with E-SPART Analyzer Type-1 (Hosokawa Micron Corporation), which detects the phase delay and drift of the toner particles in an electric field. Nitrogen gas pressure of nozzle for separating the toner from the developer was set at 0.1 kgf/cm². Field voltage of 100 Volt was applied across the electrodes in the measurement cell. In this paper, charge distribution means q/d spectra for all sized particles.

Discussion and Results

To confirm charge level and polarity of two toners, carrier C-01 was mixed with positive toner P-01 and negative toner N-01 for 3 minutes as varying wt % of P-01 toner against N-01. The Q/m values by blow off method are plotted in Figure 1. It shows the linear relationship passing nearly through the origin, consequently it is shown that these two kinds of toners have opposite polarity of equal value for C-01.

The reason why the agitation time was set for 3 minutes is, when agitation time is prolonged to 60 minutes, significant time dependency for Q/m is not observed as shown in Figure 2. In case of developer sample in the ratio of one to one of N-01 toner and P-01, the flow ability was obviously poor and it seemed to be formed a soft agglomerate.

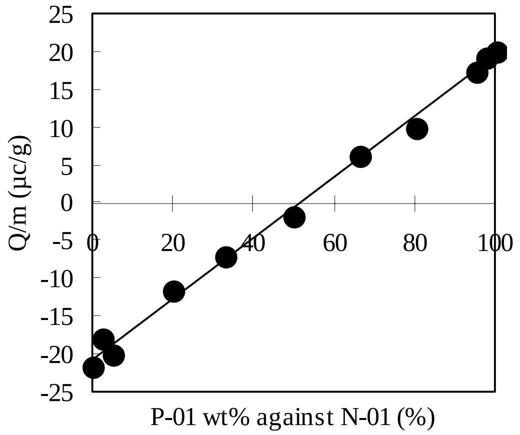

Figure 1. Q/m of developer with mixed toners of P-01 and N-01 by blow off method

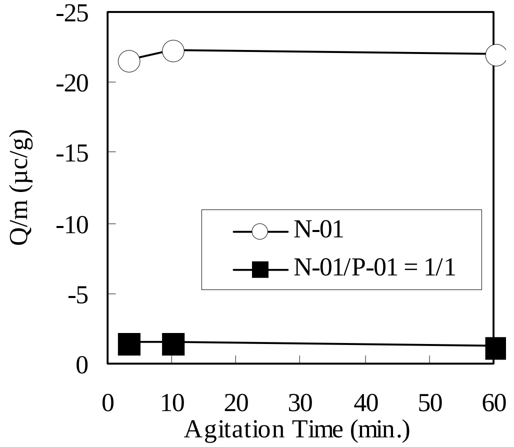

Figure 2. Q/m behavior of developer with two kinds of toners

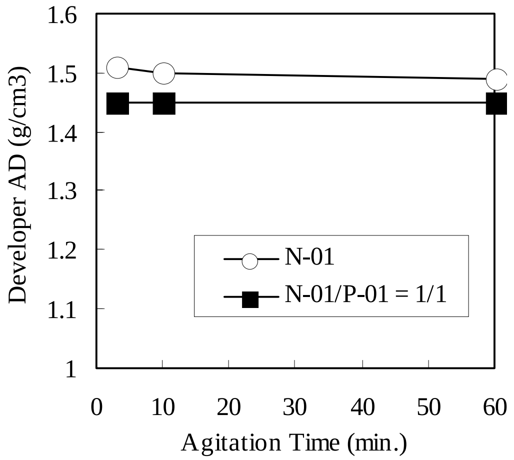

Figure 3. AD of developer with two kinds of toners

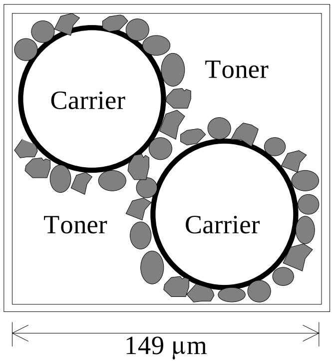

Figure 4. Mesh opening size

In order to compare the flow ability of those developers, the AD was measured and was given in Figure 3. The difference, however, is not as significant as they are looked.

To express the difference numerically, cohesiveness of the developer was measured by sieving method using mesh with 149 µm of opening size.

As shown in Figure 4, the opening size was considered so that two carriers could not go trough this opening without changing their position by disobeying the cohesiveness force to pass through it, because in observation by microscope, the carrier and toner made three dimensions chain in bond with toner.

Figure 5 shows that amount of P-01 wt % to N-01 in the developer is increased and when the ratio reaches 50%, the cohesiveness becomes the maximum value, and then the cohesiveness goes down with wt % of P-01.

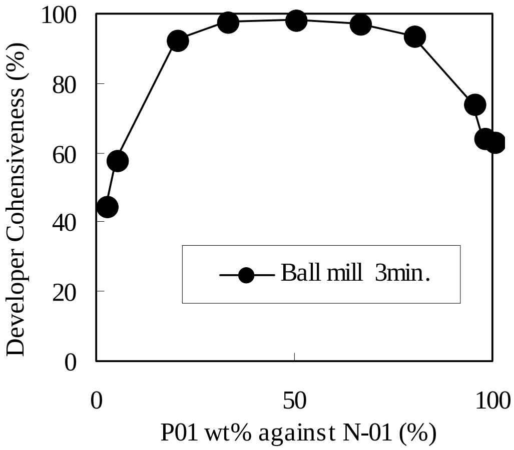

Figure 5. Developer cohesiveness for different ratio of 2 toners

Concerning the data reproducibility, enough accuracy for the comparison was confirmed in 5 times of measurements with developer using toner of P-01/N-01=95/5 in weight, although there was about 5 % of measurement error (see Figure 6).

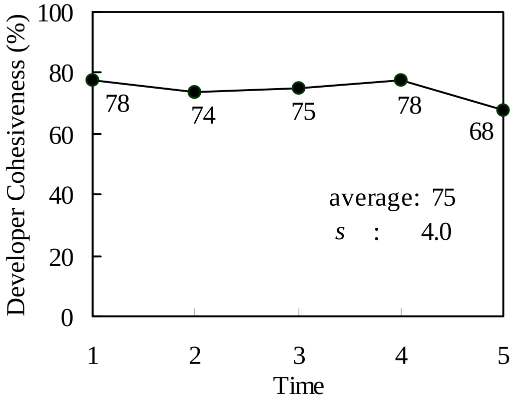

Figure 6. Reproducibility of Developer Cohesiveness (%) for toner P-01/N-1 = 95/5

Thus, the result implies that decline in the developer flow is caused by electrostatic interaction between carrier particles with existence of two kinds of opposite charge toners. Probably small particle size of carrier enhanced phenomenon of the flow decline

Furthermore to confirm whether toner interaction had relevance to these developer cohesiveness, flow ability of toners without carrier was measured by changing the ratio of the two toner mixes.

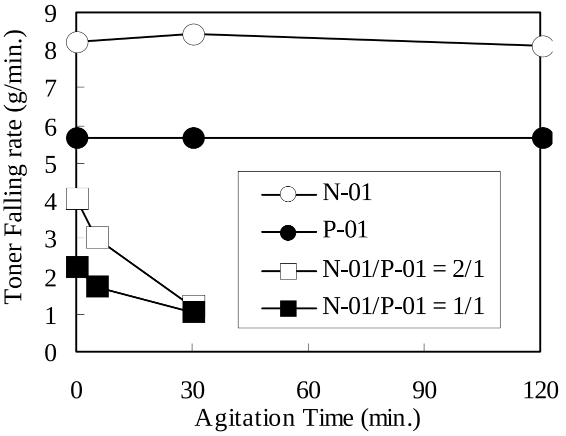

Figure 7. Toner Falling rate for 4 kinds of toner with time

In Figure 7, toner falling rate of N-01 and P-01 are constant with agitation time, but when N-01 and P-01 are once mixed in a bottle by hand shaking for 20 times, falling rate of the blended toners are lowered drastically, also the falling rate declines with further agitation time, then at 120 minutes no toner is fallen from measurement cell of toner flow tester.

It was observed that blended toner of in the ratio of N-01/P-01 =1/1 was actually an agglomerate just like clay.

Angle dispose of toners for N-01 and N-01/P-01 = 1/1 are 8 and 14 degree respectively, but determination of the value have possibly human error by this method.

Additionally since data reliability of toner falling rate remarkably decrease for below 2 g/min., we performed cohesiveness measurement for two toners to make it possible to discriminate week agglomerate from strong agglomerate.

P-01 and N-01 were mixed 15 seconds at various ratio, and the results of the toner cohesiveness are plotted in Figure 8.

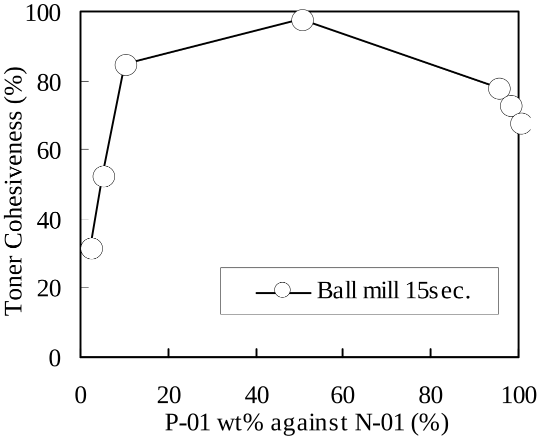

Figure 8. Toner Cohesiveness for different ratio of P-01 and N-01

The toner cohesiveness is increased with P-01 wt % to N-01, and when reaches 50% it shows the maximum value, and then goes down with wt % of P-01. The results present strong evidence toner-toner interaction and these phenomena is very similar in case of the developer cohesiveness shown in Figure 5.

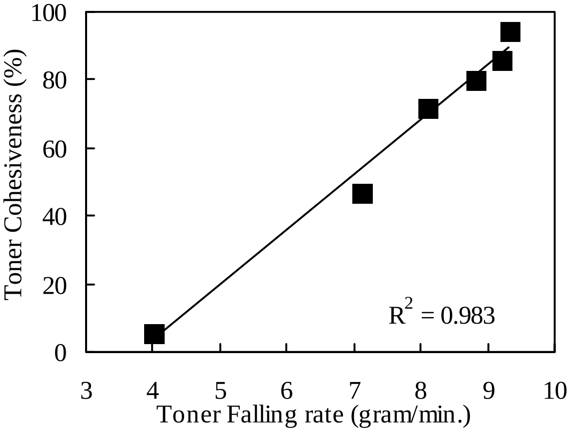

Figure 9. Correlation of Toner Falling rate and Toner Cohesiveness

Additionally Figure 9 displays that there is almost a linear relationship is seen between the toner cohesiveness and the toner falling rate, although the descried toner falling rate is over 4 gram/min.. Also from this point of view, it seems to indicate that decline of toner flow is caused by cohesive force of toner-toner interaction.

To relate this toner-toner interaction with charge distribution of the developer, in the developer preparation, toner ratio of N-01 and P-01 were varied quantitatively and the developers with 5 kinds of toners were agitated for 20 min. and 1 min. respectively. Their charge distributions were analyzed by E-Spart Analyzer. Figure 10 and 11 show the results.

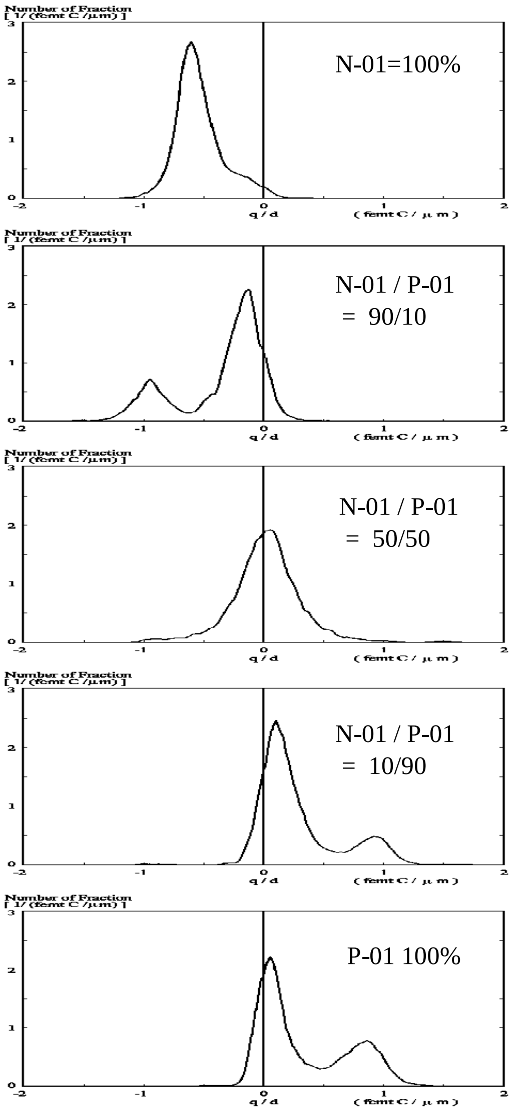

Figure 10. Q/d for P-01, N-01 with Carrier 1 at 20 minutes agitation

P-01 charge distribution is not a single peak even at 20 min. of agitation time in Figure 10, because Carrier C-01 is designed for negative chargeable toner N-01. However, most of P-01 toner exist in plus charge region, then there is worth discussing for interaction by the charge distribution. When two toners are blended in the ratio of one to one of N-01 and P-01, each plus and negative peak are fallen and only single peak in the vicinity of zero charge is observed, and the bi-model peak is not observed by contraries. It is not also clear yet why the separated higher charge peaks are observed in N-01/P-01=90/10 and 10/90 than N-01=100 and P-01=100.

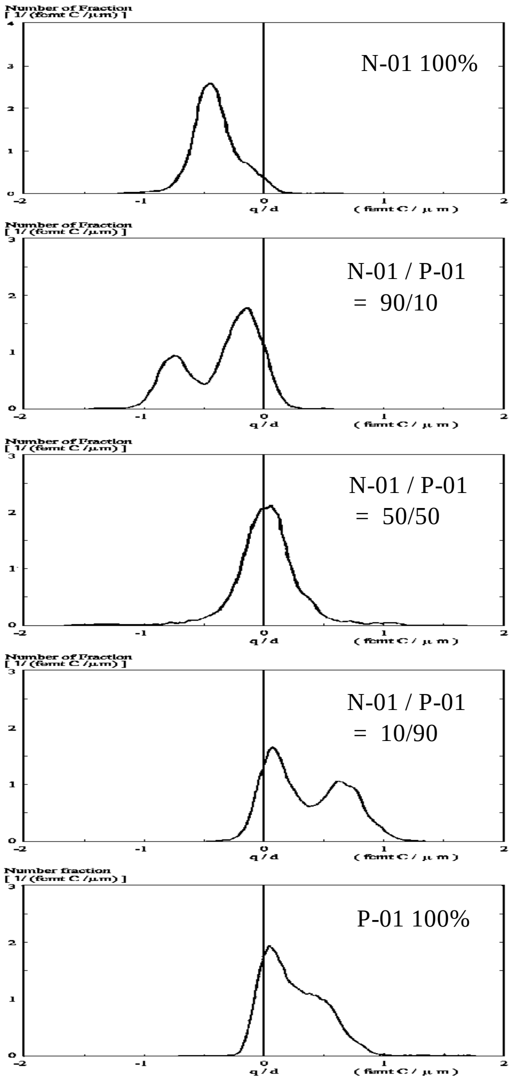

Figure 11. Q/d for P-01, N-01 with Carrier 1 at 1 minutes agitation

In Figure 12, toner average diameter (D_{50}) in counter base and volume base are plotted to each mixed ratio of toner N-01 and P-01. Both N-01 and P-01 was designed to have 11.0μm of D_{50} in volume base with Multisizer of Coulter Electronics, and when N-01 and P-01 toner are not mixed, their D_{50} in volume by E-Spart are close to D_{50} of Multisizer, but in case of other mixed toners of N-01 and P-01, the values of D_{50} in volume by E-Spart are around 15 μm, and they are rather bigger than that of Multisizer.

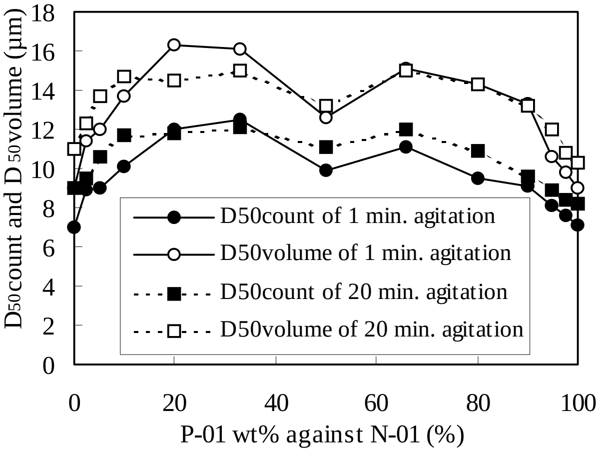

Figure 12. Mediam diameter by E-Spart Analyzer of mixed toner of P-01/N-01 = 50/50

Principally, E-Spart Analyzer utilizes dry measurement and obstructions for reliable measurement by toner agglomeration or cohesion are intrinsically higher than wet method, and even in case of D_{50} in count, which is more accurate than D_{50} in volume, the D_{50} in count shows also a similar tendency to increase when two toners are mixed. Therefore it is clear that such a trend concerns presence of agglomeration of toners. That is, it seems that agglomeration of toners by electrostatic force are detected as a particle, which was neutralized in charge by each their own charge.

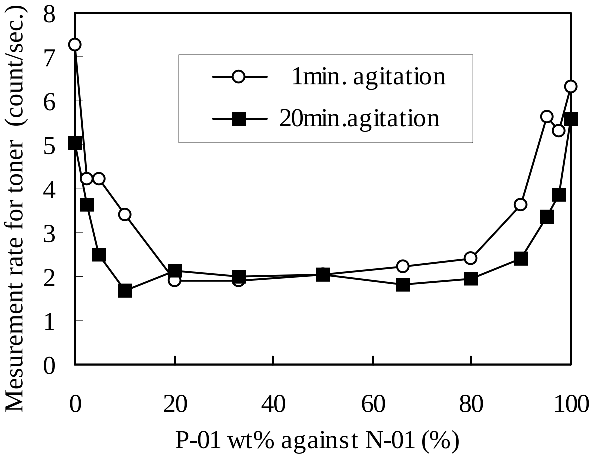

Figure 13. Measurement rate by E-Spart Analyzer for 1 and 20 min. agitated developers

Figure 13 shows measurement rate for toner particle by E-Spart Analyzer. By mixing N-01 and P-01, the measurement rate decreases less than 2 count/min. from ca. 6 count/min. Since toner particles are detected by phase delay and drift in the electric field cell, there is a limitation for counting particles rate, and particle which has more than 26 µm of diameter is canceled, therefore if there are a lot of particles over 26 µm of diameter, the measurement time to reach 3,000 counts will be longer in proportional to the amount by cancellation. This results also indicates that there are agglomerations of toner in measurement cell when they were measured. As the results, those agglomerations are treated as a neutral bigger particle and are observed a single peak in the vicinity of zero charge in charge distribution.

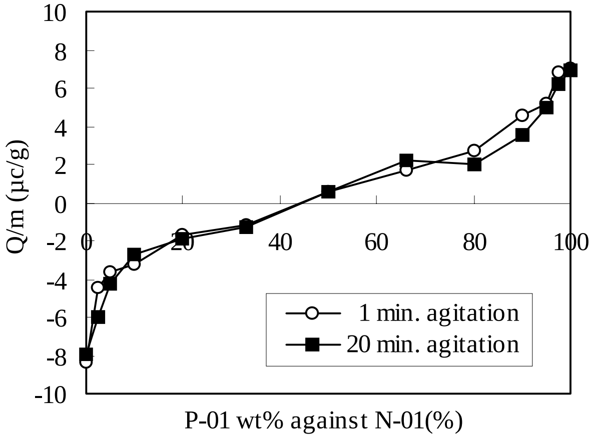

Figure 14. Q/m of developer with mixed toners of P-01 and N-01 by E-Spart Analyzer

Q/m values by E-Spart Analyzer were measured for developers mixed with different mixing ratio of P-01 and N-01 for 3 minutes. In Figure 14, it does not show linear relationship, though it shows a correlation of the neutralization and is passing nearly through the origin. The difference from results of Q/m by blow off method as shown in Figure 1 is probably caused from existence of agglomeration, because some of them were not contributed to the results.

There is a report on charge stabilization of developer by using both positive and negative charge control agents as internal additives for the toner[6], however it is obvious that by mixing positive and negative toner, charge stabilization of developer is impossible because of toner-toner interaction on flow ability decline for both toner and developer.

Julian reports the presence of toner-toner charge exchange process that can assist in maintaining narrow charge distributions in mixing toner particles containing carbon black with the same charge polarity[4-5]. In this present paper, tested two toners contain carbon black and the charge exchange process is also occurred among opposite polarity toners as charge neutralization. However as opposite polarity toners showed electrostatic agglomeration, there may be possibility of electrostatic interaction between the already charged toner and the added toner in the admix process even in the same polarity toners.

Considering the energy difference by contact charge model, it is temporary and too small to be detected as compared to energy difference like between $\Phi_{TonerP\text{-}01}$ and $\Phi_{Toner\ N\text{-}01}$ as shown in Case A of Figure 15.

Ott et al. suggest a non-uniform distribution of charge on the non-spherical toner particles and the neighboring effect[8]. It is not yet clarified the morphology of this cohesion for opposite charged particles as they proposed, but localized charge may cause polarization of the charge, then charged sites attract non-charged sites, although the time for toner-toner charge exchange may be very short. Of course, if each particle toner has a uniform charge distribution, each toner must have repulsive force.

Thinking low charge and high charge toner in the contact charge process, since work function level deference determine charge polarity of the toner, there may be also electrostatic attraction between the low charge and the high charge toners (Case B in Figure 15). Because such a irregular insulative toner material has some conductive parts and it makes possible to create polarization and localization in charge.

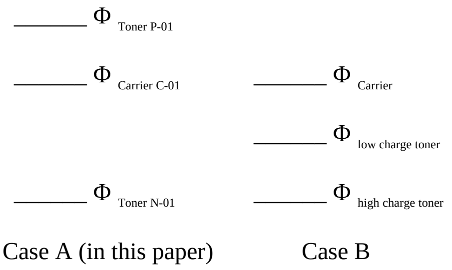

Figure 15. Contact charge model with toner and carrier. Metal-Metal, Metal-Insulater and Insulater-Insulater contact charging should not be equally compared, but they were compiled for understanding the each energy level.

Furthermore meaning of the same polarity for the low charge and the high charge toner is against one carrier. But when they are compared as toners with different work function without contact of carrier, one toner particle acts as if one carrier particle against the other toner particle. It is very difficult to proof the temporary cohesion force with existence of carrier for the time being, however, in actual developer station, if it could be confirmed, it would be very significant for study for admix process and also toner-toner interaction.

Conclusions

Two kinds of toners which had opposite polarity of equal value for each other against a Carrier C-01 were prepared. It has been shown that by mixing the carrier and toners with different mixing ratio of positive P-01 and negative N-01, the developer flow was affected by the mixing ratio and the highest cohesiveness of developer was observed in the ratio of one to one of two toners.

Additionally, visible toner agglomeration was observed when these two toners were mixed, and it was also investigated quantitatively as toner flow ability and cohesiveness by changing the ratio of the two toner mixes. The highest cohesiveness of toner was observed in the ratio of one to one of two toners same as the in developer. It was considered that such toner-toner interaction was due to electrostatic adhere force between opposite polarity toners.

Charge distribution spectrographs of those developers with varying ratio of two toners were also measured with E-SPART analyzer, and single peak in the vicinity of zero charge was additionally observed when P-01 and N-01 were blended. They have their independent charge distribution almost in plus and negative region respectively, and these two peaks were faded out by increasing amount of P-01 wt % to N-01 and finally they were fallen when blended in the ratio of one to one of two toners. It seems that a neutralized toner agglomeration is detected as a neutral bigger particle from data on the particle size and the measurement rate of E-SPART analyzer.

References

1. D. A. Hays, *J. Imaging Technol.*, **16**, 209 (1990)
2. L. B. Schein, *J. Imaging Technol.*, **16**, 217 (1990)
3. J. Gutman and W. Hollenbaugh, Jr. 13th Int'l. Cong. on Adv. in Non-Impact Printing Technol., M.H.Lee, ed., IS&T, Springfield, VA, 41-45, (1997).
4. P. C. Julien, 6th Int'l. Cong. on Adv. in Non-Impact Printing Technol., IS&T, Springfield, VA, 21-24, (1990).
5. P. C. Julien, R. Koehler, E. Connors, and R. Lewis, 10th Int'l. Cong. on Adv. in Non-Impact Printing Technol., E. Hanson, ed.,IS&T, Springfield, VA, 102-106, (1992).
6. N. Hayashi and J.Shimizu, 11th Int'l. Cong. on Adv. in Non-Impact Printing Technol., J.Anderson,ed., IS&T, Springfield, VA, 80-91, (1996).
7. N. Hayashi, 6th Int'l. Cong. on Adv. in Non-Impact Printing Technol., R. Nash, ed., IS&T, Springfield, VA, 85-86, (1990).
8. H. Mizes, M. Ott, E. Eklund, and D. Hays, 12th Int'l. Cong. on Adv. in Non-Impact Printing Technol., IS&T, Springfield, VA, 313-319, (1996).
9. L. B. Schein, Electrophotography and Development Physics, 2nd Ed., Springer-Verlag. Berlin (1992), p. 64.

Biography

Norihiro Hayashi received the M.E. degree in organic chemistry from the Mie University in 1984. He has been working for Wakayama Research Laboratories of Kao Corporation Japan since 1984, where he has been involved with the development of polyester resin, toner and developer materials. He was a committee member of The Society of Electrophotography of Japan (SEPJ) in Kansai branch in 1995-1997. He currently is R&D Manager of Kao Corporation Spain Toner Division in Barcelona, Spain.