

# Charge Stabilization of Toner using Polyester Resin

*Norihiro Hayashi and Jun Shimizu*

*Kao Corporation, Recording & Imaging Science Laboratories, Japan*

## Abstract

It is well known that an advantage of branched/crosslinked polyester resin for toner and developer are low temperature fusing ability, keeping the long life due to the high mechanical strength and quick negative charge ability in the field of high speed copier and printer. Especially, crosslinked polyester resin which has both branched chain and high acid value gives the toner excellent fusing ability to many kinds of papers. In general, however, the toner employing such a resin tends to cause a high charge level in the combination of some carriers, which complicates charge stabilization of the developer. Indeed, since there have been several kinds of CCA (charge control agent)-free toners using polyester resins in the market, it will be also possible to design a long-life developer by utilizing only the charge ability of polyester resins. On the other hand, it is also possible to diminish the polyester resin charge by selecting a proper carrier, which makes it easier to control the charge of the polyester toner with CCA like styrene acrylic toners.

This paper experimentally presents a charge stabilization of the toner using a polyester resin which has excellent fusing ability, by selecting the carrier and by adding some CCA in a dual component system. Finally, the high charge level of the polyester resin having over 30 KOH mg/g in acid value has been diminished by using a dimethyl silicon coated carrier. Hence, charge stabilization of the toner has been achieved in copy test by changing the balance of positive and negative CCAs. Finally, this lead to a long-life toner/developer based on the polyester resin.

## Introduction

Charge stabilization of a toner/developer in xerographic development system is one of the most important key designs and an unavoidable challenge for researchers to introduce a product to the market. Aside from development process, of course, for other processes like fusing, transfer and cleaning, toner must be optimized simultaneously. In general, however, the matching of toner function to each process makes it difficult to design a toner, because one optimization to one process does not necessarily give good effect to the others. Additionally, even if the toner recipe is the same, its charging rate, charging level and charge distribution are strongly influenced by the dispersion state of internal additives.<sup>1-5</sup> Consequently, the design for charging properties does not only need the know-how of the chemical components but also the process engineering in the production. Nash and other researchers studied toner charge stability on a dual component system in detail from theoretical viewpoint, and they reported that yet there must

be a way to attain it by many strategies, some parts of which were imperfectly understood in physics and chemistry.<sup>6-8</sup>

On the other hand, polyester resin for toner binder becomes more and more popular because of several advantages as compared to conventional styrene acrylic, styrene butadiene or epoxy resin.<sup>9-11</sup> Some of the advantages of polyester resin are as follows. For full color toner, linear type polyester resin having low melt viscosity with slightly toughness is preferred, because it gives high transparency, excellent color reproduction after fusing and sufficient developer life. Additionally, polyester resin has polar substituents, then it affords good pigment dispersion and dye solubility for the toner compared to those of styrene acrylic resin. For high speed copier and printer, branched/crosslinked type polyester resin is also preferred, since it affords good fusing ability, offset resistance and long life by less impaction onto carrier surface. Further, for non magnetic mono component system, branched/crosslinked type polyester resin is also used, because the toughness (high mechanical strength) gives frequent high charge ability without filming of charging blade surface.

Further, as common advantages, polyester resin enables continuous negative charge, and good fusing ability to many kind of papers, possible plastisizer resistance and good deinkability. Concerning the advantage of fusing ability, one of the aspects is that polyester resin has closer value of critical surface tension to plain paper than that of styrene acrylic resin.<sup>9</sup> Additionally, cohesive force of the polyester resin is enhanced by increasing polar groups like COOH and COOR. Therefore, the fusing ability of the toner rises with increasing acid value (AV) of the polyester resin. Thus, from material side, utilizing polyester resin for toner leads to energy savings, which will be in accordance with recent ecological trends in the world.

On the other hand, if amount of carboxylic group in the resin increases, the charge-to-mass ratio ( $q/m$ ) level also increases as well as the fusing ability. The polyester resin with high  $q/m$  level allows us to design in two major ways, that is, whether by utilizing the high resin charge to achieve a CCA-free toner system, or by diminishing the resin charge level to attain a CCA-toner system.

In this paper, to establish a long life developer having low temperature fusing ability, the latter way has been examined by selecting an appropriate carrier type. To Simplify the interpretation of test results, IMB (Insulative Magnetic Brush) was applied as a dual component system to minimize the effect on charge stability by leakage through the carrier. As a polarity of the toner, negative charge was chosen, although positive chargeable toner was also obtainable.<sup>12, 13</sup> Furthermore, charge stabilization of toners employing the polyester resin has been mainly discussed by

combining negative CCA with positive CCA comparing results of copy test (open test) and roll mill test (closed test).

## Experimental

### (a) Material

**Carrier S:** Spherical ferrite powders of nominal 100  $\mu\text{m}$  diameter were solution coated with 0.5% of dimethyl silicon. The resistivity value was  $2.0 \times 10^{10} \Omega\text{cm}$  applying 500 volts and 1.0 kg of pressure. **Carrier A:** Spherical ferrite powder of nominal 100  $\mu\text{m}$  diameter were solution-coated with 0.5% of acrylic polymer. **Carrier N:** Spherical ferrite of nominal 100  $\mu\text{m}$  diameter (non coated). **Carrier I:** Irregular oxidized iron powder of nominal 70  $\mu\text{m}$  diameter (commercially available as TEFV 200/300 from Powder Tech Co., LTD.).

**Polyester Resin:** Polyoxypropylene (2.2)-2,2-bis (4-hydroxyphenyl) propane, fumaric acid, octenyl succinic anhydride and telephthalic acid were allowed to react for condensation polymerization at 230°C 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 32 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 measured by a differential scanning calorimeter (DSC) "DSC Model 200" manufactured by Seiko Instruments Inc., at a heating rate of 10°C/min. The obtained resins had Tg of 63°C.

**Charge Control Resin (CCA-2):** Styrene, 2-ethylhexylacrylate and dimethylaminoethyl methacrylate were copolymerized in xylene with dicumyl peroxide as a initiator at 130°C, then up to 200°C followed by removal of xylene. The obtained resin has 130°C of Tsp and 65°C of Tg. This resin gave positive charge when it is combined with Carrier S.

**Polyester Toners:** Polyester resin having AV value of 32 KOH m/g was used. CCA-1 was chrome azobenzene complex, which donates negative charge. CCA-3 was nigrosine compound which gives positive charge. To 100 percent by weight (wt%) of resin, 2 wt % of a polypropylene wax, carbon black (CB) and CCA were incrementally added. The amount and the type of the CCAs were varied and the amount of CB was changed as listed in Table 1.

They were compounded by a twin screw extruder, then they were micronized and size-classified to produce a volume median diameter of 11  $\mu\text{m}$ . All toners were externally treated with 0.3 % of hydrophobic silica to get efficient flowability for test operation.

**Developer:** For aging tests, Carrier S and corresponding toner at 3.0 % of the toner/developer mass ratio (T/D) were blended for 10 minutes prior to start of copy test.

### (b) Measurement Procedures

**Charge-to-Mass Ratio (q/m):** For the measurement of q/m with roll mill, all the toner powders were combined to Carrier S at 3.0% of T/D, and roll milled at 250 rpm for appropriate time. 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<sup>2</sup>) through a wire screen with 36  $\mu\text{m}$  opening. The carrier beads were recovered for further analysis. The q/m values of the powders were calculated from the charge measured with Kawaguchi Universal Electrometer (model MMA2-17A).

**Table 1. Formulation of Polyester Toner Samples**

Name	CCA-1 (wt%)	CCA-2 (wt%)	CCA-3 (wt%)	CB (wt%)
Toner 1	0	0	0	6.0
Toner 2	2.00	0	0	6.0
Toner 3	0.50	0	0	6.0
Toner 4	1.00	0	0	6.0
Toner 5	1.50	0	0	6.0
Toner 6	1.50	0	0	10.0
Toner 7	1.50	8.0	0	6.0
Toner 8	1.50	0	0.50	6.0
Toner 9	0.25	0	0	6.0
Toner 10	0.50	0	0.10	6.0
Toner 11	0.50	0	0.20	6.0
Toner 12	0.50	0	0.30	6.0
Toner 13	1.00	0	0.18	6.0
Toner 14	1.00	0	0.20	6.0
Toner 15	1.00	0	0.22	6.0

The amount of carbon percentage of developer samples was measured with a HORIBA carbon analyzer (model EMIA-110). Then the value was calibrated to the line which was previously prepared concerning to T/D versus carbon percent, and the T/D was calculated from the plot.

**Quantitative Analysis of CCA-1 on the Surface of Carrier S:** The blown carrier samples were observed with scanning electron microscope (SEM) in order to confirm the absence of the residual toner particles on the surface. The concentration of transferred CCA-1 on the carrier was determined by UV-visible absorption spectrum according to the Beer-Lambert Law. Each 1.0 gram of sampled carriers was added to 20 ml of methanol and the mixture was sonicated for 1 minute, then the UV-visible spectrum of the decanted solution was measured. The absorption peak detected for CCA-1 was 578nm and the measured absorption values of each samples were compared to the calibrated curve by authentic samples, and the concentration was calculated.

### (c) Aging Fixture

2 kg of developer were placed in a single roll development housing set to operate against a selenium alloy photoconductor drum, and image development was set to occur at 7% of black/white ratio for a imaging cycle. The average toner throughput was about 200 gram/hour. The T/D was maintained at 3% by magnetic sensor in the housing. The fixture has two modes; one mode can create actual image on the paper and the other can consume the toner without using paper. In case of the paperless aging, development images were continually cleaned by cleaner blade from the photoconductor drum. Periodically, small samples

of the developer were removed from the developer roll for measurements of  $q/m$ , T/D and toner impaction. Image density (ID) was also measured for each sampling point at a black solid area on the paper with Macbeth Densitometer (RD-914). The climate condition was kept at  $23 \pm 3^\circ\text{C}$  and  $55 \pm 10\%$  RH to minimize the effect of ambient dependency.

## Results and Discussion

### Comparison of $q/m$ level of two Polyester Toners Against 4 Carriers

Figure 1 shows that comparison of  $q/m$  levels of CCA-free and CCA-toners against 4 kind of carriers. The saturation  $q/m$  level of the polyester resin having 30 KOH mg/g of AV was obviously depended on the carrier type. Both Toner 1 and Toner 2 showed almost same level of saturation  $q/m$  against Carrier A and Carrier I respectively, but in case of Carrier S and Carrier N, they gave lower level of  $q/m$ . Especially, with Carrier S, Toner 1 gave lower  $q/m$  by  $10 \mu\text{C/g}$  than that of Toner 2. It seems that dominant factor for the toner charge level against Carrier S is charge ability of CCA-1. Therefore, it will be possible by using Carrier S, to control charge level by CCA for such a polyester resin like styrene acrylic resin.

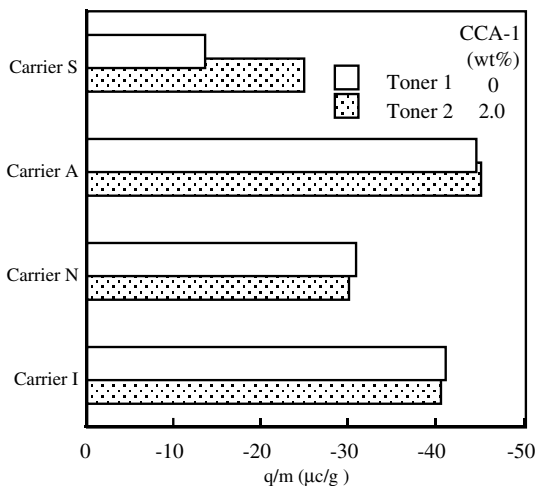


Figure 1. Effect of 4 type Carriers on  $q/m$  with Toner 1 and Toner 2.

### $Q/m$ Behavior of Polyester Toners in the Copy Test

Further, to discuss practical  $q/m$  stability in copy test, the amount of CCA-1 in the toners was varied. Figure 2 shows that  $q/m$  values increased with increasing amounts of CCA-1 until 15 K counts except CCA-free Toner-1 in actual copy test. Subsequently, all toners except Toner-1 indicated steep declining in image density (ID) with copy count, although the ID data are not shown in the figure. On the other hand, Toner 1 only showed undesirable background on the paper and toner dust. It means negative CCA is necessary to maintain sufficient image qualities with Carrier S.

Mechanistically, since the degree of  $q/m$  increase in the copy test corresponds to the CCA-1 amount, it seems that the charging sites in the vicinity of toner surface are increased by increasing CCA-1 amount. Then it leads to faster charge generation process and higher saturation charge.

Indeed, in Figure 2, Toner 1 which has no CCA-1 showed the gradual  $q/m$  declining, which implies this hypothesis, because the charge generation process is not sufficient in the absence of charging sites of CCA-1. Now, to relate the  $q/m$  increase behavior in copy test with the charging rate, roll mill test was examined by changing contents of negative CCA-1.

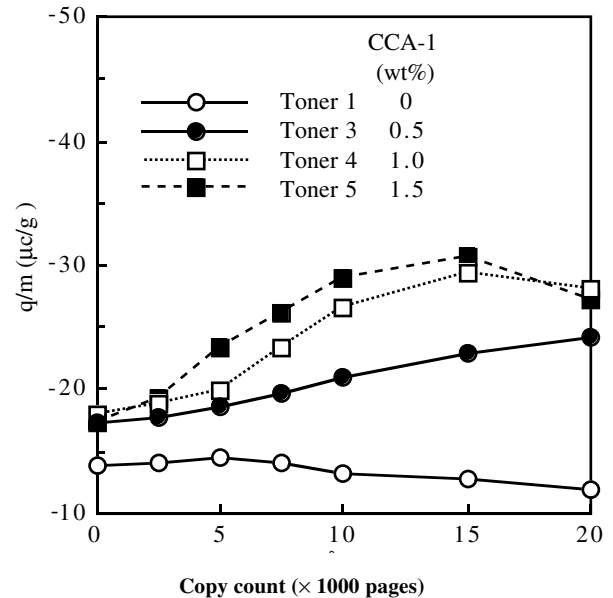


Figure 2.  $q/m$  versus copy count from tests made at different CCA-1 amounts of polyester toners with Carrier S.

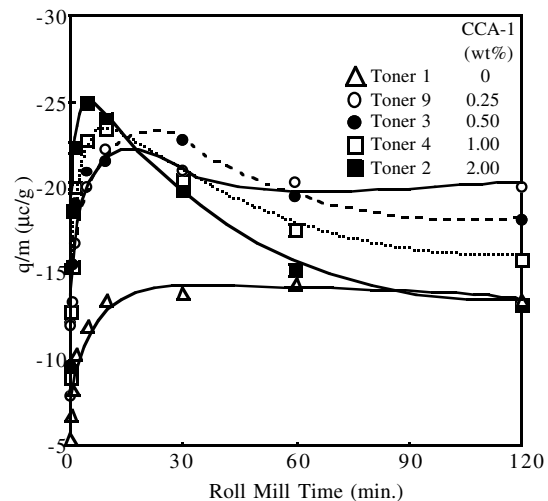


Figure 3.  $q/m$  as a function of roll mill time of toners with different amount of CCA-1.

### Effect of CCA-1 Amount in Toner to the Charging Rate with Roll Mill Test

In Figure 3,  $q/m$  of toners with varying content of CCA-1 were measured with roll mill. Except Toner 1,  $q/m$  of toners containing CCA-1 did not increase monotonically with the CCA-1 amount, and plateaus of the  $q/m$  appeared at shorter rolling times for higher amount of CCA-1. Further, the maximum  $q/m$  values at the plateaus became high

in proportion to CCA-1 amount, however, at roll mill times longer than 30 minutes, well mixed developers showed lower  $q/m$  levels with increasing CCA-1 content. Though CCA transfer can occur from toner to carrier surface even with such a gentle agitation, in order to determine the charging rate in quite initial steep increase until the plateau,  $q/m$  values were measured at each roll mill times of 0.25, 0.5, 1.0 and 2.0 minutes.

Here, charging curves of almost all dual component developers are expressed by the following equation (1), which shows a saturating exponential dependence on time.<sup>14, 15</sup>

$$q = q_{\max} [ 1 - \exp (- t / \tau ) ] \quad (1)$$

where  $q_{\max}$  is the maximum charge of the toner and  $\tau$  is the time constant for the charging rate. The  $\tau$  is obtained by the following transformed equation as a reciprocal of the slope in the plot of  $\log (q_{\max} - q)$  against the roll mill time.

$$\log (q_{\max} - q) = - t / \tau + \log q_{\max} \quad (2)$$

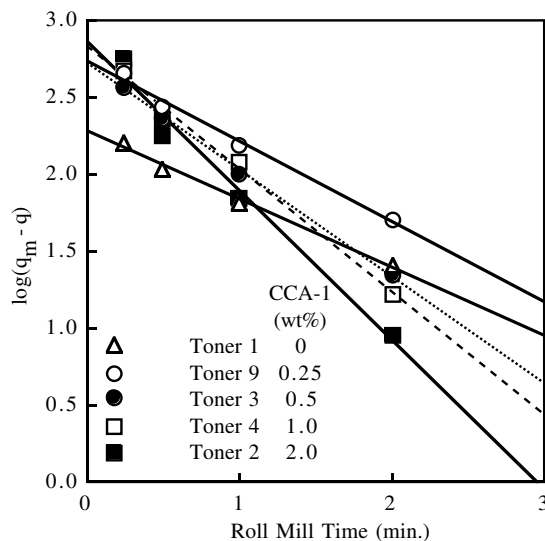


Figure 4.  $\log(q_{\max} - q)$  as a function of the roll mill time (the slope is represented by  $-1/\tau$ ).

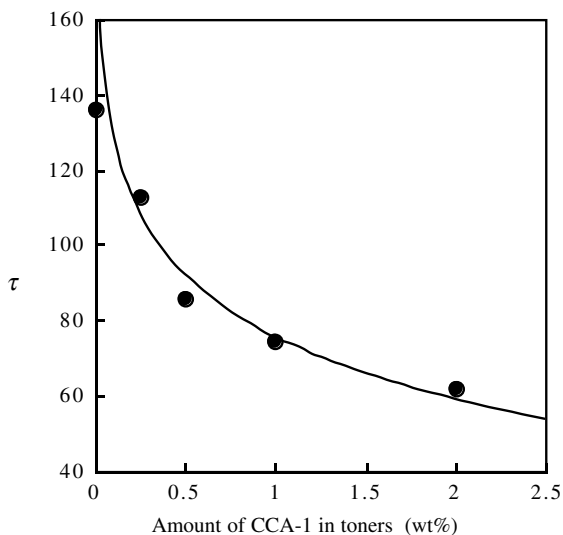


Figure 5. Charging time constant  $\tau$  as a function of CCA-1 amount in toners.

As shown in Figure 4, the linear relationships were seen, and the slope of each line was regressed as a straight line. Then the  $\tau$  for each toner was calculated according to equation (2) by the least squares method, and they were plotted against the CCA-1 amount in Figure 5. Since low  $\tau$  means quicker charging rate, increasing the amount of CCA-1 leads to faster charging toners. Hence, the reason of increase of charging rate would be interpreted that number of charging sites on the toner surface is increased in proportion to CCA-1 amount at a same kneading condition for all toners. Thus, there is a correlation between the  $q/m$  increase in copy test and the charging rate in roll mill test.

On the other hand, such a fast charging toner like Toner 2 showed the rapid decline in  $q/m$  after the plateau in Figure 3. As mentioned earlier, the CCA transfer to carrier will not be negligible with increasing milling time. Anderson reported that high surface charge levels associated with phase-separated toners with CCA leads to lower  $q/m$  and more rapid developer aging than non-phase-separated toners with low surface concentrations of CCA.<sup>2, 3</sup> The observation of cross sections of our toners by transmission electron microscope-energy dispersive X-ray spectroscopy (TEM-EDS) showed no aggregates greater than  $0.5 \mu\text{m}$  of CCA-1 in the resin, but the surface concentration and the surface accessible CCA are not confirmed. Considering that similar results were obtained in our tests, it seems that such accessible CCA-1 exists on the surface of the toner. As seen in Figures 6 and 7, the concentration of CCA-1 transferred to the Carrier S increased with the CCA-1 amount in the toners, and with the roll mill time respectively. Similarly, in case of copy test, Toner 4 and Toner 5 showed the declines in  $q/m$  after 15 K counts in Figure 2, and the degree of decline in  $q/m$  was enhanced with the amount of CCA-1. These behavior in copy test would be also caused by the CCA transfer.

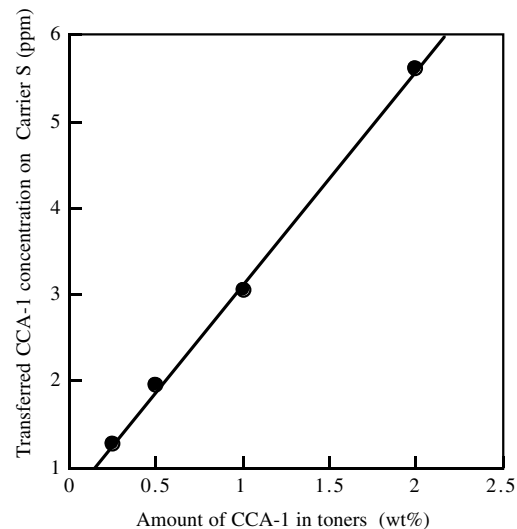


Figure 6. Transferred CCA-1 concentration Carrier S agitated 120 minutes as a function of CCA-1 amount of toners.

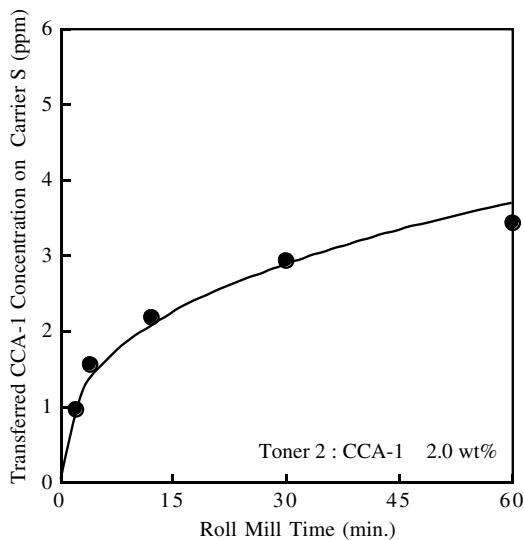


Figure 7. Transferred CCA-1 concentration on Carrier S agitated 120 minutes as a function of roll mill time for Toner 2.

### Q/m Stabilization of Polyester Toners in the Copy Test

Now, as discussed earlier, it seems that more charging sites associated with higher amount of CCA-1 in toners lead to the more rapid increase in  $q/m$  as shown in Figure 2. Accordingly, in order to make the  $q/m$  level of toners more stable in copy test, two approaches were examined. One is reducing the toner resistance and enhancing charge leakage process by increasing CB amount from 6 wt% to 10 wt%. The other one is controlling the charge generation at a certain level by adding another CCA which has opposite polarity against the CCA-1.

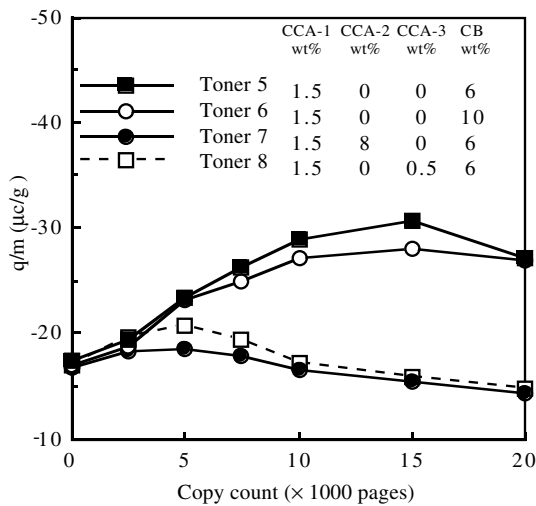


Figure 8.  $q/m$  versus copy count from tests using polyester toners varied CB amount or CCA combination with Carrier S.

In Figure 8, Toner 6 which has CB of 10 wt % slightly diminished the increase in  $q/m$  as compared to Toner 5, though the stabilization in  $q/m$  is not still sufficient. If CB amount in the toner were increased more than 10 wt%, less  $q/m$  increase might be attained, however, it would simultaneously cause the difficulty in dispersion with the same kneading condition. On the contrary, Toner 7 and Toner 8

which contain plus chargeable agent showed the moderate decline in  $q/m$ , and the ID was stabilized without degrading other image qualities like background. Thus, combining negative CCA-1 with positive CCA is significantly effective to reduce the  $q/m$  increase and stabilize the  $q/m$  with Carrier S in copy test.

### Effect of CCA-3 Amount in Toner to the Charging Rate

As indicated in Figure 8, plus chargeable CCA stabilized the tendency of increasing  $q/m$  in the copy test. Then the effect of plus chargeable CCA-3 to the charging rate in the presence of 0.5 wt % of CCA-1 will be also discussed. Figure 9 shows that maximum  $q/m$  level was lowered with increasing CCA-3 amount, however, the charging rate until the plateau did not seem to be affected. Then, the  $\tau$  until 2 minutes of roll mill time was calculated on the basis of the equation (2) as shown in Figure 10. It seems that CCA-3 did not affect the  $\tau$  in the range from 0.1 to 0.3 wt% of CCA-3 content, and the values of  $\tau$  were only owed by the 0.5 wt% of CCA-1 in these toners. However, the decline in ID was diminished by combining negative CCA-3 with positive CCA-1 as indicated in Figure 8. There might be other  $q/m$  stabilizing function in the CCA-3.

Conceptually, considering the results of roll mill test, following interpretation will be available. In this IMB system, the residual charge is induced on the carrier surface by elimination of developed toners. Since Carrier S has high resistivity, negative charging sites of CCA-1 give continuous accumulation of the positive residual charge on the carrier during successional copy test. Further, if CCA-1 amount in the toner is raised, the charging sites are increased and it enhances the accumulation of the residual charge. Finally, it causes the decline in ID because the accumulated positive charge diminishes the toner elimination from the carrier. However, when positive CCA-3 is added to the toner, charging site of CCA-3 partially neutralizes the residual charge which caused by the charging site of CCA-1. As a result, the average charge level of each toner particles is controlled at a optimum level, which can afford sufficient image qualities in copy test.

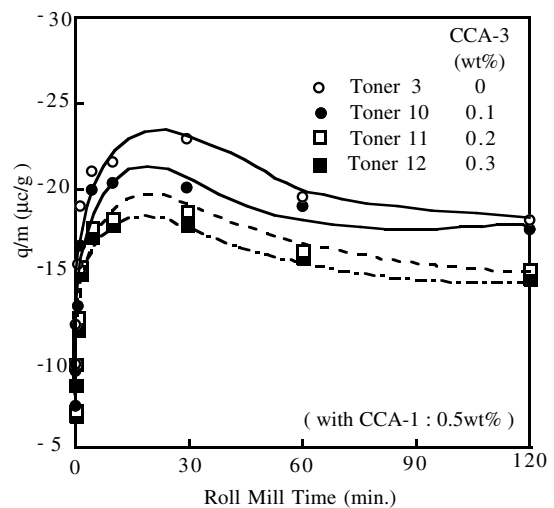


Figure 9.  $q/m$  as a function of roll mill time for toners with different amount of CCA-3.

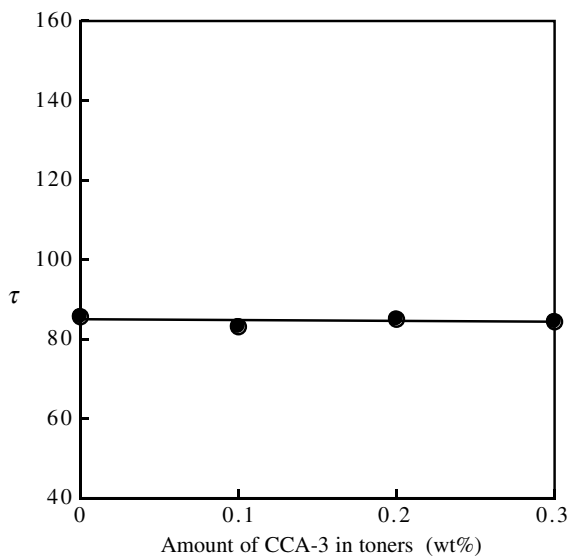


Figure 10. Charging time constant  $\tau$  as a function of CCA-3 amount of polyester toners.

On the other hand, the amount of CCA-3 transferred to the Carrier S has not been measured quantitatively, considering the results of observation with TEM-EDS, the CCA-3 is dissolved in the polyester resin. Therefore, carrier contamination of the CCA-3 itself can hardly occur, and another reason will be the used amount of CCA-3 is smaller than that of CCA-1 by one order of magnitude.

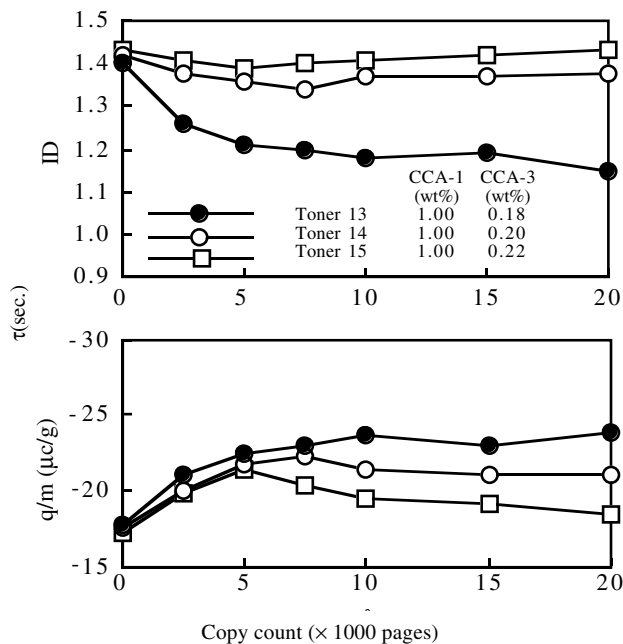


Figure 11.  $q/m$  and ID versus copy count from tests made at 3 CCA-3 amount of polyester toners with Carrier S.

#### $q/m$ Stabilization in the Long Copy Test

Figure 11 shows that both the rise in  $q/m$  and the decline in ID were stabilized with increasing CCA-3 amount in the copy test. It seems that there will be an appropriate CCA-3 amount, which differs depending on the CCA-1 amount, toner

throughput rate and other factors related to  $q/m$ . Additionally, instead of CCA-2 and CCA-3, other plus chargeable CCA may be also available to use as a charge stabilizers, if the dispersion is sufficiently optimized.<sup>13, 16</sup>

From a viewpoint of toner design, finding the best balance needs experimental data with an engine. On the contrary, if there were two points which showed increasing and decreasing trends in  $q/m$  and they were content with specification of image qualities, it would be possible to determine the best combination by pincer movement. Figure 12 shows an example of the best balance in  $q/m$  stability for long life developer, and Toner 14 has a medium amount of CCA-3 between Toner 13 and Toner 15. The moderate decrease in  $q/m$  was seen after 50 K until 500 K counts, however, even if the CCA-3 amount were increased in order to raise the  $q/m$  level after 400 K counts, the  $q/m$  instability at initial 10 K counts would be enhanced. Obviously, the priority of design in  $q/m$  stabilization should be given to long-term stability more than short-term, unless the  $q/m$  instability in short-term is intolerable.

Generally, CCA transfer process to carrier is inevitable in a CCA-toner system, more or less, until the point of toner/carrier CCA equilibration. Nash reported that a developer will reach the zero aging rate, which is produced by the long-term toner/carrier CCA equilibration in a CCA-toner system.<sup>6,7</sup> It is not clear whether this developer using Toner 14 has reached the zero aging rate.

By analysis of Carrier S which is obtained from aged developer in copy test, toner impaction and coating loss were found with a carbon analyzer and SEM observation. Therefore, the moderate decline in  $q/m$  after 100K counts might be mainly caused by the toner impaction and the coating loss. Considering that  $q/m$  behavior until 50 K counts was less stable than after 100K counts in Figure 12, this developer might have reached a CCA equilibrium state until 100 K counts as a pre-aged state.

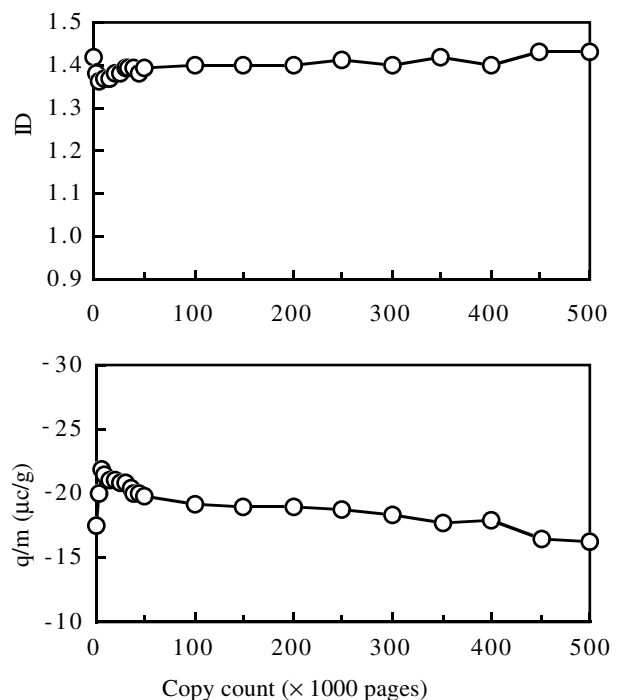


Figure 12.  $q/m$  and ID vs. copy count with Toner 14 and Carrier S.

## Conclusions

In order to use a polyester resin which is superior in fusing ability for toner, charge stabilization of the toners were examined by changing amount of carbon black and combination of negative and positive charge control agents (CCA) in a dual component system, and the foregoing results lead to the following conclusions:

1. The high charge level of the branched/crosslinked polyester resin having 32 KOH mg/g of acid value has been diminished by using a dimethyl silicon coated carrier.

2. Charge stabilization of the toner having low temperature fusing ability has been achieved by changing the balance of the two CCAs, and experimentally a long life toner/developer has been established over 500 K counts in a copy test.

3. In roll mill test without toner throughput, charging rate and saturation q/m level of the toner increase with amount of the negative CCA until agitation of 2 minutes. On the contrary, effect to the charging rate of the positive CCA is not found significantly, while saturation level of the q/m is lowered.

4. There is a correlation between the q/m increase in copy test and the charging rate in roll mill test, that is, increasing the amount of negative CCA leads to charging sites of toners, and it increases the residual charge on the carrier surface, subsequently the q/m increase in the copy test is enhanced. On the contrary, positive CCA would partially neutralize of the residual charge which induced by the negative CCA on the carrier. Hence, the stabilization of q/m in the copy test could be achieved.

5. The transfer of negative CCA to carrier is confirmed in roll mill test, and the concentration of the CCA on the carrier increases both with the amount of CCA in the toners and with the roll mill time.

## Acknowledgments

The authors wish to thank the helpful discussions and criticisms by Dr. Kuniyasu Kawabe of Kao Corporation Recording & Imaging Science Laboratories.

---

## References

1. N. Hayashi, *6th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, R. Nash, ed., IS&T, Springfield, VA, 85-86, (1990).
2. J. H. Anderson, D. E. Bugner, L. P. DeMejo, R. Guistina and N. Zumbulyadis, *8th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, E. Hanson, ed., IS&T, Springfield, VA, 107-115, (1992).
3. J. H. Anderson, D. E. Bugner, R. Guistina, *8th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, E. Hanson, ed., IS&T, Springfield, VA, 144-149, (1992).
4. J. Guay, J. L. Miller, H. Nguyen and A. F. Diaz, *8th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, E. Hanson, ed., IS&T, Springfield, VA, 116-118, (1992).
5. A. R. Gutierrez, H. T. Nguyen and A. F. Diaz, *8th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, E. Hanson, ed., IS&T, Springfield, VA, 122-125, (1992).
6. R. J. Nash and J. T. Bickmore, *9th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, M. Yokoyama, ed., IS&T, Springfield, VA, 68-71, (1993).
7. R. J. Nash, S. M. Silence and R. N. Muller, *10th Int'l. Cong. on Adv. in Non-Impact Printing Technol.*, A. Melnyk, ed., IS&T, Springfield, VA, 95-107, (1994); (see page 169, this publication).
8. J. Gutman and G. C. Hartmann, *J. Imaging Sci.* Vol. **36**, No. 4, pp. 335 (1992).
9. S. Tanaka, Symposium at Osaka of The Society of Electrophotography of Japan, *Proceeding of Technological Innovation on Toner and Developer*, 19-23, (1993).
10. USP 4387211
11. USP 4804622
12. USP 4933252
13. USP 5173387
14. I. Shinohara, *J. of the Soc. of Electrophotography of Japan*, vol. **10**, No.1, pp. 2, (1971).
15. K. Karakita, *J. of The Soc. of Electrophotography of Japan*, vol. **27**, No.3, pp. 14, (1988).
16. USP 493905