

Study on Positively Chargeable Polyester Toner

Hidenori Tachi, Shinichi Sata and Shinji Moriyama
Kao Corporation, Performance Chemical Research Laboratories
Wakayama, Japan

Abstract

To apply polyester resin to positively chargeable toner, the relation between the acid value of its resin and toner charge, and also dispersion of charge control agent in low acid polyester resin were investigated. The mixing condition of polyester resin and charge control agent was also investigated for the most suitable positively chargeable toner. It was found CCA should be dispersed as certain aggregates, to get higher charging-up speed and the charge stability. That means low acid value of polyester does not always mean disadvantages, and we could make positively chargeable polyester toner with high durability, and low energy fusing.

Introduction

Positively chargeable toners are indispensable for high speed printer and copier with electrophotographic system. In this field, styrene-acrylic resin has been mainly used for toners, because it is easy to control chargeability. However, the high speed, continuous printing and print quality require toner to have durability, low energy fusing, and charge-up speed, charge value, and stability. Those requirements have not been made little success with styrene-acrylic resin, generally because of its molecular distribution and structure.

On the other hand, toner using polyester resin has been also used for electrophotographic system, because of high fixing ability at low temperature, high dispersion quality of ingredients, and high durability. However polyester resin is itself negatively chargeable, it has been mainly used for negatively chargeable toner. The development of positively chargeable toner has been desired earnestly for making use of those advantages.

Now we have developed positively chargeable polyester toner that showed higher charging-up speed, and charge stability, without impairing any advantage of polyester resin nor increasing the amount of Charge Control Agent (CCA). In this paper, we described the detail of relation between the acid value of polyester resin and toner charge, and also dispersion of charge control agent in polyester resin. The mixing condition of polyester resin and charge control agent was investigated for the most suitable positively chargeable toner.

Experimental

Toner Samples

(a) Preparation of Polyester Resin

Bisphenol A propylene oxide adduct, ethylene oxide adduct, Terephthalic acid, C_{12}-Succcinic anhydride, and Trimellitic anhydride were allowed to react for condensation polymerization at 230ºC with small amount of catalyst in a glass flask, which was equipped with a thermometer, a stainless steel stirring rod, a reflux condenser and nitrogen inlet tube. The acid value was adjusted by changing ratio between acid and alcohol, keeping the each resin's softening point about 136ºC.

Table 1. Properties of the Polyester Resin

	acid value (KOHmg/g)	T1/2 (ºC)	Tg (ºC)
Resin A	3	135	62
Resin B	10	135	63
Resin C	20	136	64

1. The acid value was measured according to ASTM D-1980-67
2. The softening point (T1/2) was measured according to ASTM E-28-67
3. The glass transition temperature (Tg) was measured by a differential scanning calorimeter "DSC Model 200" manufactured by Seiko Instruments Inc., at the heating rate of 10ºC/min.

(b) Preparation of Toner Samples

Toner samples were comprised of those resin, charge control agent (Nigrosine), and polypropylene wax (2wt%). Those toners were pre-mixed, kneaded, pulverized and classified to obtain 10μm in average size. Colorant and Silica were not contained to investigate the relation between CCA and polyester resin.

Dispersion quality is influenced mainly by pre-mixing time and kneading condition. From the point of view, Toner 7 to Toner 12 was made under the different production condition.

Pre-mixing time was set from 1 to 30 minutes. The longer pre-mixing time disperses CCA better in resin.

Kneading condition was created by changing feed rate (kg/h) only. The lower feed rate disperses CCA better, because it is to be kneaded for more time.

These processes could destroy agglomerated CCA and then reduce the particle size, which is to be uniformly dispersed in resin.

Table 2. Formulation of Polyester Toner Samples

	resin wt%	CCA wt%	pre-mix min.	feed rate kg/hr
Toner 1	A	1	1	15
Toner 2	A	2	1	15
Toner 3	A	3	1	15
Toner 4	A	4	1	15
Toner 5	B	2	1	15
Toner 6	C	2	1	15
Toner 7	A	2	1	10
Toner 8	A	2	10	10
Toner 9	A	2	30	10

Measurement of Toner Charge (q/m)

The q/m is determined by the Blow-off method: Toner was mixed with carrier at 3.0% of toner concentration by roll mill at 250rpm. The carrier was silicon-coated magnetite and 100μm in size. The q/m value was measured with reliable q/m-meter (Epping GmbH). The charged developer is transferred into measuring cell (45μm) inside both ends. Air pressure blowing for 90sec. separates carrier from toner. The resulting voltage was measured and q/m value was calculated.

Measurement of UV-Visible Spectrum of CCA on Toner Surface

The relative amount of CCA on toner surface (hereafter surface CCA amount) was measured by UV-visible absorption spectrum. 0.5 gram of toner sample and 20 ml of ethanol were poured into a glass bottle. This bottle was mixed by roll mill for 20 minutes, and then another 20 ml of ethanol was poured. Finally, the UV-visible spectrum of this solution was measured. Toner sample contains resin, wax, and CCA, and the spectrum of CCA on toner surface was only observed.

Results and Discussion

Affinity between Polyester Resin and CCA

Polyester resin has been thought to have a good affinity with ingredients (Wax, Colorant, CCA) because of the polarity group -COOH. Naturally, this affinity influences the amount of CCA on the toner surface and dispersion quality. Carboxylic acid group bonds to ingredients with hydro bond, which destroys agglomerates or aggregates, and decreases particle size. Ultimately, primary CCA particles would be dispersed uniformly into toner.

There is considerable evidence to show that polyester resin has good affinity with CCA. Very small amount of Toner 2 (AV=3), and Toner 6 (AV=20) were molten on the slide glass by a hot plate at 200ºC for 5minutes. Then molten toner on the glass was observed by microscopy at 500 times' magnificent. Figure 1 and Figure 2 are their microscopic pictures. Toner 2 has much black agglomerate, while Toner 6 has nothing to be observed. That means primary CCA particles were dispersed uniformly in resin.

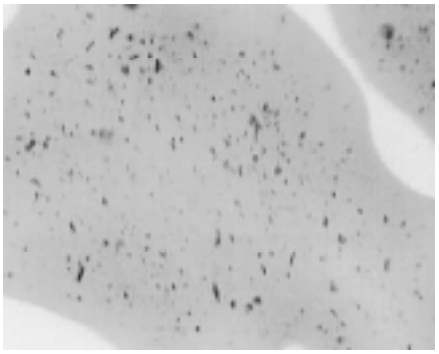

Figure 1. microscopic picture of Toner 2(AV=3)

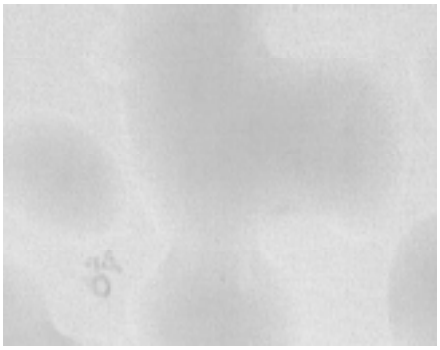

Figure 2. microscopic picture of Toner 6(AV=20)

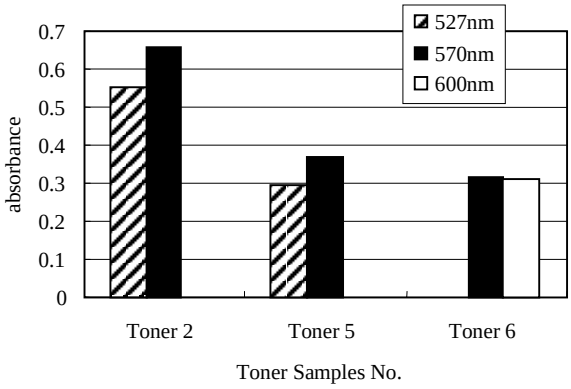

Figure 3. UV-visible absorption at toner

Figure 3 shows the surface CCA amount measured by the UV-visible absorption spectrum. The spectrum decreases in proportion to the acid value. The high dispersion quality of polyester resin could reduce CCA particles from agglomerates to aggregates, finally to primary particles. So, primary CCA particles dispersed well in toner, and relatively the surface CCA amount decreased.

However, Toner 6 having 20 (KOHmg/g) of the acid value shows peak in 600nm of wavelength, where other toners show not any peak.

To understand the CCA affinity with polyester, the solubility of Nigrosine was measured into two kinds of solvent. The one is ethanol, which has no polarity group, and another is acetic acid, which has the polarity group -COOH. Those solutions were measured by UV-visible absorption. The result was listed in Table 3. The wavelength of the spectrum for each solution corresponds to that of Figure 3. Namely, ethanol corresponds to the resin having lower acid value, while acetic acid does to the resin having higher acid value. Those results indicate that polyester resin having higher acid value had a certain interaction with Nigrosine, which results in shifting the wavelength. This interaction might destroy the agglomerates.

Table 3. UV-Visible Absorption of CCA (Nigrosine)

	ethanol	acetic acid
wave length	570nm	600nm
absorbance	0.217	0.214

Figure 4 shows charging performance on agitation time. Toner charge increases inversely proportional to the acid value because polyester resin is negatively chargeable. The higher acid value could reduce CCA particles to primary particles and decreased toner charge after reaching the saturated toner charge.

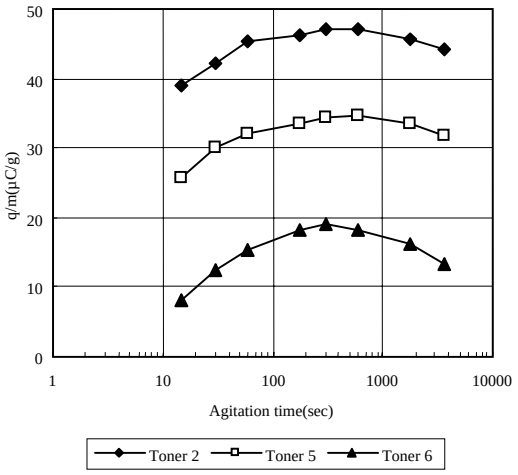

Figure 4. q/m at toner with different acid values

Relation between the Amount of CCA and Toner Charge

Figure 6 shows the surface CCA amount measured by the UV-visible absorption spectrum. Naturally, the absorption spectrum increased in proportion to the amount of CCA.

Figure 7 shows charging performance on agitation time. Toner charge increased proportionally with the amount of CCA, keeping same toner charging performance. However, toner containing more than 2 wt% of CCA had the same saturated toner charge, but different charging-up speed, which means, in this region, toner with more amount of CCA gets more stable toner charge. This result indicates CCA on toner surface is very important to increase charging-up speed as well as toner charge.

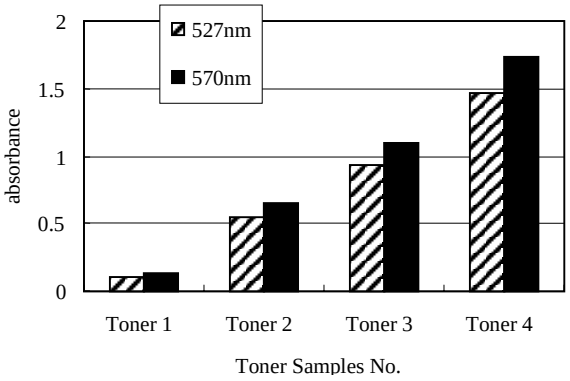

Figure 6. UV-visible absorption at toner

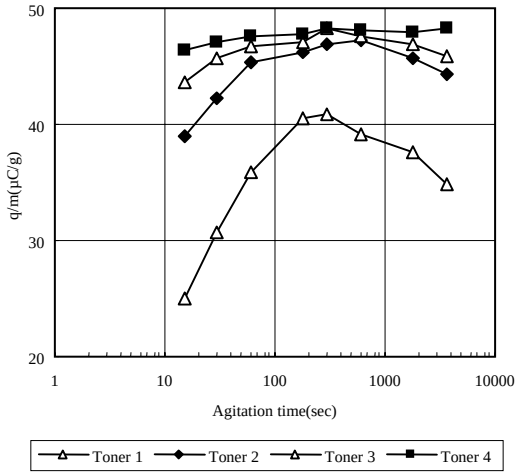

Figure 7. q/m at toner with different amount of CCA

Performance of CCA According to Different Producing Condition

Figure 8 shows the surface CCA amount measured by the UV-visible absorption spectrum. The dispersion quality increased with sample number, which means Toner 9, has the best dispersion, and Toner 2 has the worst. However, Toner 7 has more surface CCA amount than Toner 2.

This difference indicates surface CCA amount depends on how agglomerated or aggregated CCA was dispersed in resin. Too much agglomerated CCA is likely to isolate from toner particle at the interface of resin and CCA during pulverizing process, because of its volume. Therefore Toner 2 has less surface CCA amount than Toner 7 which has less aggregated CCA. On the other hand, the much better dispersion process by longer pre-mixing time and lower feed rate destroys CCA agglomerates to primary

particles. It takes a similar dispersion effect like dispersing CCA in resin having higher acid value. That is why surface CCA amount of such toners decreased.

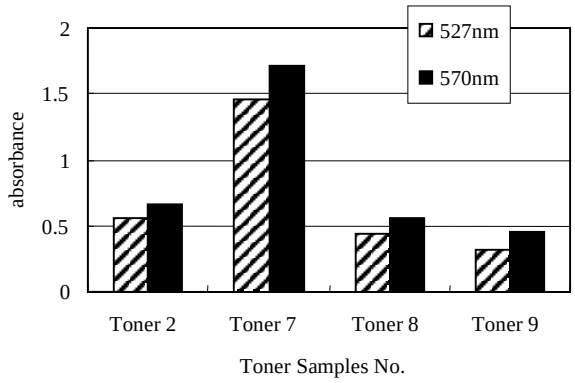

Figure 8. UV-visible absorption at toner

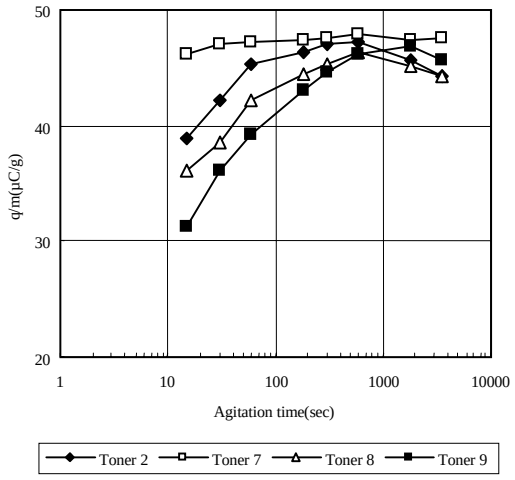

Figure 9. q/m at toner with different production condition

Figure 9 shows charging performance. The charging-up speed increased with the surface CCA amount. But except Toner 7,toner charge decreased after reaching the saturated toner charge. Only Toner 7 has stable toner charge.

These results indicate CCA should be dispersed as certain volume (aggregates) on toner surface to obtain higher charging-up speed and charge stability. Too much dispersed CCA results in slower charging-up speed, and unstable toner charge.

Conclusion

The conclusion of this study on positively chargeable polyester toner can be summarized as follows.

1. Polyester resin having low acid value shows highly positive chargeability.
2. Polyester resin having high acid value interacts with Nigrosine, and it causes toner charge value to decrease.
3. CCA should be dispersed as certain volume on toner surface, which increases charging-up speed, and keeps toner charge. The much better CCA decreases charging-up speed and toner charge becomes unstable.

References

1. Ruediger Bauer, Hans-Tobias Macholdt, Eduard Michel and Chrisrian Zeh, *13th International Congress on advances in Non-Impact Printing Technologies,163-167(1997).*
2. Shinji Otani,Yuto Matsumoto and Manabu Takeuchi, *14th International Congress on advances in Non-Impact Printing Technologies,341-344(1998).*

Biography

Hidenori Tachi received his master degree in physics from Nihon University in 1994. Since 1994 he has been working in the Wakayama Research Laboratories at Kao Corporation in Wakayama, Japan. He has been involved in research and development of toner and toner binding with polyester resin, including full color toners.