

# Particle Size and Composition Effects on Charging Properties of Toner

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## Abstract

The charging properties of pseudo toners of different compositions have been studied by measuring the charge-to-mass ratio dependence on the particle size and toner concentration in toner-carrier mixtures. The results have been compared to the current models of toner charging. It is shown that the data are inconsistent with the current surface state theories. A simple charge exchange mechanism between toner and carrier is proposed.

## Introduction

In dry toner electrophotography the toner charge  $Q$ , and particle size are key parameters control print quality. However, the relationship between charge-to-mass ratio,  $Q/M$ , and toner size is still ambiguous. Indeed, the toner  $Q/M$  is not always inversely proportional to the toner radius,  $r$ , as most theories predict.<sup>1,2,3</sup> Furthermore, the size-charge relationship can be different depending on whether the electrostatic charge is obtained from multiple developer mixtures prepared with toners of different sizes or from one developer mixture containing a toner with a distribution of size.<sup>4</sup> This last case has been studied by several authors and it has been shown that  $Q$  often deviates from its ideal value, i.e.,  $Q$  is not proportional to the surface area of the toner.<sup>4,5,6,7</sup> In these systems, the relationship between  $Q$  and  $r$  is complicated by the fact that toner particles may exchange charge among themselves in order to maintain the same electrostatic potentials<sup>5,8</sup> and the data show a lot of scatter. On the other hand, systematic study of the relationship between  $Q/M$  and toner particle size for multiple carrier-toner mixtures is limited.<sup>2</sup> Moreover, the data is for non-pigmented toner resin only. In the study published by Gutman et al.,<sup>2</sup>  $Q/M$  of five resin powders with average particle sizes ranging from 5.8 to 15.1 microns departed substantially from the theoretical behavior, i.e.,  $Q/M$  ratio of 5.8 and 15.1 micron toners was not equal to the toner size ratio. Validation of surface state theories of toner charging, however, is usually based on the linear relationship between  $M/Q$  and toner concentration  $C_t$ , without even considering the size-charge relationship of toners.<sup>1,2,3,9</sup> The purpose of this paper is to investigate the particle size effect on the electrostatic charge of pseudo toners and show that the data can be rationalized by two simple cases: a) the charge of the toner is limited by its surface area, b) the charge of the toner is limited by the surface area of the carrier. The simple surface area argument is based on the observation that in the latter case the charge per unit surface area of the toner,  $Q/A$ , increases linearly with toner size, whereas  $Q/A$  is independent of

toner size for the first case. Based on those results and the observation that  $M/Q$  is independent of  $C_t$ , the validity of the surface state theories of toner charging is questioned.

## Experimental

The pseudo toners were prepared by melt mixing styrene-butylmethacrylate copolymer resin and dry blends of resin/non-oxidized carbon black (9%), resin/charge control agent TRH (2%), and resin/0.5 micron iron oxide (30%). The compounded materials were then milled to powders with average volume sizes of ca. 5, 7, 10, 15, and 20 microns. The charge on the pseudo-toners was activated by rolling the powders against a 200 micron steel spherical carrier. The charge  $Q/M$  was measured at different roll times using the total blow-off method.

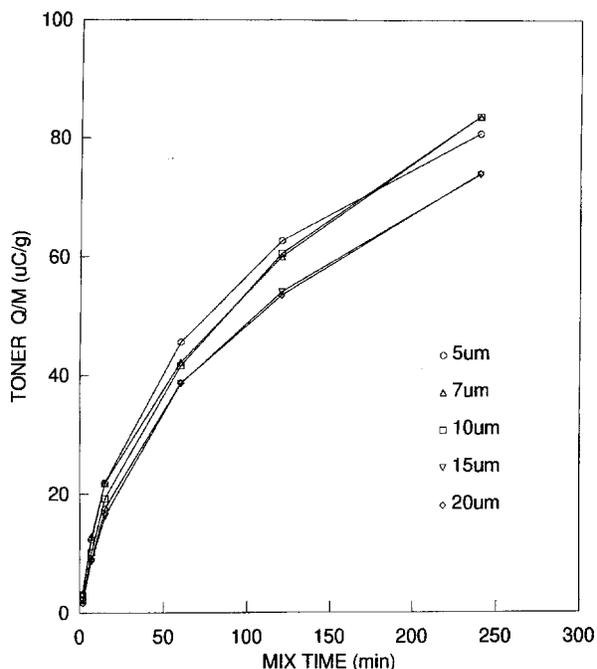


Figure 1. Charge ( $Q/M$ ) of resin pseudo-toner powders as a function of rolling time.  $C_t$  is equal to 1%.

## Results and Discussion

Four pseudo-toners made of styrene-butylmethacrylate resin (1), resin containing 9% non-oxidized carbon black (2), 2% TRH (3), and 30% iron oxide (4) were mixed with 200 micron spherical carrier at different concentrations and the

blow-off charge was measured for several roll times. Figures 1, 2, 3 and 4 show  $Q/M$  for the resin, resin/9% carbon black, resin/30% iron oxide, and resin/2% TRH pseudo-toners as a function of the rolling time, respectively.  $C_t$  is equal to 1% in all cases. Based on the observed charging behavior, the pseudo-toners can be divided in two categories; one which shows a toner size effect on the magnitude of  $Q/M$  (Figures 3 and 4), and one where the average diameter of the powder has very little effect on  $Q/M$  (Figures 1 and 2). For the sake of clarity, we will use only one example from each category.

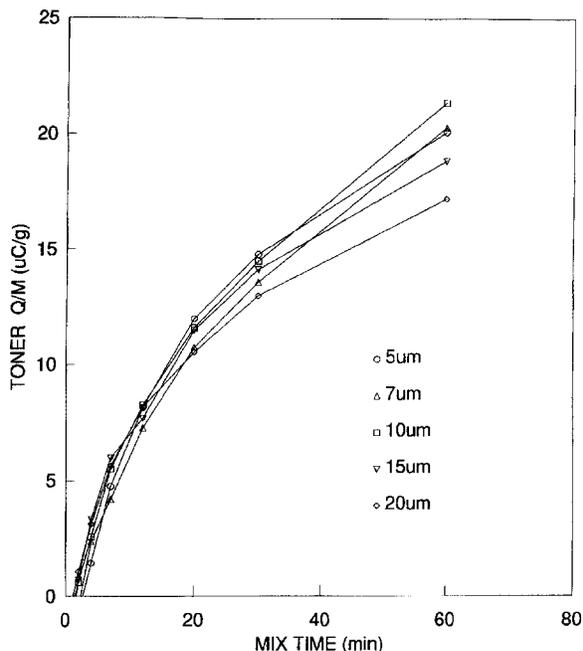


Figure 2. Charge ( $Q/M$ ) of resin/9% carbon black pseudo-toner powders as a function of rolling time.  $C_t$  is equal to 1%.

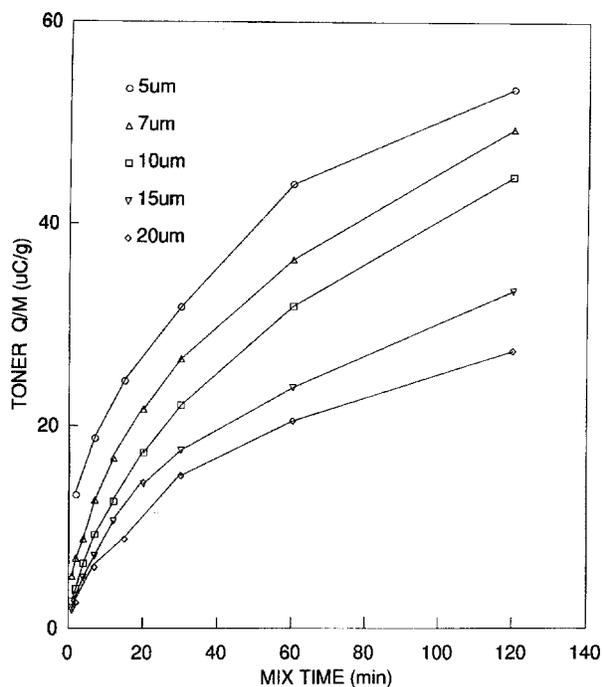


Figure 3. Charge ( $Q/M$ ) of resin/30% iron oxide pseudo-toner powders as a function of rolling time.  $C_t$  is equal to 1%.

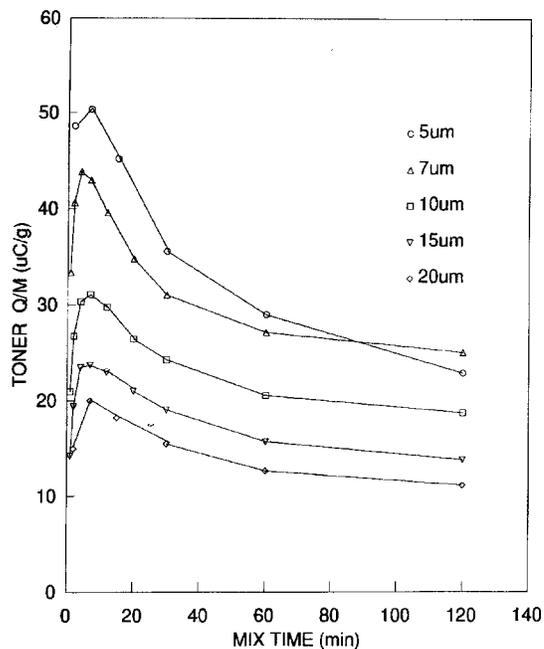


Figure 4. Charge ( $Q/M$ ) of resin/2% charge control agent pseudo-toner powders as a function of rolling time.  $C_t$  is equal to 1%.

Surface state theories predict a linear relationship between  $M/Q$  and  $r$ , with a non-zero slope and intercept.<sup>1,2,3</sup> Based on Lee's model,<sup>3</sup> this relationship can be expressed the following way<sup>1</sup>:

$$\frac{M}{Q} = RC_t \left[ \frac{\rho_c}{3N_c \Delta\phi_e} \right] + r \left[ \frac{\rho_t}{3N_t \Delta\phi_e} \right] \quad (1)$$

where  $M/Q$ ,  $C_t$ , and  $r$  are the toner mass to charge ratio, concentration, and radius; and  $R$  is the carrier radius. The toner ( $t$ ) / carrier ( $c$ ) bulk density and surface state density are represented by  $N$  and  $\rho$ , respectively.  $\Delta\phi$  is the surface work function difference between the carrier and toner. Thus, the theory predicts that for any given carrier size at any fixed  $C_t$ , the slope of the plot  $M/Q$  vs.  $r$  will equal the second term in brackets with an absolute value greater than zero, whereas the intercept will equal the first term of equation 1 and also be greater than zero.

Figure 5 shows the relationship between  $M/Q$  and  $r$  for resin and resin/iron oxide pseudo-toners.  $M/Q$  values used in Figure 5 were obtained after 7 minutes of rolling time in order to minimize the impact of other chemical and/or physical processes on the charging event (a linear relationship is maintained for 60 minutes data, but the slope for the resin/30% iron oxide powders decreases and the intercept is no longer equal to zero, whereas the slope for the resin powder is practically unchanged). This time is orders of magnitude larger than the time usually required to exchange electrons or ions between two surfaces and therefore represents an accurate measurement of the electrostatic charge resulting from the contact between two dissimilar materials. In Figure 5, the full line going through the data for the resin/iron oxide pseudo-toner represents the ideal case where  $M/Q$  is proportional to the toner radius. The line was obtained by using  $M/Q$  value for the 10 micron toner as reference value. The fact that the experimental points fall on

one line indicates that this toner system is well behaved and responds to toner size changes as expected with most theories. The straight line, however, passes through the zero point. This last observation is not in agreement with surface state theories.<sup>1,2,3</sup> In contrast to the previous example,  $M/Q$  of toner made of resin only is insensitive to size variation as shown in Figure 5. This result is also not consistent with the proposed surface state models.<sup>1,2,3</sup>

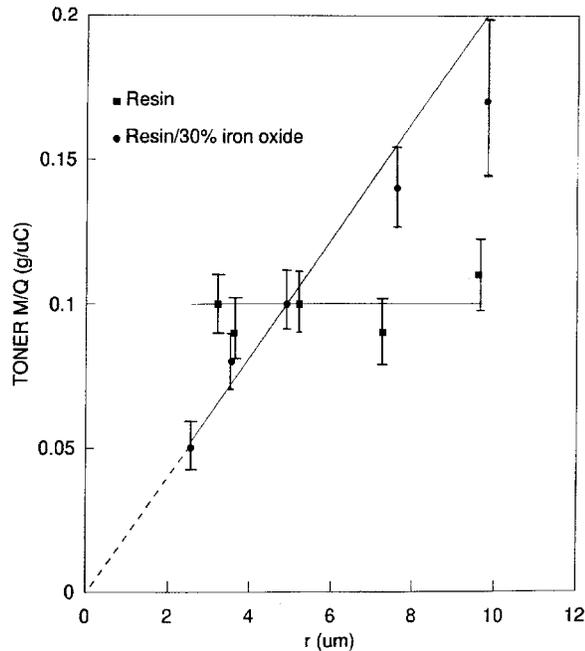


Figure 5. Mass-to-charge ratio ( $M/Q$ ) of resin and resin/30% iron oxide pseudo-toner as a function of toner radius ( $r$ ).  $C_t$  is equal to 1%.

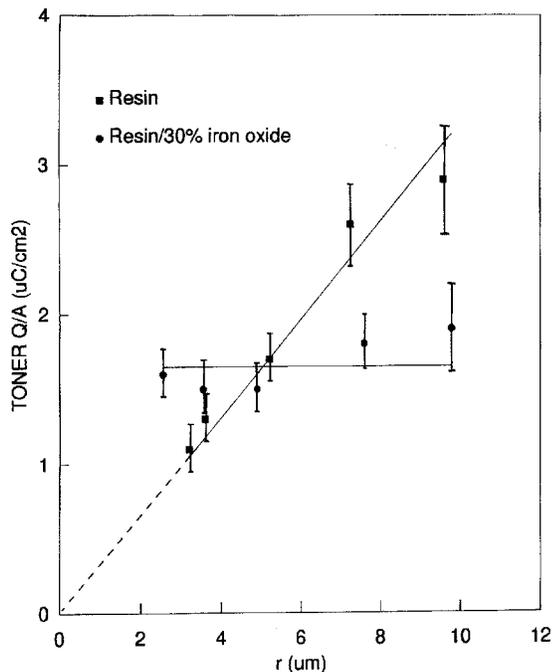


Figure 6. Surface charge density ( $Q/A$ ) of the resin and resin/30% iron oxide pseudo-toners as a function of toner radius ( $r$ ).  $C_t$  is equal to 1%.

Figure 6 shows the relationship between the surface charge density  $Q/A$ , and toner radius.  $Q/A$  values were calculated from  $Q/M$  data and the specific area expressed in  $\text{cm}^2/\text{g}$  of toner. The specific area was estimated assuming a density of  $1 \text{ g}/\text{cm}^3$  and spherical shape for toner. Figure 6 shows that  $Q/A$  for the resin/iron oxide pseudo toner is the same for particle sizes ranging between 5.2 to 19.2 microns. This result suggests that the charge on the pseudo-toner is limited by its surface area. On the other hand,  $Q/A$  for the resin increases linearly with toner size suggesting that the charge on the resin particles is limited by the carrier surface area.

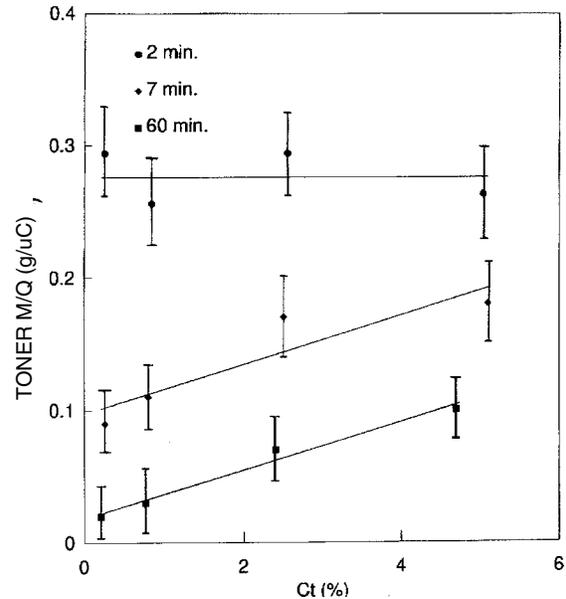


Figure 7. Mass-to-charge ratio ( $M/Q$ ) of resin/30% iron oxide 10 micron pseudo-toner as a function of toner concentration ( $C_t$ ) for three roll times.

$Q/M$  data obtained at different roll times and toner concentrations for the 10 micron powders of resin/iron oxide and resin/carbon black pseudo toners are displayed in Table 1. The corresponding  $Q/M$  values for the carrier are also reported in Table 1. Figure 7 shows  $M/Q$  data for the resin/iron oxide powder after 2, 7 and 60 minutes of rolling as a function of  $C_t$ . Interestingly,  $M/Q$  data after 2 minutes of roll time are insensitive to  $C_t$ . This result has major implications. First, it suggests that the charge on the toner is limited by its surface area for  $C_t$  ranging from 0.25% to 5% (a range that corresponds to 0.5-14 monolayers coverage of the carrier). This last affirmation is also supported by the fact that the corresponding  $Q/M$  values for the carrier (Table 1) is proportional to  $C_t$ . But more significantly, the insensitivity of  $M/Q$  vs.  $C_t$  is not reconcilable with the surface state theories,<sup>1,2,3,9</sup> since they all predict an increase in  $M/Q$  as a function of  $C_t$  in toner-carrier mixtures. The universally observed and theoretically expected relationship between  $M/Q$  and  $C_t$  is, however, observed for longer roll times as shown in Figure 7. The fact that the relationship between  $M/Q$  and  $C_t$  is influenced by the roll time indicates that the tribocharging event is accompanied by other processes that alter the charge data. Contamination of the carrier surface by the toner and surface modification of the toner during agitation may lead to the observed modifica-

**Table 1. Toner and carrier charge (Q/M) for two pseudo-toners at different rolling times and concentrations.**

Toner Rolling Time	$C_t$ (%)	Toner ( $\mu\text{C/g}$ )	Q/M Carrier ( $\text{nC/g}$ )
Resin/30% Iron Oxide	2 min	0.25	8
		0.84	33
		2.55	90
		5.04	200
	7 min	0.26	28
		0.80	75
		2.50	150
		5.10	300
	60 min	0.21	125
		0.77	250
		2.40	330
		4.70	500
Resin/9% Carbon Black	7 min	0.25	34
		0.68	41
		2.44	38
		4.50	37
	60 min	0.20	130
		0.77	170
		4.70	150
		3.1	150

tions in the  $M/Q$  vs.  $C_t$  curves. The carrier charge data reported in Table 1 are also in line with the contamination argument. Since most of the charge data in the literature were obtained for roll times ranging from 15 minutes to three hours, it is not surprising to find that most toner charging studies have data supporting the surface state theories.<sup>1,2,3,9</sup> Interestingly,  $M/Q$  insensitivity to  $C_t$  can also be observed in Lee's study<sup>3</sup> for developers made of toner resin different sizes and different carrier surfaces (see his Figures 3 and 4; a straight line with slope equal to zero fits through the data for toner concentrations up to 1.5% and 2.5% respectively).

The charging behavior of the resin/carbon black 10 micron powder is shown in Figure 8. It can be seen that  $M/Q$  scales linearly with  $C_t$  and, interestingly, the linear regressions show that the straight lines go through the origin for both 7 and 60 minutes data. Once more, none of the current surface state theories are consistent with an intercept equal to zero. The linear relationships observed in Figure 8 are consistent with the carrier surface limiting charging since as  $C_t$  increases the toner charge decreases proportionally and the carrier  $Q/M$  values remain the same within the experimental error (Table 1).

### Conclusion

Many experimental evidences have been presented in this study to demonstrate that current surface state charging theories are inconsistent with the charging behavior of pseudo-toners. Our results are better explained by a simple charge exchange mechanism between toner and carrier where one of the two surfaces controls the magnitude of the charge. It is also proposed that the universally observed and theoretically expected  $M/Q$  vs.  $C_t$  relationship may be

brought about by a combination of physical and chemical processes occurring during the charging event, since most of the charge data used in the literature are for relatively long rolling times. Clearly, the observation of a linear relationship between  $M/Q$  and  $C_t$  is not enough to validate surface state theories.

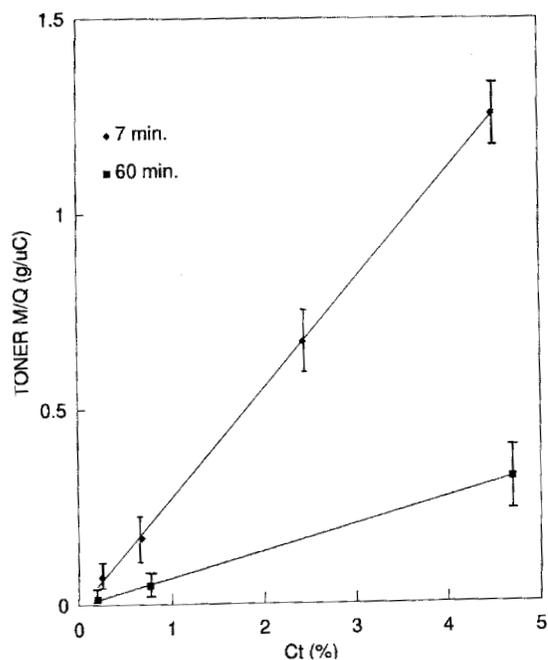


Figure 8. Mass-to-charge ratio ( $M/Q$ ) of resin/9% carbon black 10 micron pseudo-toner as a function of toner concentration ( $C_t$ ) for two roll times.

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