

CHAPTER 4

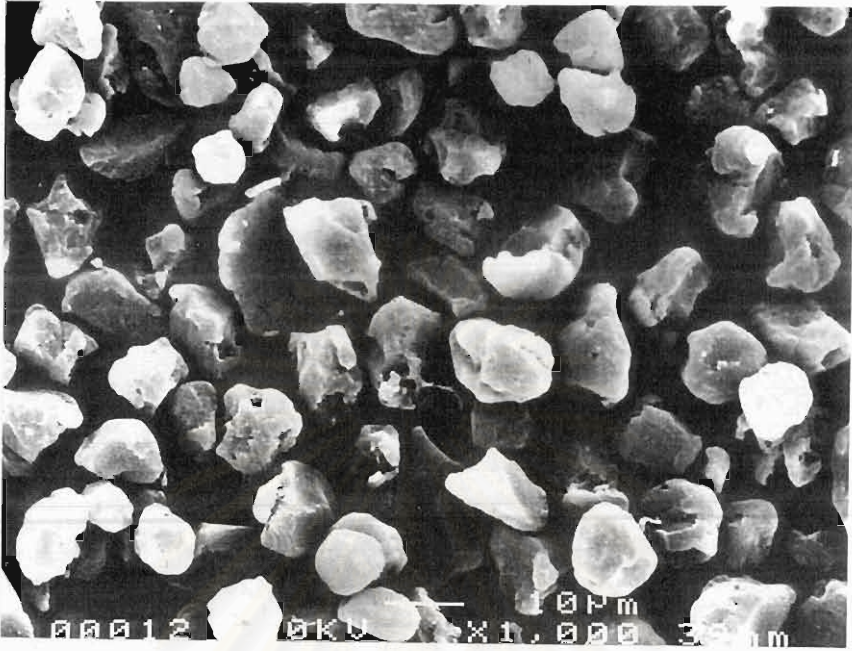
RESULTS AND DISCUSSION

4.1 Morphology of the Toner and the Carrier Particles

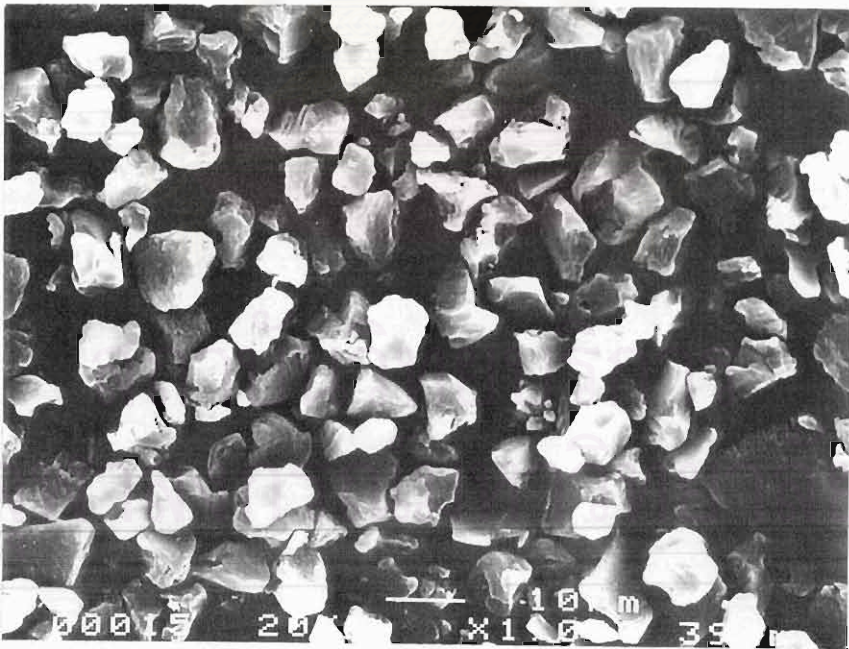
The scanning electron micrographs (x1,000) of the red and cyan toner particles are shown in Figure 4-1 that the red toner particles are larger than the cyan toner particles, and both toner particles are of relatively irregular shape. However, the toner particle shape can be approximately assumed as a spherical shape.¹⁹ The micrographs (x5,000) in Figure 4-2 shows that the cyan toner surface is slightly rougher than is the red toner surface.

The micrographs (x100) in Figure 4-3 show the different particle sizes of the carriers A to D, and also show that the particle shapes are almost spherical. The different surfaces of the carriers B, E, F and G, coated with fluorine/acrylate, acrylate, silicone and uncoated, respectively, are shown by the micrographs (x1,000) in Figure 4-4, which also show that the ferrite carriers are nearly spherical and smooth, but the iron carrier (H) shown by the micrographs in Figure 4-5 is very irregular and rough. The irregular shapes of carrier H can be evidenced by the dependence of toner contact charging on the carrier shape.

The scanning electron micrographs in Figures 4-1 and 4-3 show that the particle sizes of the red toner, the cyan toner, and the carriers A to D are varied, but the average particle diameter can be measured from the 300 enlargement of these micrographs by the Size Distribution System, as shown in Table 4-1.

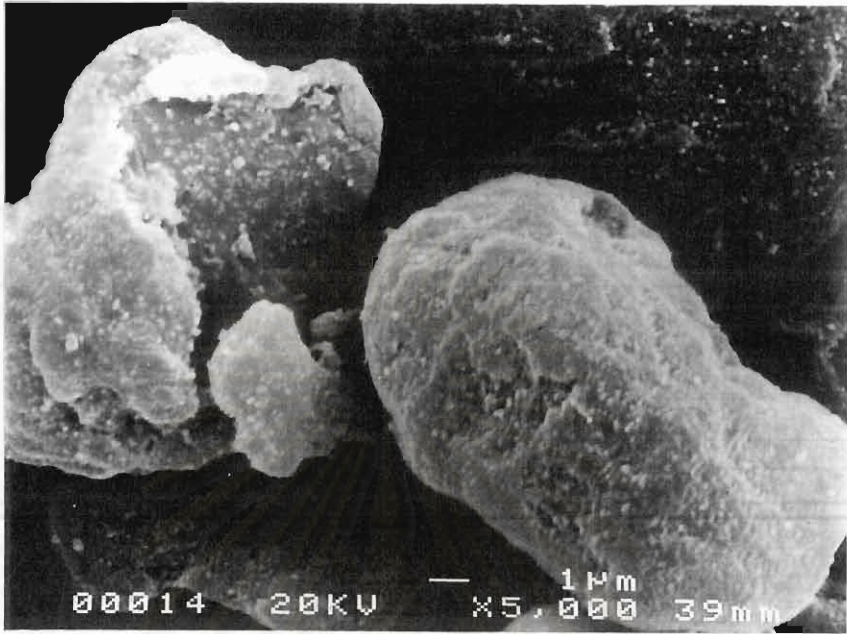


Red toner

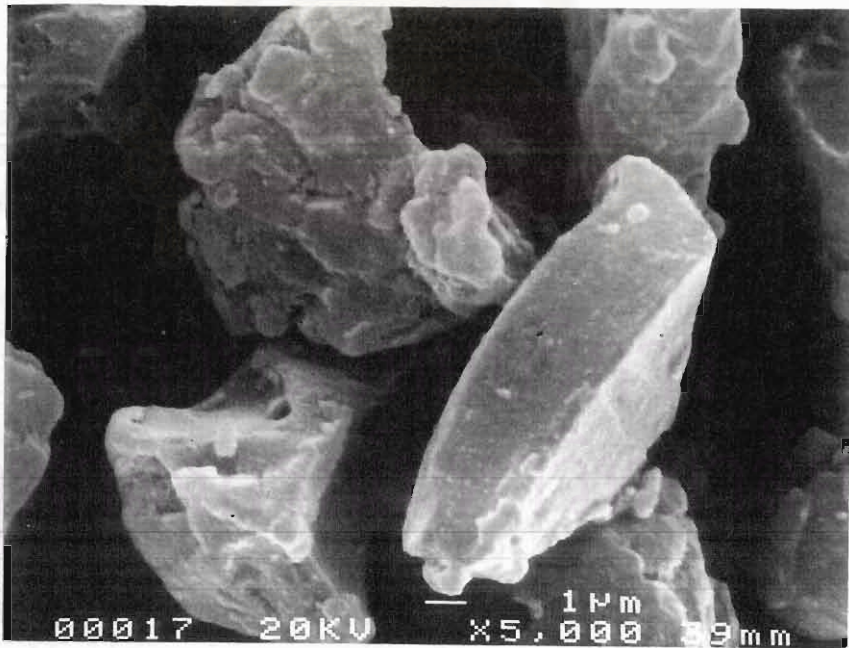


Cyan toner

Figure 4-1 Scanning electron micrographs of the red and cyan toner particle shape

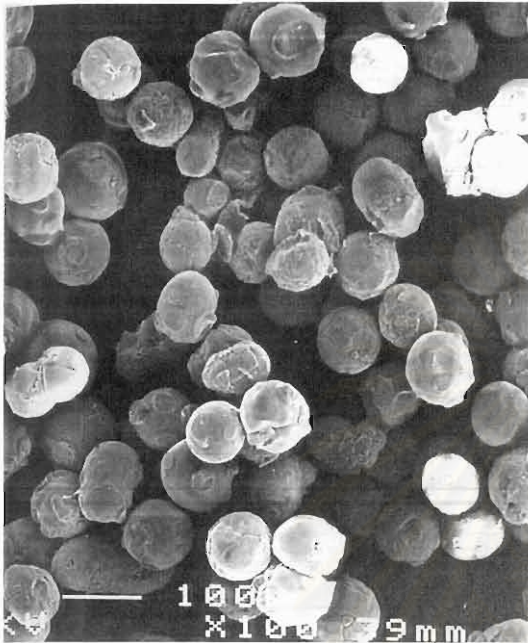


Red toner

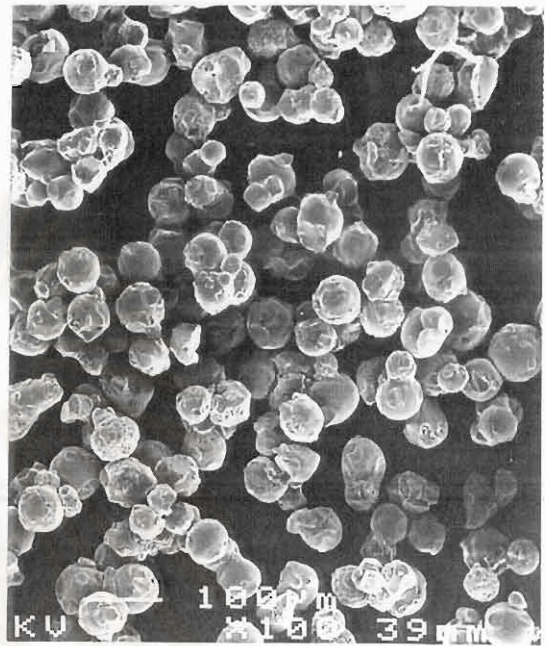


Cyan toner

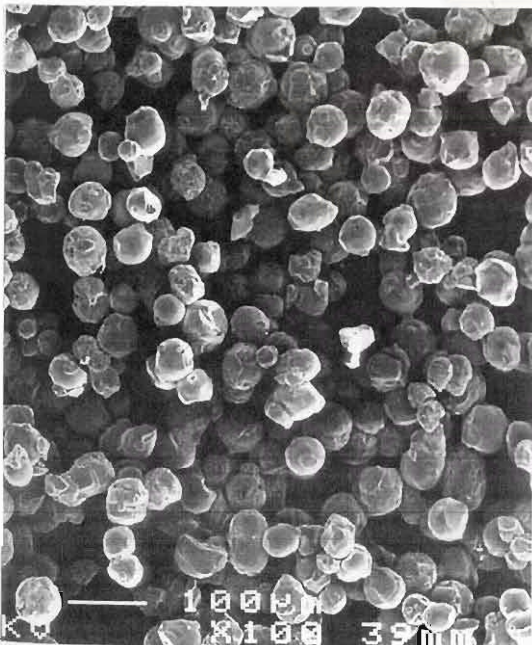
Figure 4-2 Scanning electron micrographs of the red and cyan toner particle surface



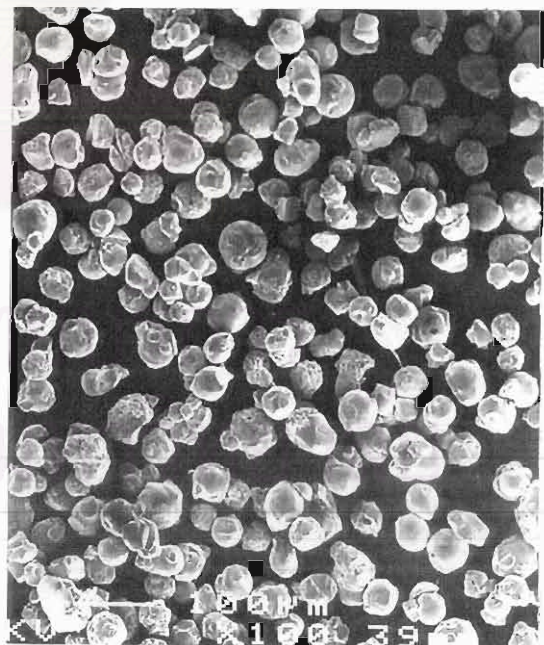
Carrier A



Carrier B

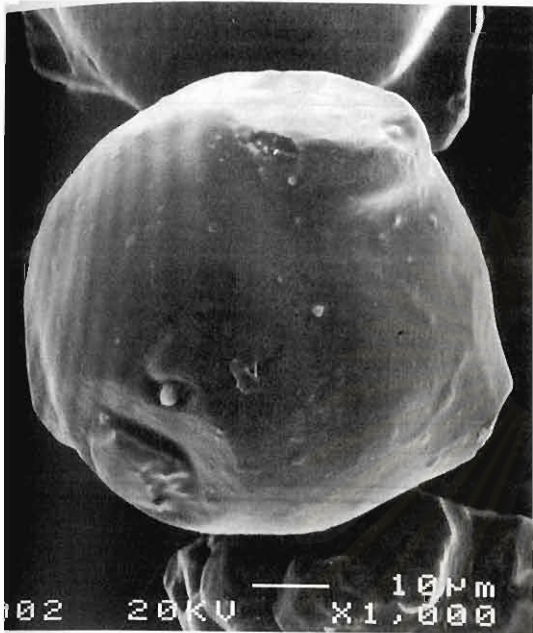


Carrier C

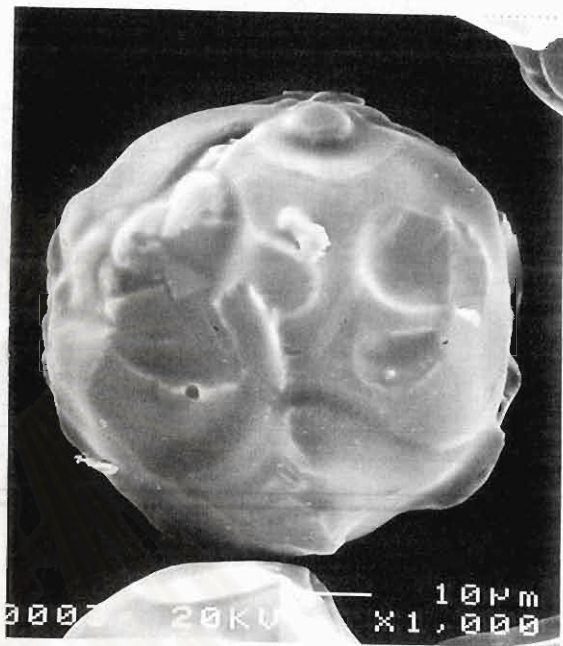


Carrier D

Figure 4-3 Scanning electron micrographs of the different carrier sizes (A - D)



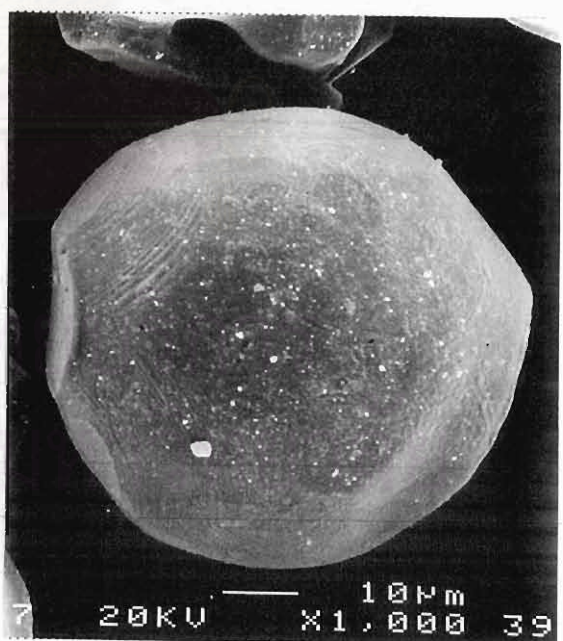
Carrier B



Carrier E



Carrier F

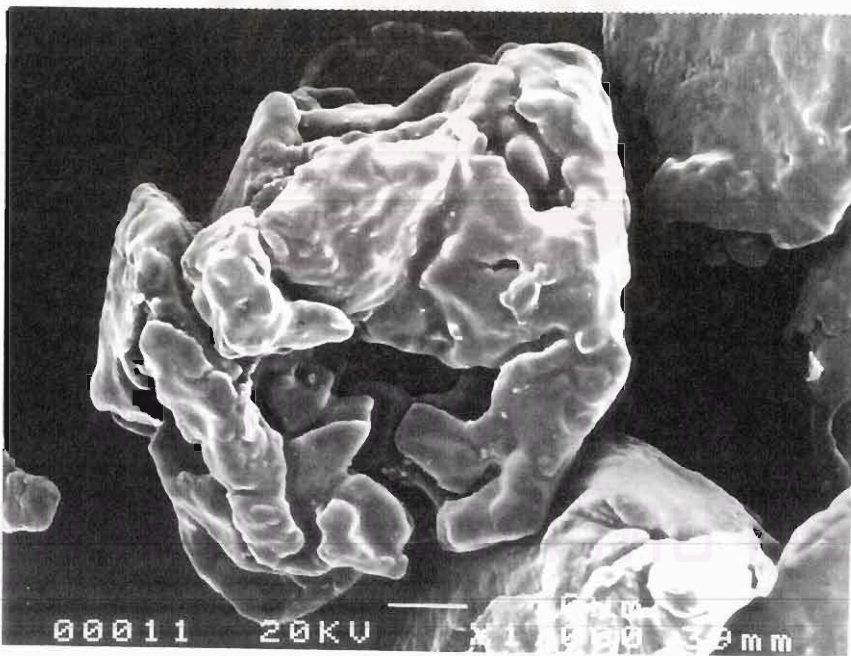


Carrier G

Figure 4-4 Scanning electron micrographs of the different carrier surfaces (B - G)



(a)



(b)

Figure 4-5 Scanning electron micrographs of the carrier H : (a) Shape (b) Surface

Table 4-1 Particle size and distribution of the toner and carrier particle sizes

Data	X (μm)	X _d (μm)	X _{P1-P2} (μm)	X _{P3-P4} (μm)	MIN (μm)	MAX (μm)	S (cm^2/g)	SD
Red toner	9.492	10.249	9.663	9.322	3.716	19.959	6320.871	2.647
Cyan toner	6.465	7.154	6.504	6.426	2.862	14.148	9280.595	2.091
Carrier A	86.570	87.347	86.406	86.733	53.796	107.059	138.617	8.268
Carrier B	57.579	58.816	58.025	57.133	31.441	75.997	208.410	8.578
Carrier C	48.346	49.723	49.174	47.517	30.73	70.626	248.213	8.168
Carrier D	45.992	47.378	46.759	45.225	29.316	69.486	260.917	7.999
Carrier E	55.983	57.352	56.35	55.615	28.484	75.657	214.352	8.896

X is the mean diameter, X_d is the median diameter, X_{P1-P2} and X_{P3-P4} are the vertical and horizontal diameter, MIN and MAX is the minimum and the maximum diameter, S is the surface area per mass, and SD is the standard deviation.

The data in Table 4-1 show that the particle size of the cyan toner is smaller than the red toner, and the carrier particle size of A is larger than those of B, C, and D, respectively, and also show that the larger particles have a smaller surface area per mass than do the smaller particles as shown by curve in Figure 4-6. It means that at the same weight of the carriers, the smaller carriers have more surface area to be covered by the toner particles than do the larger carriers. Therefore, the smaller carriers can be mixed with higher toner concentration and have less amount of the free toners than do the larger carriers.

The average diameter and particle size distribution of the cyan toner are also obtained by an E-SPART analyzer, as shown in Appendix A.

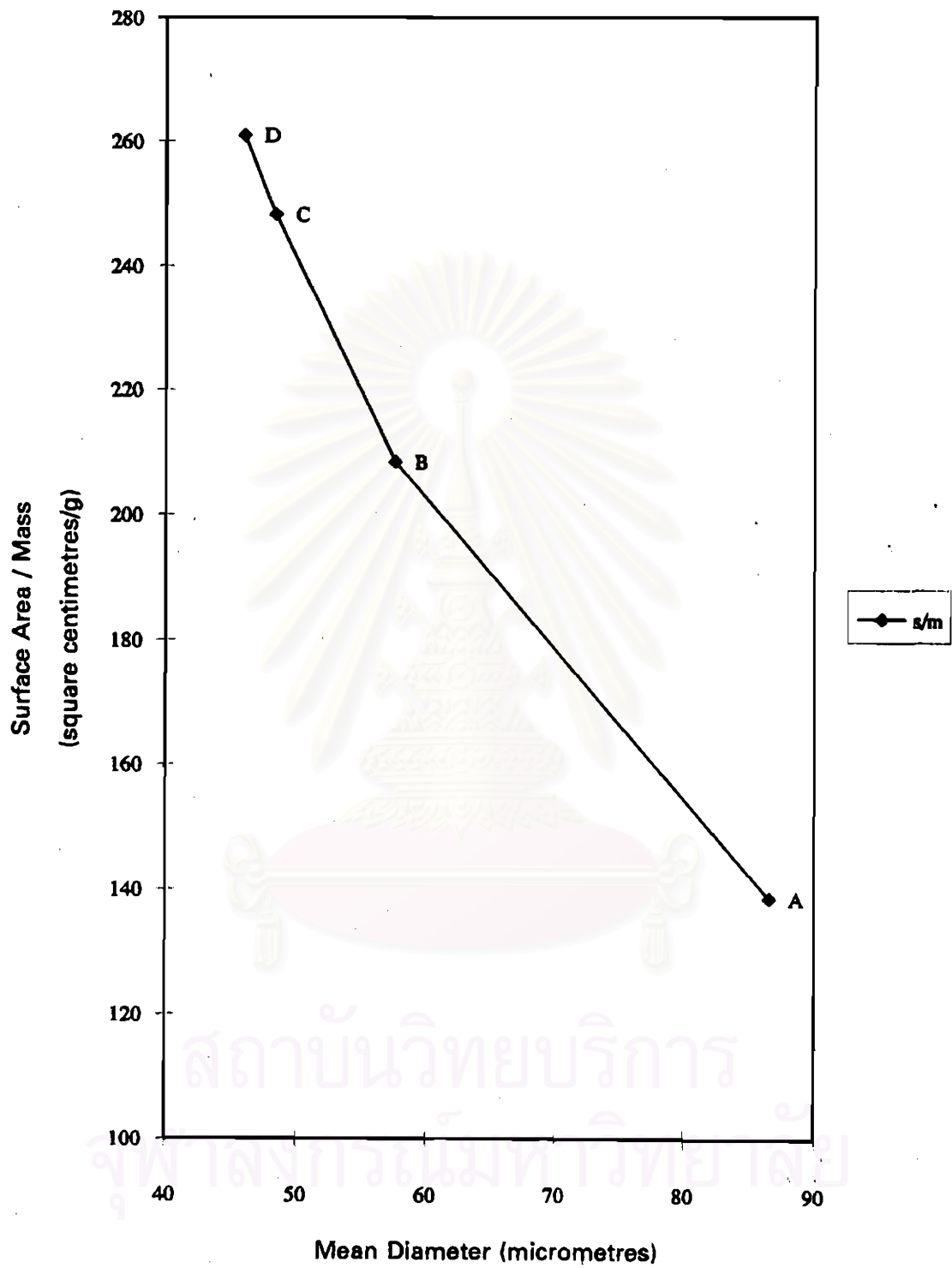


Figure 4-6 Surface area/mass vs. mean diameter of four carriers

4.2 Determination of Developer Charge Properties and the Effective Parameters

The developers, toners and carriers, are subjected to a charge measurement by the blow-off technique. This experiment shows that the red toner, is of positive charge, but the cyan toner is of negative charge with the carriers A to H and K. The charges of the red and the cyan toner depend on the surface work function difference between the carrier coating polymer and the toner resin.¹⁵ We predict that the carriers coating polymers probably lie between the red toner resin (positive site) and the cyan toner resin (negative site) in the triboelectric series. The red toner resin has an electron donating affinity with the carriers coating polymers, such as fluorine/acrylate, acrylate, silicone, fluorine/silicone and even the uncoated ferrite, so the carriers can accept electrons and become negatively charged. Likewise, the cyan toner resin has a tendency to accept electrons from these carriers coating polymers, and induce the carriers to be positive charges. Triboelectric series of some copolymers is shown in Appendix B.

4.2.1 The dependence of the red toner charge on the shaking time

The dependence of the red toner charge-to-mass ratios (q/m) on the shaking time of the carriers A, B, C and D shown in Figures 4-7 to 4-10 implies that the red toner q/m is not stable during 10 - 30 seconds, and reaches a saturated value in 60 seconds. At the low T/Cs (1-5%) the q/m values of red toner increase with increasing the shaking time, but at the high T/Cs (8-15%) the q/m values decrease with increasing the shaking time.

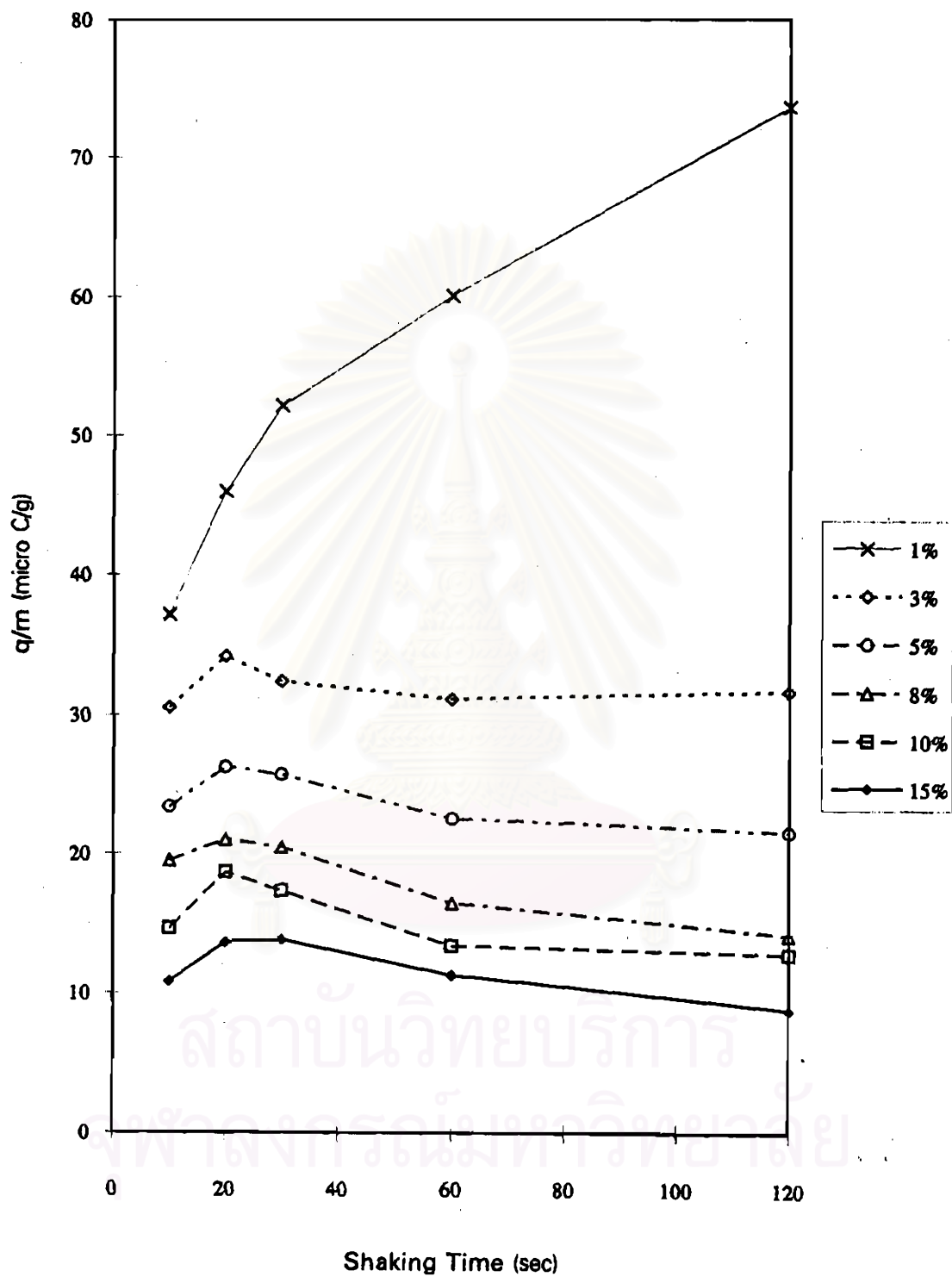


Figure 4-7 Red toner q/m versus shaking time of carrier A

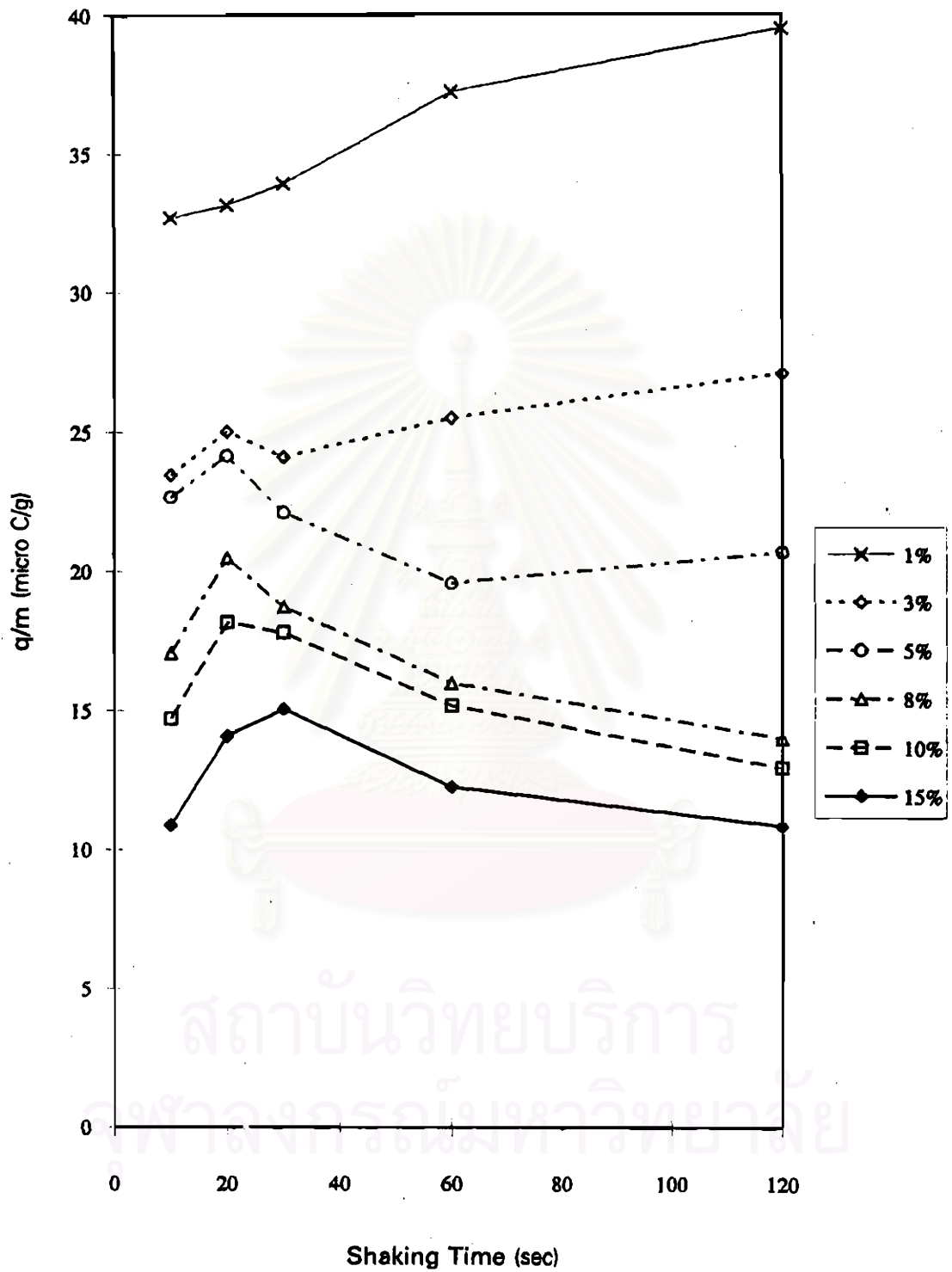


Figure 4-8 Red toner q/m versus shaking time of carrier B

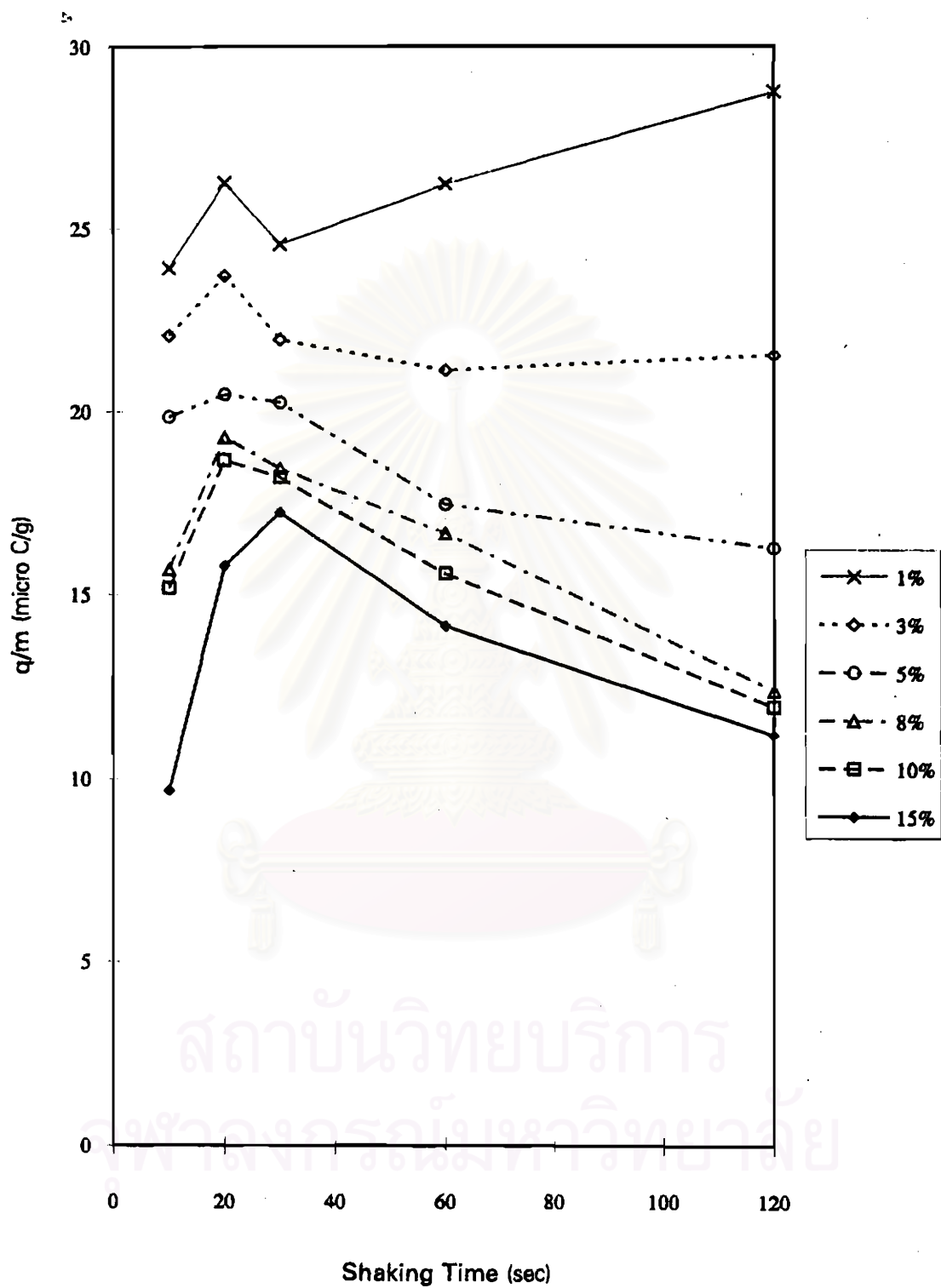


Figure 4-9 Red toner q/m versus shaking time of carrier C

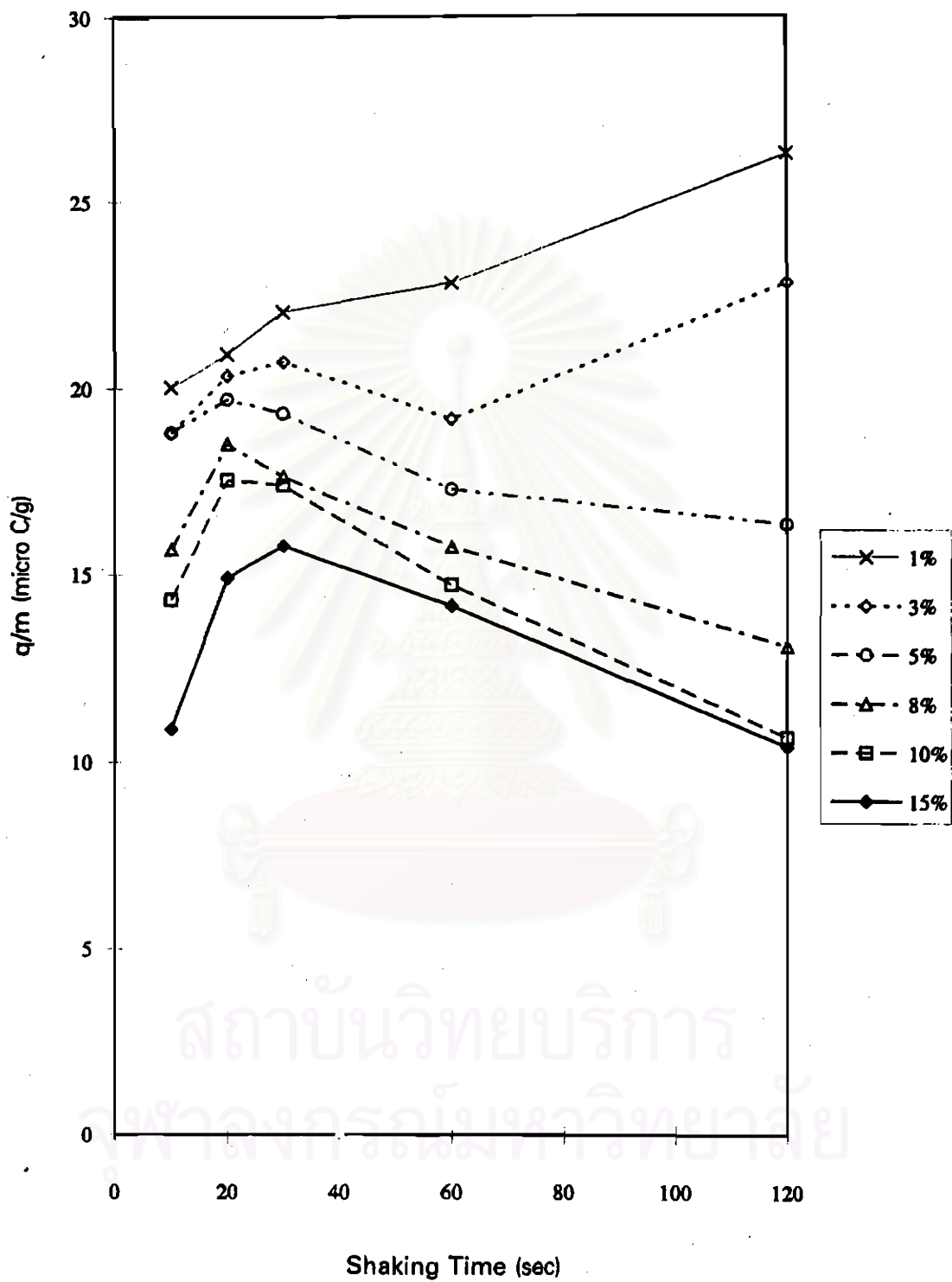


Figure 4-10 Red toner q/m versus shaking time of carrier D

The plots of the red toner q/m versus the shaking time of the carriers E, F, G and H in Figures 4-11 to 4-14 show the same dependence of the shaking time as those of the carriers A to D. For some T/Cs of the developers E (1-3%), F (1%), G (1-10%) and H (1-5%), the toner q/m values increased with increasing the shaking time, but other toner concentrations, the toner q/m values decreased with increasing the shaking time.

To conclude, tribocharging rate of any red developers is rapid in mixing and reaches to saturated value in 60 seconds. The equilibrium value of tribocharge during mixing was determined by the balance of charging and discharging rate.¹⁶ At some low T/Cs, the red toner q/m values increase by increasing the shaking time, because the friction between the red toners and the carriers during the longer shaking time is higher and then the tribo-electrification is higher, resulting in a higher q/m value. If the T/Cs are high, many toner particles will be better off to adhere on a carrier when increasing the shaking time, resulting in a lower q/m value, which means indirectly that the tribocharge is distributed to many toners on a carrier surface.

The red toner q/m with the carriers E, F and G are far too lower than those of the carriers A to D, because the different carrier coated resins give different charge properties. The carriers A to D (fluorine/acrylate coated) have a higher tendency to accept electrons from the red toner than do the carrier E (acrylate coated), the carrier F (silicone coated), and the carrier G (uncoated).

The q/m curve of the carrier H, the fluorine/acrylate coated iron carrier, has the same dependence of the shaking time as the carriers A to D, because they are all coated with the same material, resulting in the same charging behavior.

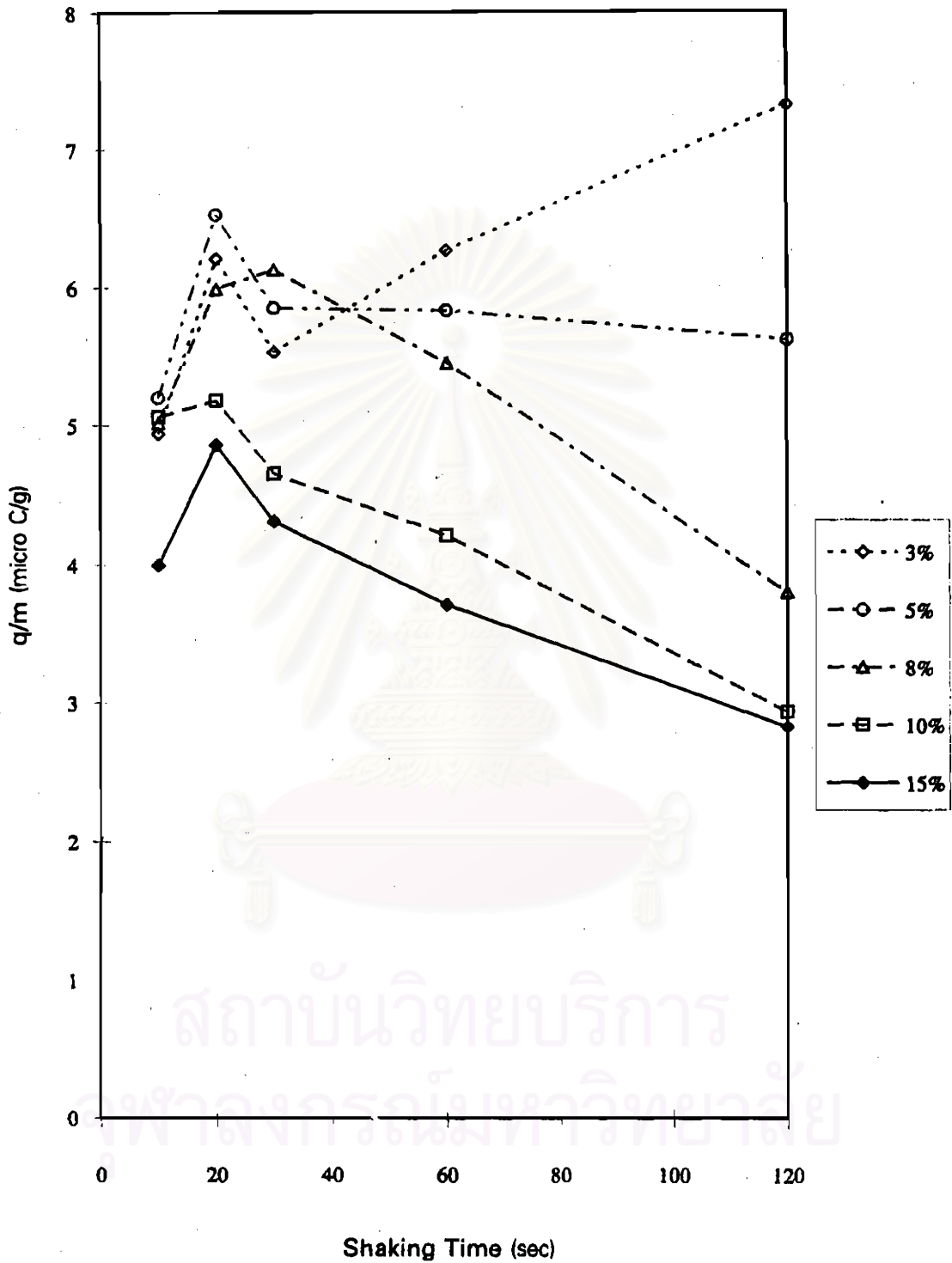


Figure 4-11 Red toner q/m versus shaking time of carrier E

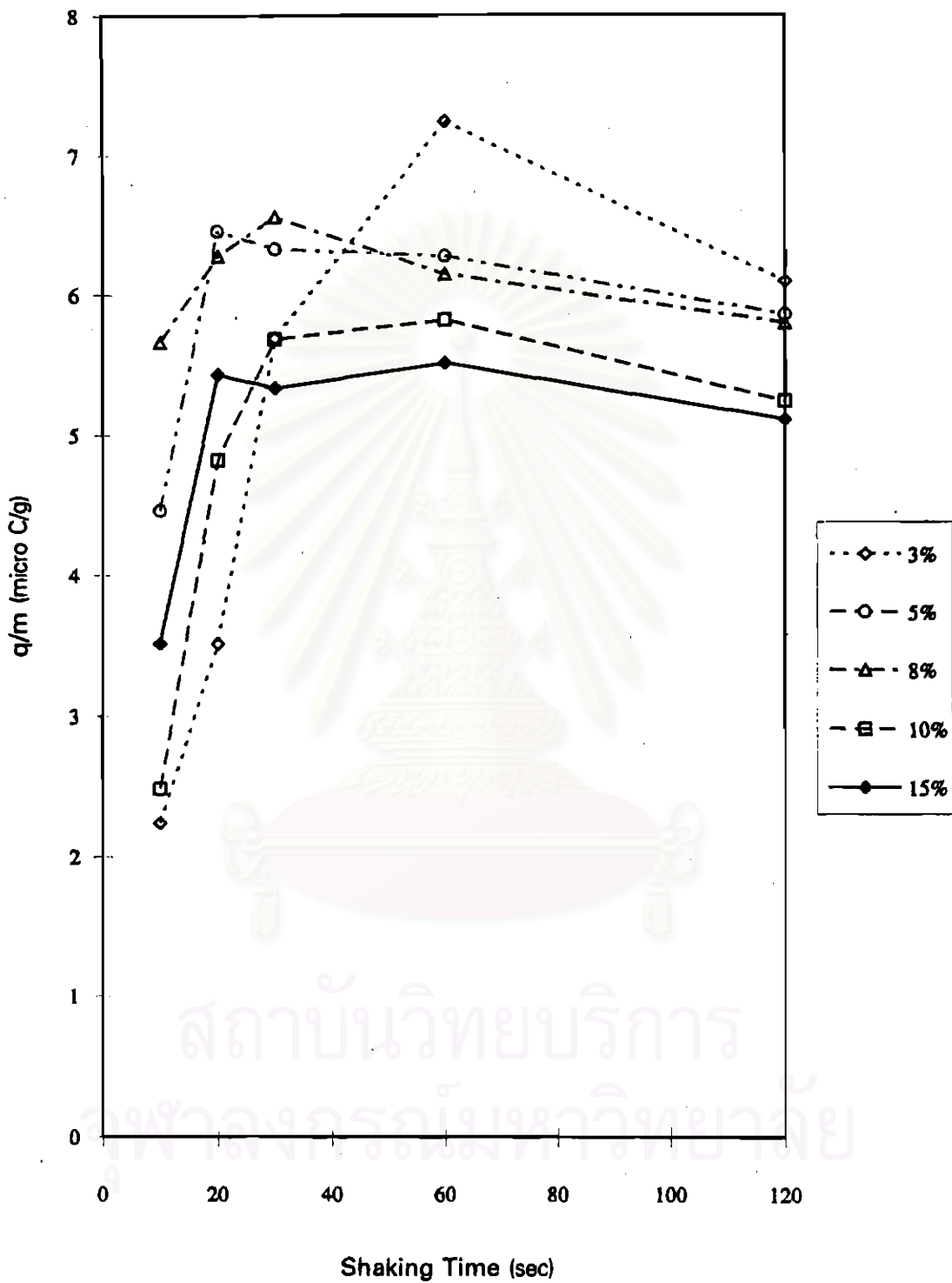


Figure 4-12 Red toner q/m versus shaking time of carrier F

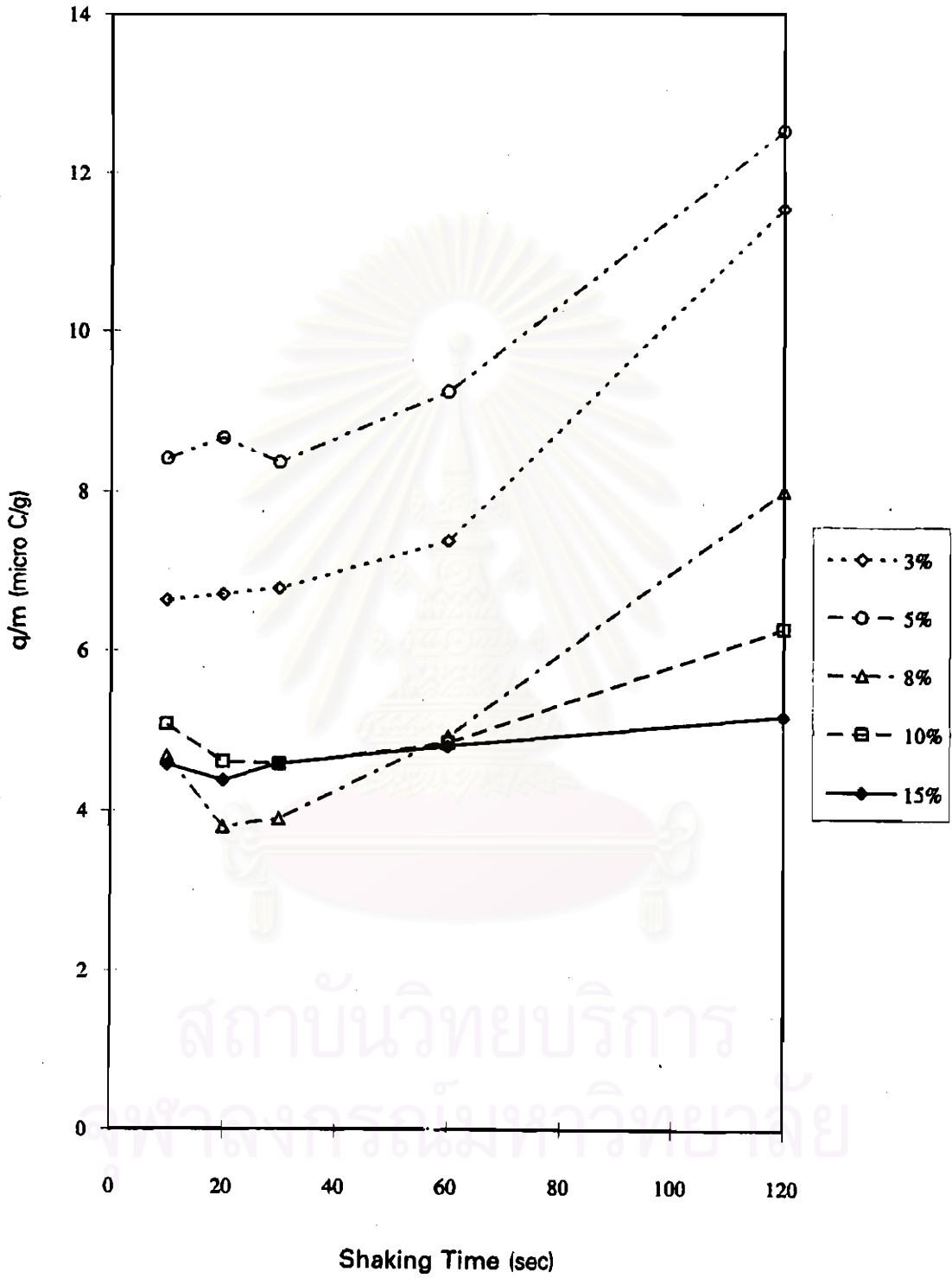


Figure 4-13 Red toner q/m versus shaking time of carrier G

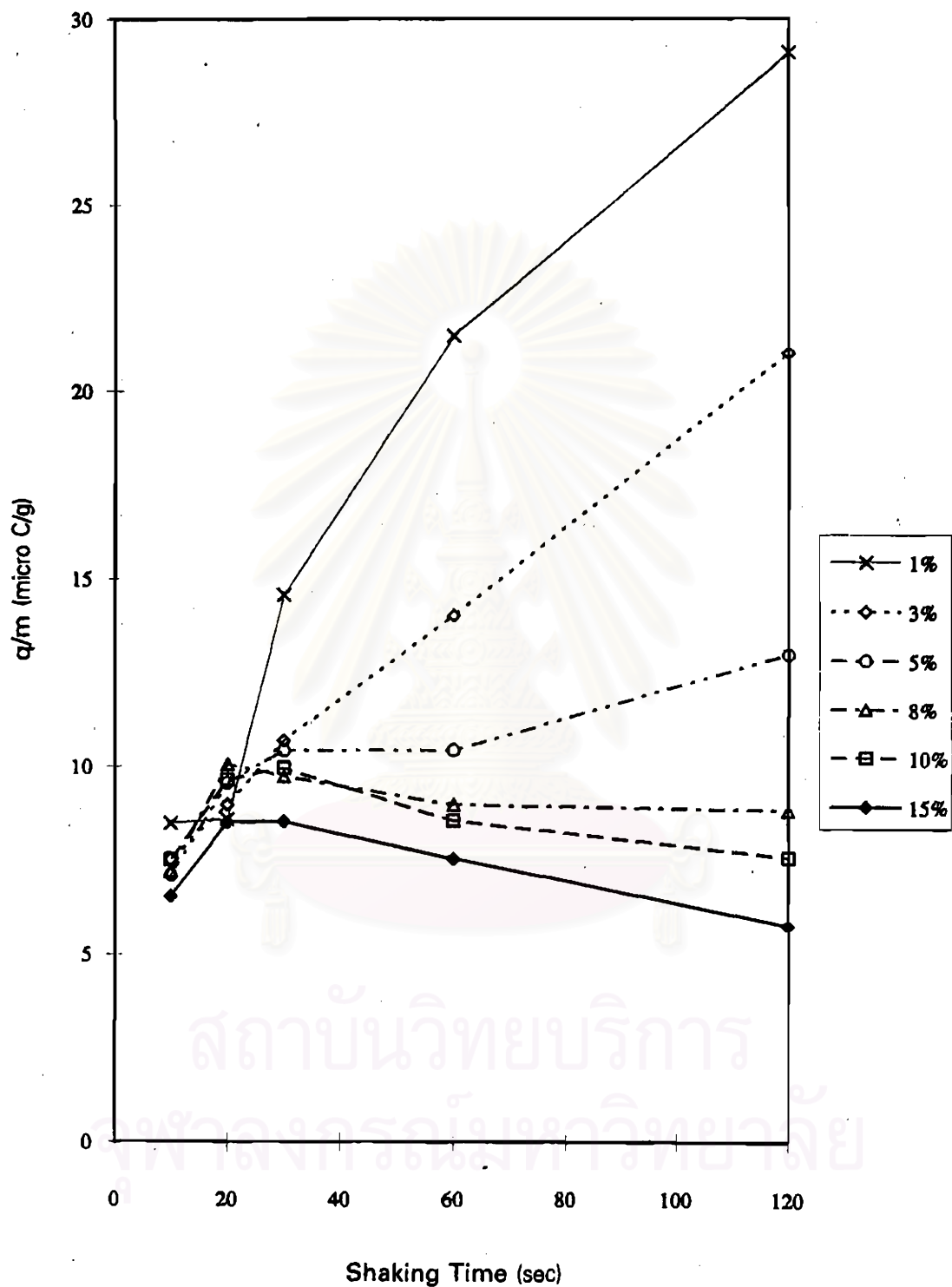


Figure 4-14 Red toner q/m versus shaking time of carrier H

4.2.2 The dependence of the red toner charge on the toner concentration

The dependence of the red toner q/m on T/C of the carriers A to D at 60 seconds of shaking time in Figure 4-15 shows that the red toner q/m decrease with increasing the toner concentrations. The curves of q/m versus T/C of the carriers B, E, F and G in Figure 4-16, and of the carriers B and H in Figure 4-17 show the same dependence as those of the carriers A to D. The toner coverage on a carrier surface is higher at higher T/C, therefore, the toner charge distributed to one toner on a carrier surface decreases with increasing toner concentration, similar to that observed by Takahashi,¹⁶ and there are free toners if the toner concentration and coverage is too high.

4.2.3 The dependence of the red toner charge on the carrier size

Figure 4-15 shows that the red toner q/m values of the larger carriers are higher than the smaller carriers at the low T/Cs (1-5%), but are lower than the smaller carriers at the high T/Cs (8-15%). At some low T/Cs, the average charge of a toner particle is not affected by the number of toners under the condition of $N_c > N_t$, and the number of tribocharge sites is determined by the maximum of carrier charging sites.¹⁶ Therefore, a larger carrier with larger surface charging sites can give higher q/m values to the toner than does a smaller carrier. When the T/C is higher than 5%, the q/m values of the larger carriers depend on T/C under the condition of $N_c < N_t$, according to the model types II and III of Takahashi, as shown in Figure 2-17.¹⁶ The toner q/m value of the larger carrier rapidly decreases, while the smaller carrier gradually decreases with increasing T/C, determined by a slope of the curve.

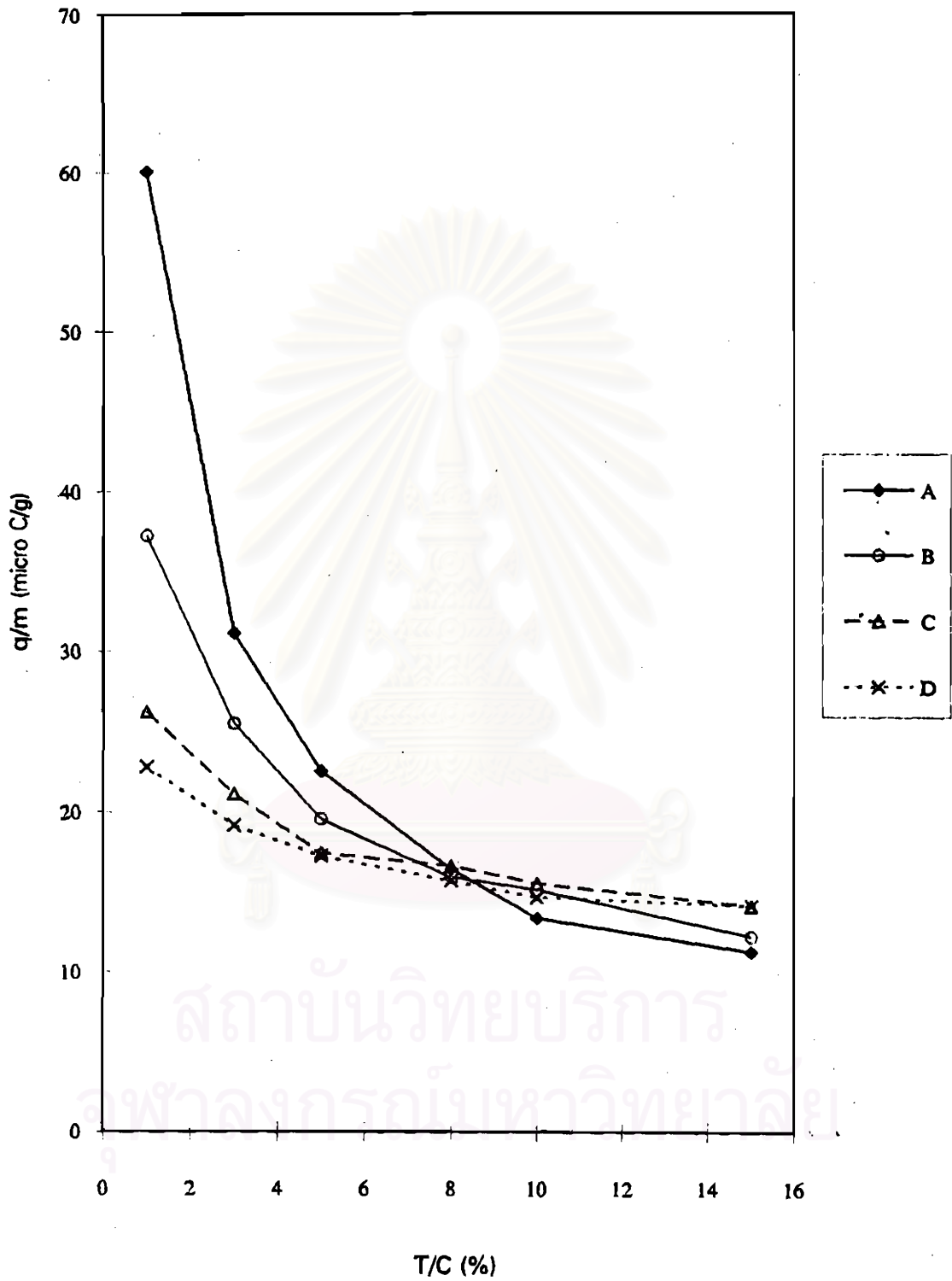


Figure 4-15 Red toner q/m versus T/C of carriers A - D

The larger carrier gives lower q/m to the toner than does the smaller carrier at higher T/C than 8% because the toner coverage on a larger carrier surface is higher than that on a smaller carrier surface. It means that the carrier with a smaller particle diameter tends to be slightly affected by changing the toner concentration, which is in agreement with those reported by Yamamoto and Takashima.²⁰ Because the larger carrier has smaller surface area per mass to be mixed with high toner concentration than does the smaller carrier. Therefore, the larger carrier has more free toner particles surrounding and lower q/m than does the smaller carrier, at the high T/C. Basically, the latitude of T/C corresponds to the level of q/m values. The latitude of T/C then becomes higher when a carrier size becomes smaller.

4.2.4 The dependence of the red toner charge on the carrier surface coating

The red toner q/m values of the carriers B, E, F, G and K in Figure 4-16 show the effect of the different carrier surface coatings. The carrier B has a much higher tribocharging ability than do the carriers E, F and G, but has a much lower tribocharging ability than does the carrier K. It means that the carrier K gives too high q/m , and the carriers E, F and G give too low q/m to the red toner. These results are correlated to the charging ability or the work function difference between the carrier coating polymer and the toner resin, which have different positions in the triboelectric series. We predict that the carriers E and F coating polymers lie closely to each other to the slightly lower position of the red toner resin; the carrier B coating polymer is at the middle position, and the carrier K coating polymer is at the highest position (work function difference) in the triboelectric series.

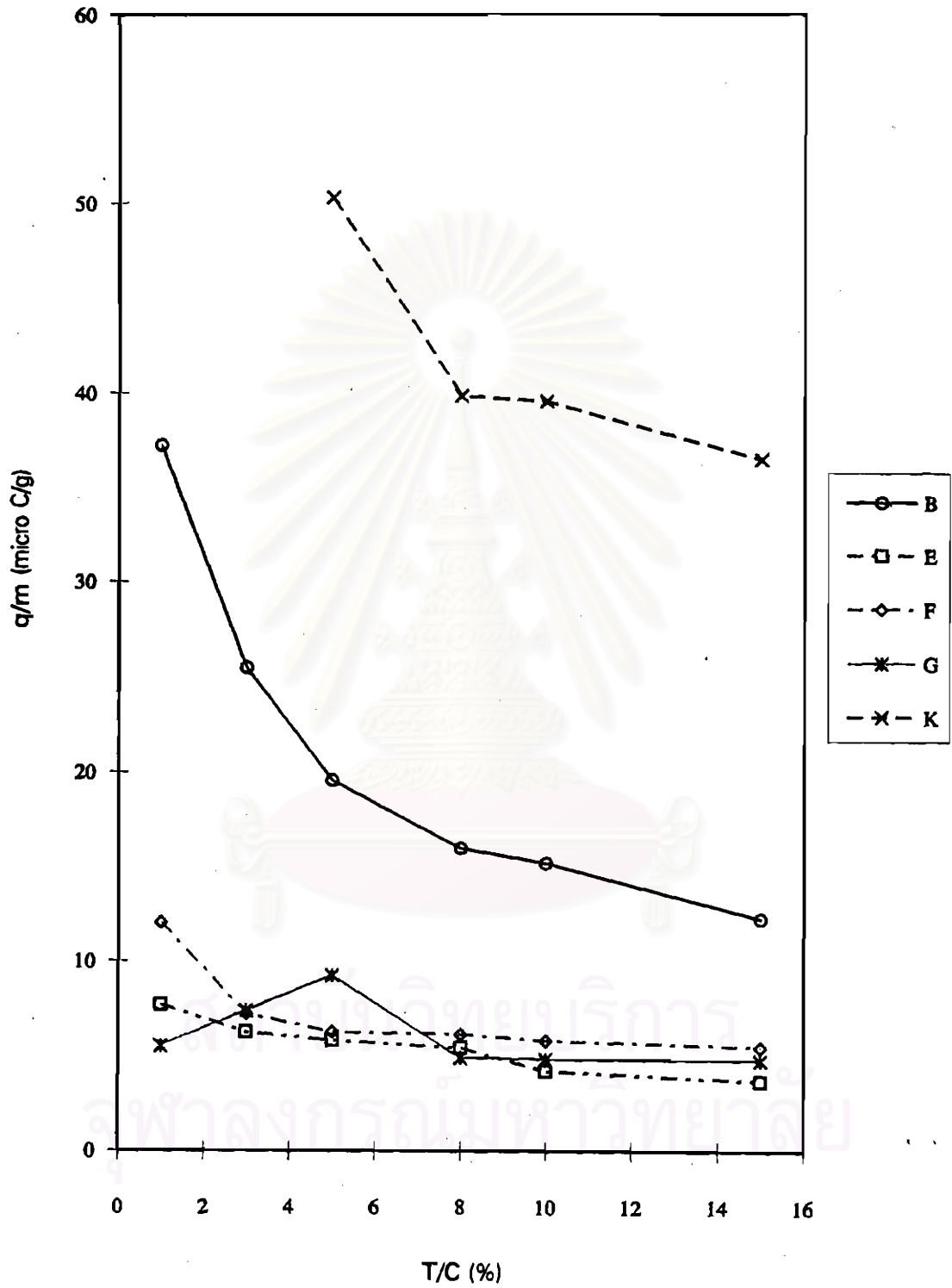


Figure 4-16 Red toner q/m vs. T/C of carriers B, E, F, G and K

Therefore, the tendency of the carrier B coating polymer to accept the electrons from the red toner resin is higher than those of the carriers E and F coating polymers, but lower than that of the carrier K coating polymer. And then, the carrier B induces the red toner to accept a higher positive charge than do the carriers E and F, but a lower positive charge than does the carrier K. By these results, the print quality producing by the high-, the medium-, and the low-charge toners can be analysed in section 4.3.2.

The carrier G without a coating resin also giving an unstable low charge value, indicates that the contact charging between the red toner and the ferrite surface is poor. Similarly, Anderson explained that the toner positively charged against the carrier had a higher D/A than the carrier. The greater the difference in D/A of the toner and the carrier, the greater q/m would be.⁸

4.2.5 The dependence of the red toner charge on the core carrier particle

The different toner q/m values between the carriers B and H as shown in Figure 4-17 show the effect of the different core carrier. The spherical ferrite carrier (B) has a higher negatively tribocharging ability than does the irregular iron carrier (H) by about 1.5 - 2 times. The lower charge value of the carrier H was probably related to the irregular shape, the amount of coating resin or the resistivity of the core carrier materials.

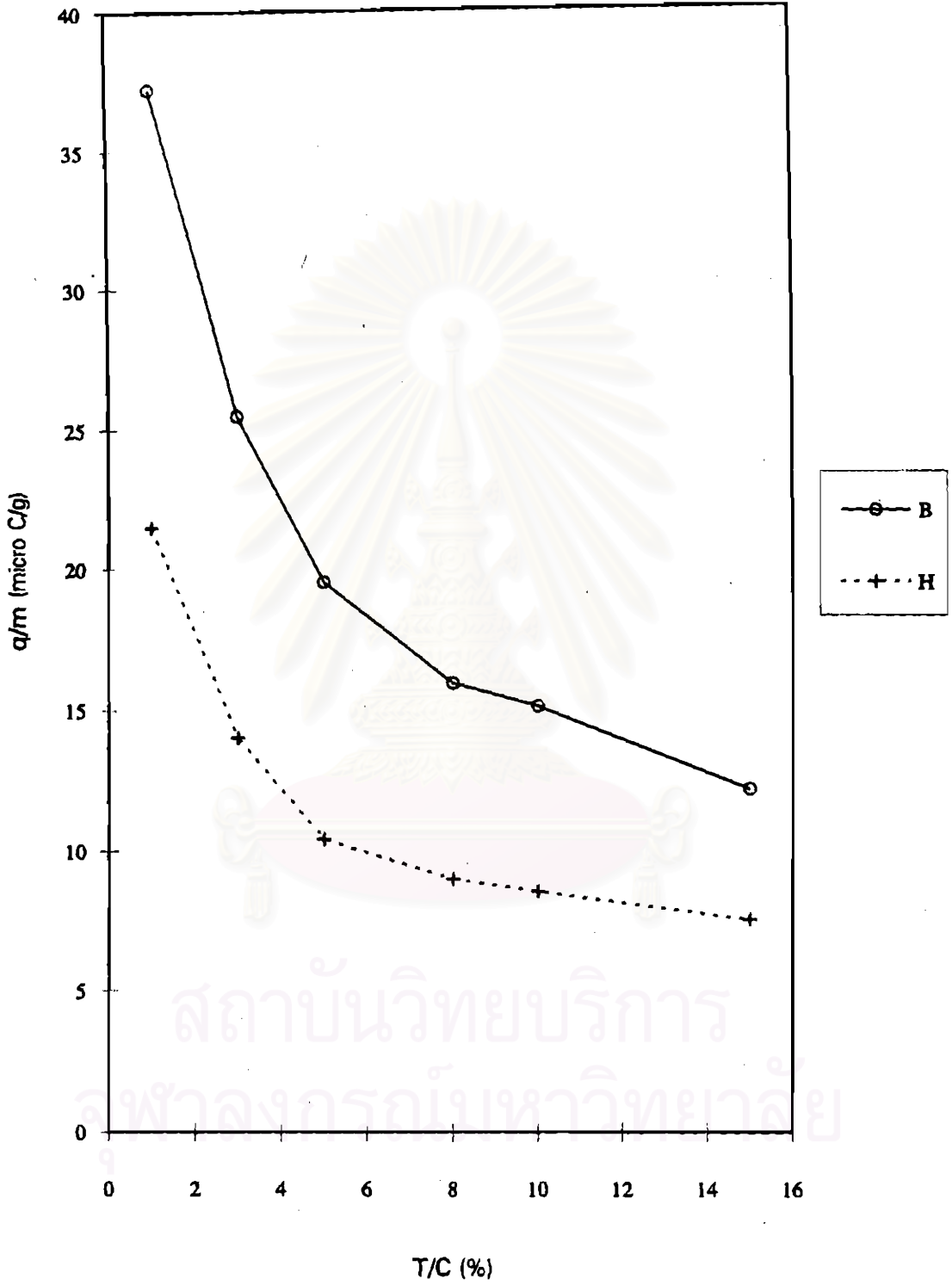


Figure 4-17 Red toner q/m versus T/C of carriers B and H

Referring to the carrier shape, the spherical shape has less surface area than that of the irregular shape, resulting in a better contact charging. Yamamoto and Takashima discussed that when irregularly shaped carrier particles were employed, the real limit of the toner concentration would be higher than that of spherical shaped carrier particles,²⁰ as shown in Appendix C. Therefore, the carrier H surface is more covered by the toner particles than is the carrier B, resulting in very lower q/m .

Another reason similar to the result by Gutman and Hartmann, the average surface density of states was changed by varying the amount of polymer coating on the carrier.¹¹ The carrier B has a more ratio of coating resin on the surface than does the carrier H due to its spherical shape. When these carriers have the same amount of coating resins, much resin is spent for filling pores of the carrier H leading to a less amount of coating resin on its surface.

Regarding the resistivity, the ferrite has more resistivity⁴ and has a higher tendency to accept electrons than does the iron to enable the red toner to accept higher positive charge. It also shows that the different core carriers coated with the same coating resin give the similar characteristics of charge properties, because the q/m values of the developers B and H tend to decrease in the same rate with increasing toner concentrations. These results can be explained that the same resin coated carrier, which control the electrostatic charging, is affected by the same parameters.

4.2.6 The dependence of the cyan toner charge on the shaking time

The dependence of the cyan toner charge on the shaking time of the carriers A to D shown in Figures 4-18 to 4-21, shows that the cyan toner has a negative charge and the q/m reaches a saturated value in 60 seconds. At the concentrations lower than 5%, the toner q/m value increase with increasing the shaking time, but the concentrations higher than 5%, the toner q/m values were nearly constant from 60 seconds to 120 seconds.

The cyan toner q/m versus the shaking time of the carriers E, F, G and H in Figures 4-22 to 4-25 show the same result as that the charge is saturated in 60 seconds and nearly stable after 60 seconds.

In summary, the optimum charging time of all carriers is 60 seconds. The cyan toner q/m value is less affected by the long shaking time than is the red toner. It shows that the small particle size of cyan toner, can adhere fully on the carrier surface within 60 seconds, and the toner coverage on carriers is slightly increased after 60 seconds. This consequence gives the same result in q/m values, i.e. the values are slightly decreased after 60 seconds. For another possible reason for the above result, the cyan toner is used for the high quality full-color copier from the the toner charge must be constant during agitation.

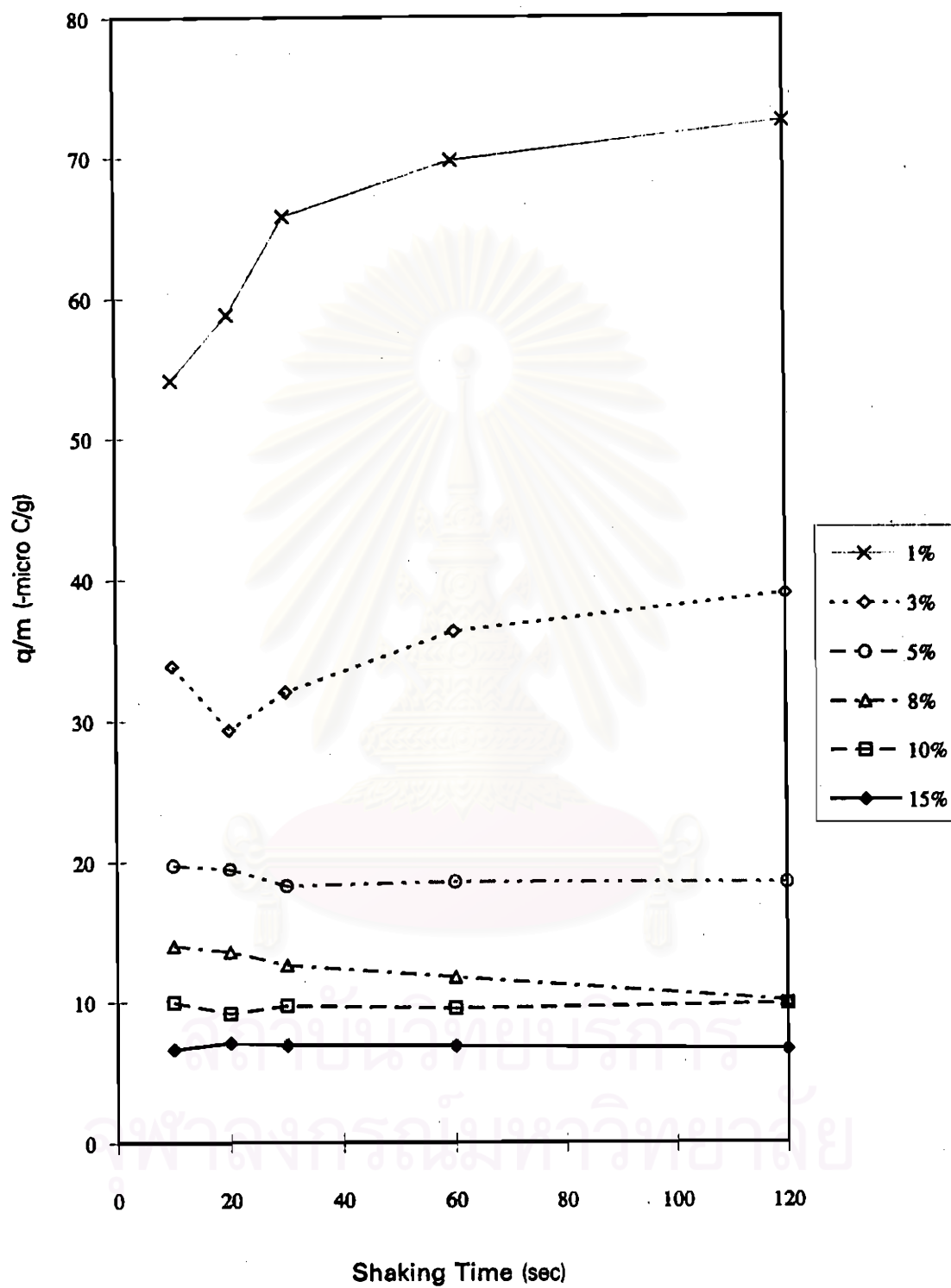


Figure 4-18 Cyan toner q/m versus shaking time of carrier A

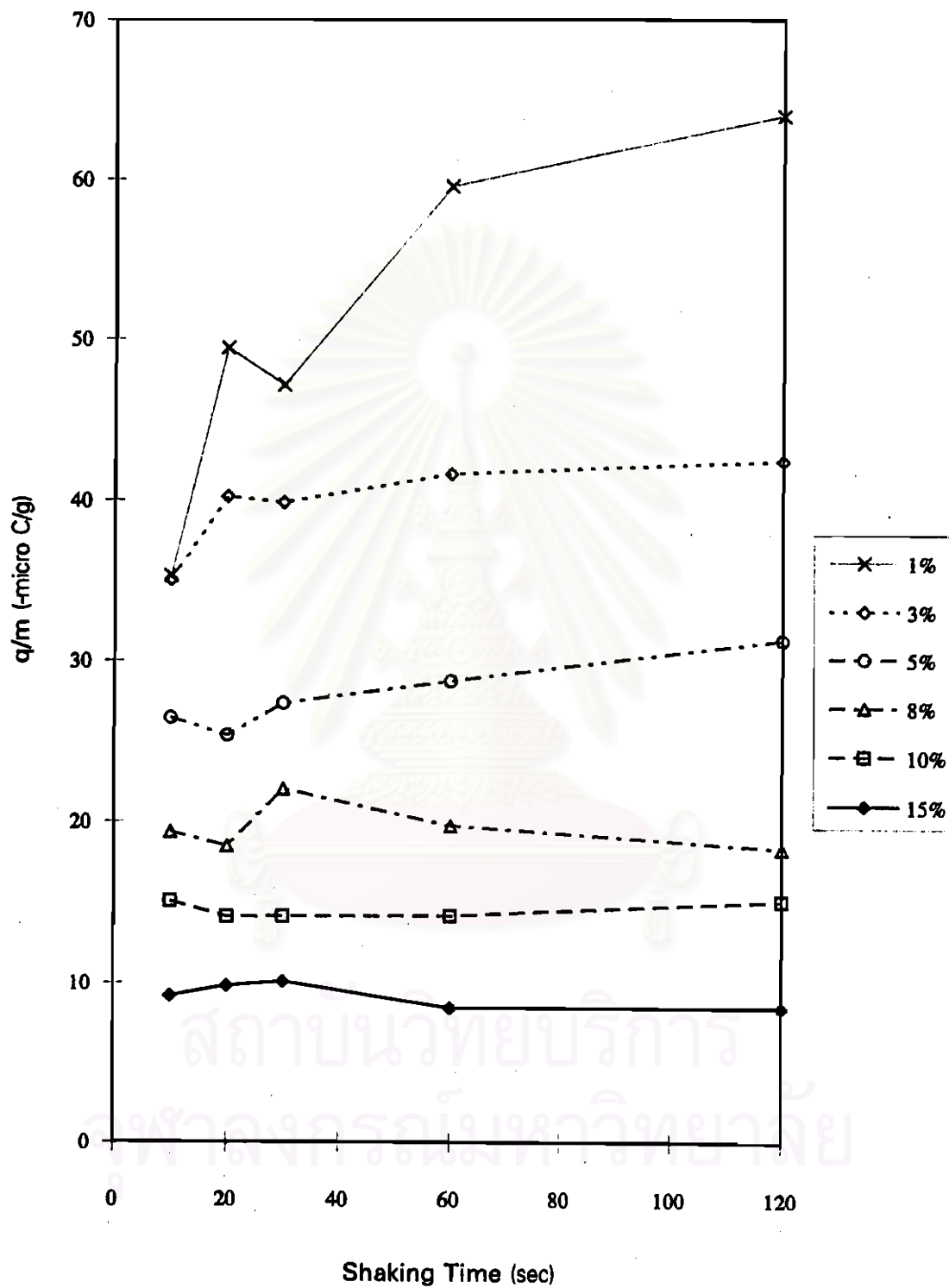


Figure 4-19 Cyan toner q/m versus shaking time of carrier B

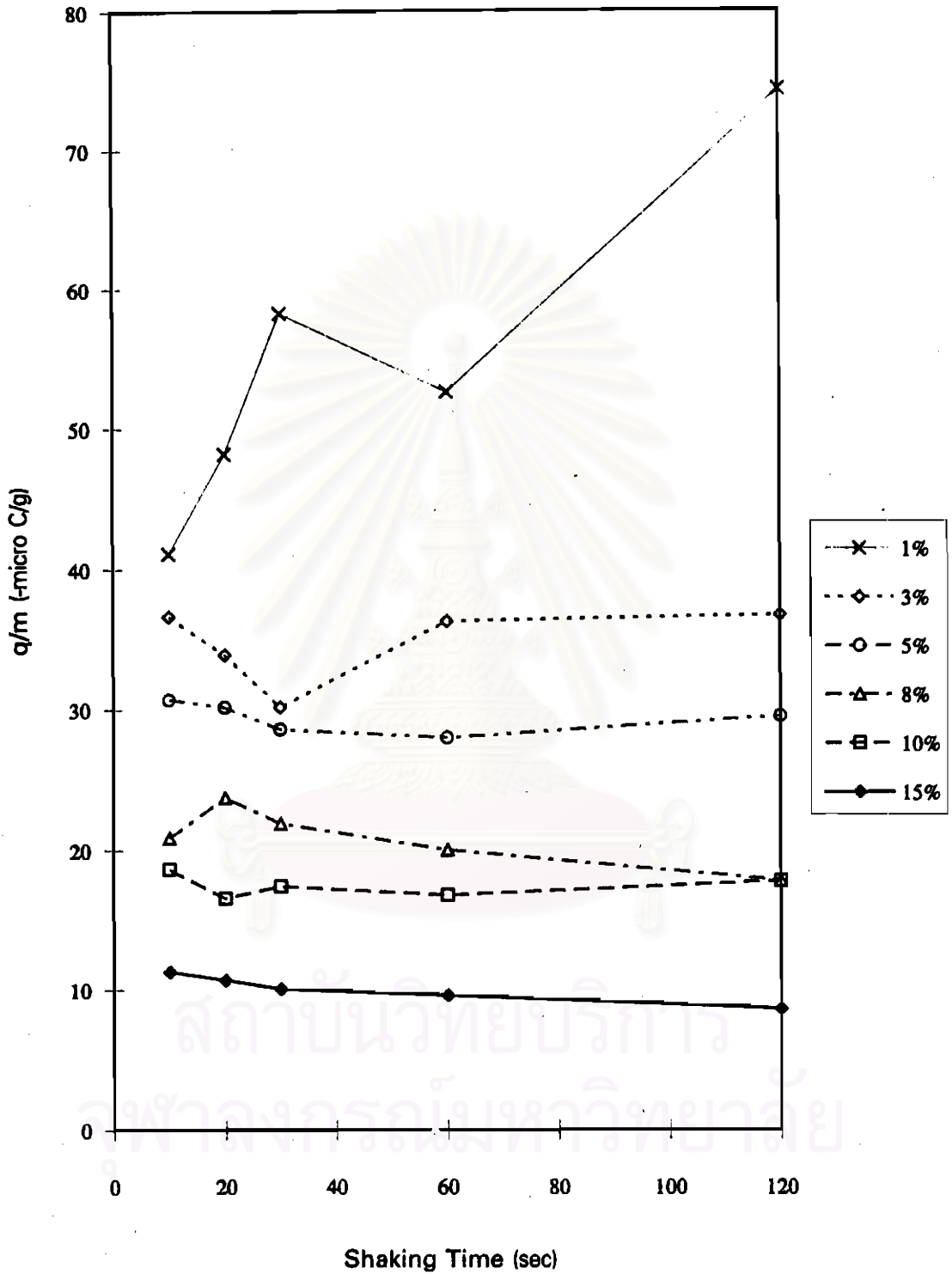


Figure 4-20 Cyan toner q/m versus shaking time of carrier C

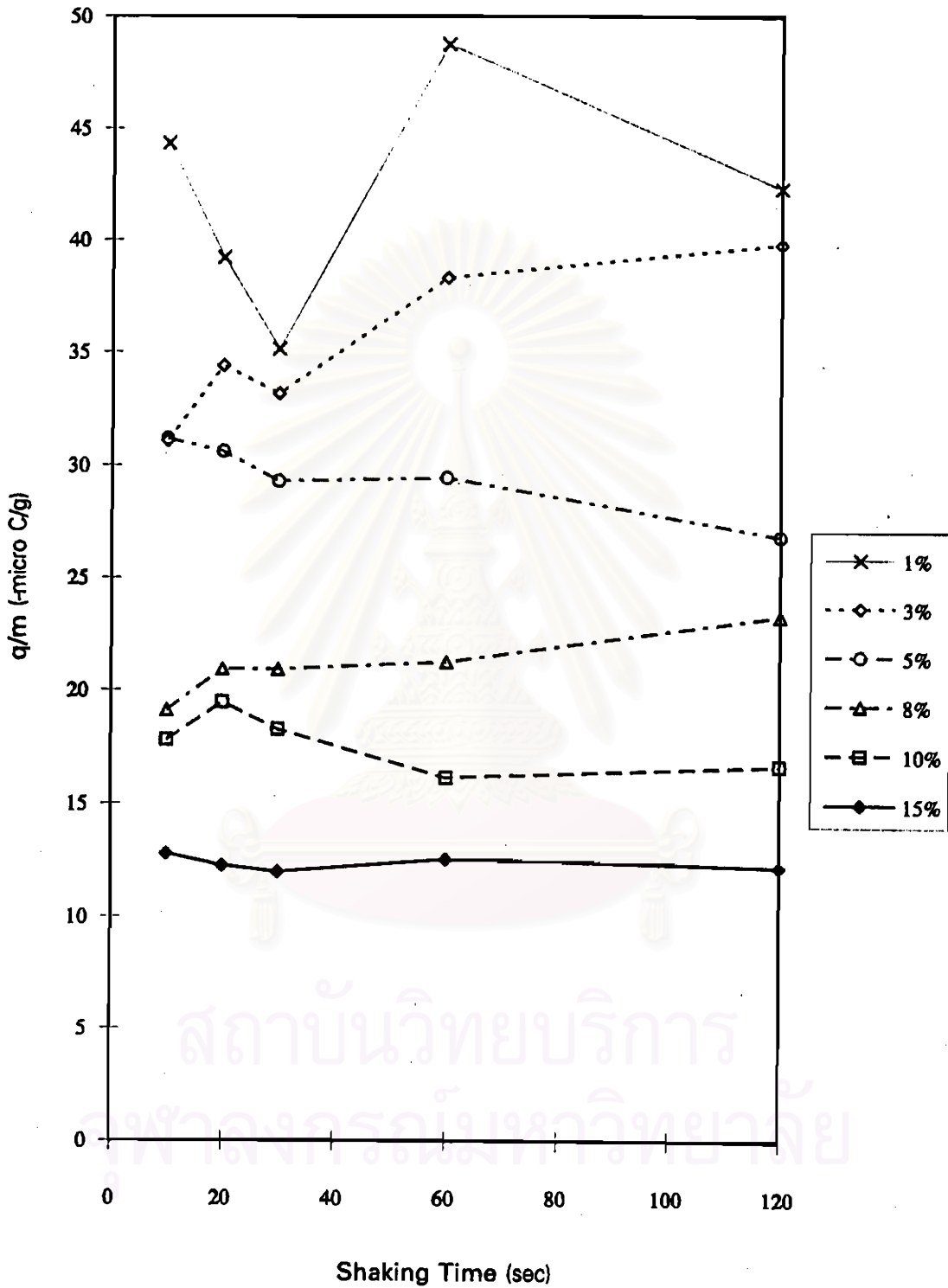


Figure 4-21 Cyan toner q/m versus shaking time of carrier D

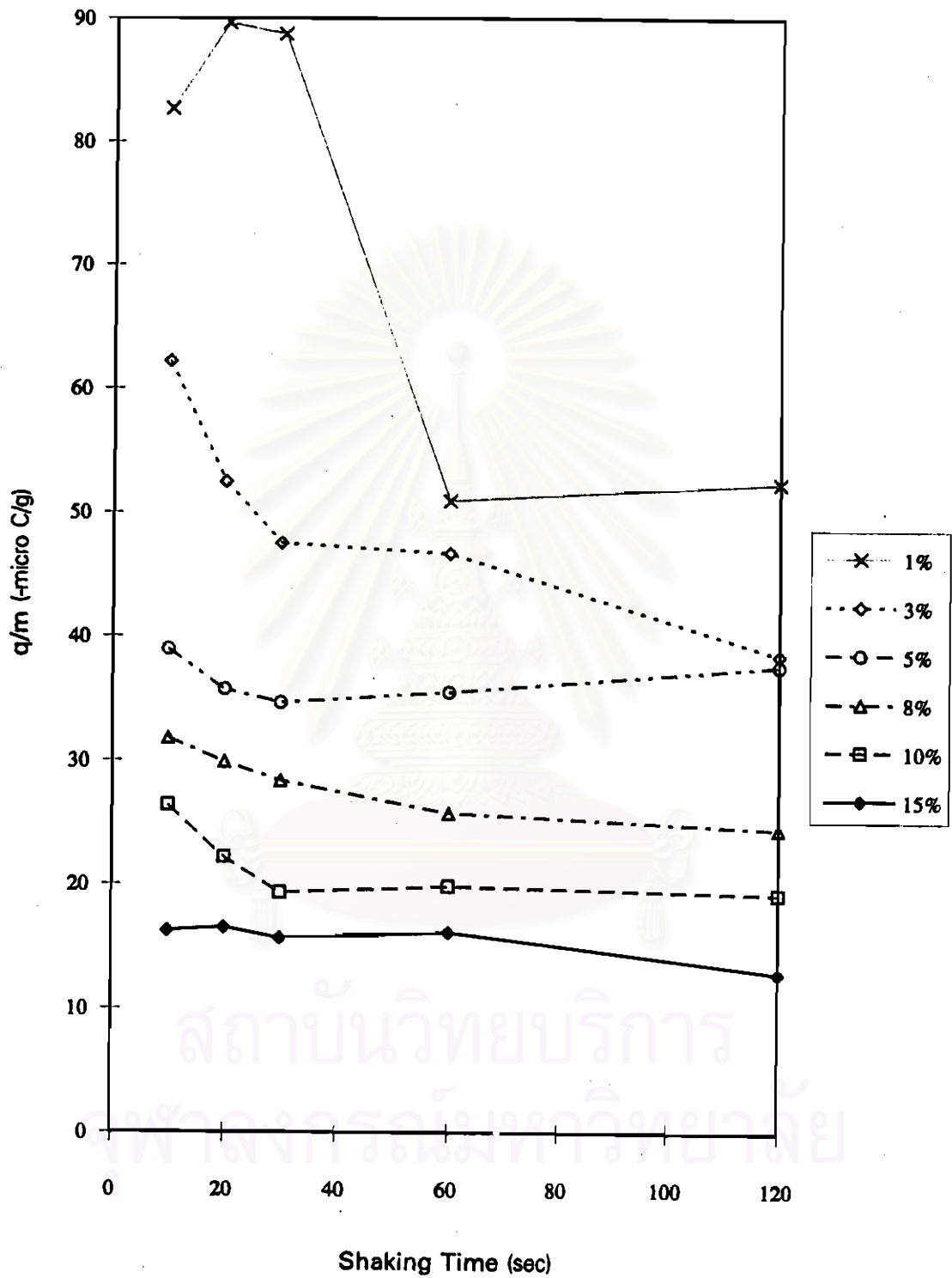


Figure 4-22 Cyan toner q/m versus shaking time of carrier E

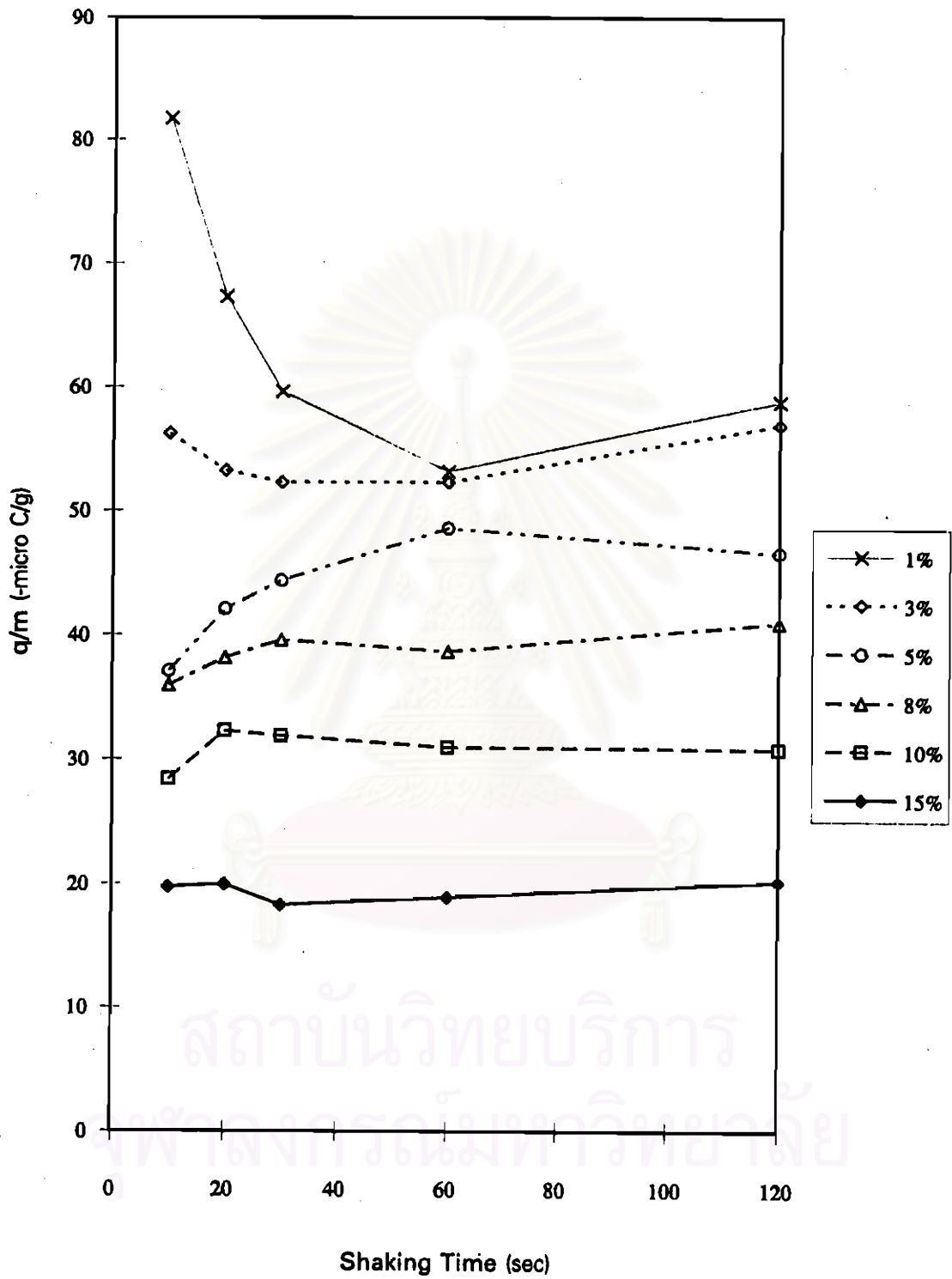


Figure 4-23 Cyan toner q/m versus shaking time of carrier F

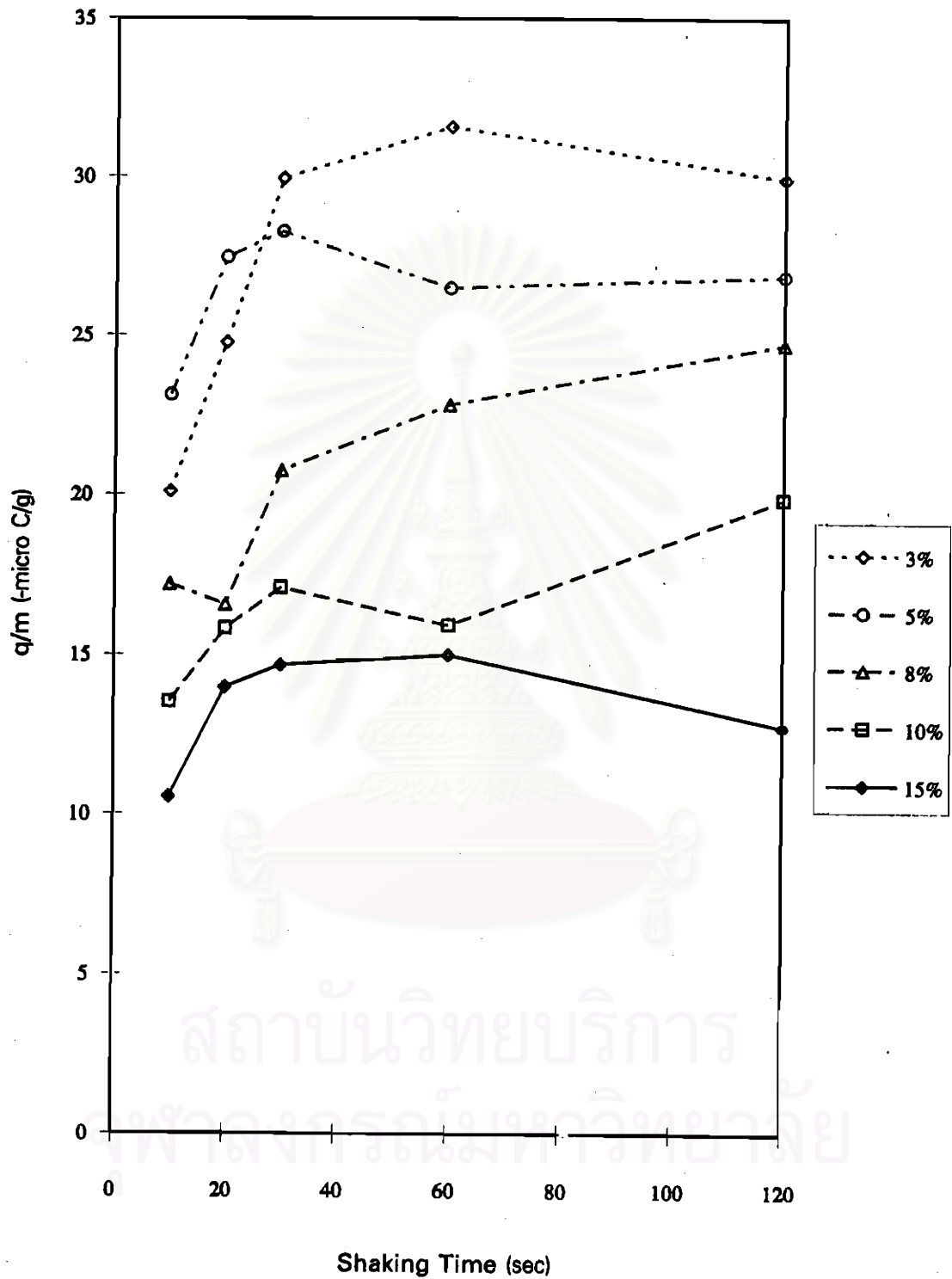


Figure 4-24 Cyan toner q/m versus shaking time of carrier G

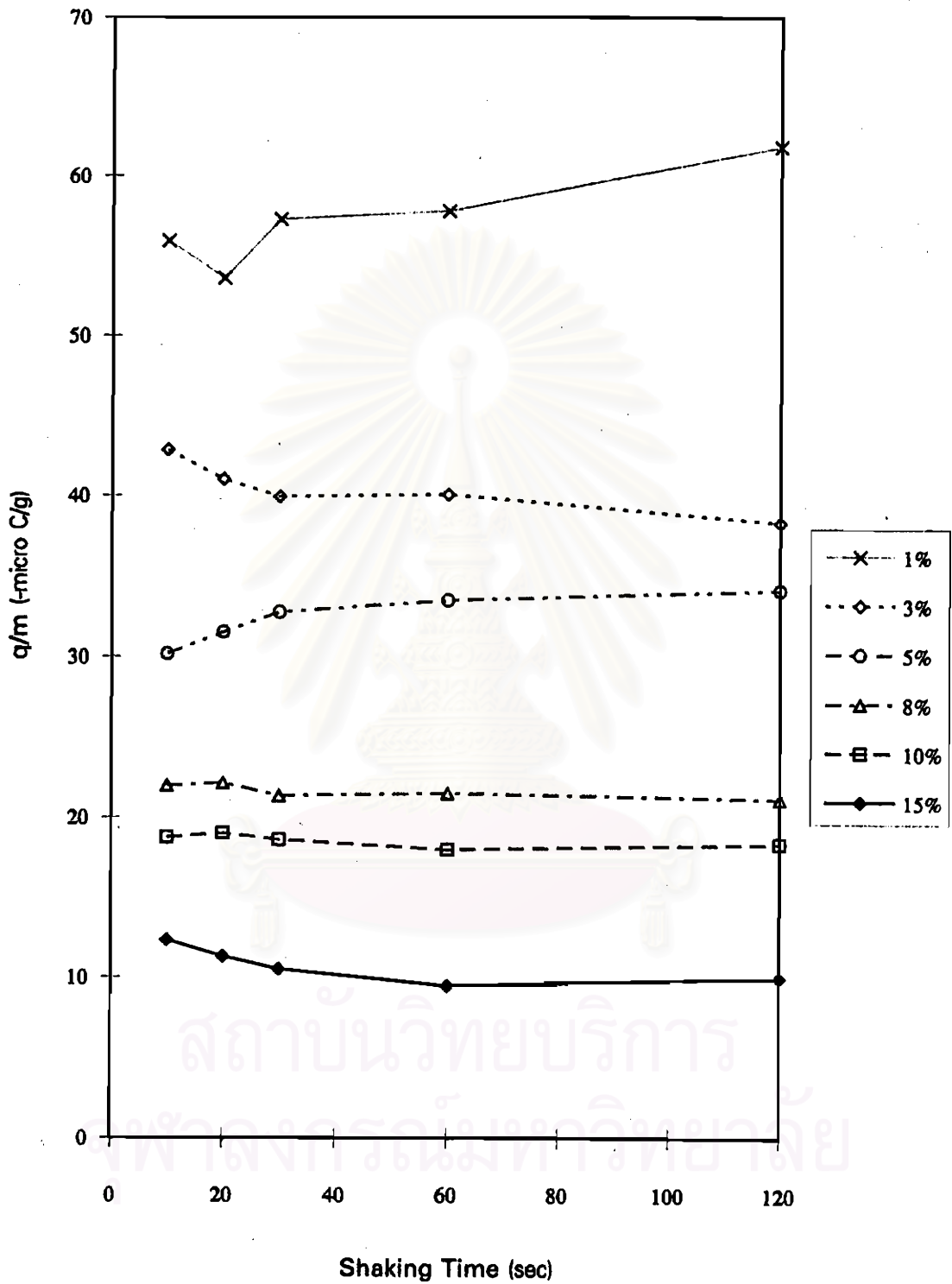


Figure 4-25 Cyan toner q/m versus shaking time of carrier H

4.2.7 The dependence of the cyan toner charge on the toner concentration

The plots of cyan toner q/m values versus T/C of the carriers A to D for 60 seconds of shaking time in Figure 4-26, show that the cyan toner q/m values decrease with increasing T/C. The q/m values of cyan toner mixed with the carriers B and D with various T/C were also evaluated by an E-SPART analyzer, as shown in Appendix A, which the q/m values are relatively closed to the blow-off method. All the q/m curves of the cyan toner of B, E, F, G (Figure 4-27), and B and H (Figure 4-28) depend on T/C as do the carriers A to D and the red toners. The q/m values decrease with increasing T/C by following the trends of the higher the T/C, the greater the toner coverage on carrier and the more free toners. Likewise, the dependence of q/m values of the cyan and red toner on T/C is accorded to the results by Anderson,⁹ Kishimoto and Takahashi,¹⁶ and Gutman and Hartmann.¹⁷

4.2.8 The dependence of the cyan toner charge on the carrier size

Figure 4-26 also shows that the cyan toner q/m values of the larger carriers are much lower than the smaller carriers at the higher T/Cs. The charge of carrier A is lower than that of carrier B when the toner concentration is higher than 3%. Likewise, for the carrier B and C pair, the carrier C and D pair, the T/C when the charges $B < C$, and $C < D$ are observed at 8% and 11%, respectively. The cyan toner q/m of the larger carrier rapidly decreased, but that of the smaller carrier gradually decreased with increasing T/C. The toner charge of the smaller carrier depends less on the toner concentration than does the larger carrier.

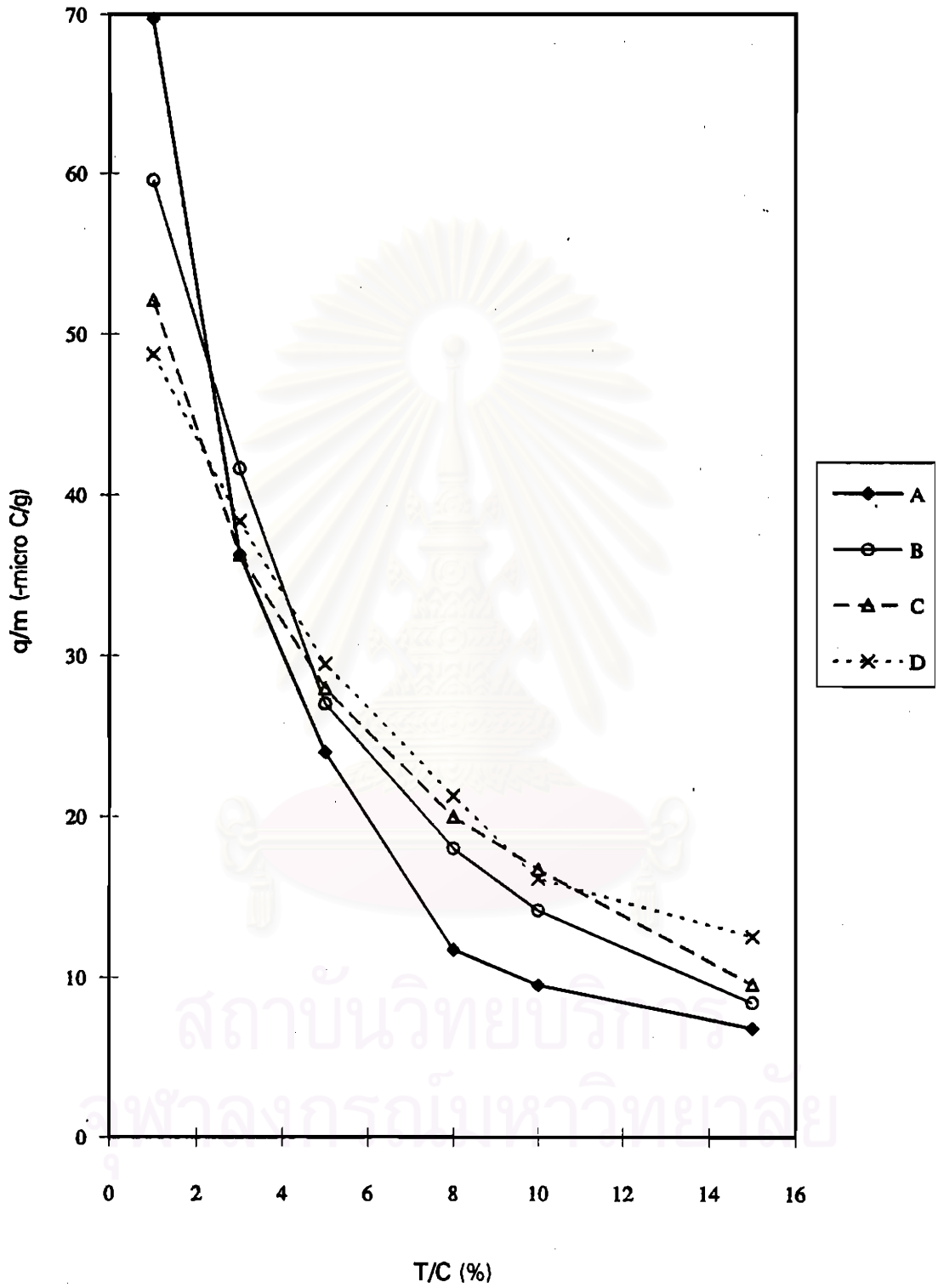


Figure 4-26 Cyan toner q/m versus T/C of carriers A - D

The same reason as for the red toner, the larger carrier has a smaller surface area per mass than does the smaller carrier at the same T/C. The former is fully covered by the cyan toner particles at lower T/C than is the latter. This result agreed well with Anderson's, which found that increasing carrier particle size led to higher slopes of a plot of M/Q versus T/C, and increasing the number of charging sites on the surface of the carrier per gram of carrier led to decrease in the slope.⁹ The smaller toner (cyan toner) give higher covering percentage than that of the larger toner (red toner) in the same T/C, so the carrier is more covered by the cyan toner at lower T/C than is the red toner, and consequently has more free toner particles at the same high T/C. Therefore, the decreasing rate of the cyan toner q/m with each carrier is higher than is the red toner q/m . For the smaller-sized toner, the q/m depends significantly on T/C and carrier size rather than the larger-sized toner.

4.2.9 The dependence of the cyan toner charge on the carrier surface coating

The cyan toner q/m with the carriers B, E, F and G in Figure 4-27 shows the influence of the different carrier surface coatings. The cyan toner charge with the carrier F is higher than those of the carriers E, B and G. These results are also correlated to the work function difference between the carrier coating polymer and the cyan toner resin. The carrier F coating polymer has a higher tendency to donate electrons to the cyan toner resin than does the carrier E and the carrier B coating polymer, and induces the cyan toner to accept higher negative charges from the carrier F than the carrier E and the carrier B. The carrier G, uncoated ferrite, also gives an unstable low charge value because the ferrite without coating polymer has a low tendency to donate electrons to the cyan toner resin.

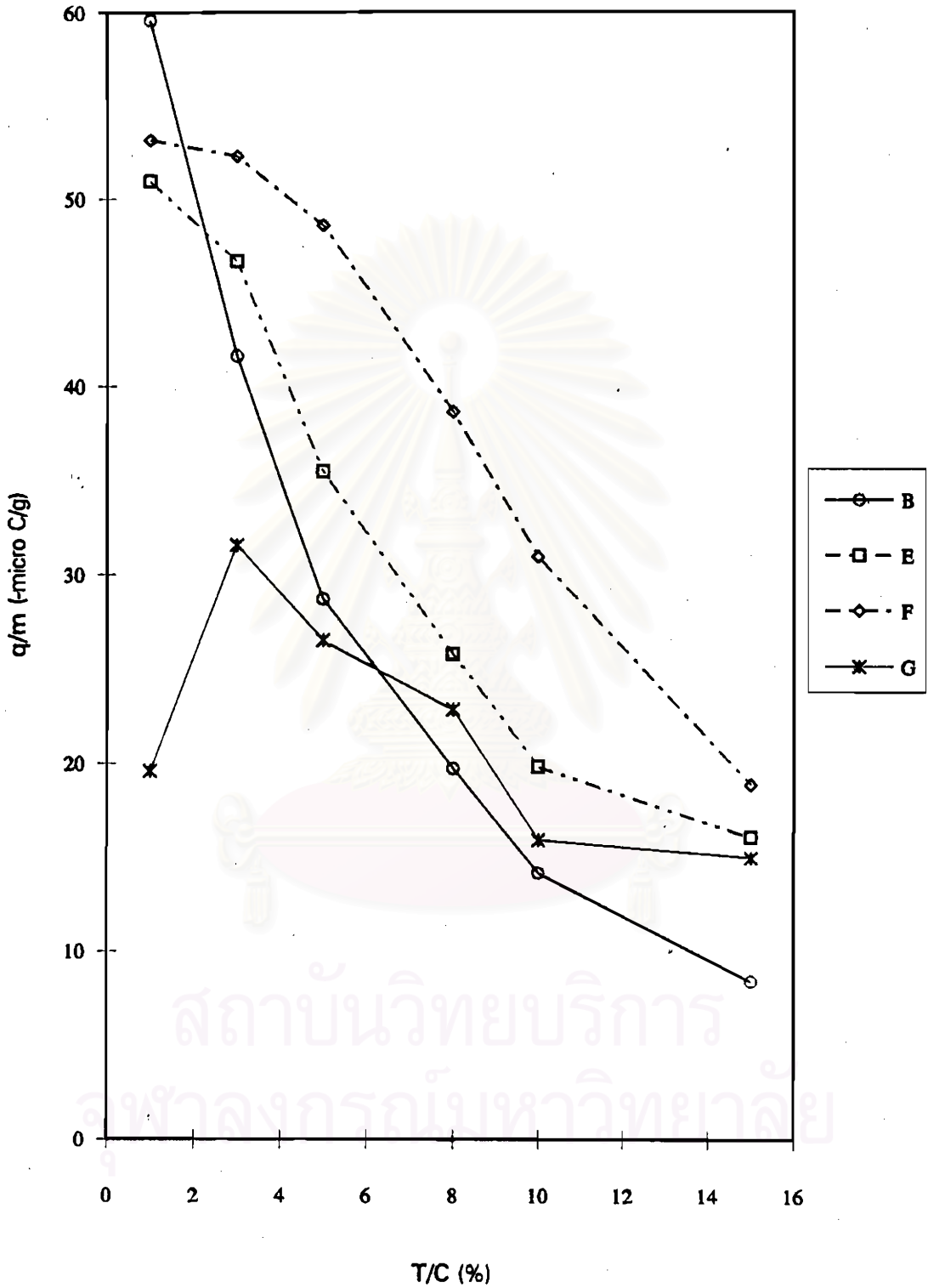


Figure 4-27 Cyan toner q/m versus T/C of carriers B, E, F and G

Referring to Anderson's paper,⁹ the cyan toner charged negatively with these carriers because it has a lower D/A than those of the carriers. Furthermore, the greater the difference in D/A of the cyan toner and the carrier F, the greater q/m would be.

4.2.10 The dependence of the cyan toner charge on the core carrier particle

The different cyan toner q/m s values between the carriers B and H affect different core carriers as shown in Figure 4-28. Unlike the red toner, the cyan toner negative charge of the carrier B is lower than that of the carrier H. We predict that the low charge value of the carrier B is probably correlated to the resistivity of the core carrier materials. Because the iron has lower resistivity than does the ferrite, therefore the iron has a higher tendency to donate electrons to cyan toner resin than does the ferrite. In contrast, the iron has a lower tendency to accept electrons from the red toner resin than does the ferrite. Therefore, the carrier H gave a higher negative charge to the cyan toner than did the carrier B, and gave a lower positive charge to the red toner than did the carrier B.

The curve in Figure 4-28 show that the carrier H gave slightly higher q/m to the cyan toner than did the carrier B because the irregularly shaped particle of carrier H had less amount of coating on the surface, and had higher toner coverage on a carrier,¹⁹ so the toner q/m was not high enough. However, the same coating materials of the carriers depend on the same parameters, because the cyan toner q/m of the developers B and H tend to decrease in the same rate with increasing toner concentrations.

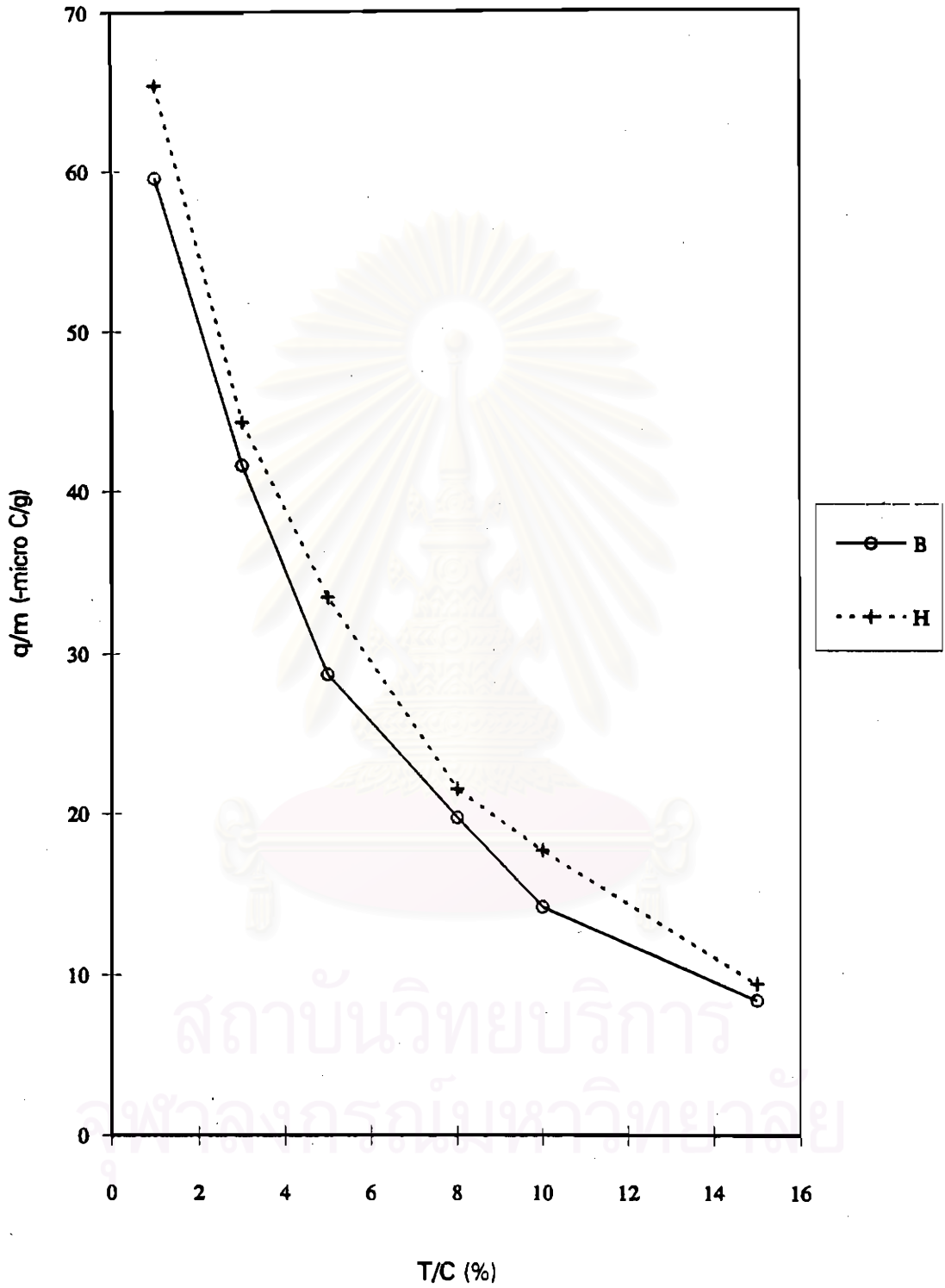


Figure 4-28 Cyan toner q/m versus T/C of carriers B and H

4.3 Analysis of Quality of the Copy Print

4.3.1 Dependence of the maximum copy density and the background density on the red toner concentration and the carrier size

The optimum red density of the solid area is determined from the copies, which is found somewhat higher than 1.35. The plot of the maximum density versus the toner concentration in Figure 4-29 shows that the minimum toner concentration of the red developer A producing the high red density is about 6%, whereas the minimum T/C of other carriers (B to D) is 5%. However, the developer A with 5% T/C has enough amount of toners to produce a copy density, but the toner q/m of carrier A is too high to give high density.

According to the calibration of the null density on a reference white paper, the background density should be normally lower than 0.03. The curves of the background density versus the toner concentration in Figure 4-30 show that the toner concentrations of the red developers A, B, C and D, which produce a fog density on the background, are higher than 9%, 12%, 14% and 15%, respectively. Therefore, these are the maximum toner concentration of the developers being capable of producing the good print quality.

To conclude, the T/C latitude of the red developers A, B, C and D, which produced high print density without background fog, are 6-9%, 5-12%, 5-14% and 5-15%, respectively.

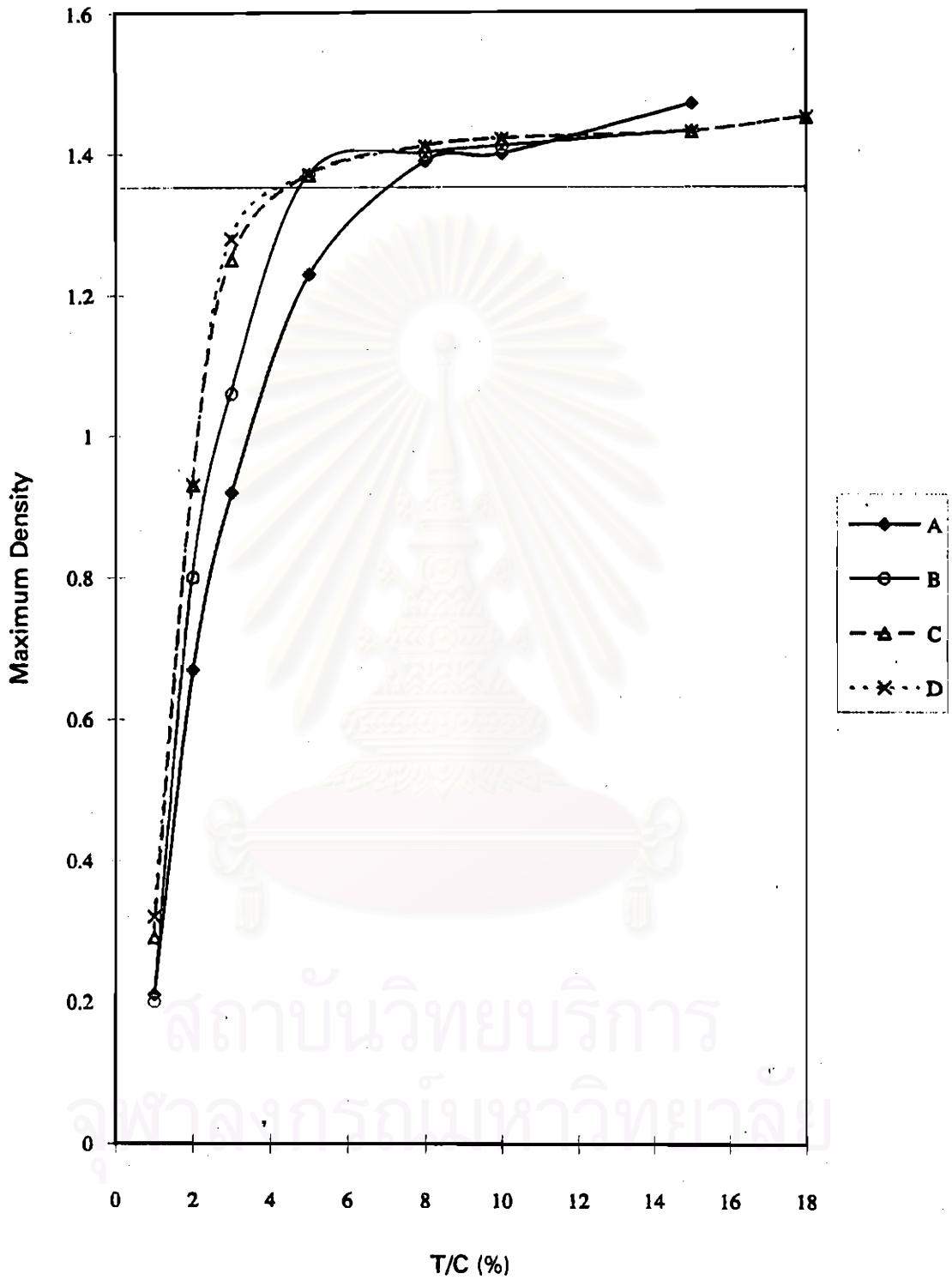


Figure 4-29 Maximum density versus T/C of red developers A - D

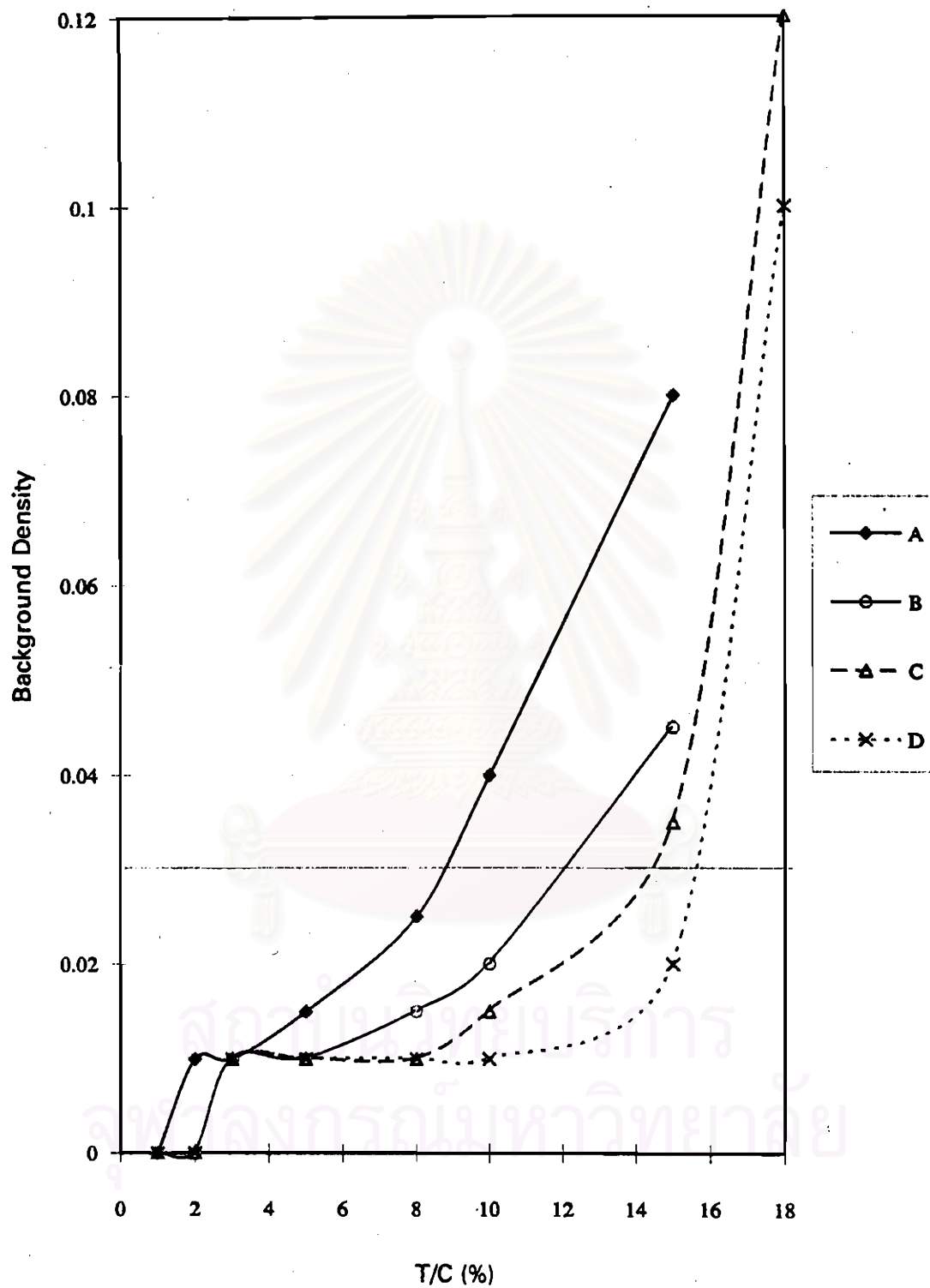


Figure 4-30 Background Density vs. T/C of red developers A - D

These print results are correlated with the toner charge (q/m) in Figure 4-15, that the density increases with increasing T/C by the way of decreasing toner q/m . Similarly, Ming-Chu showed that the lower q/m was, the larger M/A on the photoreceptor was.¹⁴ If the toner charge is too high at low concentrations, the toner cannot be stripped from the carrier, resulting in a low print density. If the toner charge is too low at high concentrations, the toner particles are not held by the carrier, and low charged toners would float around the machine, causing dirt, or sediment in nonimage areas, causing unpleasant background on the copy.⁴ Therefore, the T/C latitude correspond to the q/m latitude, which is not too high or too low.

Accordingly, the optimum ranges of toner concentrations for the red developers containing carriers A, B, C and D show that the smaller carriers with more surface area per mass, are able to accommodate more toners with a wider latitude of toner concentrations than are the larger carriers to result in an optimum range of charge and a good print quality. Likewise, Yamamoto discussed that the small carrier allowed a wider range of toner concentration than did the large carrier.²⁰

4.3.2 Dependence of the maximum copy density and the background density of the red toner on the carrier surface coating

The curves of the print density versus the toner concentration of developers E, F, G and K shown in Figures 4-31, indicate that the red developers E, F and G can produce the high print density at 4% toner concentration because the toner charge is very low ($< 10 \mu\text{C/g}$), though the T/C is too low (2%). But the developer K produced too low print density (< 1), though the T/C is too high (15%) because the toner charge is very high ($> 35 \mu\text{C/g}$).

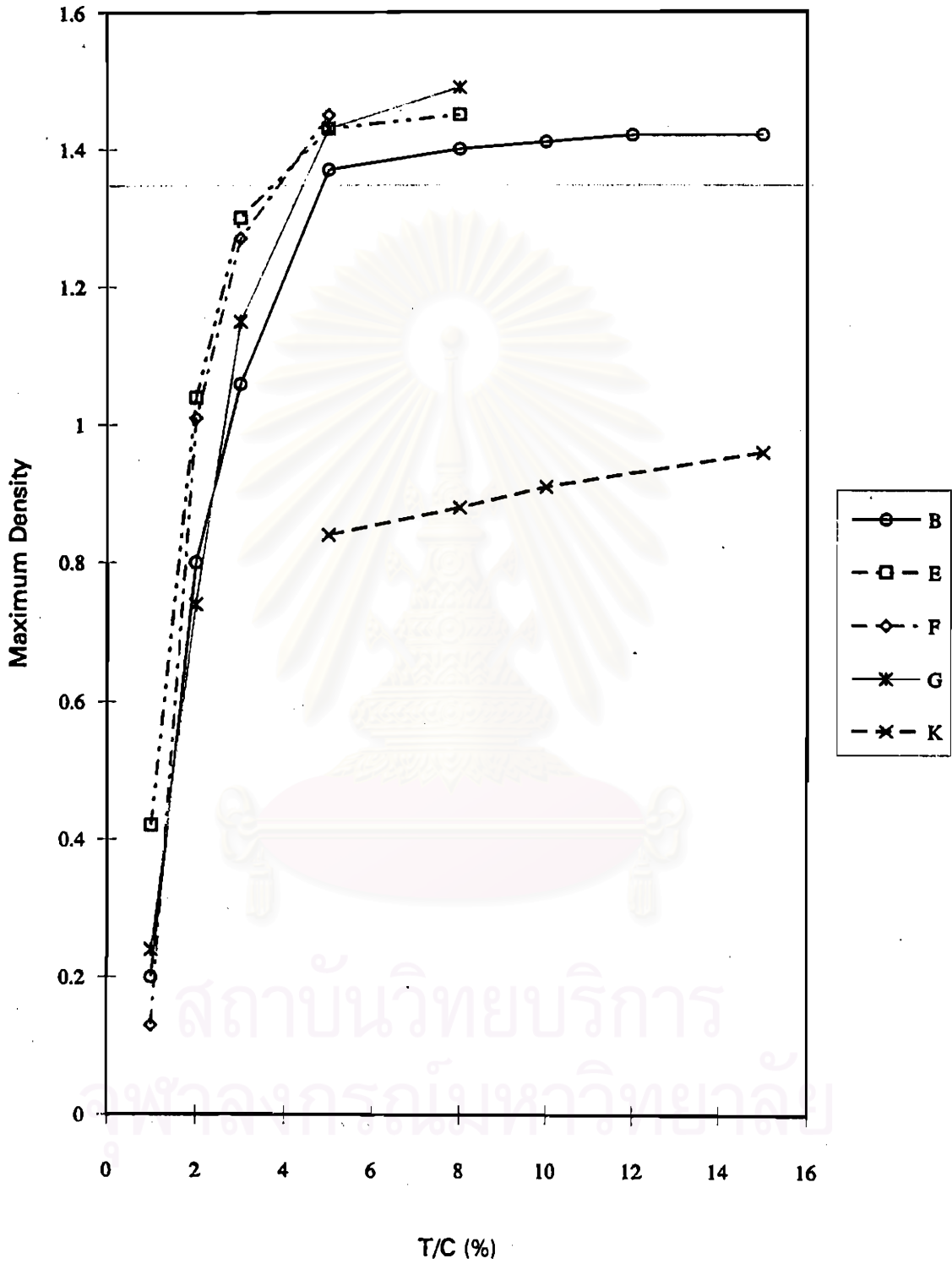


Figure 4-31 Maximum density versus T/C of red developers

B, E, F, G and K

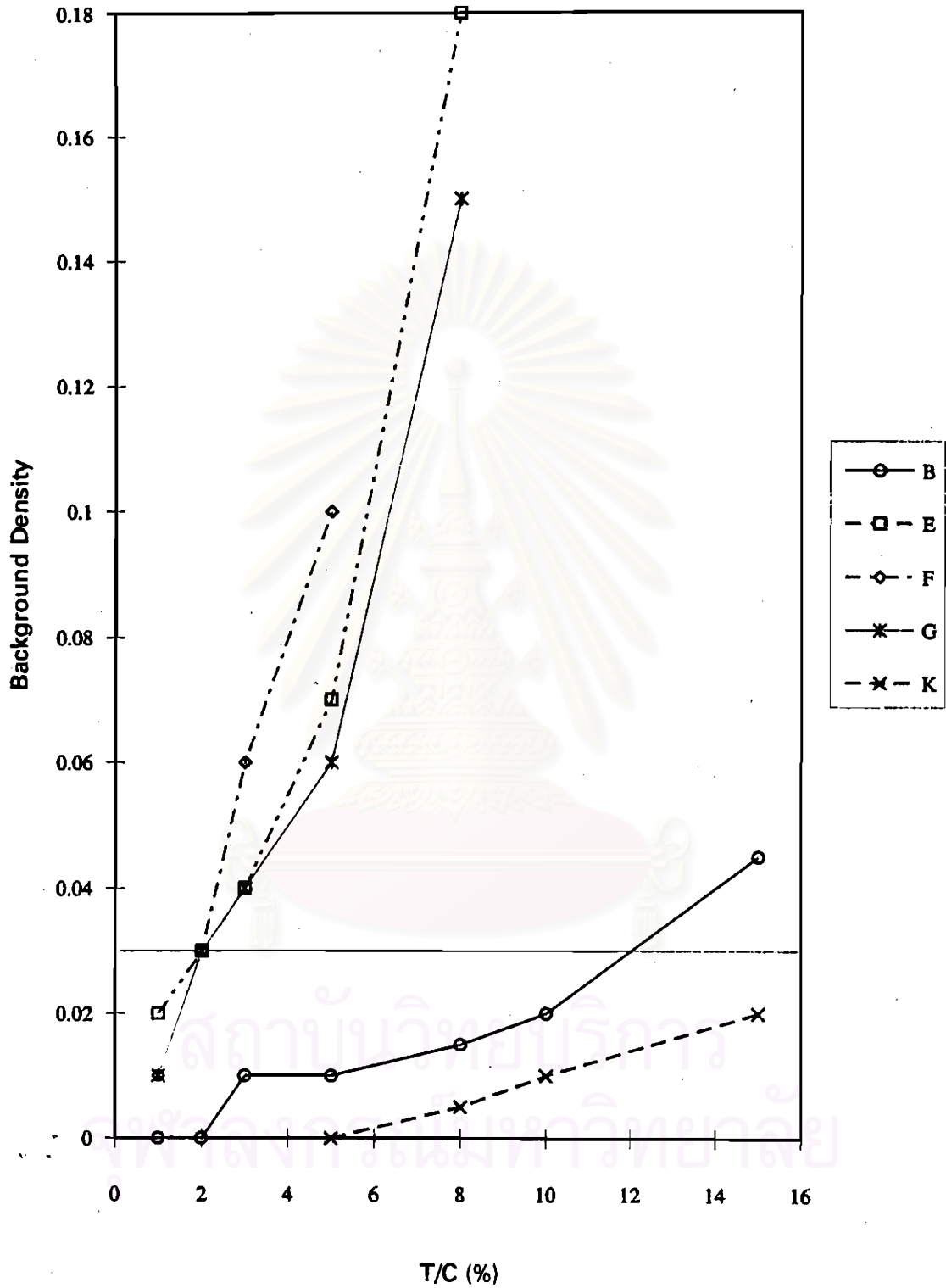


Figure 4-32 Background density versus T/C of red developers

B, E, F, G and K

The curves of the background density versus the toner concentration in Figure 4-32, indicated that the red developers E, F and G began to give a fog density on the print background at 2% toner concentration because the toner q/m was too low, so the high print density with high background density was produced. The developer K did not produce fog on the background, though the toner concentration was too high (15%), because the toner q/m was too high to produce the high print density and the background density. The results of this experiment show that the red developers using acrylate-, silicone-, and fluorine/silicone coated ferrite carriers, and even the uncoated ferrite carrier are not suitable for the present copier. Because the low charge of red toners by the carriers E, F and G produce a high fog background, and the high charge of red toner by the carrier K produces a low print density.

4.3.3 Dependence of the tone reproduction of the red toner on the toner concentration and the carrier size

The curves of the copy density versus the original density of 14 continuous gradation levels in Figures 4-33 to 4-36, show the tone reproduction of red copies. The print contrast increases with increasing T/C; and the smaller carrier produces a higher print contrast than does the larger carrier, due to the toner q/m values. Because the larger carrier gives a higher toner charge at some low T/Cs, and resulting in lower density and contrast. It means that the larger carrier can produce a better tone reproduction for the red toner than does the smaller carrier.

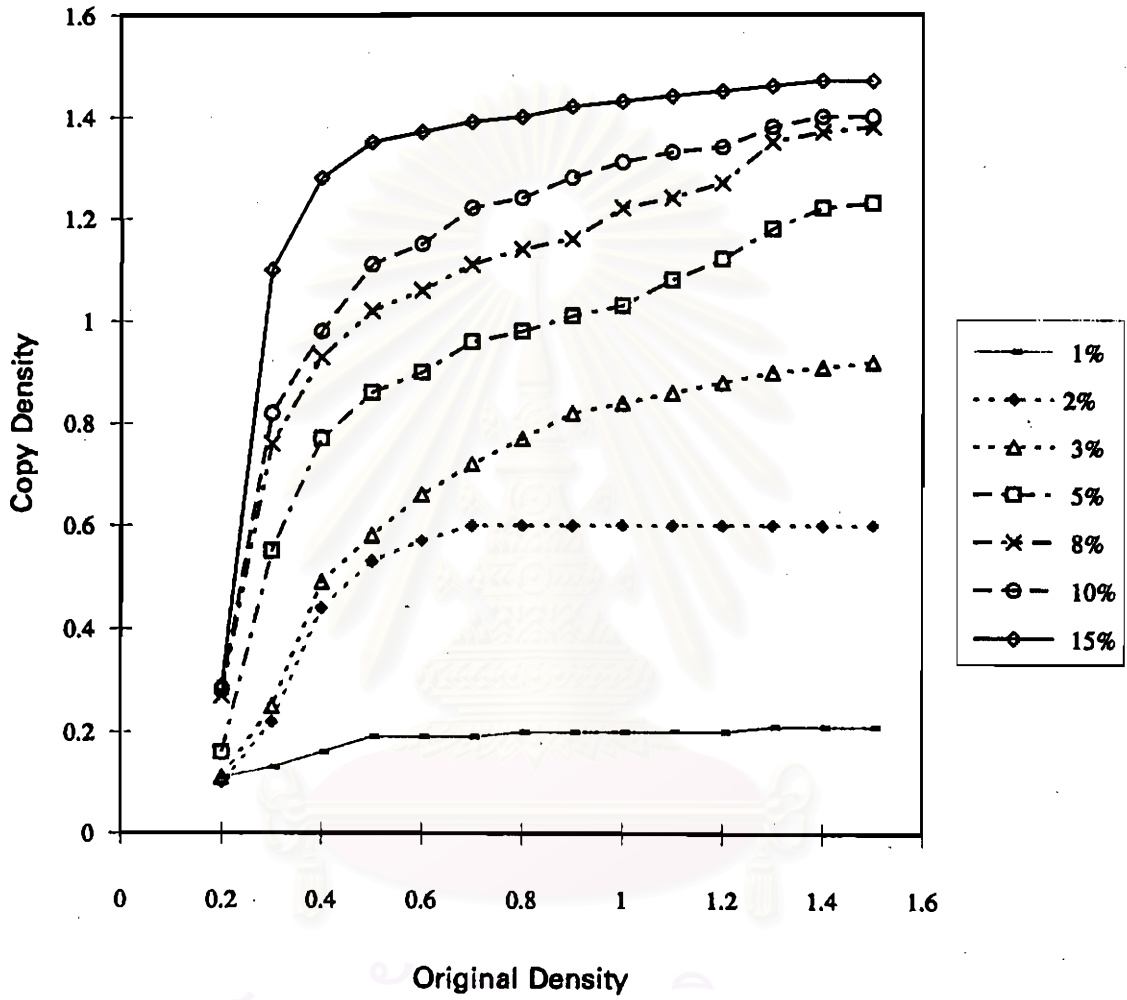


Figure 4-33 Copy density versus original density of red copy produced by the red developer A

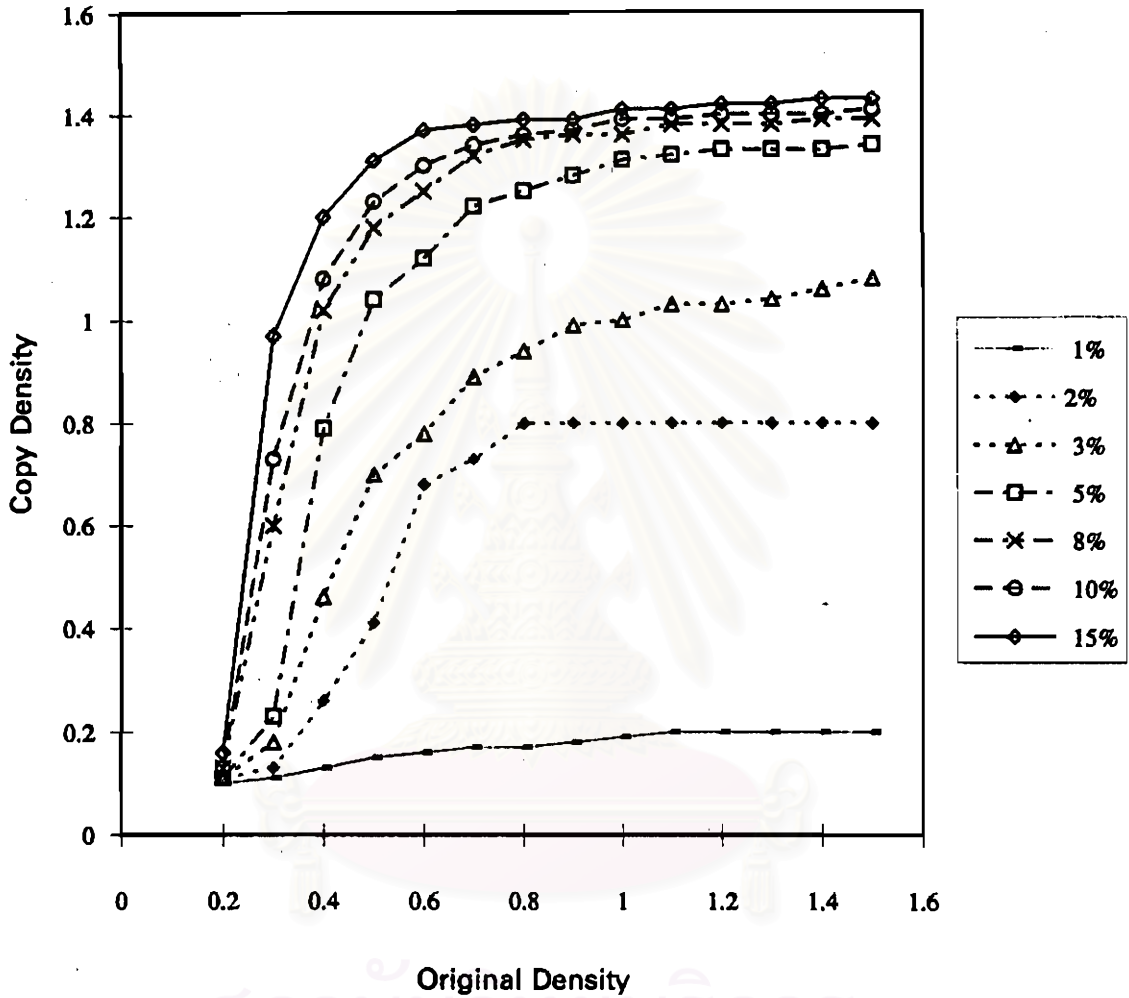


Figure 4-34 Copy density versus original density of red copy produced by the red developer B

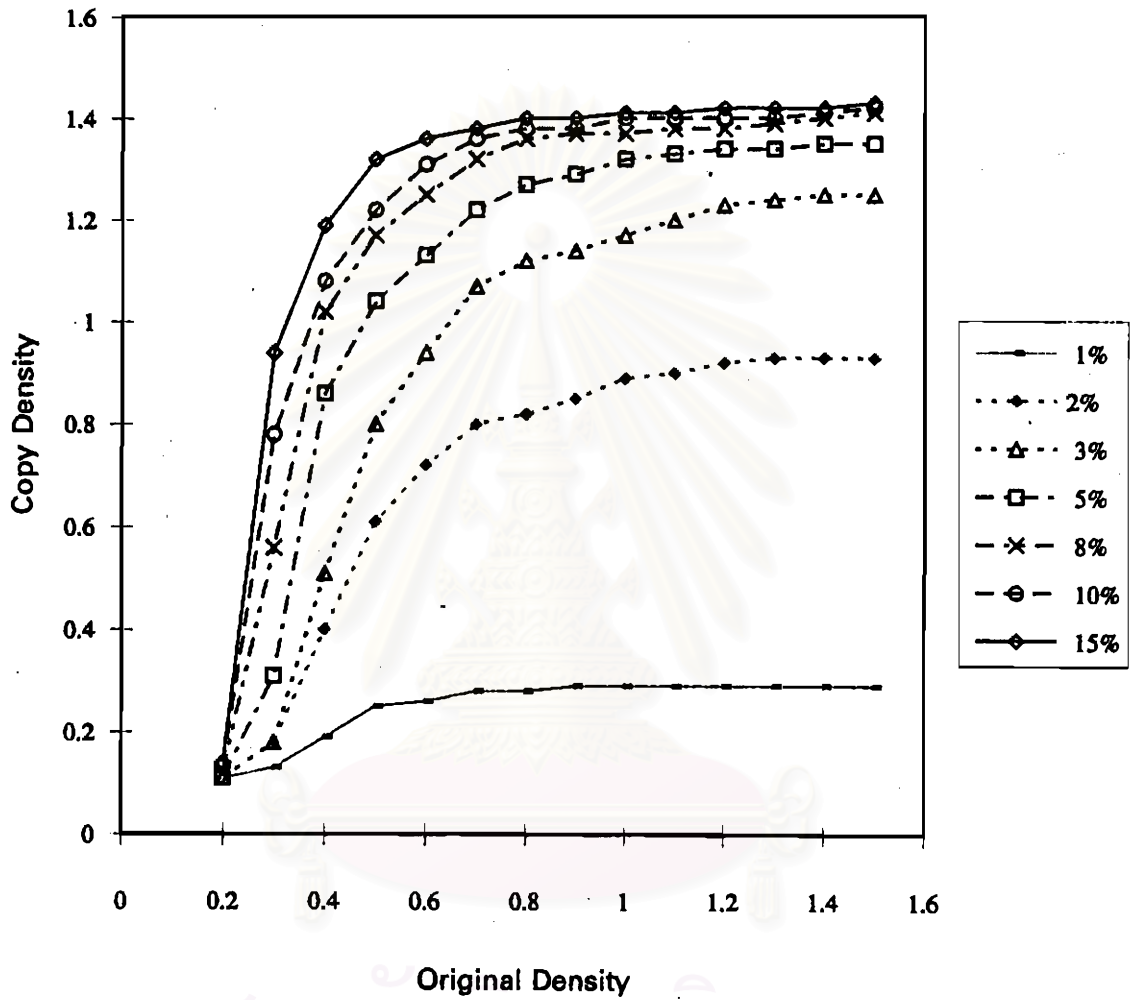


Figure 4-35 Copy density versus original density of red copy produced by the red developer C

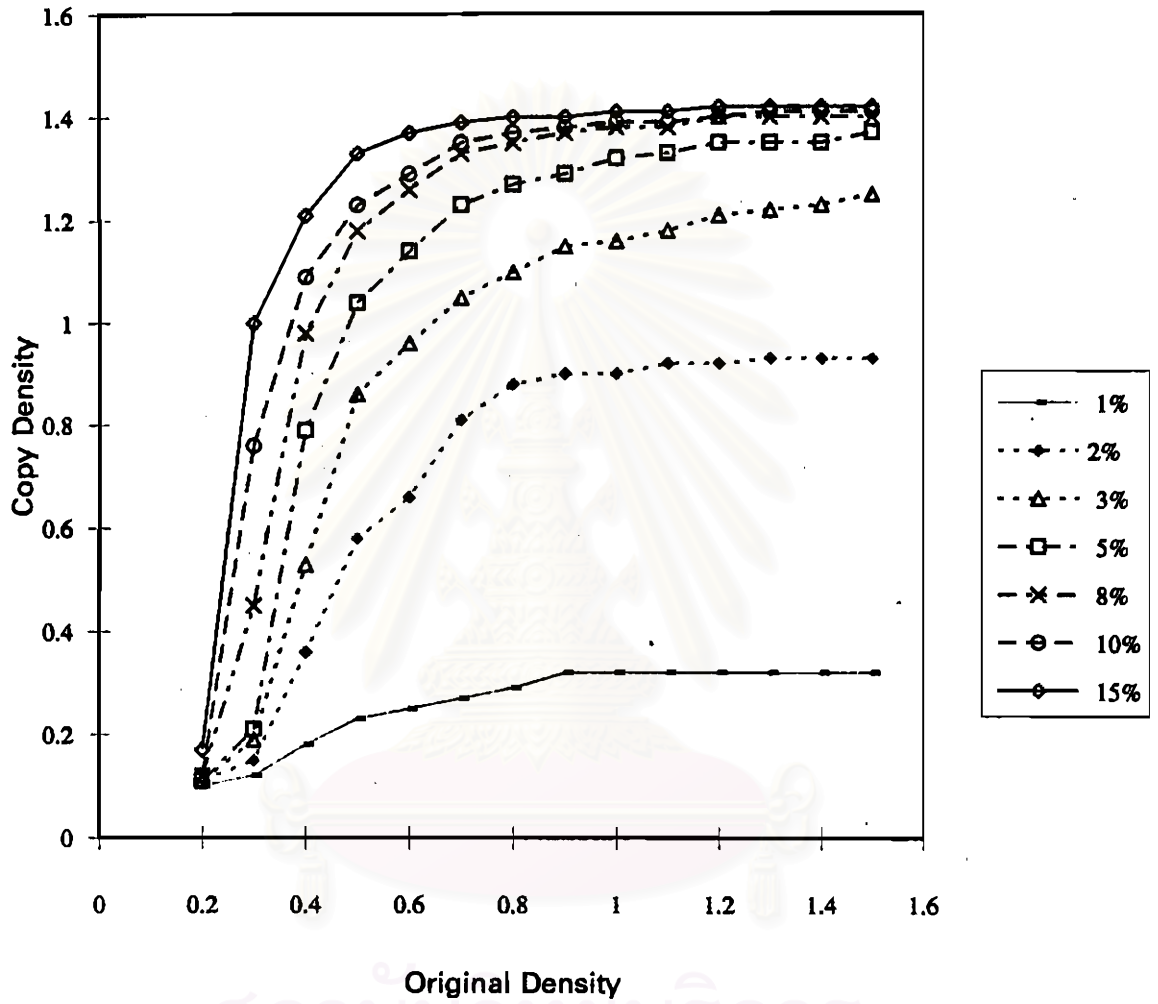


Figure 4-36 Copy density versus original density of red copy produced by the red developer D

4.3.4 Dependence of the tone reproduction of the red toner on the carrier surface coating

Figures 4-37 to 4-39 also show that the print contrast increases with increasing toner concentration; and the carriers E and F gave a higher print contrast at the low toner concentration than did the others, because their too low toner charge result in a high development on the photoreceptor and transfer on the substrate.

4.3.5 Dependence of the resolution and dot gain of the red toner on the carrier size

The resolution of the red line copies A to D, measured of the line width at 5 lines/mm, is shown in Figure 4-40, that the carrier D gives the optimum resolution from 1-15% toner concentrations, because the slightly wide lines were produced at low toner concentrations and least enlarged at high toner concentrations. The carrier C gives a better resolution than do the carrier B and the carrier A, respectively. The smaller carriers as if a finer dispersion give thus a better resolution than do the larger carriers as expected.

Fourteen steps of the halftone copy producing by the developers A to D containing 5% toner concentration were measured for the dot gain, as shown in Figure 4-41. It is found that the large carrier (A) produced a higher dot gain from highlight to midtone areas than did the smaller carriers (B to D). Because the toner coverage on a large carrier is high, so the toners can be developed exceedingly on the line and halftone image areas. But the small carrier produced more dot loss in highlight area because it has less amount of toner particles to be developed on the highlight halftone area than does the large carrier.

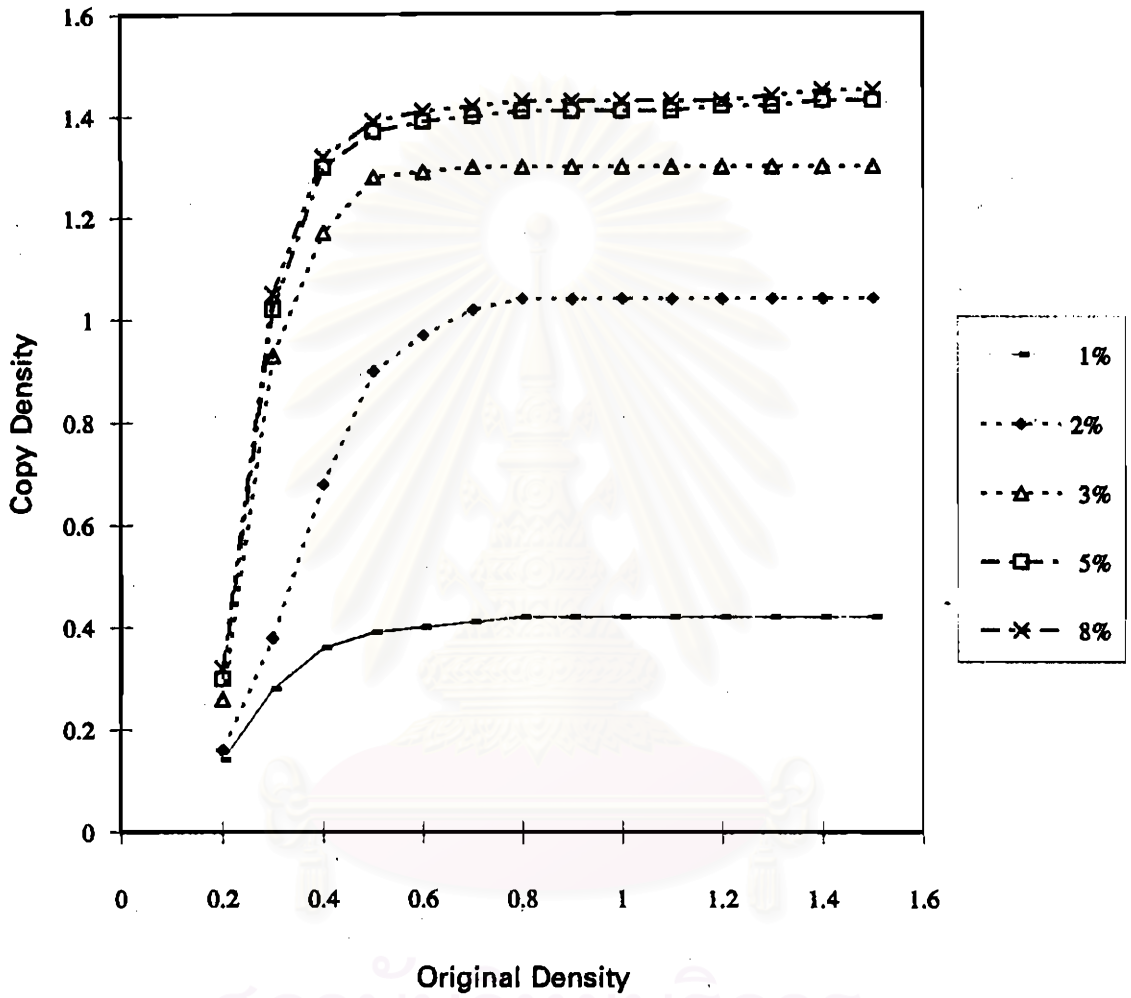


Figure 4-37 Copy density versus original density of red copy produced by the red developer E

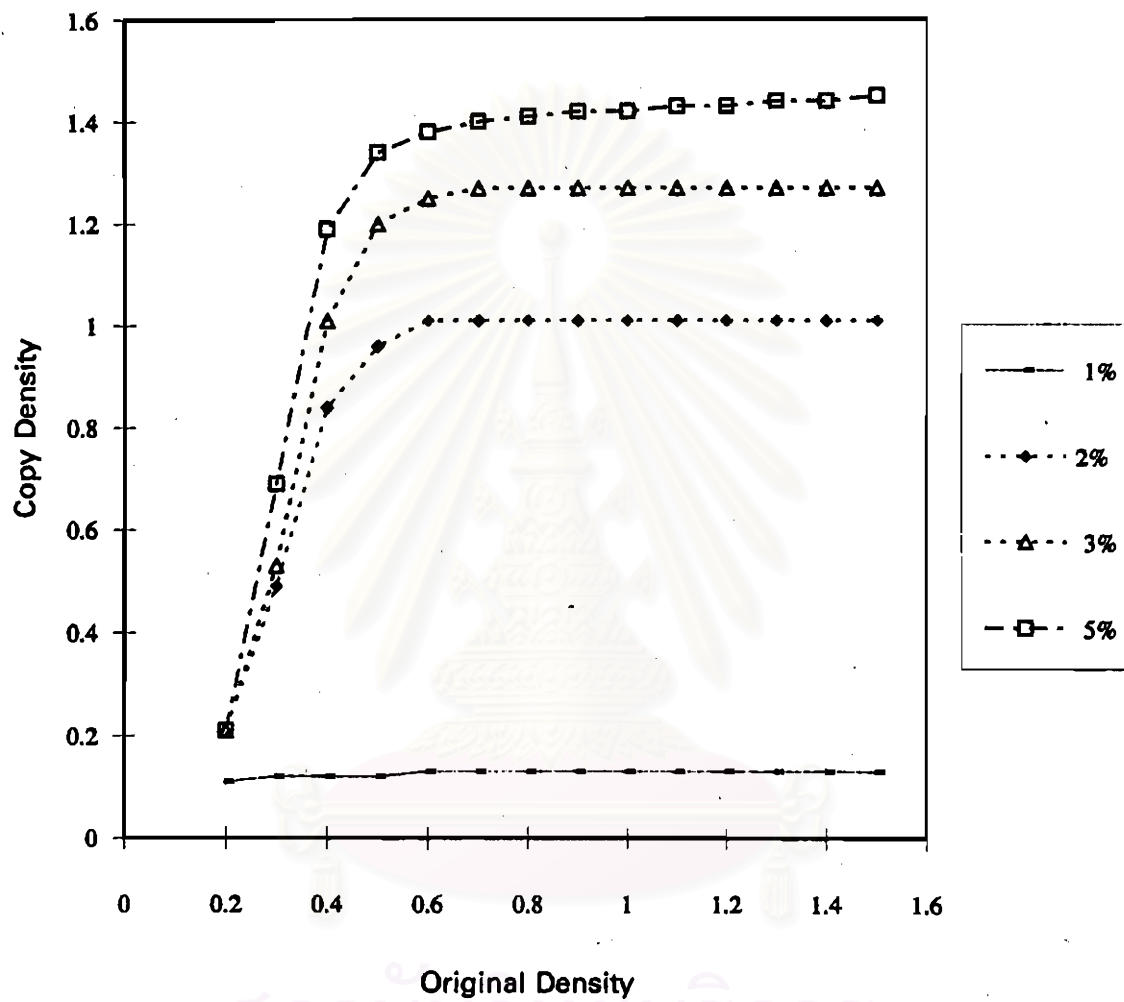


Figure 4-38 Copy density versus original density of red copy produced by the red developer F

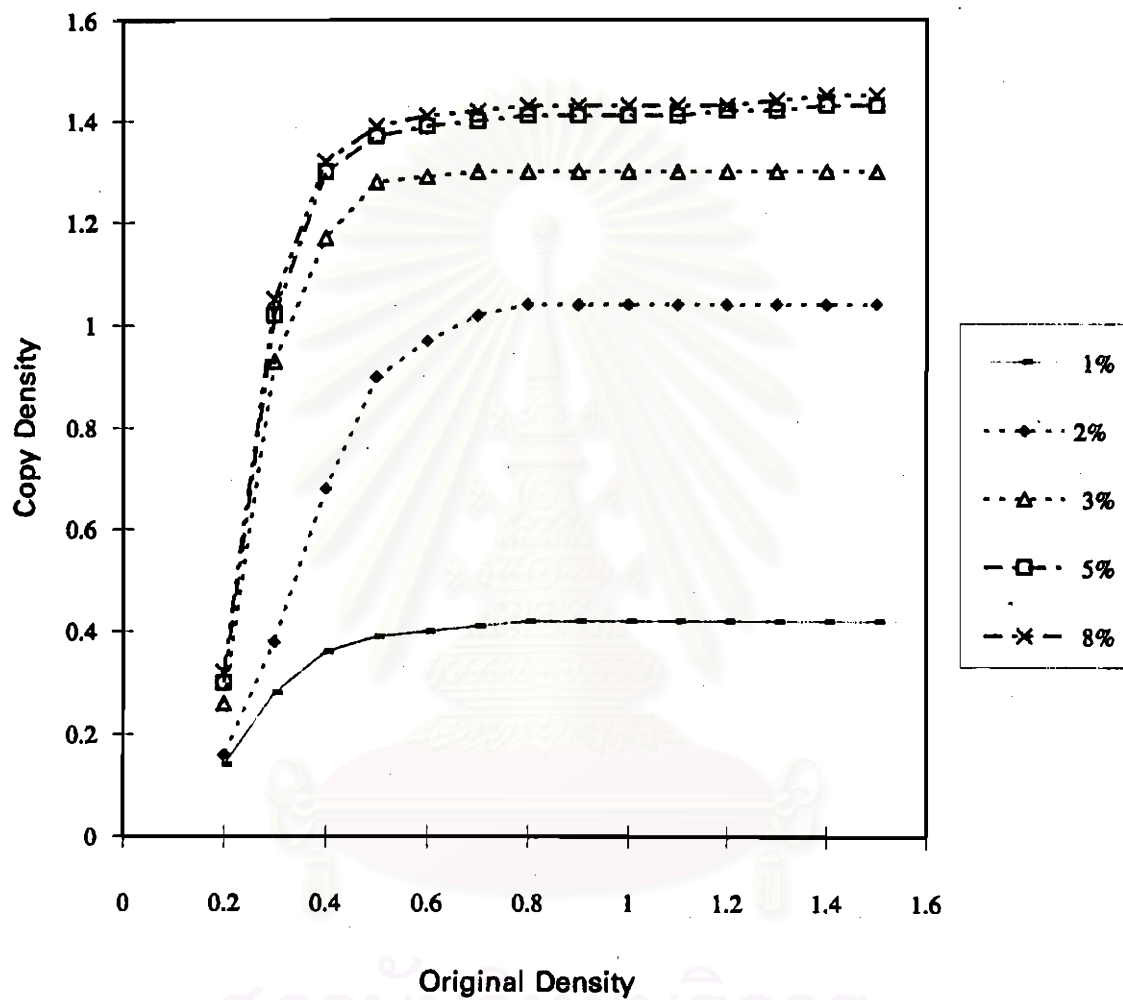


Figure 4-39 Copy density versus original density of red copy produced by the red developer G

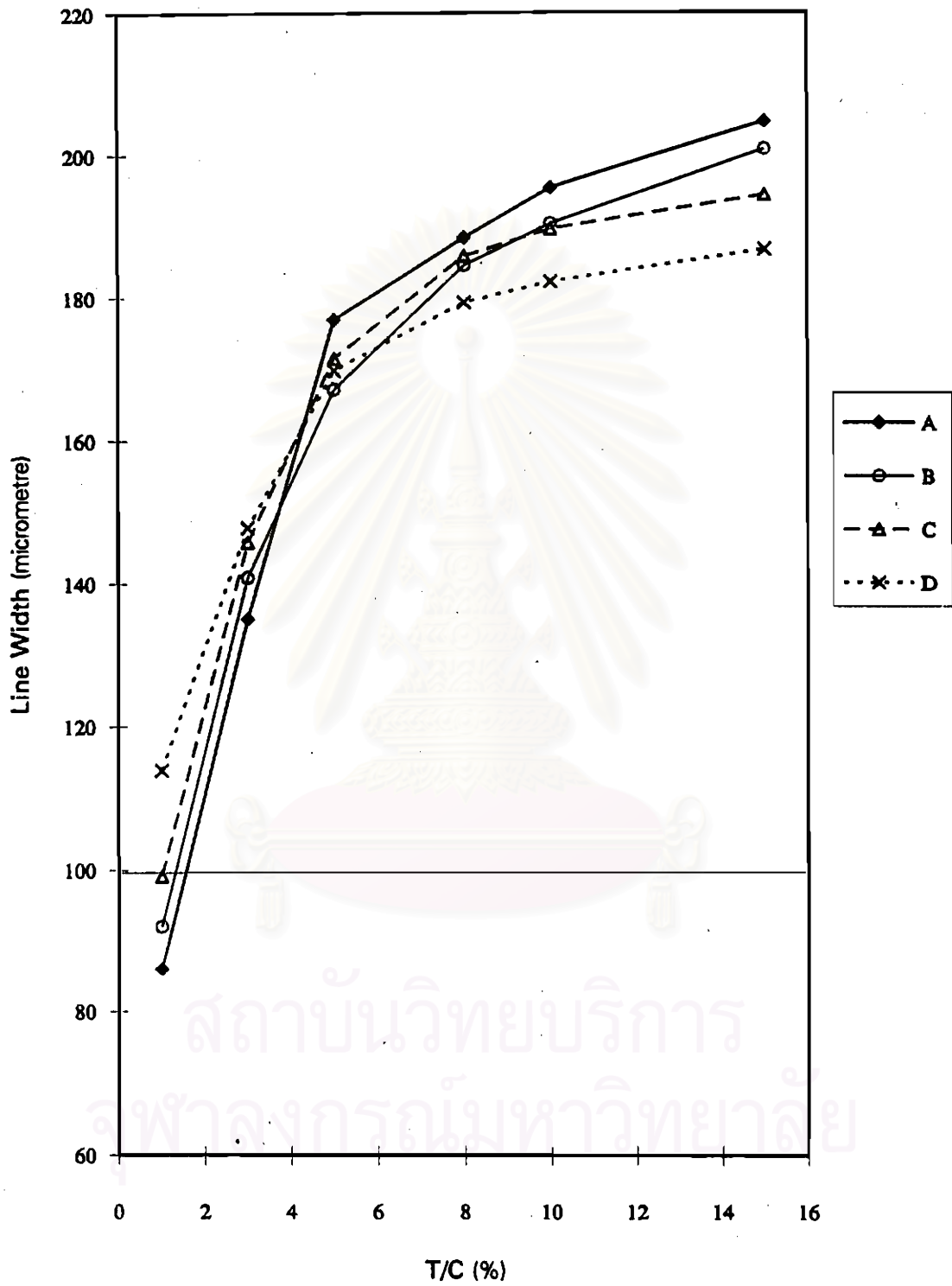


Figure 4-40 Line width versus T/C of red copies A - D

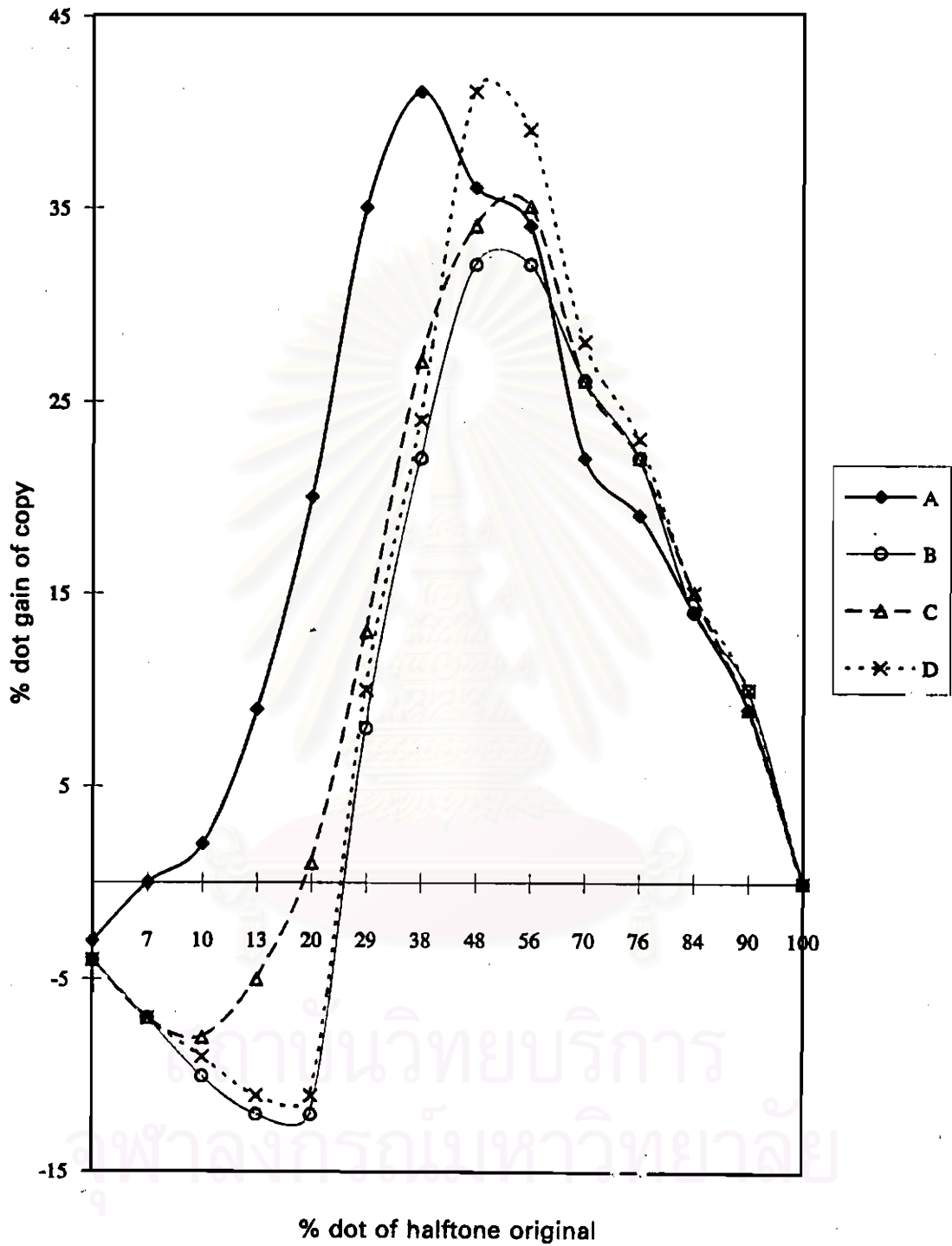


Figure 4-41 Dot gain of halftone copies produced by the red developers A to D with 5% toner concentration

4.3.6 Dependence of the maximum copy density and the background density of the cyan toner on the toner concentration and the carrier size

The maximum density of the cyan copies are 1.8 to 2, and the optimum solid density is determined from 1.8. The plot of the maximum density versus the toner concentration in Figure 4-42 shows that the minimum toner concentrations of the cyan developers A, B, C and D producing the optimum print density are 5%, 6%, 7% and 8%, respectively.

According to the calibration of the null density on a reference white paper, the background density of the cyan copies should be lower than 0.03, same value as the red copies. The plot of the background density versus the toner concentration in Figure 4-43 show that the maximum toner concentrations of the cyan developers A, B, C and D without a fog density on the background are 7%, 10%, 12% and 14%, respectively.

The optimum ranges of toner concentrations for the cyan developers A, B, C and D are 5-7%, 6-10%, 7-12% and 8-14%, respectively. The results of the cyan toner are similar to the red toner that the T/C latitude corresponding to the q/m latitude becomes higher when a carrier size become smaller. But the T/C latitude of the smaller cyan toner is narrower than that of the larger red toner.

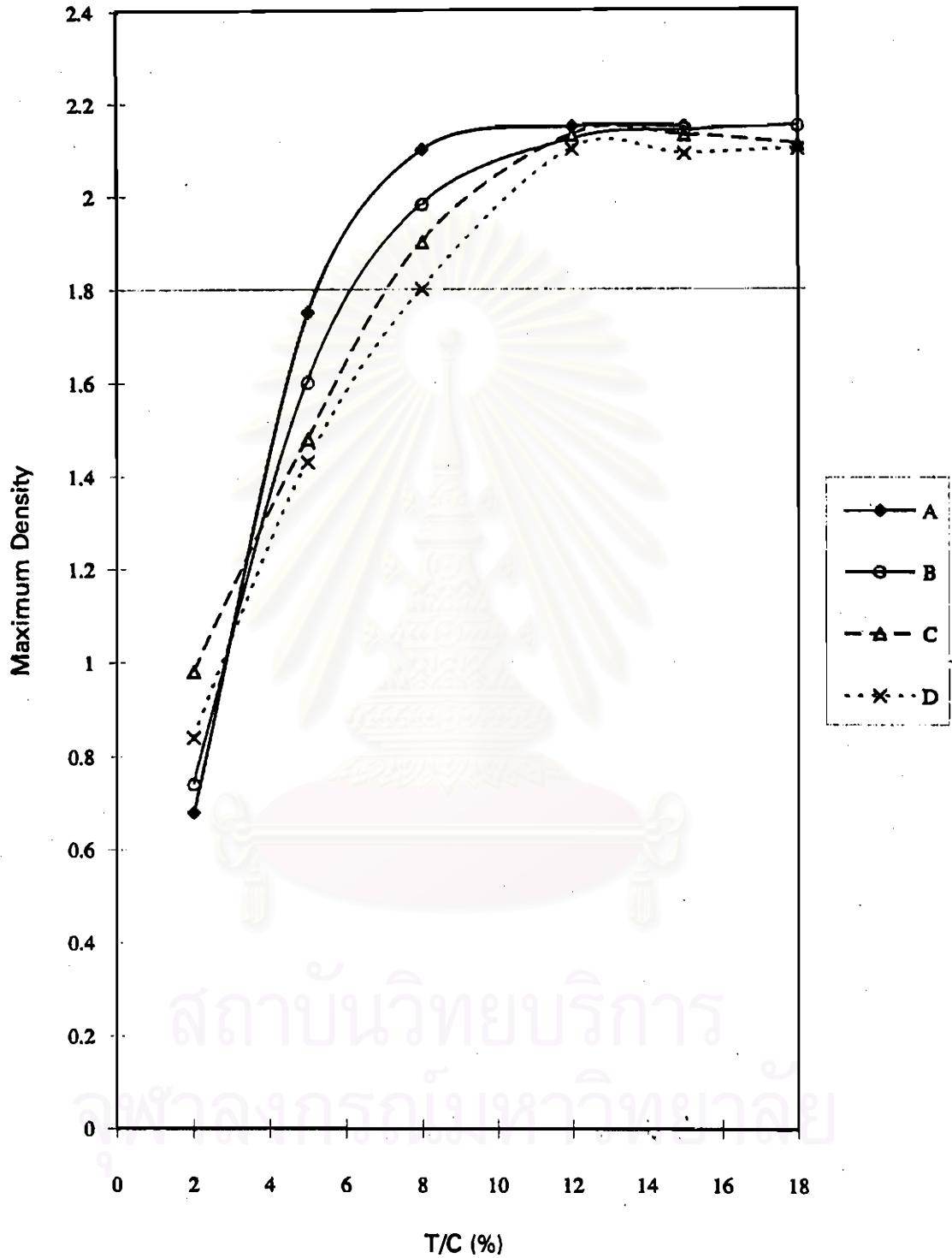


Figure 4-42 Maximum density vs. T/C of cyan developers A - D

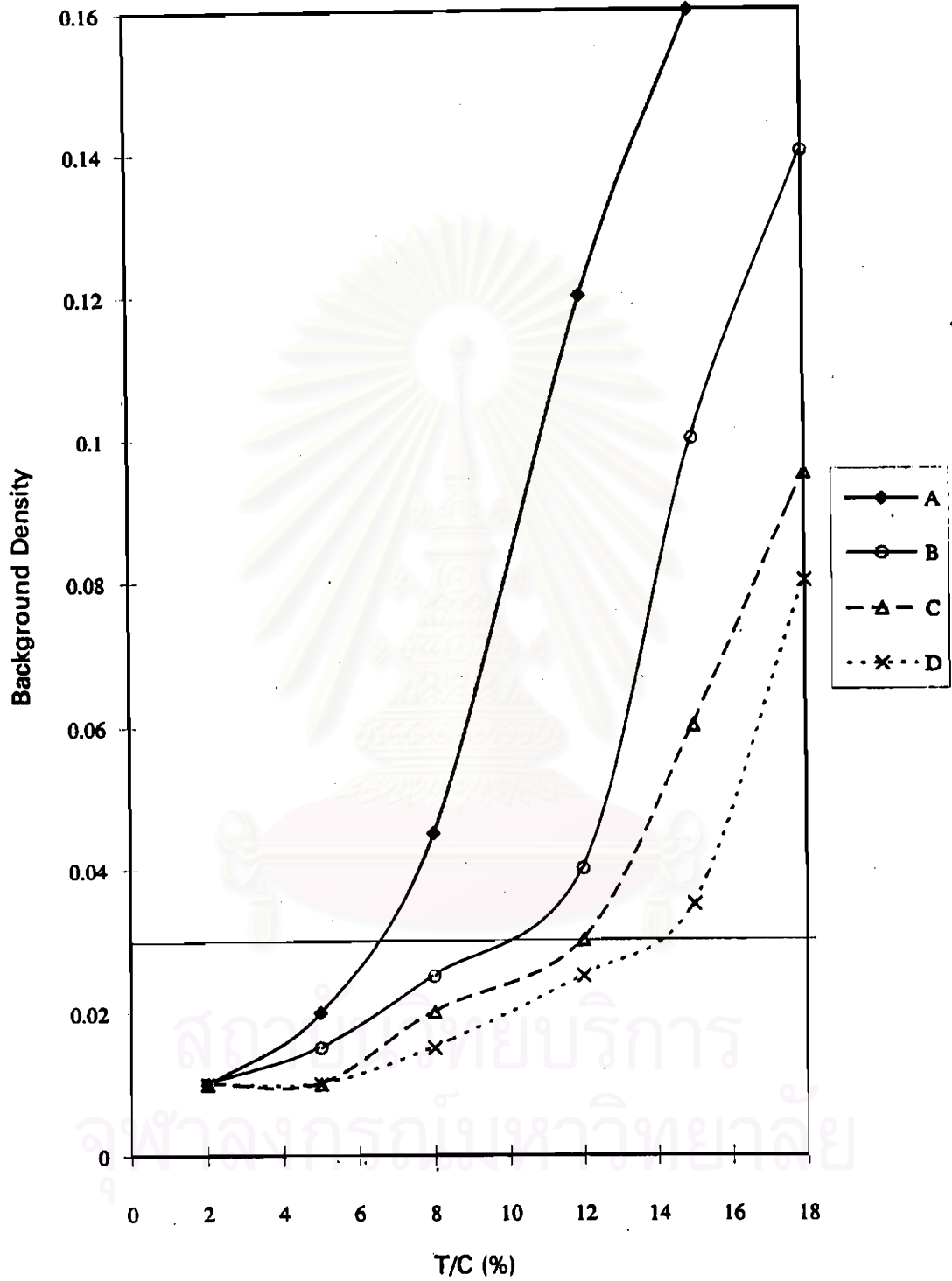


Figure 4-43 Background density vs. T/C of cyan developers A-D

4.3.7 Dependence of the tone reproduction of the cyan toner on the toner concentration and the carrier size

The curves of the copy density versus the original density of 14 gradation levels are shown in Figures 4-44 to 4-47, that the print contrast increases with increasing toner concentration and carrier size. These results are also related to the cyan toner charge in Figure 4-26, which are of low density and contrast by the low toner charge. The larger carrier gave lower q/m to the cyan toner at higher than 5% T/C than did the smaller carrier. In addition, the higher toner coverage on the larger carrier, the higher development on the photoconductor, and the higher print density would be.

4.3.8 Dependence of the resolution and dot gain of the cyan toner on the carrier size

The resolution of the cyan copies A to D measured of the line width at 5 lines/mm, is shown in Figure 4-48. It shows that the carrier D gives the optimum resolution from 1-15% of the toner concentrations, because the lines can be produced at the low toner concentrations (2%) and the lines are least enlarged at the high toner concentrations (5-15%). The carrier C gives the better resolution than do the carrier B and the carrier A.

The dot gain of cyan halftone copies produced by the cyan developer A to D with 5% toner concentration is shown in Figure 4-49 that the larger carrier produces slightly higher dot gain value than does the smaller carrier. Comparing the Figures 4-41 and 4-49, the small-sized cyan toner can produce a lower dot gain value than does the large-sized red toner.

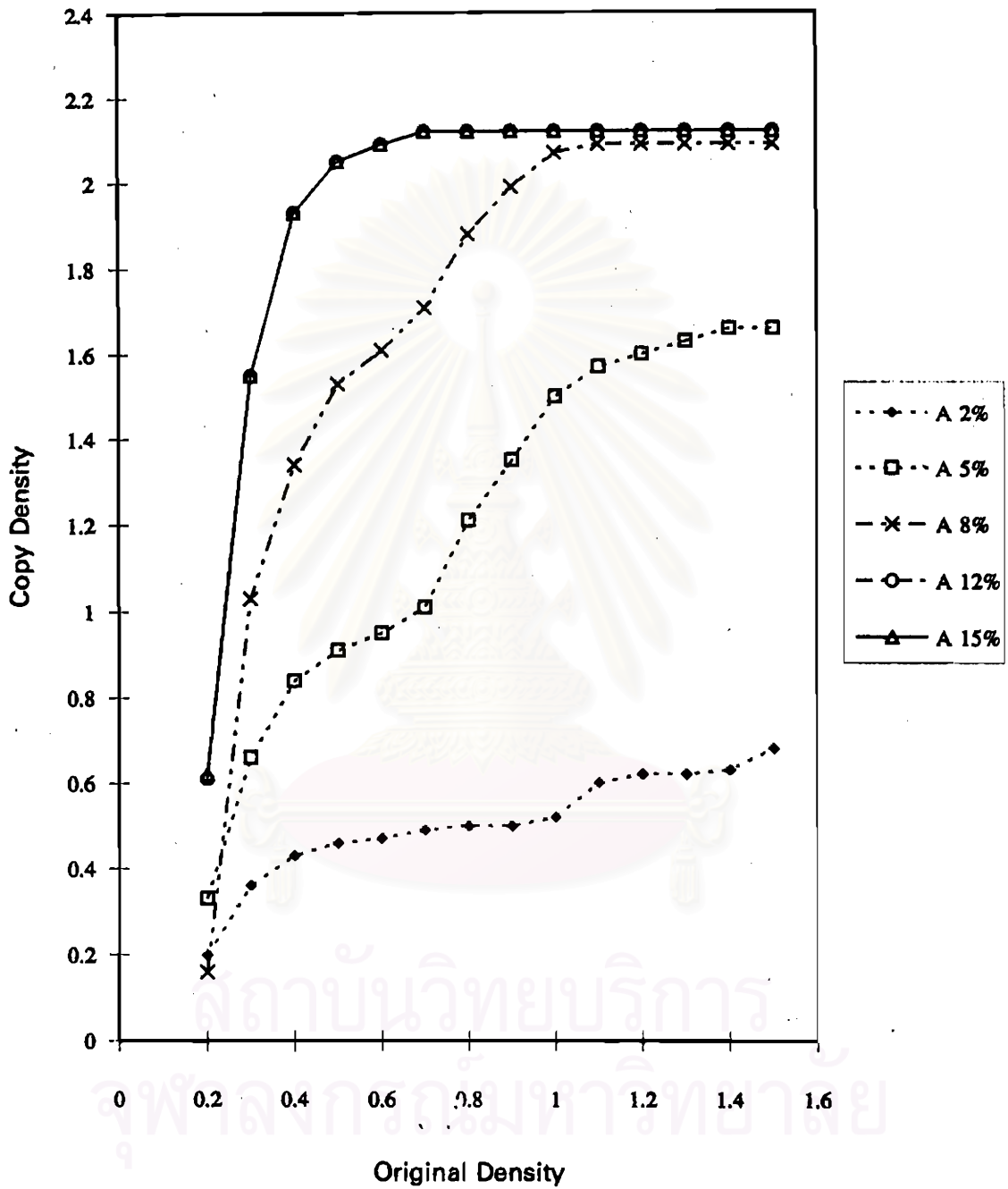


Figure 4-44 Copy density versus original density of cyan copy produced by the cyan developer A

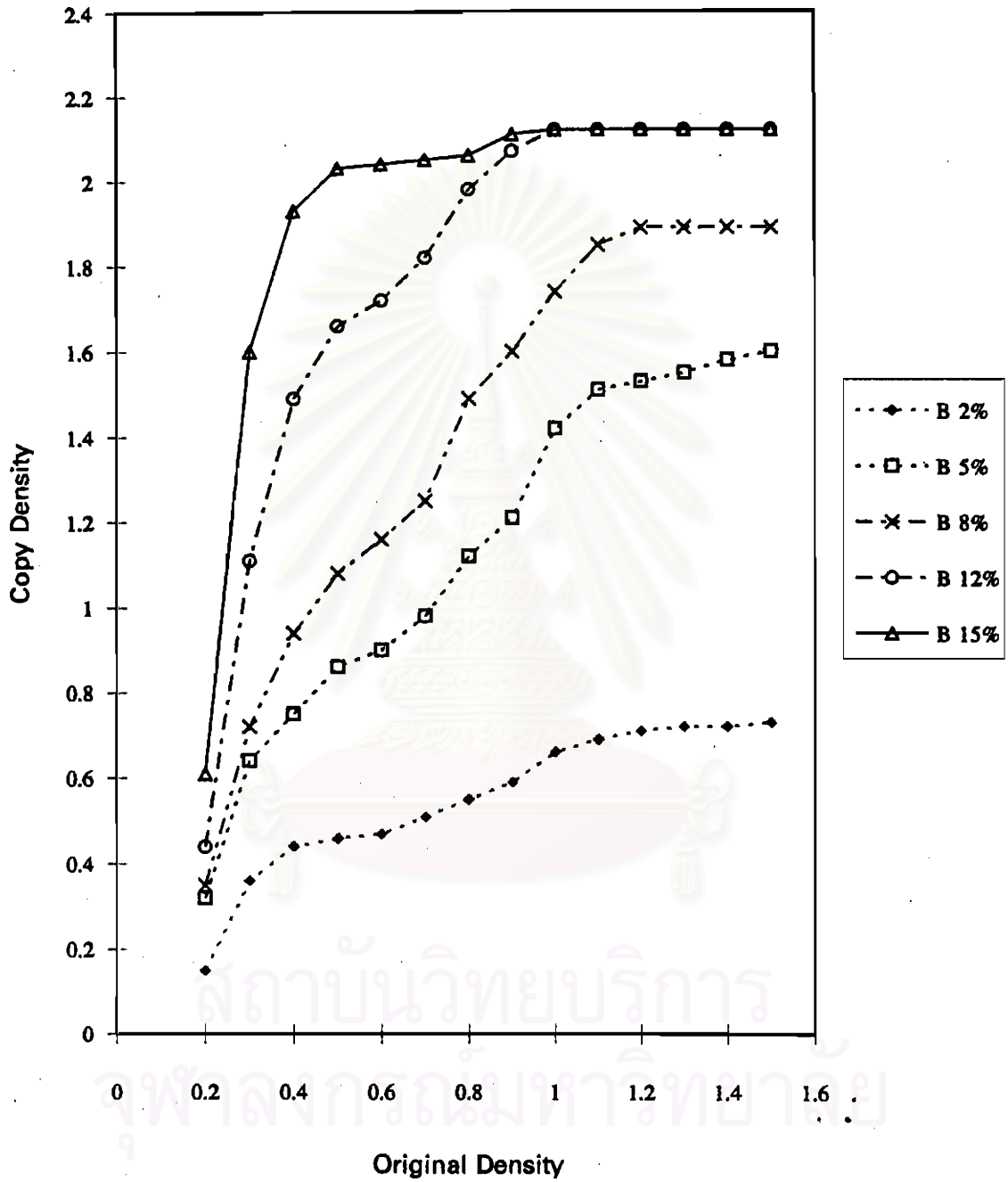


Figure 4-45 Copy density versus original density of cyan copy produced by the cyan developer B

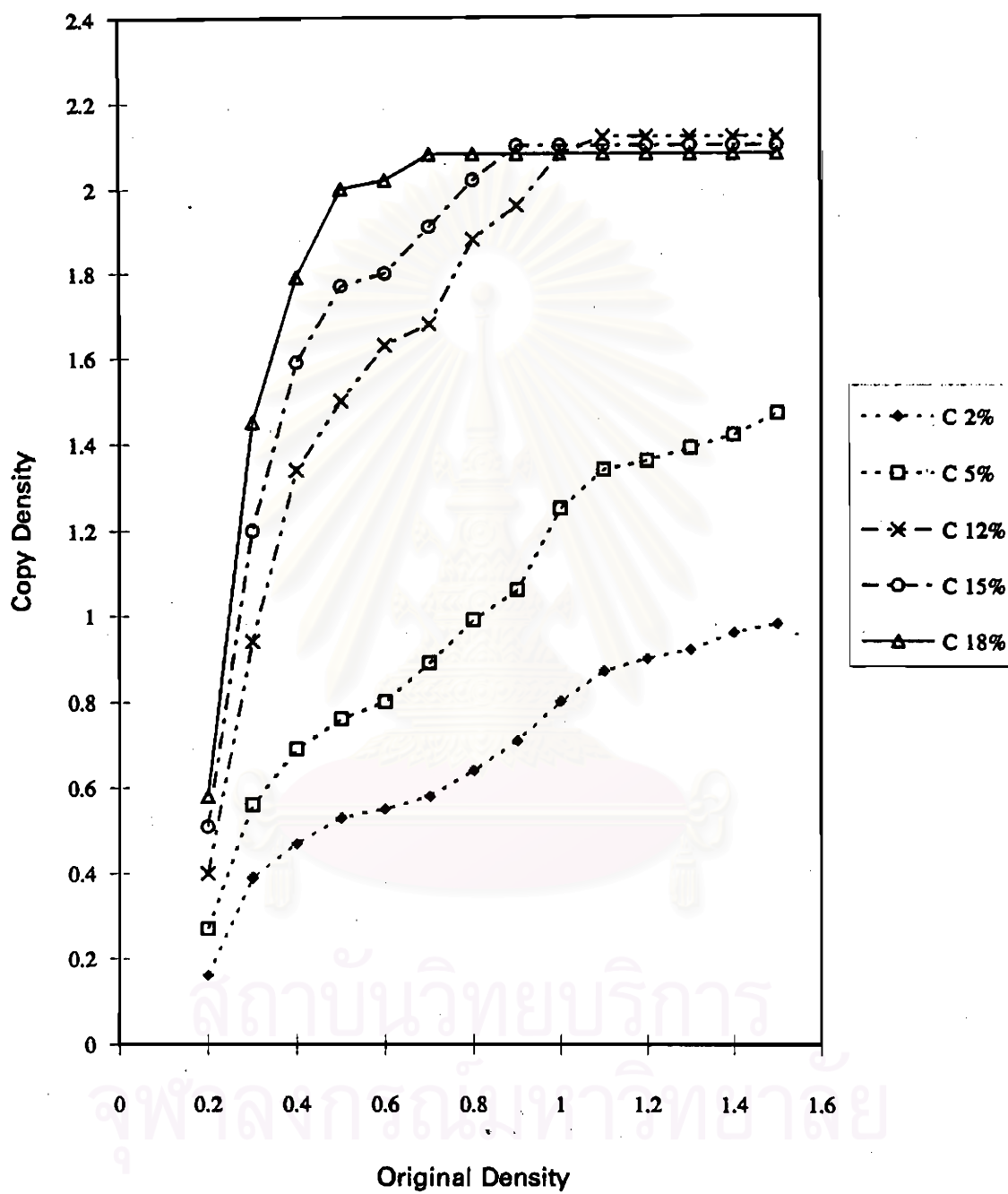


Figure 4-46 Copy density versus original density of cyan copy produced by the cyan developer C

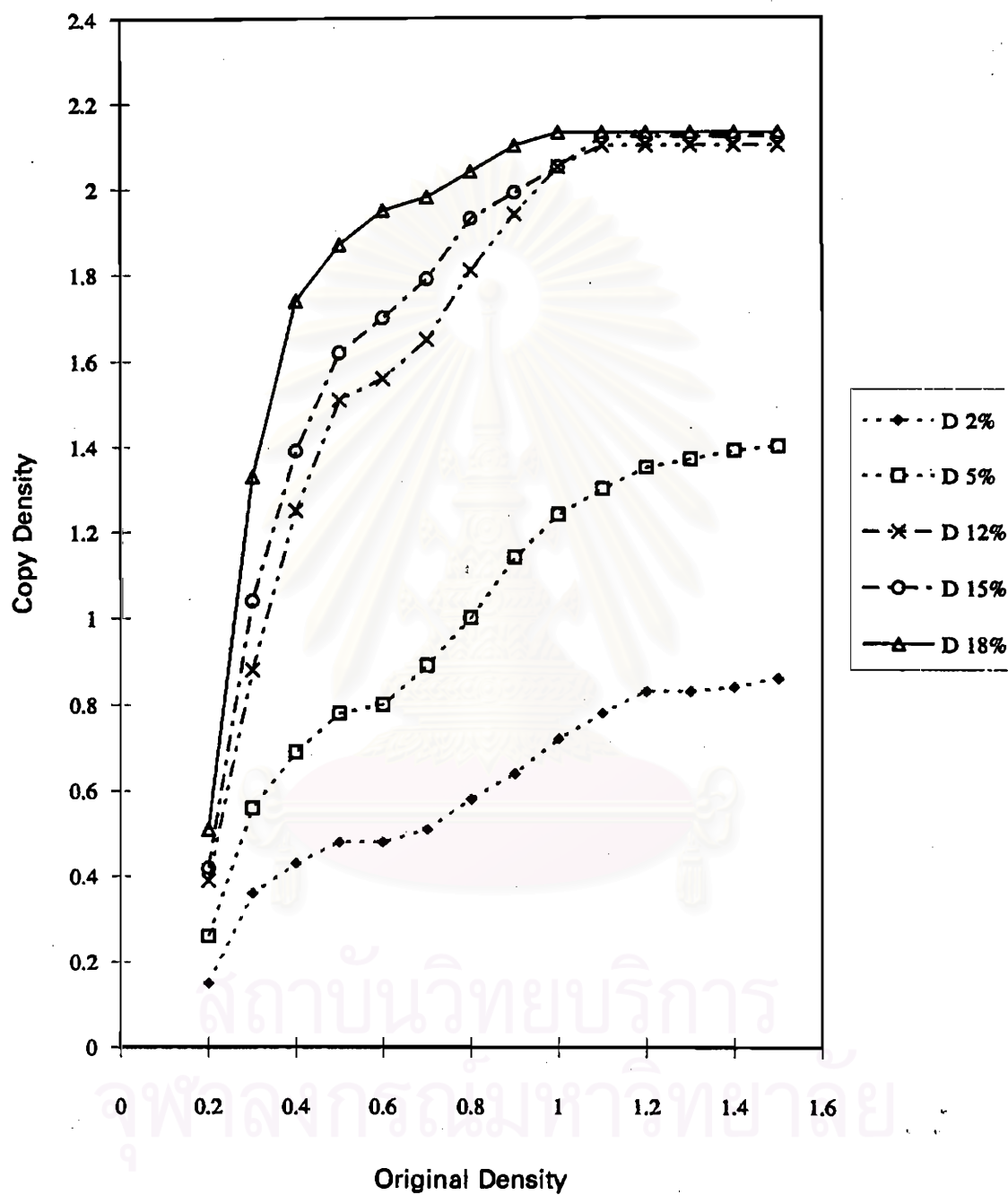


Figure 4-47 Copy density versus original density of cyan copy produced by the cyan developer D

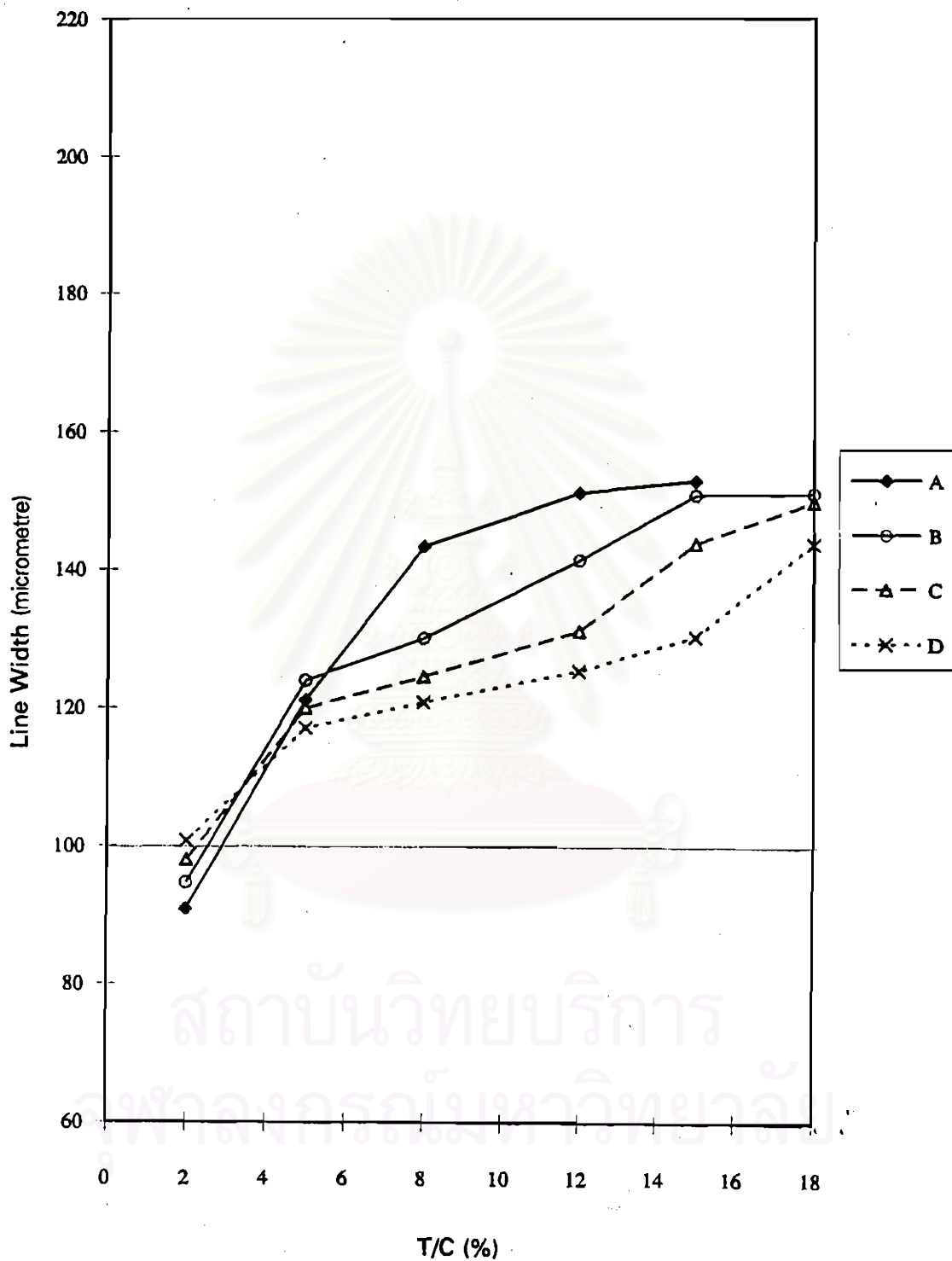


Figure 4-48 Line width versus T/C of cyan copies A - D

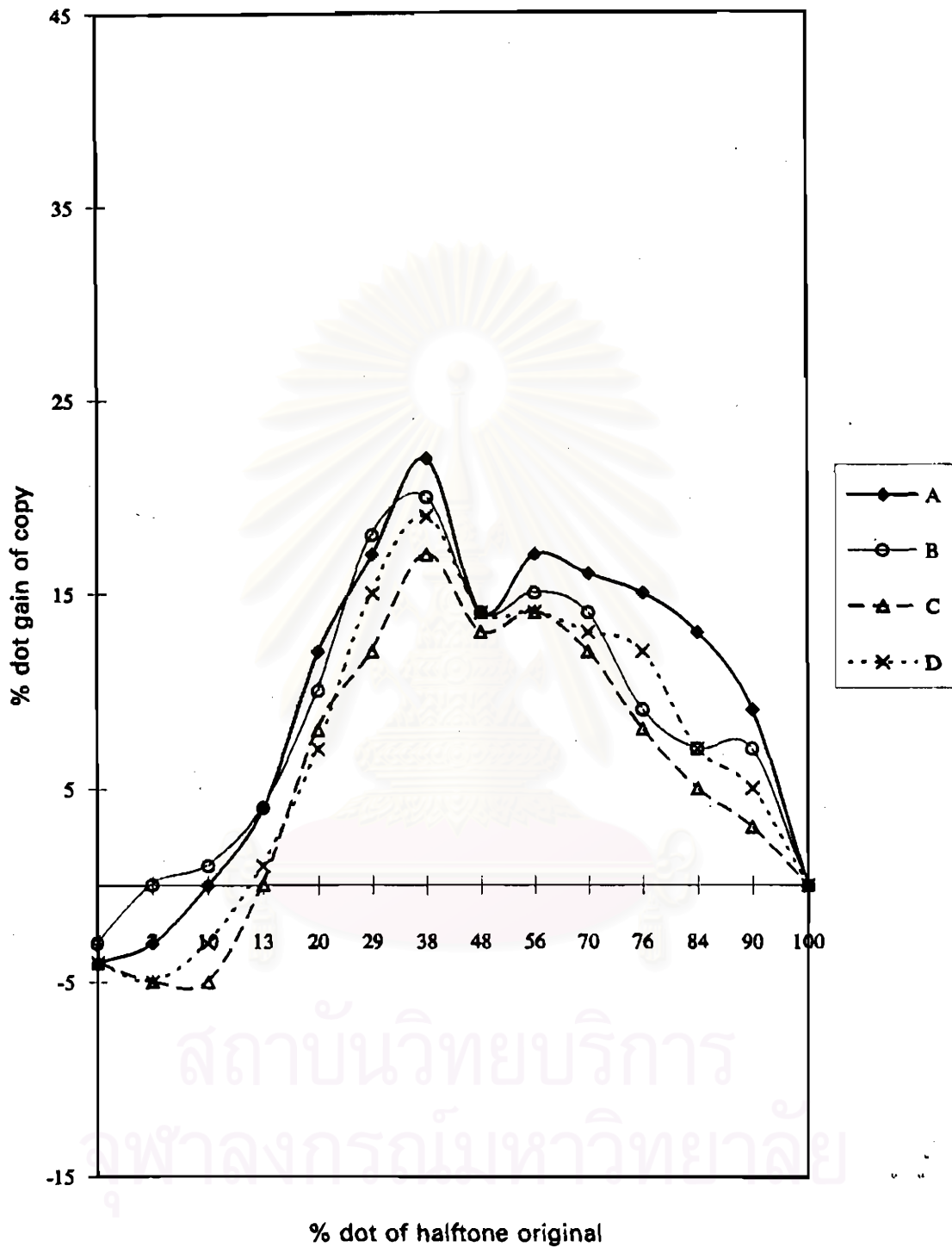


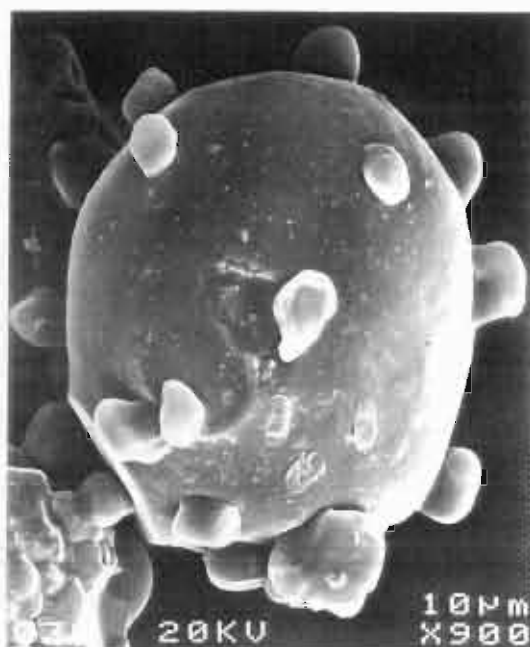
Figure 4-49 Dot gain of halftone copies produced by the cyan developers A to D with 5% toner concentration

4.3.9 Consideration on the covering ratio

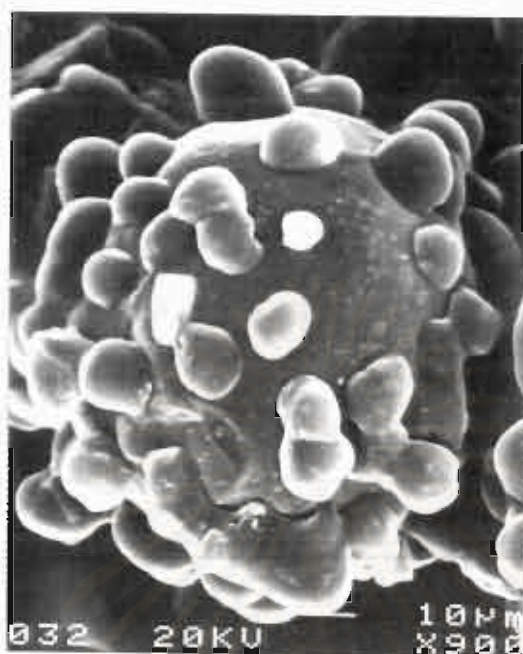
The scanning electron micrographs of the red and the cyan developers for the carrier B are shown in Figures 4-50 and 4-51, in order to determine a model of toner coverage on carrier surface at the various toner concentrations of 1, 3, 5, 8, 10 and 15%, and to compare with a model of Gutman and Hatmann.¹⁷ The micrographs show that the toner coverage on a carrier increase with increasing T/C, and the toner particles cover on the carrier with double layers at the high toner concentration.

The color optical micrographs of the two-component developers, the red and the cyan toner mixed with the carriers A to D at the various T/Cs of 3, 5, 8, 10 and 15%, are shown in Figures 4-52 to 4-59 as a real condition of the toners cover on the carriers. The color pictures also show that the toner coverage on a carrier increases with increasing T/C, and the larger carriers have more toner coverage than do the smaller carriers. In addition, the amount of small toner covering on a carrier surface is higher than that of the large toner in the same toner concentration.

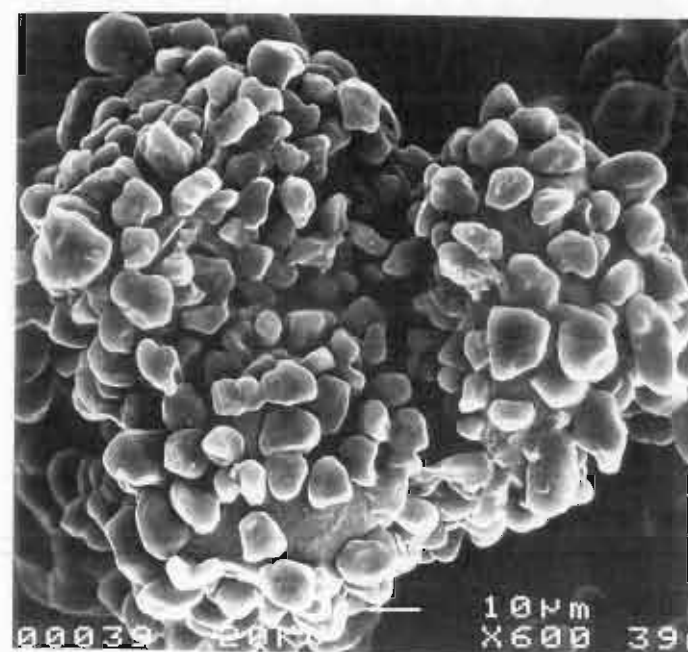
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จุฬาลงกรณ์มหาวิทยาลัย



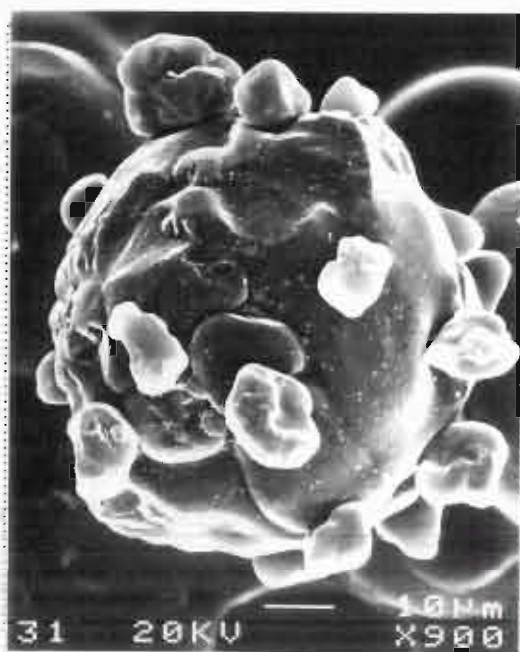
B 1%



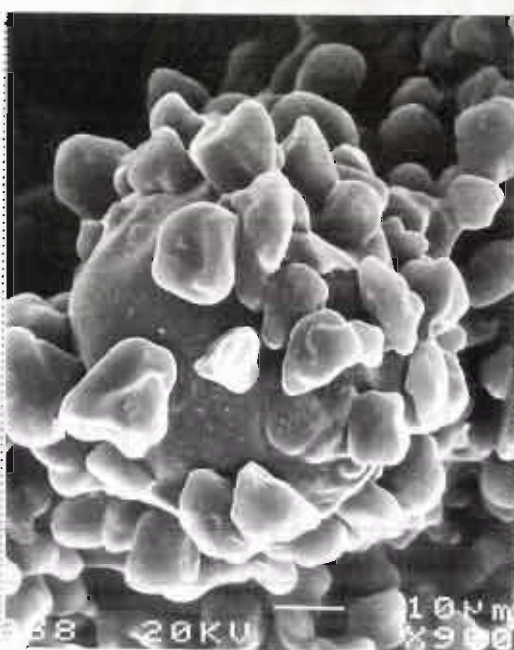
B 5%



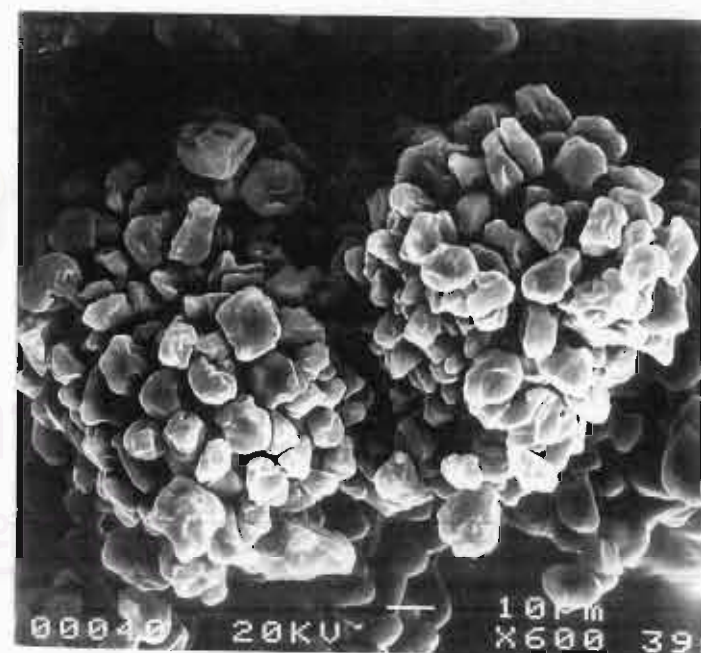
B 10%



B 3%



B 8%



B 15%

Figure 4-50. Scanning electron micrographs of the developers, red toner covering on carrier B with the various T/C of 1, 3, 5, 8, 10 and 15%

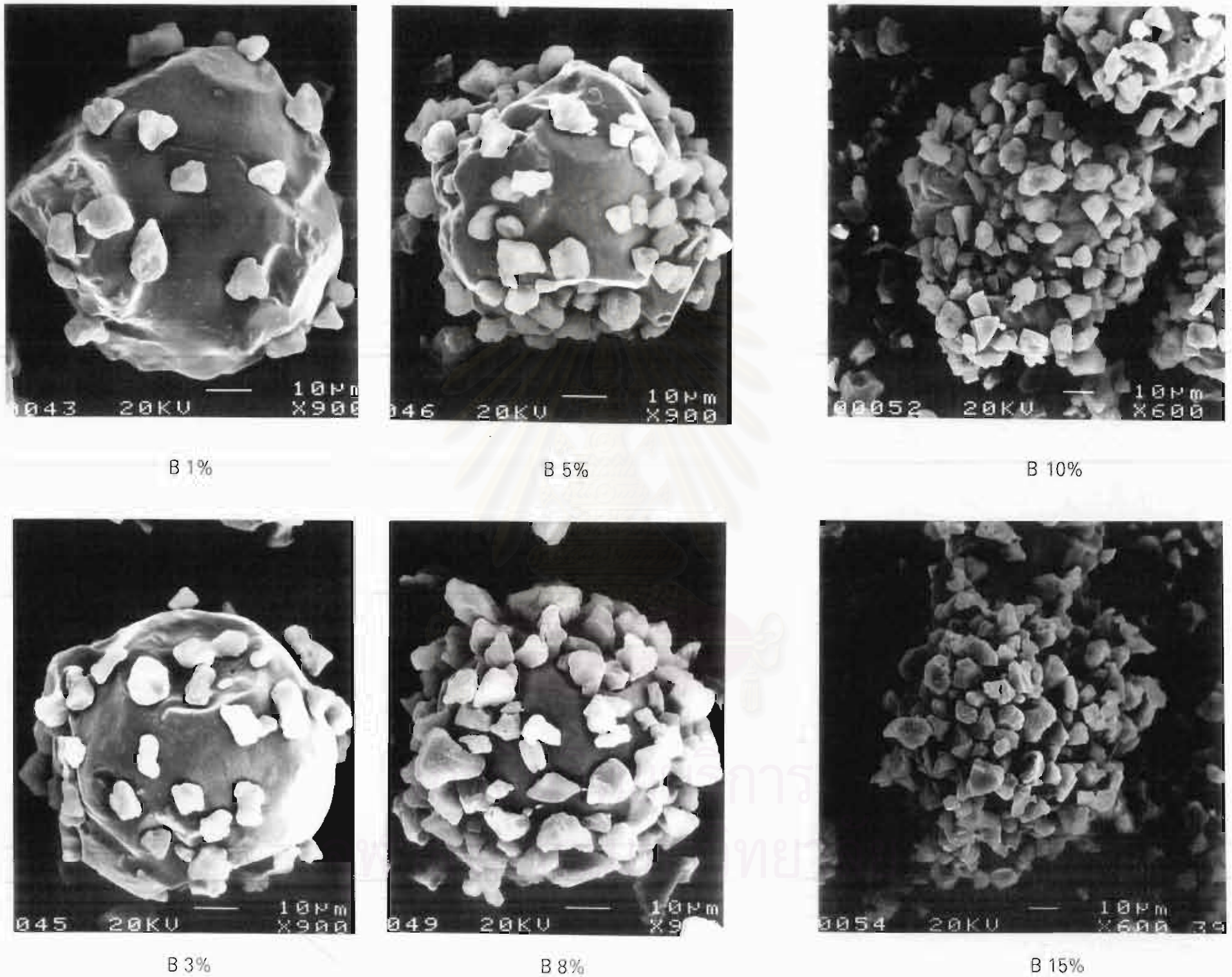


Figure 4-51 Scanning electron micrographs of the developers, cyan toner covering on carrier B with the various T/C of 1, 3, 5, 8, 10 and 15%

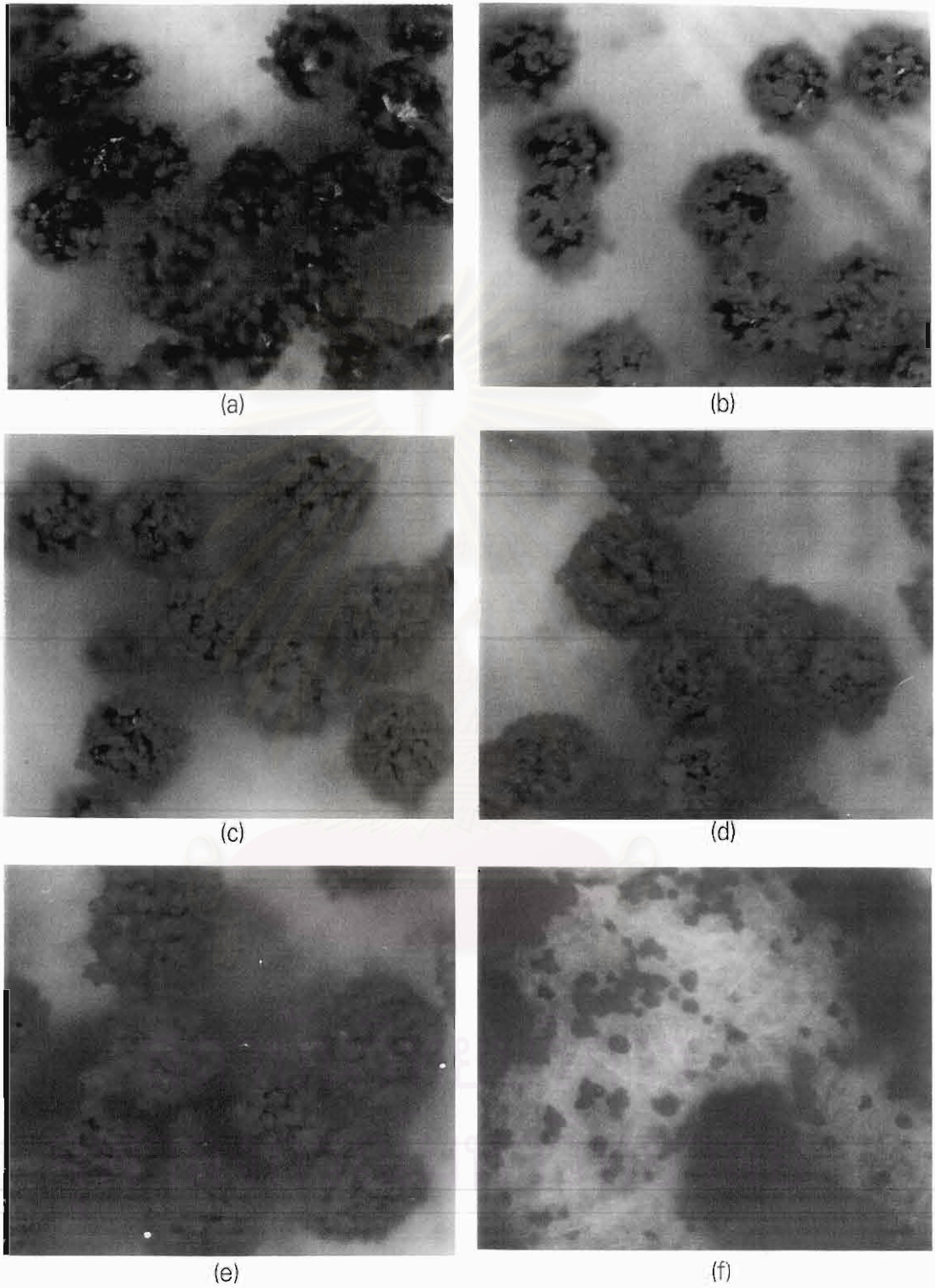


Figure 4-52 Color optical micrographs (x140) of the red developer A with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

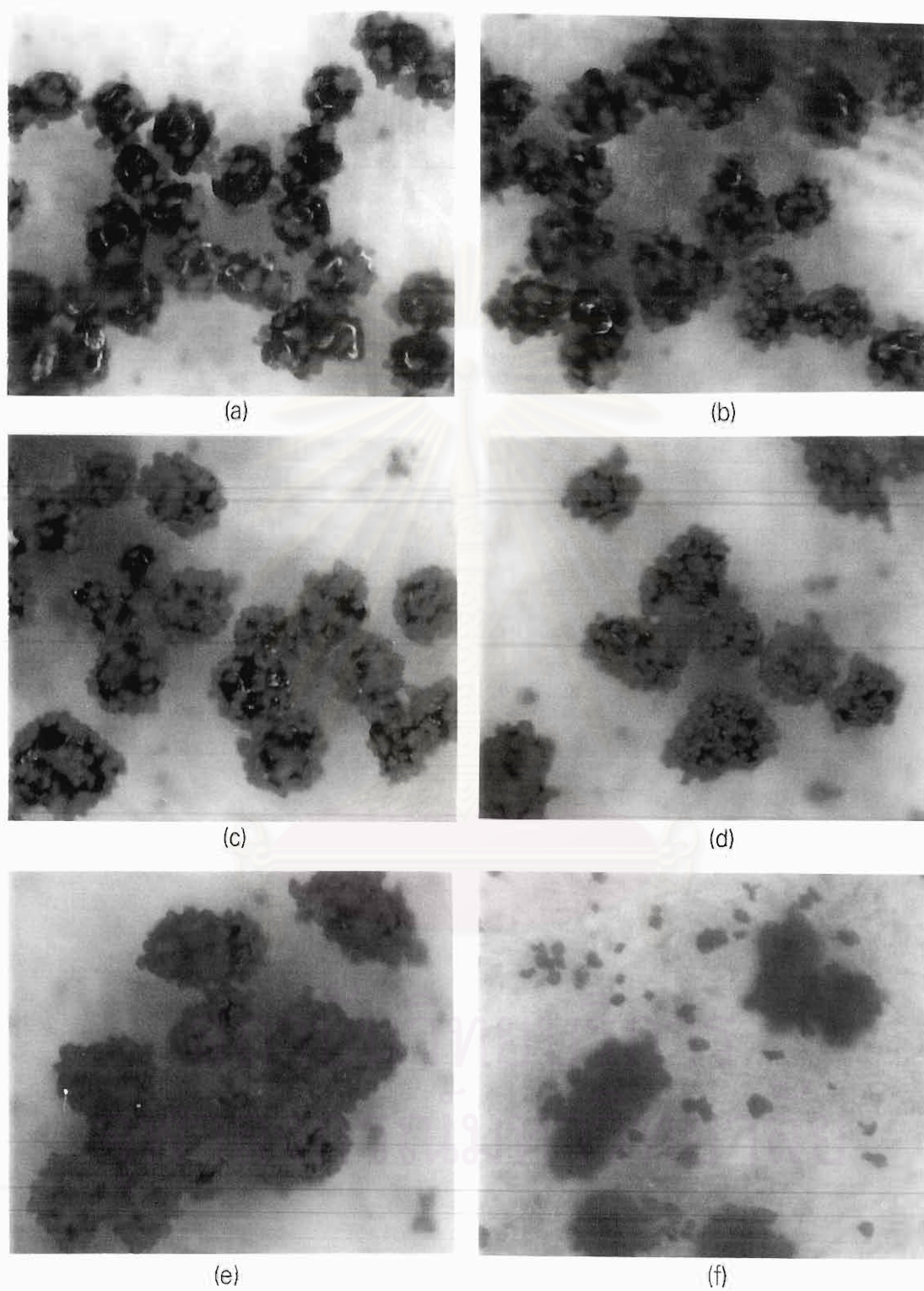


Figure 4-53 Color optical micrographs (x140) of the red developer B with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

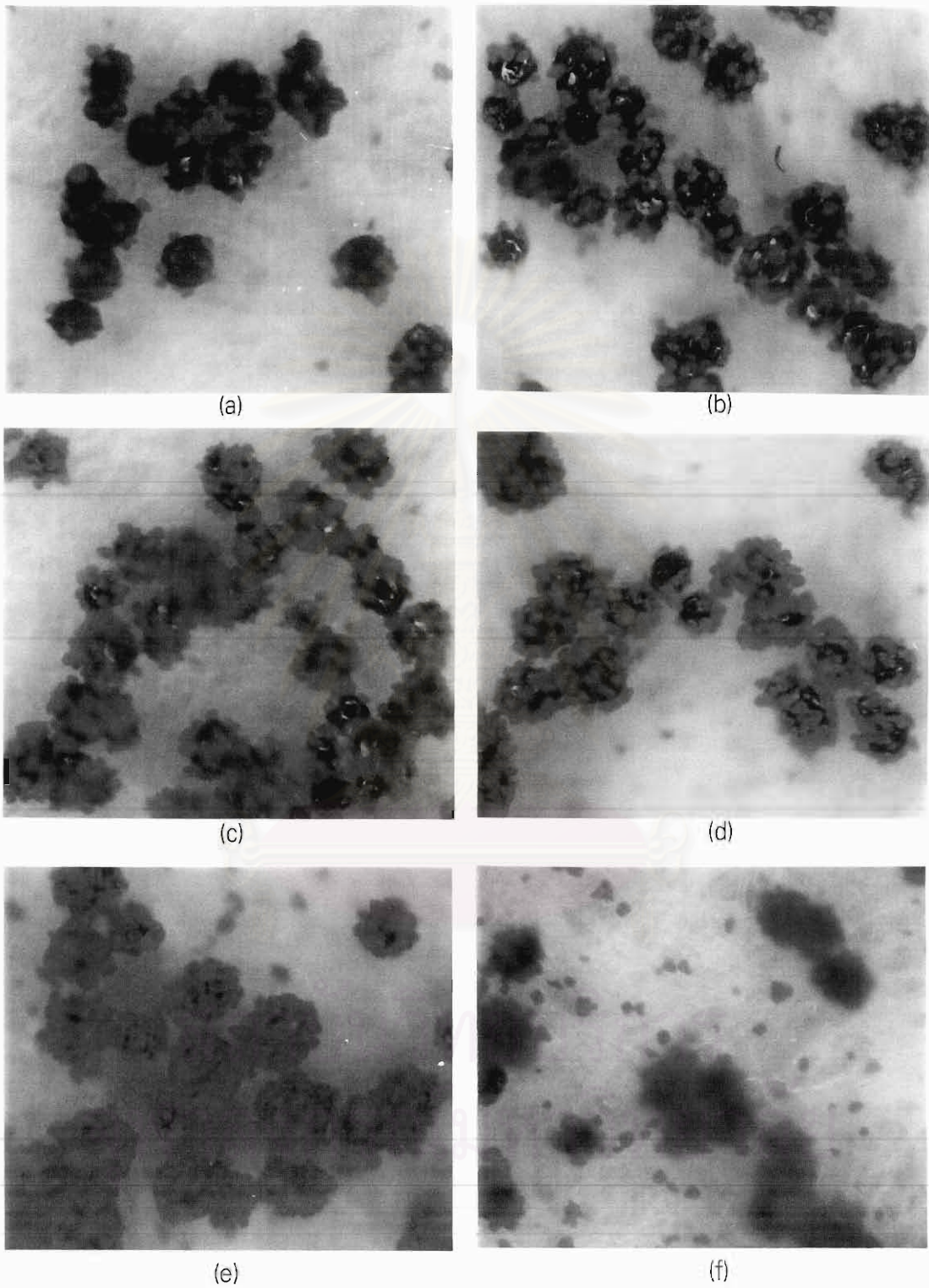


Figure 4-54 Color optical micrographs (x140) of the red developer C with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

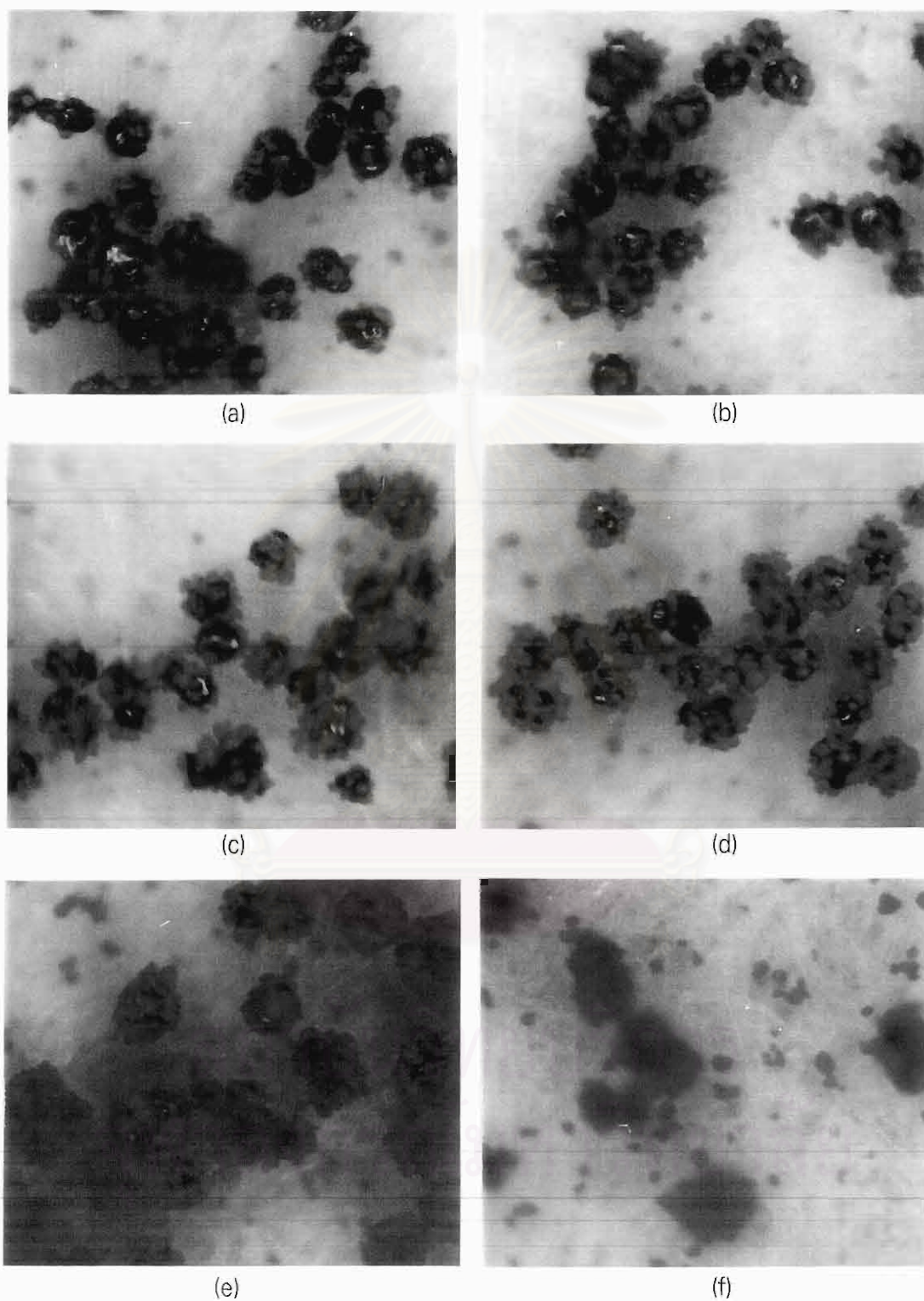


Figure 4-55 Color optical micrographs ($\times 140$) of the red developer D with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

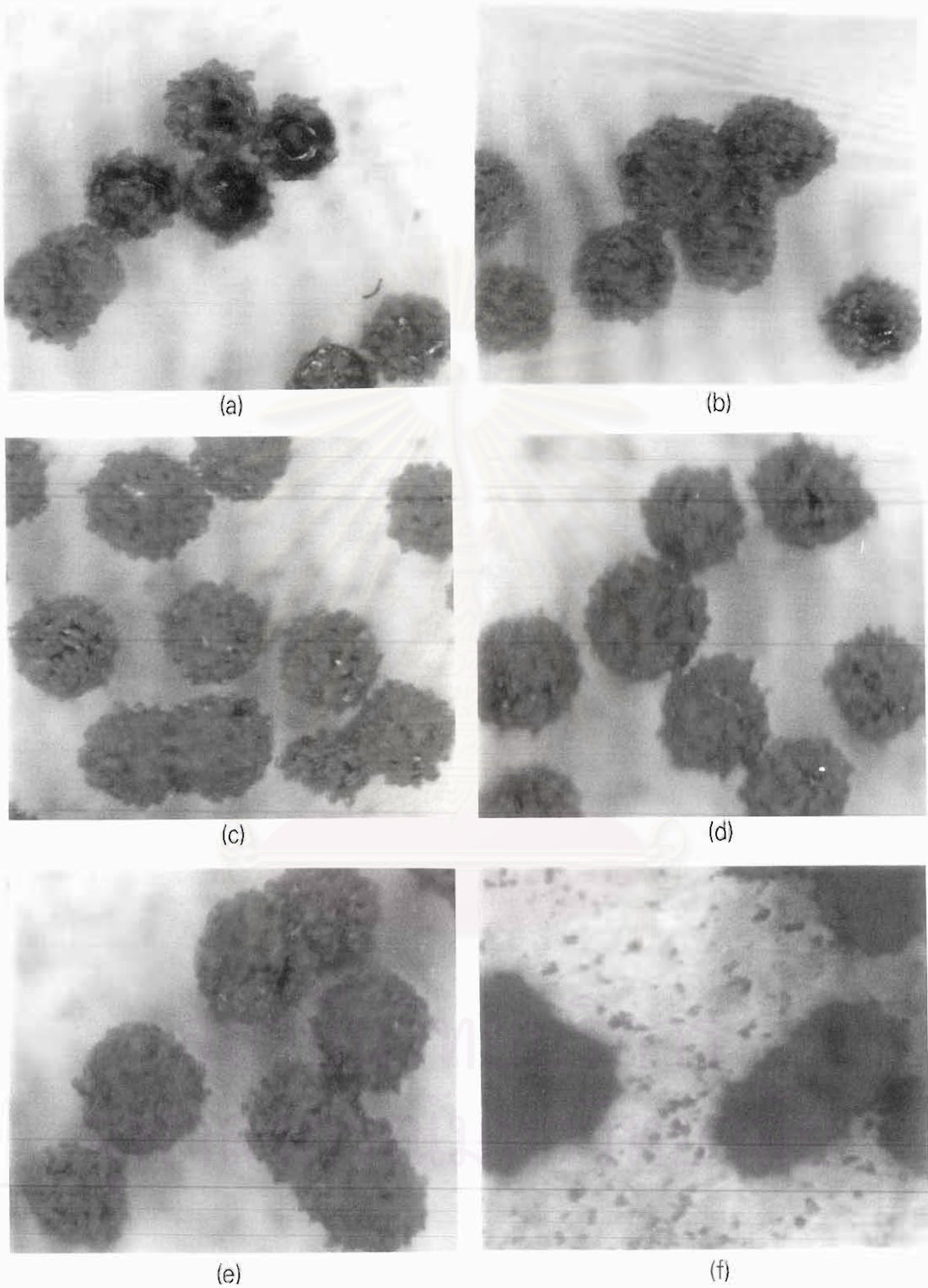


Figure 4-56 Color optical micrographs (x140) of the cyan developer \underline{A} with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

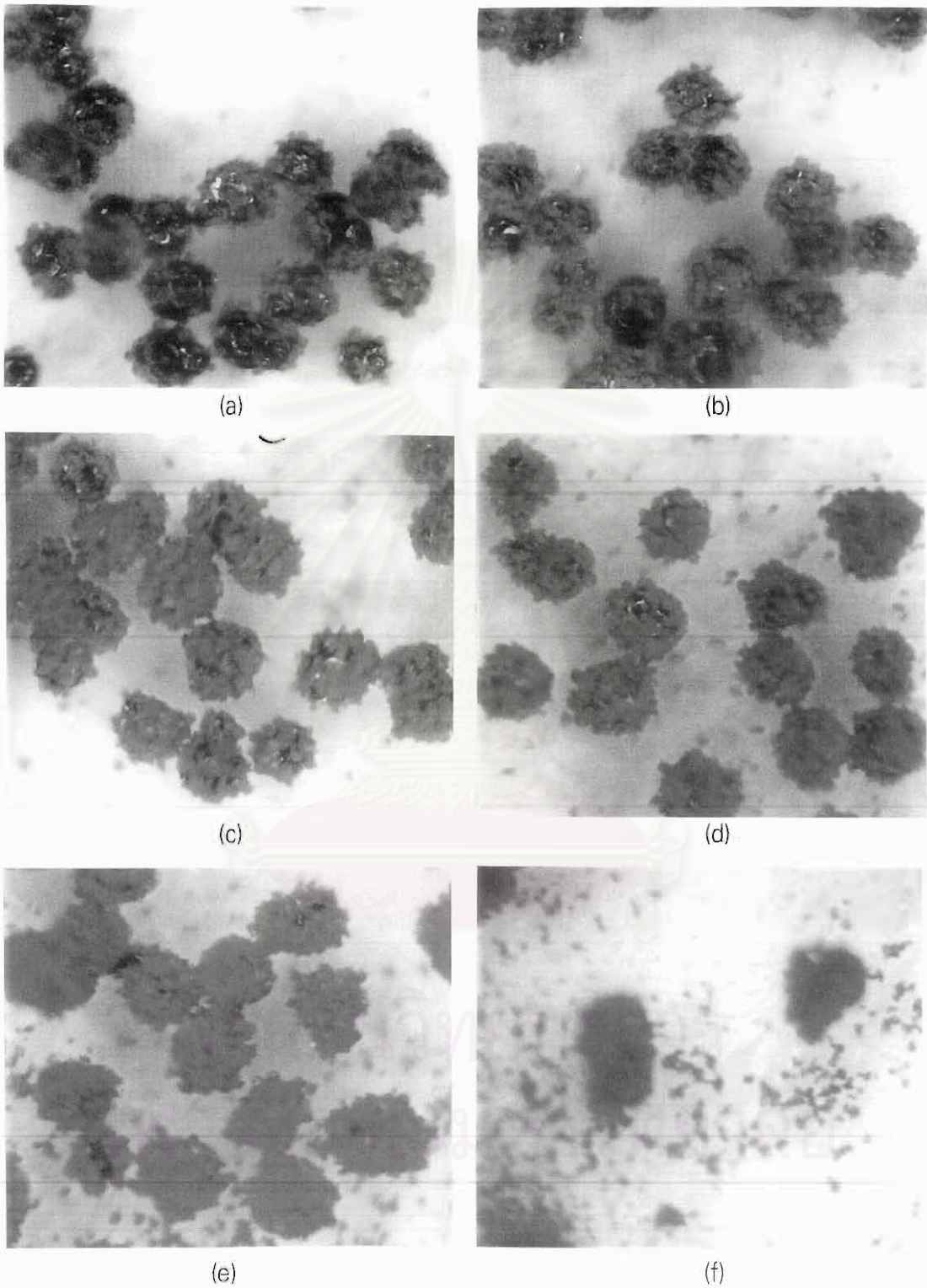


Figure 4-57 Color optical micrographs (x140) of the cyan developer B with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

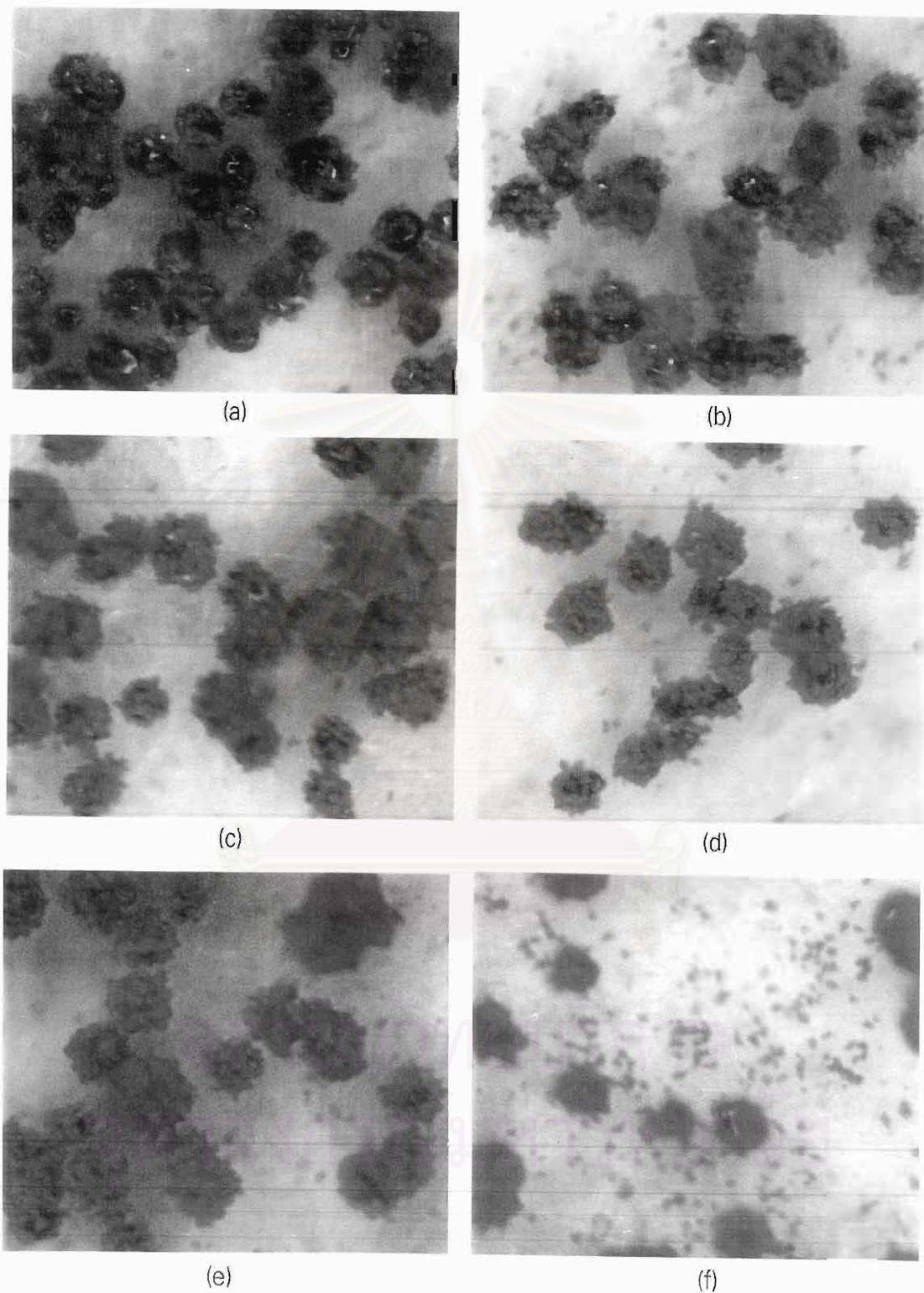


Figure 4-58 Color optical micrographs (x140) of the cyan developer C with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

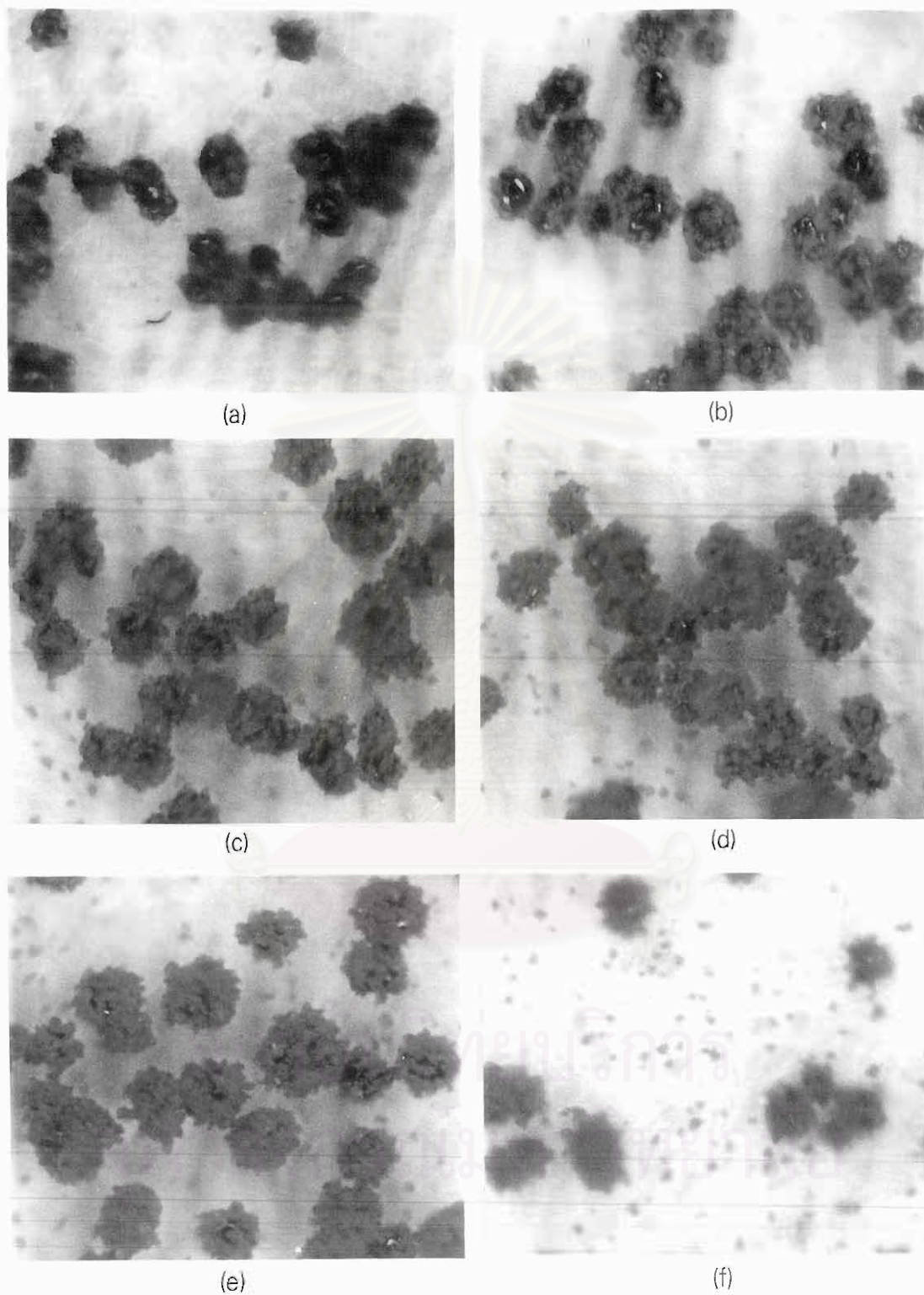


Figure 4-59 Color optical micrographs (x140) of the cyan developer D with various T/C : (a) 3%, (b) 5%, (c) 8%, (d) 10%, (e) 15%, (f) free toners of 15%

Table 4-2 Analysis of a developer particle

Developer	Diameter (micro m)	Radius (micro m)	Volume (cubic mm)	Surface area (square mm)	Mass (mg)
carrier A	86.57	43.285	3.40E-04	2.35E-02	1.73E-03
carrier B	57.58	28.79	9.99E-05	1.04E-02	5.10E-04
carrier C	48.35	24.175	5.92E-05	7.34E-03	3.02E-04
carrier D	45.99	22.995	5.09E-05	6.64E-03	2.60E-04
red toner	9.49	4.745	4.47E-07	2.83E-04	4.47E-07
cyan toner	6.47	3.235	1.42E-07	1.31E-04	1.42E-07

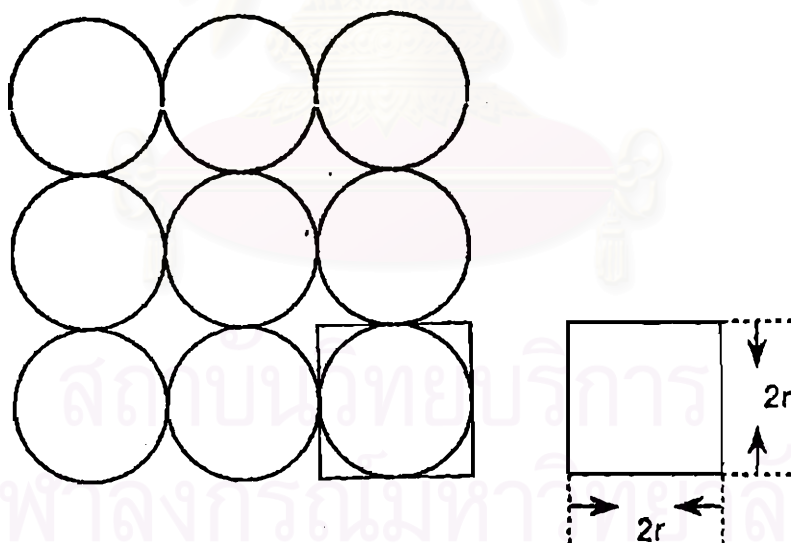


Figure 4-60 Schematic of a toner effective cross area

Table 4-2 shows the carrier radius (R), the toner radius (r), a carrier volume = $4/3 \pi R^3$, a toner volume = $4/3 \pi r^3$, a carrier surface area = $4 \pi R^2$, a carrier mass = a carrier volume x carrier density (5.1), and a toner mass = a toner volume x toner density (1.0). The calculated coverage area of a toner on a carrier surface is $4 r^2$ (a toner effective cross area) as the schematic in Figure 4-60. Consequently, the maximum number of toner particles on a carrier ($\max T_n / 1C$) can be obtained by Equation 4-1 as shown in Table 4-3.

$$\max T_n / 1C = \text{a carrier surface area} / \text{coverage area of a toner} \quad (4-1)$$

Table 4-3 Maximum number of the red and the cyan toner particles covering on a carrier (A - D)

Carrier	Max $Tr_n / 1C$	Max $Tc_n / 1C$
A	261	562
B	116	249
C	82	175
D	74	159

Tr_n : The number of red toner particles

Tc_n : The number of cyan toner particles

Table 4-4 The amount of red toner-to-carrier A-D ratio

T/C	Tn	Cn(A)	Tn/C(A)	Cn(B)	Tn/C(B)	Cn(C)	Tn/C(C)	Cn(D)	Tn/C(D)
1%	2,237,136	57,225	39	194,118	12	327,815	7	380,769	6
3%	6,711,409	56,069	120	190,196	35	321,192	21	373,077	18
5%	11,185,682	54,913	204	186,275	60	314,570	36	365,385	31
8%	17,897,092	53,179	337	180,392	99	304,636	59	353,846	51
10%	22,371,365	52,023	430	176,471	127	298,013	75	346,154	65
15%	33,557,047	49,133	683	166,667	201	281,457	119	326,923	103

Table 4-5 The amount of cyan toner-to-carrier A-D ratio

T/C	Tn	Cn(A)	Tn/C(A)	Cn(B)	Tn/C(B)	Cn(C)	Tn/C(C)	Cn(D)	Tn/C(D)
1%	7,042,254	57,225	123	194,118	36	327,815	21	380,769	18
3%	21,126,761	56,069	377	190,196	111	321,192	66	373,077	57
5%	35,211,268	54,913	641	186,275	189	314,570	112	365,385	96
8%	56,338,028	53,179	1,059	180,392	312	304,636	185	353,846	159
10%	70,422,535	52,023	1,354	176,471	399	298,013	236	346,154	203
15%	105,633,803	49,133	2,150	166,667	634	281,457	376	326,923	323

The amount of red and cyan toner-to-carrier ratio at the various toner concentrations can be calculated as shown in Tables 4-4 and 4-5 by the equation of Yamamoto and Takashima,²⁰ which gives the total number of toner particles deposited onto one carrier particle as Equation 4-2.

$$n = \frac{\rho_c d_c^3 C}{\rho_t d_t^3 (100 - C)} \quad (4-2)$$

where ρ_c , ρ_t = mass density of the carrier and toner, d_c , d_t = diameter of the carrier and toner, and C = toner concentration (%).

The coverage percentages of the red and the cyan toner on a carrier are then obtained as Tables 4-6 and 4-7 by the expression of Equation 4-3.

$$\text{Coverage percentage} = \frac{\text{toner-to-carrier ratio}}{\max T_n / 1C} \times 100 \quad (4-3)$$

Table 4-6 Coverage percentage of the red toner on a carrier

T/C (%)	Carrier A	Carrier B	Carrier C	Carrier D
1	14.94	10.34	8.54	8.11
3	45.98	30.17	25.61	24.32
5	78.16	51.72	43.90	41.89
8	129.12	85.34	71.95	68.92
10	164.75	109.48	91.46	87.84
15	261.69	173.28	145.12	139.19

Table 4-7 Coverage percentage of the cyan toner on a carrier

T/C (%)	Carrier A	Carrier B	Carrier C	Carrier D
1	21.89	14.46	12.00	11.32
3	67.08	44.58	37.71	35.85
5	114.06	75.90	64.00	60.38
8	188.43	125.30	105.71	100.00
10	240.93	160.24	134.86	127.67
15	382.56	254.62	214.29	203.14

These data can be plotted for the toner coverage on a carrier as a function of T/C as shown in Figures 4-61 and 4-62.

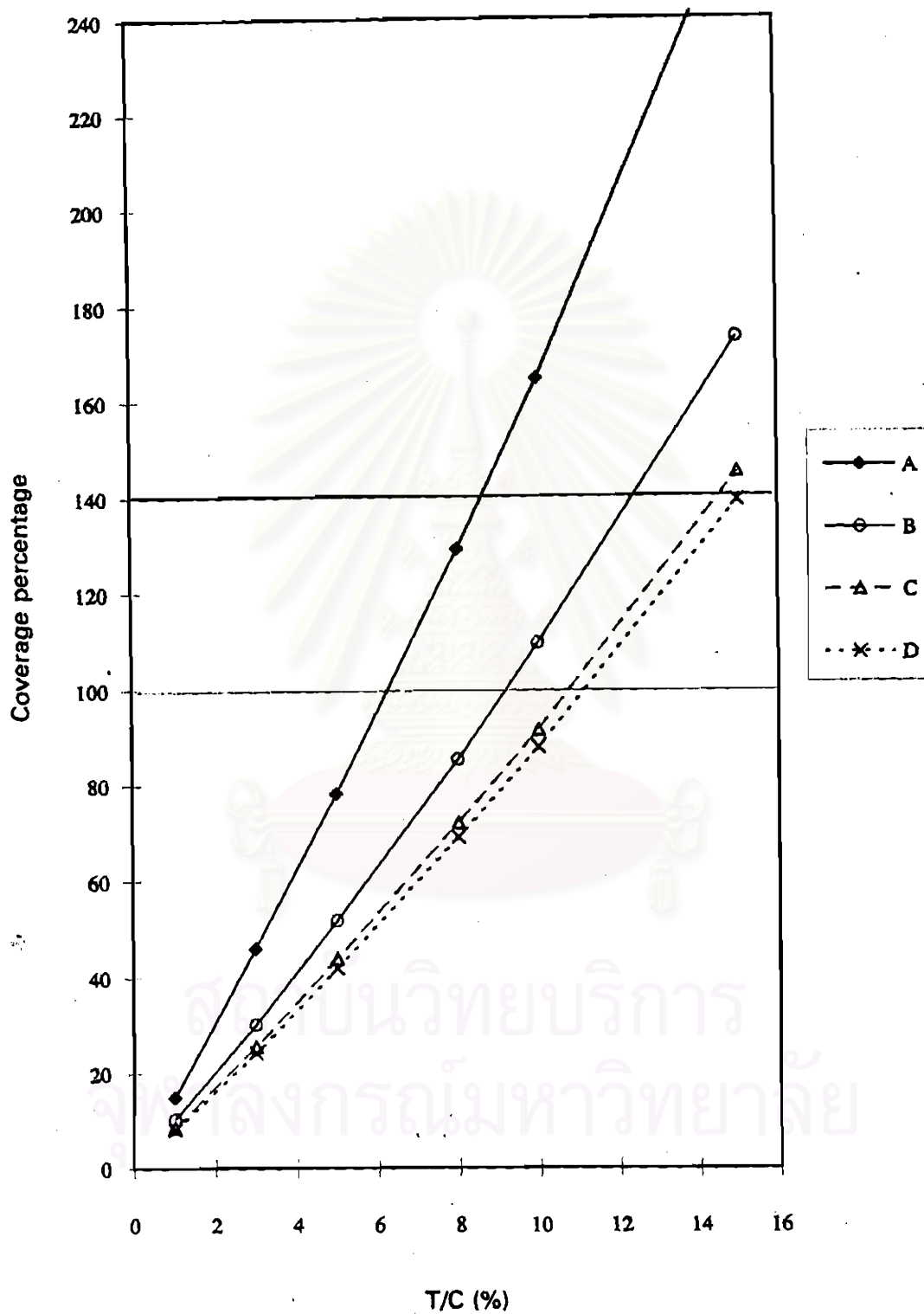


Figure 4-61 Coverage percentage of red toners on a carrier

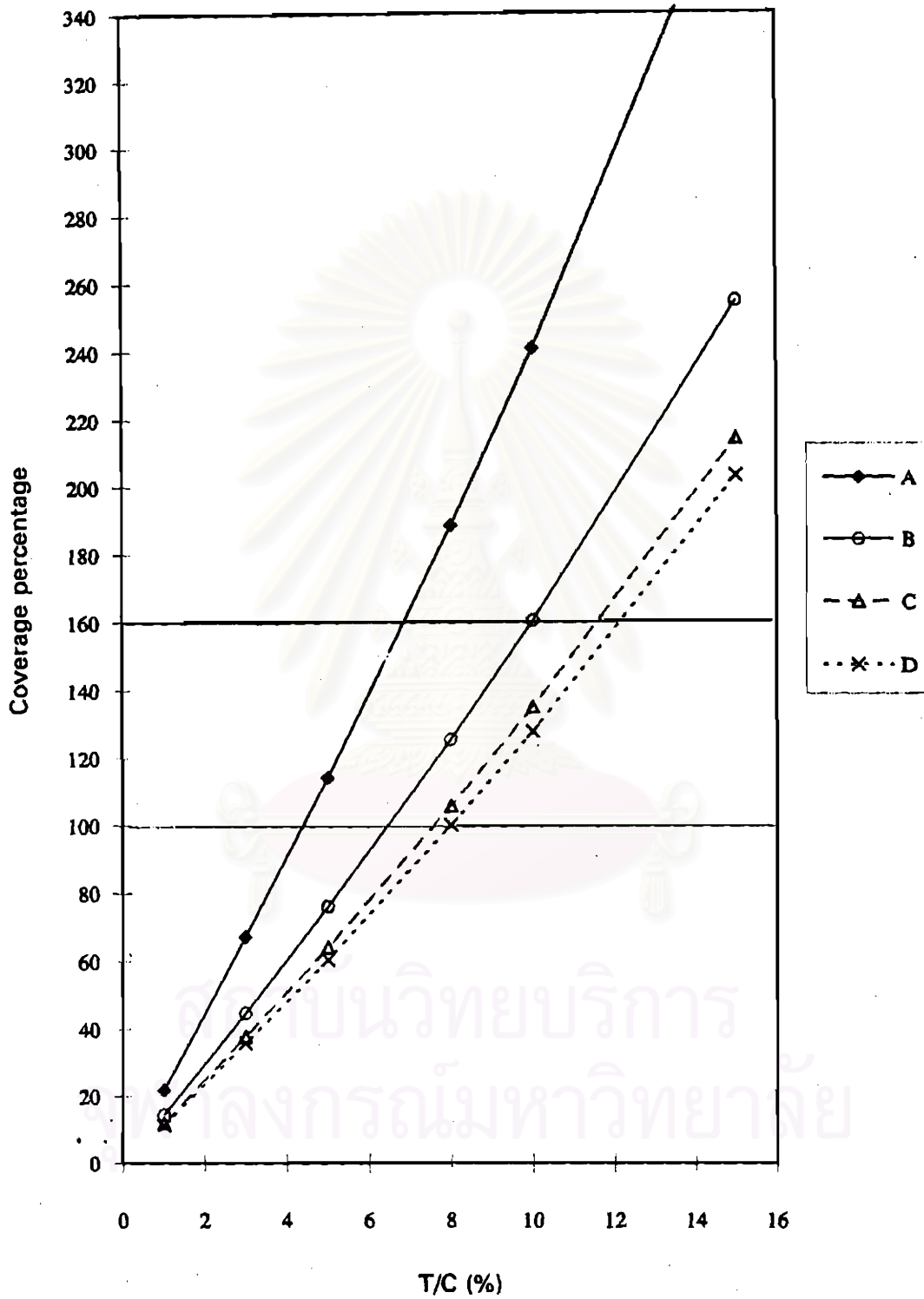


Figure 4-62 Coverage percentage of cyan toners on a carrier

Full coverage of the red and the cyan toners on a carrier A, B, C or D is 100% as indicated by the thin line. Figure 4-61 shows that the red toner concentration of 100% coverage on a carrier A, B, C and D surface is about 6.32%, 9.21%, 10.78% and 11.27%, respectively. Similarly, Figure 4-62 shows that the cyan toner concentration of 100% coverage on a carrier A, B, C and D surface is about 4.4%, 6.47%, 7.61% and 8%, respectively. We can get the T/C values at various coverage percentages either by these curves or by calculation. The limit of the amount of toner that can touch the carrier surface is determined by the toner concentration, which becomes higher when the carrier particle diameter becomes smaller,²⁰ and the limited T/C of the smaller toner is lower than that of the larger toner.

We suppose that the maximum T/C of a developer should be 100% toner coverage, in order to be fully developed without free toners. However, it is only one layer of toner covering on a carrier surface, which is not a limit of the amount of toner covering on a carrier, because the micrographs of the developers with 10-15% T/C in Figures 4-50 and 4-51 show that a carrier can be covered by double layers of toner particles, over the pores of toner particles underlay, similar to the model scheme in Figure 2-18. Therefore, the percentage of toner coverage can be assumed between 100% - 200% with a few free toners, as shown in Figures 4-52 to 4-59 (f). That is a purpose to investigate the effect of toner coverage on a carrier surface by the charge measurement and the print test of the developers with various toner concentrations, and consequently, the optimum range of toner concentration can then be obtained in Table 4-8.

Table 4-8 The Optimum range of toner concentrations and q/m values of the red toner and the cyan toner mixed with the carriers A to D

Carrier	Red toner		Cyan toner		
	T/C (%)	q/m ($\mu\text{C/g}$)	T/C (%)	q/m_1 ($\mu\text{C/g}$)	q/m_2 ($\mu\text{C/g}$)
A	6 - 9	15 - 20	5 - 7	15 - 24	25 - 32
B	5 - 12	15 - 20	6 - 10	15 - 25	23 - 29
C	5 - 14	15 - 18	7 - 12	15 - 23	22 - 27
D	5 - 15	15 - 18	8 - 14	15 - 22	21 - 25

q/m_1 : measured in a high humidity condition (50-60 %RH)

q/m_2 : measured in a low humidity condition (40-50 %RH)

We found that the toner concentrations of carriers A to D which began to produce a fog density on the background could be approximately corresponded to 140% of red toner coverage and 160% of cyan toner coverage, based on Figures 4-61 and 4-62. According to Yamamoto's explanation, when the amount of the toner exceeds the limit (140% or 160%) where the toner can contact the surface of the carrier, the triboelectrification will become insufficient. Such a developer will cause scattering of the uncharged toner or a background development by the toner of reverse polarity. Therefore, the limit of mixing is determined by the probability of the contact between two materials. If all the surface of the carrier is occupied by toner, the surplus toner will not be charged enough. The limit of the amount of toner that can touch the carrier surface is determined by the ratio of the toner and carrier, i.e., the toner concentration.²⁰

The limit of the small cyan toner is higher than that of the large red toner because the amount of small toner which can contact the surface of carrier is more than that of the large toner. The small toner particles in the first layer would open at many poles to accommodate the toner particles in the second layer which can be closer to the carrier surface, due to a smaller diameter of the toner. Consequently, the carrier can better contain more smaller toner particles with more contact electrostatic field (E_v),¹⁷ and has higher coverage of the smaller toner.

4.3.10 Comparing the red toner and the cyan toner

We found that the q/m values of the red toner and cyan toner depend similarly on the shaking time, the toner concentration, and the carrier size. That is, the q/m is saturated within 60 seconds of hand-shaking time, and the q/m value decreases with increasing toner concentration; and the latitude of T/C is wider by mixing with the smaller carrier. However, the q/m of the red toner is more decreased by a longer shaking time, but less decreased by increasing the toner concentrations and the carrier sizes than those of the cyan toner. These different results are correlated to the toner size in that the red toner is larger than the cyan toner.

In case of small toner size, the dependence of toner charge on carrier size is higher, so the latitude of q/m becomes narrow compared to the large toner size. The q/m value of the cyan toner was higher than that of the red toner at the lower 5% T/C. The q/m of cyan toner was, however, more rapidly decreased with increasing T/C and became lower than that of the red toner when the T/C is higher than 8% (see Figures 4-15 and 4-26). Because at low T/C, the toner q/m generally depends on the number of tribocharge sites on the toner and carrier. The small toner

has more surface area per mass, so the tribocharge sites are higher, and then the q/m is higher than is the large toner. According to Ming-Chu, he reported that the larger toner particle size was, the lower the toner tribo-charge would be.¹⁴ Unlikely, when the T/C is too high, the q/m depends on the toner coverage on a carrier. The q/m of the small toner is lower than that of the large toner because the coverage percentage of the small toner on the carrier is higher in the same toner concentration, as shown in Figures 4-61 and 4-62. It is necessary that a carrier size should be changed corresponding to a toner size.

The latitude of T/C which gives an optimum q/m value is wider for the larger toner, as shown in Table 4-8. The minimum of T/C value which corresponds to the maximum of q/m value can produce high density. Likewise, the maximum of T/C value corresponding to the minimum of q/m value produces a copy without background fog. It shows that the minimum T/C of the small toner is higher, and the maximum T/C is lower than that of the larger toner. The lower limit of cyan toner concentration can be determined from the charge level. Its charge is too high at low T/C, and too low at high T/C.

The cyan solid density is higher than that of the red solid density, because the amount of small toner particles accommodated on a carrier is more than that of the large toner. With the same toner mass per unit area of an image, the amount of small toner particles is more than that of the large toner particles, and the small toner can fit more easily into a space of the solid image with a smooth and glossy surface, resulting in a higher density. Though the toner size is large and the q/m value is in an adequate range, the image density becomes low due to the lack of toner particles on the image area. The large toners can not fill smoothly in the solid

image area, so the image surface is rough resulting in a lower density. The small toner can give better tone reproduction and higher resolution than does the large toner. The curves of continuous tone reproduction show that slope of the curves (gamma) of cyan copies are lower than those of the red copies, which mean that the small toner can produce a good tone reproduction of an original image. Figures 4-40, 4-41, 4-48 and 4-49 imply that the line images of the red copies were larger, and % dot gains in halftone images of the red copies were higher than those of the cyan copies, due to the large size of the red toner. According to Sato,⁵ Mizes,⁶ and Ming-Chu,¹⁴ the small toner particle size improves the print quality in solid density, line resolution, and halftone reproduction.

4.3.11 Analysis of the thermal behavior of the toners

Transition temperatures of the red and cyan toners were analyzed for the fixing behavior of the toner, which directly relates to print quality. The data of DSC shown in Appendix D indicate that the glass transition temperature (T_g) of the copolymer resin in the red toner is 59°C, with a diffuse melting temperature at around 140 - 160°C. The glass transition temperature (T_g) of the copolymer resin in the cyan toner is 54°C, which is lower than that of the red toner resin. The lower T_g of the cyan toner is also related to the print sharpness after fixation, that is, the cyan toner image can be rapidly melted and nicely fixed on the substrate. The surface of the cyan image is anticipated to be smooth and glossy, resulting in a higher density as shown in our experiment. In contrast, the red toner image is slowly melted and fixed, consequently, the lines and halftone images of the red toner are expected to be more spread than those of the cyan toner. The surface of the red image is also rough and matt to result in a lower density image.