

A Study of Mixing Characteristics for Cosmetic Fine Powder

Lee, J. W., Song, K. Y., Suh, D. S., Yoo, Y. C., Lee, H. J. and Kang, S. H.

Cosmetic Research Institute, Lucky,
150 Songjung-Dong, Cheong-Ju, 360-290, Korea

화장품용 미분체 혼합공정에서의 분산특성 연구

이종욱, 송건용, 서동성, 유영창, 이현진, 강세훈
럭키 화장품 연구소

Abstract

The cosmetic fine powders were mixed with variation of mixing time(s) in the mixers (ribbon mixer, powder mixer, micropulverizer and fine impact mill). The powders were mixed with small amount of ferric oxide as tracer. The mixed powders were measured the particle size distribution, specific surface area and surface color with mixing time (s). The color variation, particle size distribution and specific surface area of the mixed powder exist a relationship with mixing time(s) that can be expressed as mathematical equations to show the degree of the mixing of the powder mixture. The linear velocity of the impellar tip is the main factor contributing to the mixing efficiency of the mixers un this study. According to the linear velocity, the mixers used are devieded as convection mixing (ribbon mixer), shera mixing (powder mixer) and diffusion mixing (micropulverizer/fine impact mill).

1. Introduction

Powder mixing technology requires even distribution of powder mixtures which have different physical and chemical properties. Fine powder exists in the secondary

coagulated state or higher because of strong adhesiveness from the manufacturing processes both in breaking down processes and building up processes.[1]

Powder mixture contains more than two physico-chemically different kinds of powders. These might have had microscopic and macroscopic homogeneity especially in the manufacturing process of cosmetics, paint, ink, thin films and medicine. The degree of mixing of powder mixtures is related to the stability of system, surface color, viscosity (hardness), electrostatic force, conductivity (thermal and electric), surface charge and behavior in gravitational fields, because the properties of powder mixtures are influenced by specific surface area, particle size distribution, electrostatic attraction and repulsion, iso-electric point, pH and so on.

The powder mixing process isn't well understood because of large variations among characteristics of each particle. Classically, the energy consumptions during mixing were measured to evaluate the mixing efficiency of the mixers.[2] These methods have some limitations because the energy dissipates to the surroundings or is transformed into heat during the mechanical operation, and consequently, the mixing efficiency becomes too faint to measure.[3]

There are some reports for mixing and crushing.[4] Kick(1885) proposed in his study that particle size of powder is inversely proportional to energy consumption before/after crushing. A crushing law suggested by Rittinger in 1867 states that the work required in crushing is proportional to the new surface area created. These studies have shown that the measurement of particle size and/or surface area can be difficult to determine the degree of mixing or crushing. Satoh et al.(1993) reported a study on evaluation of the mixing characteristics of solid mixers using adhesive fine powders.[5] They introduced a small quantity of colorants for testing mixing efficiency.

In this study, we tried to evaluate the degree of mixing for cosmetic fine powder mixtures in various kinds of cosmetic mixers by using colorants. The color variation during mixing was measured to understand the degree of mixing with various mixing time(s), particle size distribution, specific surface area, and was correlated to the linear velocity of the impeller tip of the various kinds of mixers.

2. Theoretical

2.1 Experimental assumptions

Generally, cosmetic fine powders are manufactured by two kinds of powder manufacturing processes: a breaking down processes or a building up processes.[6] Breaking down processes composed of size reduction and classification processes while

building up processes include nucleation, crystal growth control, liquid separation, drying and atomization processes. Whatever process is used, the powder becomes thermodynamically unstable because of its high surface area. Powder tends to aggregate intrinsically because of its surface properties. Many investigators try to understand the mixing characteristics of powder mixtures by fractal theory,[7] surface chemistry[8,9] and powder characterization.[10]

In this study, we tried to understand how the aggregates are atomized during mixing process. There are several assumptions as follows: 1) Size reduction of primary particles is neglected. 2) There is no intercalation of tracer into a bulk powder. 3) There is no chemical reaction on powder surfaces and 4) The effect of heat and mass transfer are neglected.

2.2 Geometric modeling (geometrical expression for powder mixing process)

Figure 1 shows a schematic diagram of the atomization process for n-th coagulated particles by external force (mechanical stress) during mixing. The tertiary particle is aggregated with eight secondary particles or 64 primary particles without void. This means that, although the number of primary particles is constant, the number of aggregated particles is varied with mixing degree. If one primary particle has six surface areas, the surface areas of aggregated particles of 64 primary particles are expressed as 96 for tertiary, 192 for secondary and 384 for primary particle.

3. Experimental

3.1 Experimental methods

Pigments and pigment mixtures were mixed with various mixing velocities and mixing time(s) in each mixer indicated below. Each sample collected was pressed on a rectangular aluminium dish (3X4cm) at 10 pas/cm². The resulting surface color was measured by Computer Color Matching System.

3.2 Materials

Titanium dioxide (Sun Chemical, UK), calcium carbonate (Choongmu Chem, Korea), polymethylmethacrylate (Soken, Japan), nylon (Toray, Japan), spherical silica (Miyoshi, Japan), talc (Ilshin talc, Korea) and mica (Mikwang Unmo, Korea) were used as bulk powders. As tracer materials, three kinds of ferric oxides (red:Fe₂O₃, yellow:Fe₂O₃.xH₂O and black:FeO.Fe₂O₃, Miyoshi, Japan) were used. All powder materials were medical or cosmetic grade.

3.3 Mixers

Four kinds of mixers were used in this work. Ribbon mixer (Choong Chung Machine, Korea) was used as convective mixer, powder mixer (Mizuho, Japan) was used for shear mixing, and micropulverizer (Hosokawa Micron, Japan) and fine impact mill (Alpine Akiengesellschaft, Germany) were used for diffusion mixing. Table 1 shows the characteristics of the mixers used.

Linear Velocity, in table 1, is calculated for the rotating impeller tip from Eqn.(1) as follows

$$U = \pi D n \quad (1)$$

where,

U = linear velocity at impeller tip, [m/s]

D = diameter of impeller, [m]

n = rpm of impeller(X60), [-]

3.4 Measurements

Generally, for describing the properties of powders, physical parameters such as particle size distribution, specific surface area, particle shapes and density (true, loose, tapped) were measured. Particle size distribution and specific surface area were measured by a Particle Sizer (Brookhaven Inc., USA). It can be measured by two different ways, according to operational conditions, sedimentation method and disk rotation method. True density was measured by a Multi Pycnometer MVP-1 (Quanta Chrome Corp., USA). Loose and tapped density were measured by a Stampvolumeter (J. Engelsmann A.G., Germany) before and after tapping 1000 times. Particle shape was observed by using a Scanning Electron Microscope (Jeol JSM-840A, Japan) and an optical microscope (Nikon Labophot, Japan). Surface color was measured by a Chroma Sensor (ACS-5, USA) with light source D-65. Perfect dispersion was achieved by using a surfactant (STPP, 0.5wt%) with a few minutes of sonication by Ultrasonic Processor (W385, Heat System Inc., USA).

Table 2 shows the physical properties of the powder materials.

4. Discussion

4.1 Measurements of particle size distribution

A Typical results of measurements of particle size distribution for calcium carbonate by XDC Particle Sizer with disk speed 1000rpm are shown in figure 2. The sample was made of 0.5wt% calcium carbonate dispersed into 0.5wt% surfactant (STPP) solution with sonication for 1 minute. Cumulative and differential mass distribution curves showed $2.52E-6\mu$ volume mean diameter and $0.944\text{ m}^2/\text{g}$ specific surface area.

4.2 Tracing the mixing steps

Mixing mechanisms can be divided into three steps.[11] During macroscopic mixing (convective mixing), the powders are mixed as a coagulated state. Between convective mixing and perfect mixing there is a partially mixed state called shear mixing. Perfect mixing is diffusion mixing that results in a completely atomized mixing state. Diffusion mixing is composed of very high speeds or long time(s).

There are three kinds of powders in their shape of primary particles such as fine, spherical and plate types. In figure 3, schematic diagrams for fine(a), spherical(b) and plate(c) shape according to mixing steps are represented. During the mixing step the bulk powders are dispersed to primary particles and adhere the trace colorants on their surface.

Figure 4 shows SEM images for three bulk powder systems mixed with ferric oxide as a tracer colorant, a) shows mixed state of ferric oxide/titanium dioxide (X20,000), b) and c) show spherical silica and plate mica (X3,000). The tracer was observed as white spots.

4.3 Results of color change

The color change during mixing was calculated as following equation(2)

$$\Delta E = \sqrt{(L-L')^2 + (a-a')^2 + (b-b')^2} \quad (2)$$

where, ΔE = dimensionless numerical expression for total color difference on 3 axes coordinate before and/or after mixing

L = whiteness of sample surface before mixing

L' = whiteness of sample surface after mixing

a = redness of sample surface before mixing

a' = redness of sample surface after mixing

b = yellowness of sample surface before mixing

b' = yellowness of sample surface after mixing

ΔE can be expressed as the color difference between the the samples for three color components (lightness, redness and yellowness). Measured color difference expresses the vector summation of difference of each color component on

three-coordinates (L,a,b). Figure 5 shows the geometrical expression of the color difference(ΔE) and its three components.

4.4 Relationship between color difference and the degree of mixing

Figure 6 shows the relationship between mixing time(s) and color difference for three colorants and three pigments mixture systems in a powder mixer. Color difference of each component ($\Delta L, \Delta a, \Delta b$) and its vector summation (ΔE) were plotted on the same coordinates. All curves have logarithmic relationships between color difference and mixing time. The same data of figure 6 were plotted on semi-log coordinates in the figure 7 to see the linearity between mixing time and color differences in figure 7 and shows good linearity.

To understand the meaning of figure 7, simple mathematical expressions were cited. The color change of each color component ($\Delta L, \Delta a, \Delta b$) and mixing time(s) have the relationships as follows:

$$\Delta L = a_1 \log T + b_1 \quad (3)$$

$$\Delta a = a_2 \log T + b_2 \quad (4)$$

$$\Delta b = a_3 \log T + b_3 \quad (5)$$

where, ΔL = the difference of lightness, [-]

Δa = the difference of redness, [-]

Δb = the difference of yellowness, [-]

T = mixing time (X60), [s]

a_1, a_2 and a_3 = the slopes on the figure, [-]

b_1, b_2 and b_3 = the intercepts of each line, [-]

and also total color change (ΔE) is expressed as follows:

$$\Delta E = a \log T + b \quad (6)$$

where, a and b are the same notation as equation (5). Equivalent expressions are:

$$\log T = \frac{1}{a} (\Delta E - b) \quad (7)$$

$$T = \exp \frac{1}{a} (\Delta E - b). \quad (8)$$

The above equations (6-8) show that a simple relationship exists between color difference and mixing time(s)

4.5 Variation of particle size and color with mixing time(s)

Figure 8 shows the particle size distributions measured by the Particle Sizer for ferric oxide/mica system varying with mixing times in a micropulverizer. The sample was prepared without sonication to maintain the aggregated states with mixing times. Measurements were performed by sedimentation method. This method was found to be useful for tracing the effect of particle size variation with mixing time(s). Figure 9 shows that volume mean diameters of the powder mixture system were decreased with mixing time(s). Figure 10 shows the relationship between color difference and volume mean diameter. Figure 11 shows the effect of the specific surface area on the variation of volume mean diameter. From these results, the color difference was suggested to be useful in evaluation of the degree of mixing of the cosmetic fine powders.

4.6 Effect of the linear velocity of the impeller tip on the degree of mixing

Figure 12 shows the relationship between color change and linear velocity of the impeller tip. The color changes with three linear velocities (1m/s, 10m/s and 100m/s) were plotted on the semi-log scale. The mixers corresponding to each linear velocity were ribbon mixer, powder mixer and micropulverizer/fine impact mill, respectively. The degree of mixing of the ribbon mixer and the powder mixer, batch-type mixers, is increased with mixing time (minutes). The micropulverizer and the fine impact mill show the similia tendency to mixing times as the CSTR-type mixers.

The ribbon mixer showed a convection mixing region that can not give a primary mixing effect of coagulated powder, but contributes to macroscopic mixing. The powder mixer showed a partially perfect mixing effect if it was operated for a long run-time or at high speed mixing. On the other hand, since the micropulverizer and the fine impact mill run with 100m/s of linear velocity, they showed perfect mixing effects within several mixing times. It could be inferred that the mixing of the powder mixture in the micropulverizer or the fine impact mill would be atomization. This mixers belong to the mixers for diffusion mixing region in which powder mixtures can be mixed perfectly.

From figure 12, the linear velocity of impeller tip and color variation were well correlated on semi-log coordinates. Since the color change of the powder mixture indicates the degree of mixing of the powder mixture, these results mean that the main factor affecting the degree of mixing of the mixtures is the linear velocity of the rotating impeller tip of the mixers used in this study.

5. Results

To understand the main mixing characteristics of cosmetic fine powders, three groups of powders were tested with various linear velocities of the rotating mixer impeller tip in four kinds of cosmetic mixers and with the variations of mixing time(s), particle size distribution, specific surface area and surface color of the powder mixture. Among particle size distribution, specific surface area and color variation, there exists a relationship that can be easily expressed as a mathematical equations to show mixing efficiency. The linear velocity of the impeller tip is the main factor contributing to the mixing efficiency of the mixers used in this study. Although there is some possibilities of variations, this convenient method can be used to help us understanding cosmetic fine powder mixing.

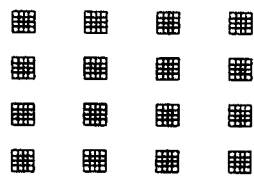
요 약

화장품에 사용되는 미분체의 혼합특성을 알기 위하여 화장품용 미분체 혼합기인 ribbon mixer, powder mixer micropulverizer, fine impact mill에 미립자, 구상 및 판상의 형태를 가진 bulk powders를 혼합시간(회수)을 변화시키면서 혼합하는 실험을 하였다. 혼합분체의 혼합정도를 평가하기 위하여 산화철을 tracer로 사용하였으며, 원료 및 혼합물의 particle size distribution, specific surface area, density(true, loose, tapped) 및 표면색상을 측정하였다. 미분체 혼합물의 혼합시간(회수)과 표면색상변화, 입도분포 및 비표면적과의 사이에 대수적 1차 상관관계가 성립되었고, 색상의 변화로부터 혼합정도를 평가할 수 있는 간단한 식을 도출하였다. 사용된 혼합기에 대해 혼합기구별 modelling과 혼합에 따른 입도 분포 및 비표면적의 변화로부터 혼합기 impeller tip에서의 linear velocity가 혼합도를 결정하는 주요인자임을 알 수 있었다. 본 실험에 사용된 혼합기의 linear velocity별 혼합기는 대류혼합(ribbon mixer), 전단혼합(powder mixer) 및 확산혼합(micropulverizer/fine impact mill)로 분류되었다.

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Schematic model
for mixing mechanism

Order	n-th	(3-rd)	(2-nd)	(1-st)
		tertiary	secondary	primary
No of Particle(p)	...	1	8	64
No of primary particle	...	64	64	64
Surface Area(q)	...	96	192	384
(p/q)	...	0.01	0.04	0.16

Figure 1. A model expressing the relationship between particle size reduction and surface area increase during mixing.

Table 1. Experimental mixers used in this work.

Mixers	rps [1/s]	Linear ¹⁾ Velocity [m/sec]	Capacity [m ³]	Impeller Type [-]	Impeller ²⁾ Diameter [m]	No. of Impeller [-]	Remark
Ribbon Mixer	1.1	1	0.02	Ribbon	0.295	6	Batch-type
Powder Mixer	16.2	10	6.28E-3	Blade	0.197	2	Batch-type
Fine Impact Mill	290.0	100	-	Studdisk	0.110	12	CSTR-type
Micro Pulverizer	253.3	100	-	Hammer	0.125	6	CSTR-type

1) Linear Velocity(U) = $\pi \cdot D \cdot n$

2) Impeller Diameter = D

Table 2. Physical properties of powders used in this work.

Materials	dp ¹⁾ [x10 ⁶]	Density [kg/M ³]		Sv ²⁾ [m ² /g]	Color Value [-]			Shape
		True	Loose Tapped		L	a	b	
Titanium Dioxide	0.55	3900	610	4.210	77.54	-0.11	0.50	fine block
Calcium Carbonate	2.52	2710	805	0.944	97.81	-0.11	0.60	fine block
P.M.M.A	6.72	1180	625	0.234	80.69	-0.23	-0.20	spherical
Nylon	16.67	1120	429	1.650	81.46	1.62	-0.34	spherical
Spherical Silica	5.62	2000	484	0.606	79.24	-0.07	0.22	spherical
Talc	5.83	2750	508	0.395	80.78	0.07	-0.11	plate
Mica	9.35	2820	366	0.237	78.65	2.08	0.37	plate
Ferric Oxide(R)	0.27	4800	500	7.180	42.99	7.48	13.94	fine block
Ferric Oxide(Y)	0.20	4050	536	9.240	55.26	29.98	9.86	fine stick
Ferric Oxide(B)	3.41	5000	484	0.397	33.69	-0.55	0.25	fine block

1) dp : volume mean diameter [m x 10⁶], 2) Sv : specific surface area [m²/g]

BI-XDC

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CUM. AND DIFF. MASS DIST.

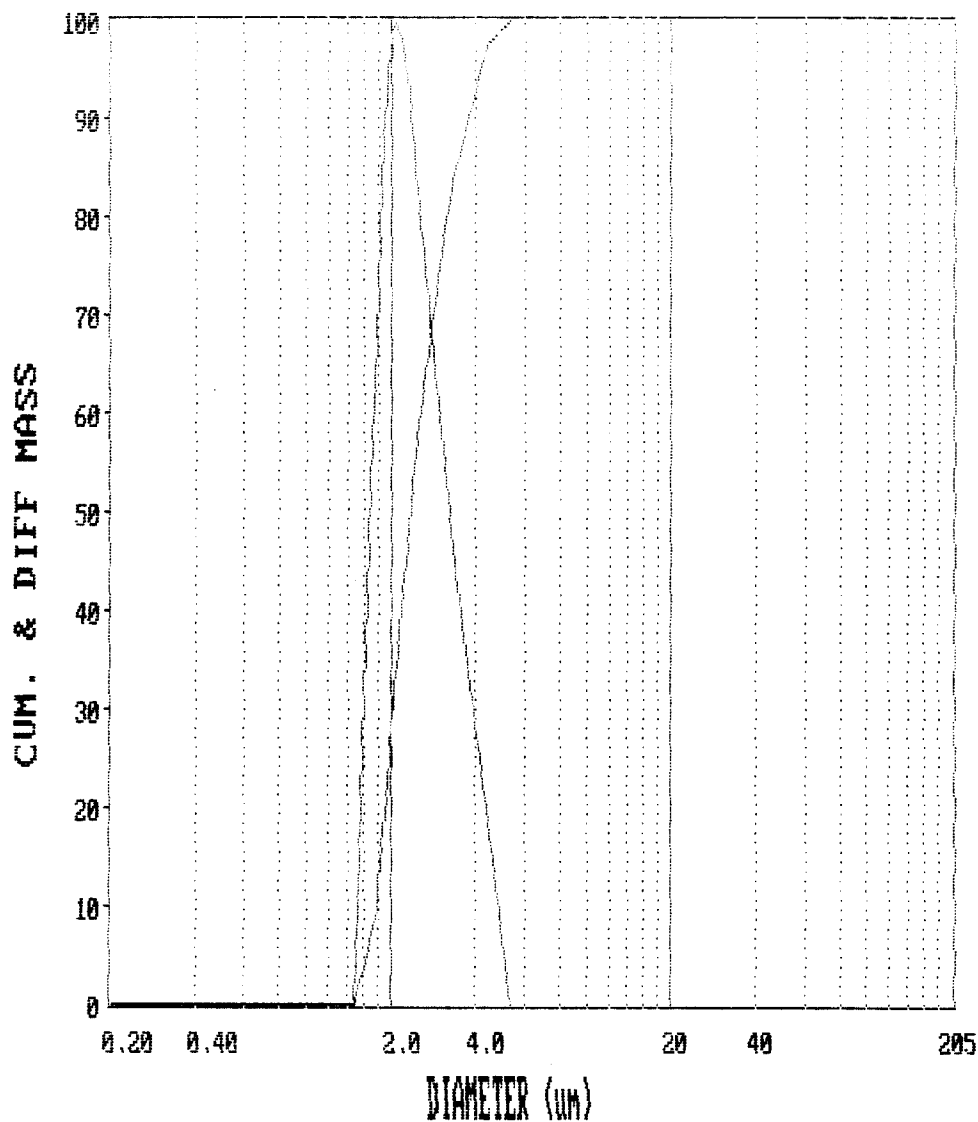
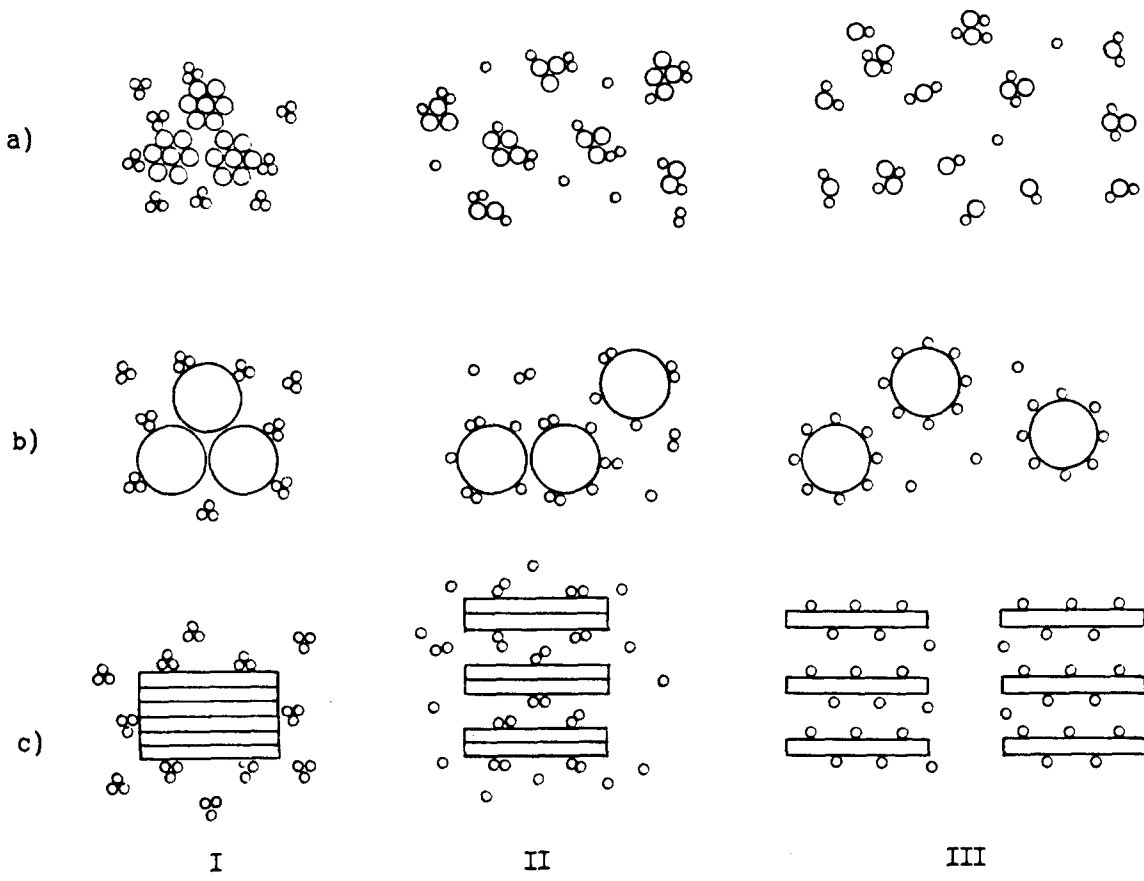


Figure 2. A Typical measurement of the particle size distribution for calcium carbonate by XDC Particle Sizer.



(M i x i n g s t e p)

Figure 3. A schematic diagram for three kinds of the mixing processes. a) fine, b) spherical and c) stratified plate powder

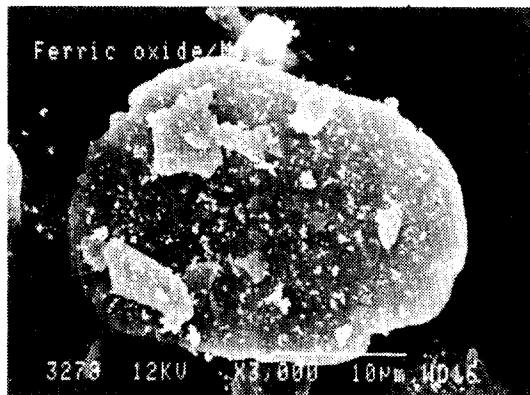
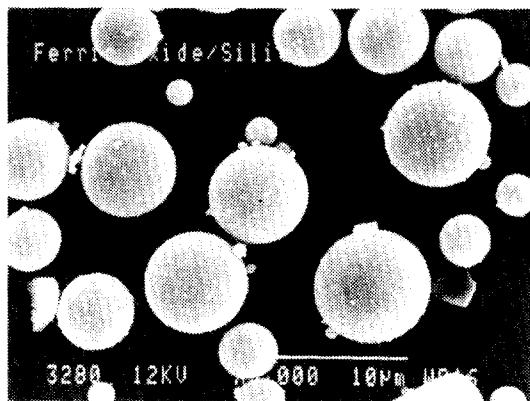
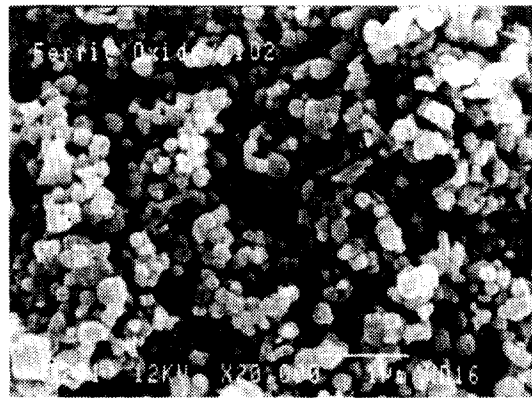


Figure 4. SEM images for three bulk powder systems mixed with tracer colorant. a) TiO_2 (x20,000), B) spherical silica (X3,000) and c) mica(X3,000)

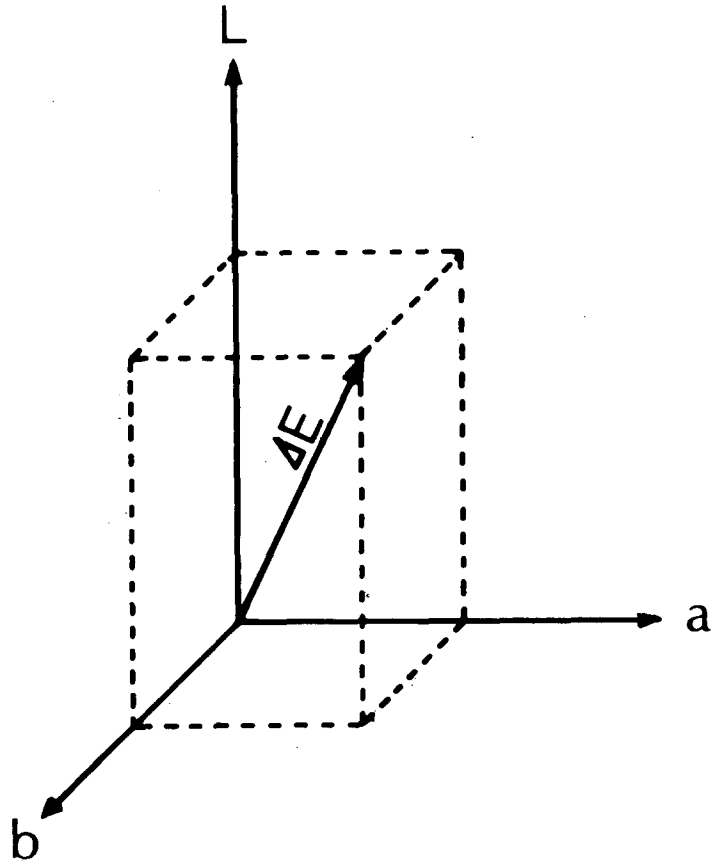


Figure 5. A geometrical expression for the color difference and its three color components, a:blue-red, b:green-yellow and L:black-white.

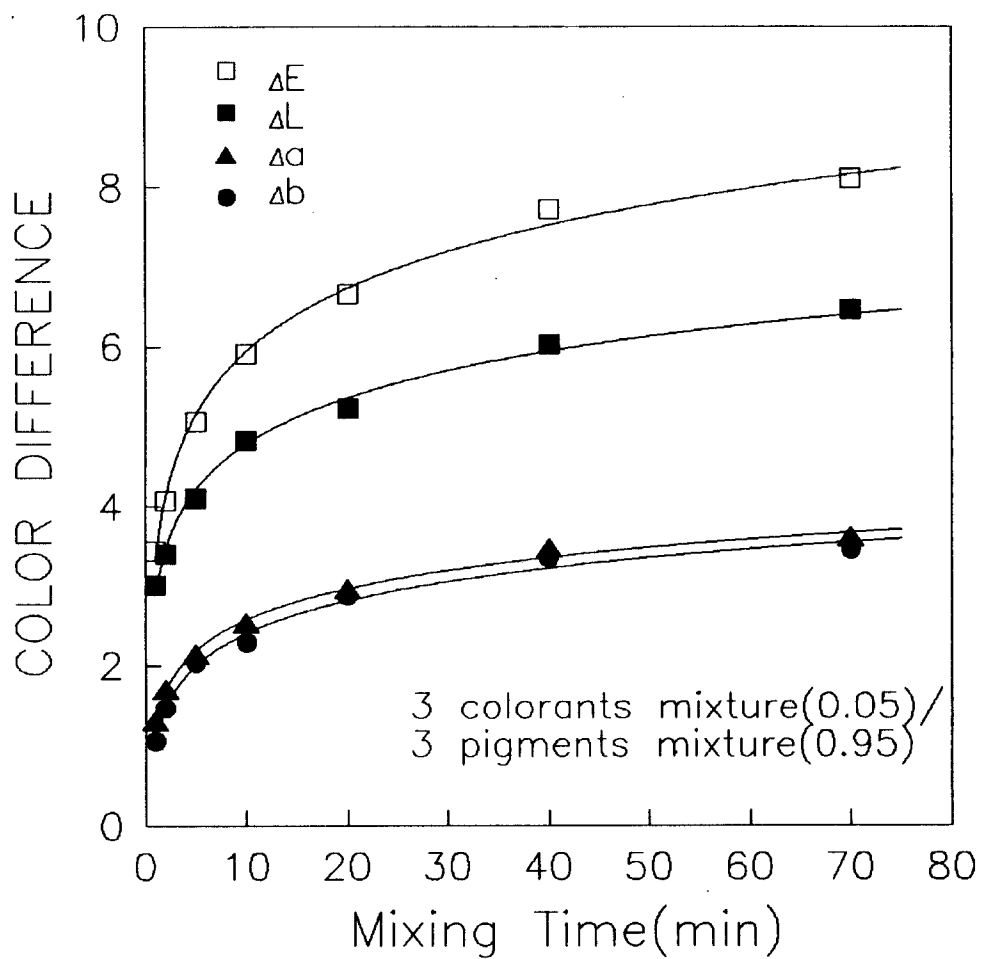


Figure 6. The relationship between mixing time and color difference for three colorants and three bulk pigments mixture systems.

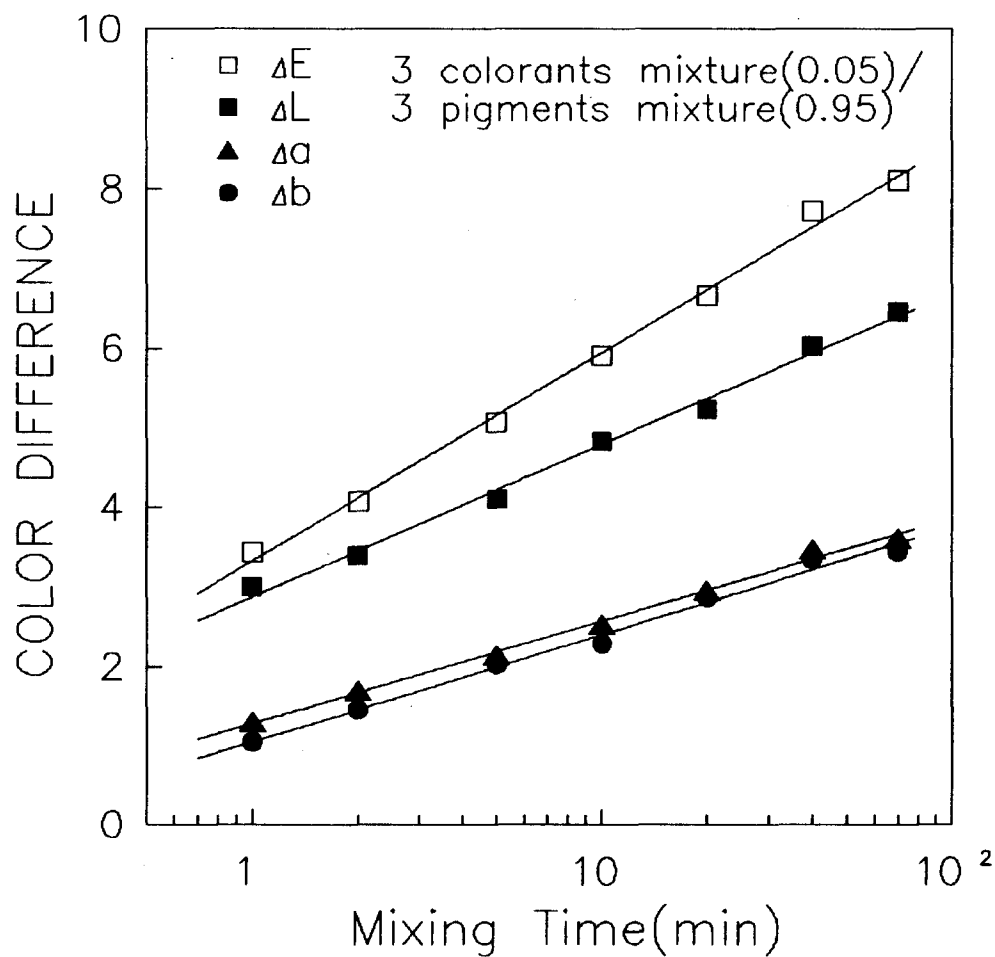


Figure 7. The relationship between mixing time and color difference for three colorants and three bulk pigments mixture systems on semi-log coordinates.

BI-XDC

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DIFFERENTIAL MASS DISTRIBUTION

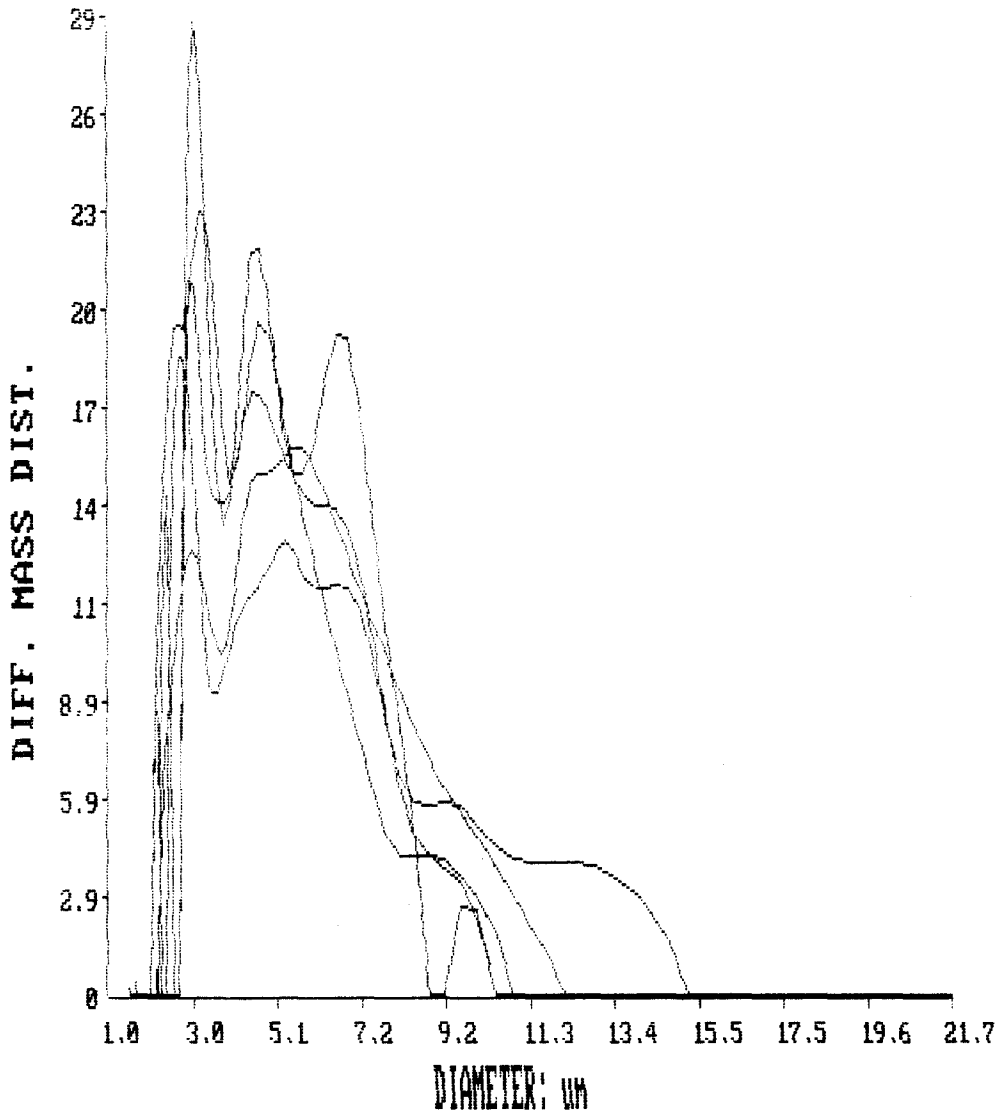


Figure 8. Comparison of particle size distribution for ferric oxide/mica system varying with mixing times in micro-pulverizer measured by XDC-Particle Sizer.

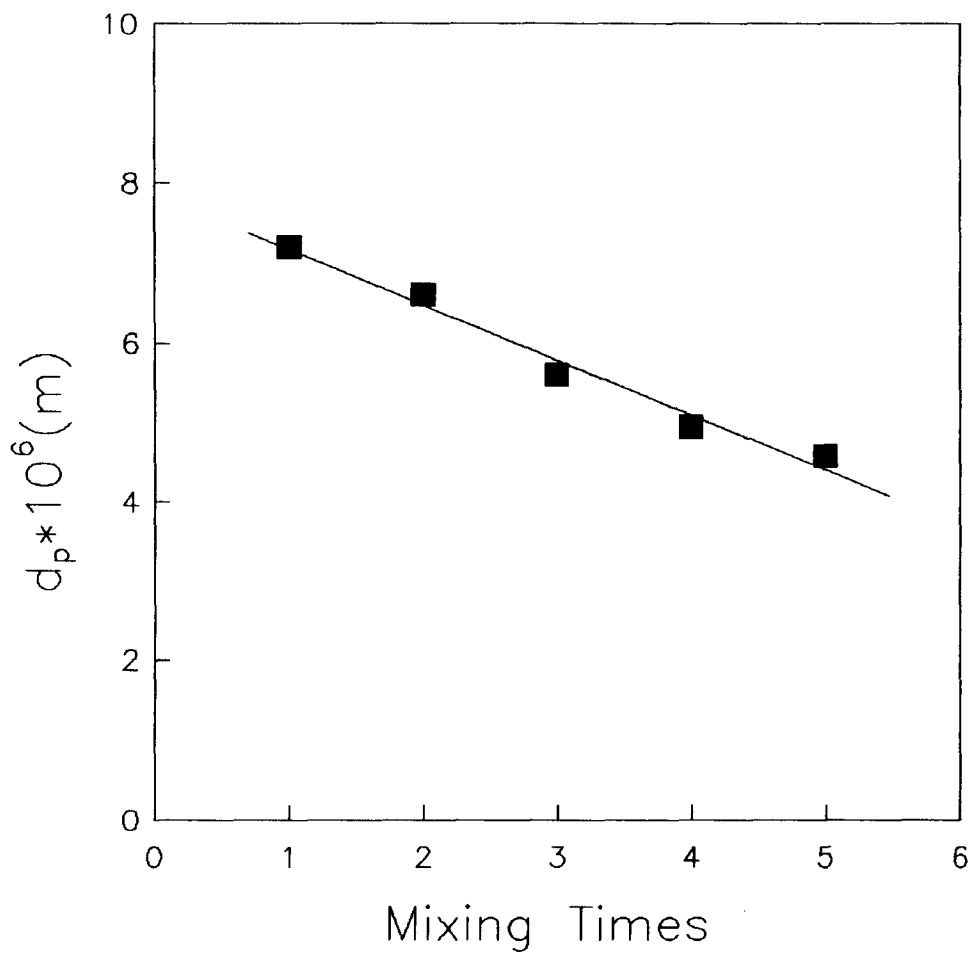


Figure 9. Effect of the mixing times on the variation of the volume mean diameter.

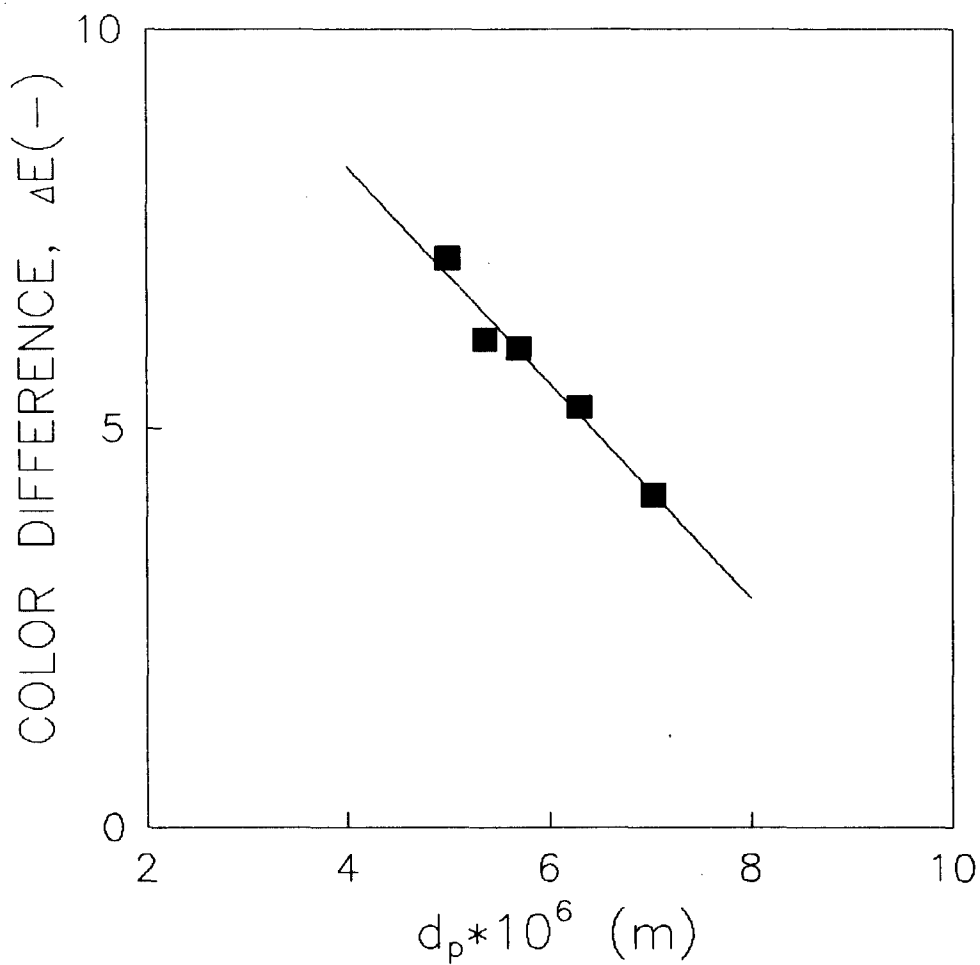


Figure 10. Relationship between the color difference and the volume mean diameter.

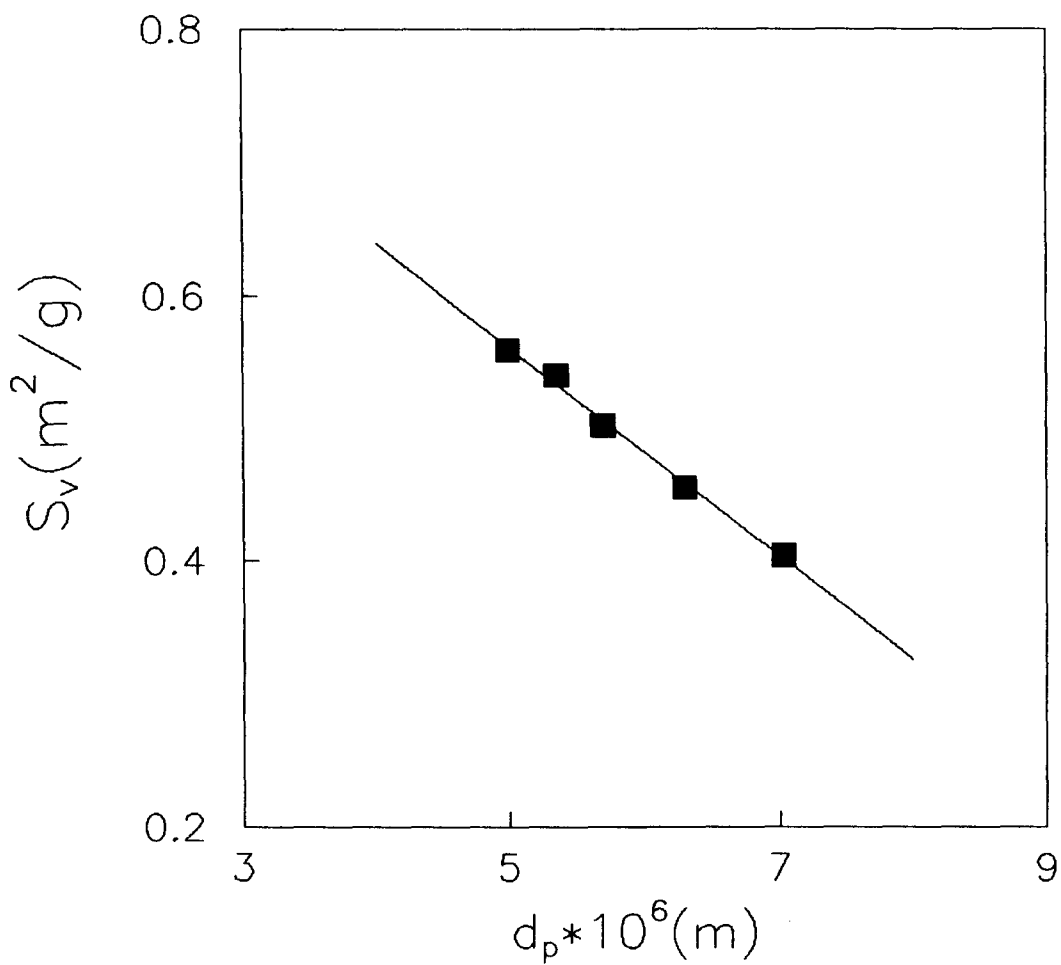


Figure 11. Effect of specific surface area in the variation of volume mean diameter.

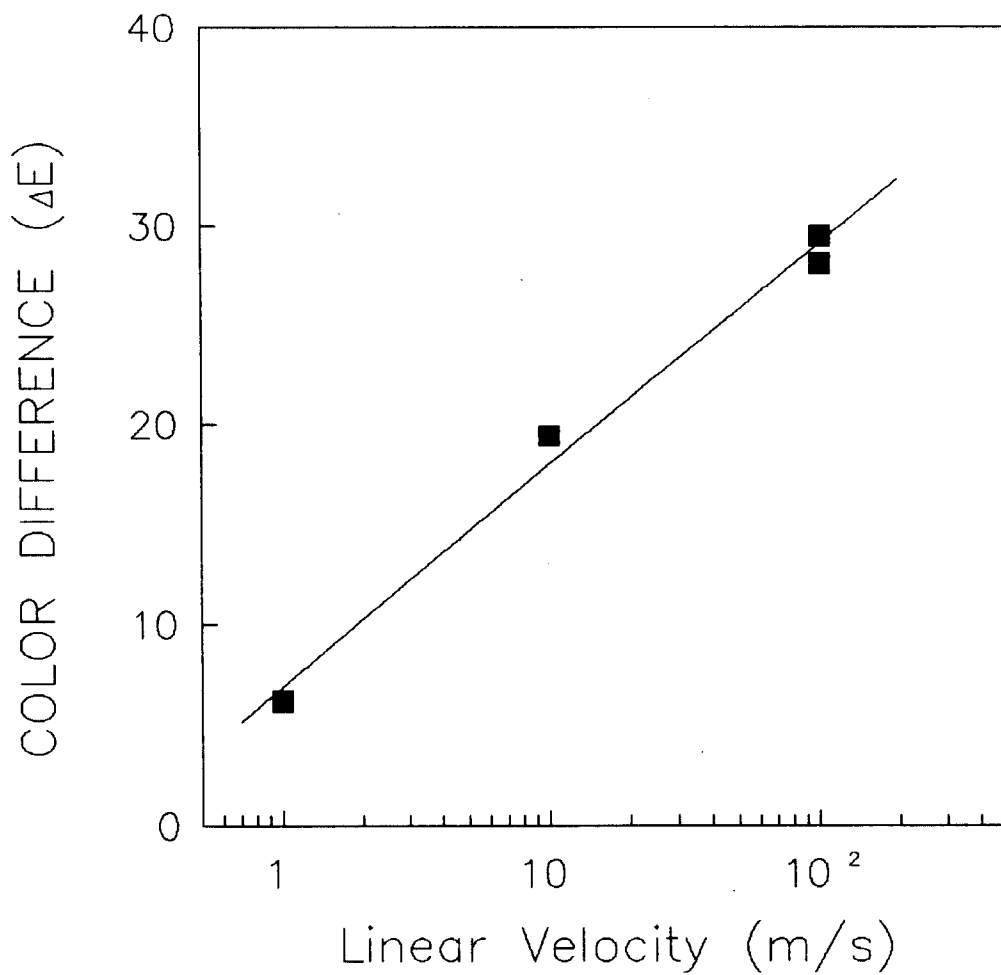


Figure 12. Relationship between the color change and the linear velocity of the impeller tips for three types of the mixers.