Measurement of the Adhesive Force between Particles and a Substrate by Means of the Impact Separation Method. Effect of the Surface Roughness and Type of Material of the Substrate

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In order to study the effect of surface roughness and substrate material type on the adhesion of particles, measurements were made using the pendulum impact separation method using a variety of powders and substrates. Two methods were used to attach powder particles to a substrate: the free falling method and the fluidized method. When the powders were deposited on a substrate by free falling (with negligible force), the force of adhesion to the substrate with a rough surface was less than the adhesion to the smooth surface substrate. The degree of reduction in adhesive force increased as the shape of sample powder more closely resembled a sphere. When the powders were attached to a substrate under a fluidized state, a remarkable increase in adhesive force was observed in organic powder/polyvinyl chloride (PVC) systems. This is probably due to the electrostatic force produced by the collision and/or friction of particles to the PVC sheet.

Keywords adhesive force; impact separation method; surface roughness; free falling method; fluidized method; surface electric potential

In our previous studies[1] of the measurement of adhesion of a variety of powders by the particle separation method, the slide glass was used as the chief substrate, in addition to moisture sorbed polymer films.[1d] However, it is well known that most pharmaceutical powder particles cause trouble when they adhere to the walls of equipment and containers during the drug manufacturing process. The adhesion of powder particles to the surface of tablets, capsules and packaging materials is also a puzzling problem related to the preparation or taking of drugs.

In the present work, the effect of surface roughness and substrate material type on particle adhesion was examined. The adhesive force between particles and a solid surface is affected by many factors. In the pharmaceutical field, the effects of particle diameter, shape,[1c] humidity,[1d,2a] temperature,[1a] static electricity[2b,c] and the presence of surface asperities on particles[1c] have been investigated. As to the surface roughness of a substrate, Corn *et al.*[3] reported a decrease in adhesive force of quartz particles to a Pyrex surface as microscopic roughness increased. The adhesive force between spherical glass particles and a steel surface of different classes of surface finish was reported by Zimon and Volkova.[4] They described that adhesive force depended upon the relative size of particles with asperities on the substrate. Okada *et al.*[5] measured the adhesive force between several pharmaceutical powders and the surface of tablets prepared with the same kind of substance by means of the centrifugal separation method, and reported that adhesive force was independent on surface roughness for all the systems. Booth and Newton[6] investigated the adhesion of two pharmaceutical powders to various types of substrates. They stated that the difference between smooth and rough surfaces was small in most cases, although the adhesive force tended to be slightly less on a rougher surface. In the above references cited, various powders and substrates were used, but the results were diverse, and no clear conclusion has been obtained on the effect of the surface roughness of substrate. This may be caused by the lack of consideration of the shape and surface asperities of particles. In the present study, several kinds of the powder particles with different shapes, and three different types of the substrates with smooth and rough surfaces, were used. In order to examine the effect of surface roughness of the substrate in detail, the adhesion of glass beads to glass substrates ground with three kinds of alumina powder which had different particle sizes was investigated.

In the measurements described above, the powders were deposited on the substrate with negligible force (free falling method). Studies were also carried out on the adhesion of particles attached to the substrate under a fluidized state, and the electrostatic effect on adhesive force was examined.

Experimental

Materials In Table I, several kinds of sample powders with various particle shapes are shown together with the physical properties of these powders. The average particle diameter (Heywood diameter), d, and the particle shape index, ψ_2, were determined by an image analyzer (Luzex 500, Nireco Ltd.). The value of ψ_2 is obtained by dividing the actual projected area of a particle, A, by the area of a circle having a circumference equivalent to the perimeter length of the projected image, PM, as shown in Eq. 1

$$\psi_2=\frac{4\pi A}{PM^2} \qquad (1)$$

TABLE I. Physical Properties of Sample Powders Used

No.	Sample	Average particle diameter d (μm)	Particle density ρ (g/cm³)	Shape index ψ_2	Symbol
1	Glass beads	40.2	2.16	0.933	○
2	Crushed glass	35.4	2.16	0.718	◇
3	Calcium carbonate P-70	26.6	2.67	0.814	⊖
4	Potato starch	41.8	1.48	0.865	⬭
5	Sulfadimethoxine	57.6	1.48	0.729	□
6	Crystalline cellulose	32.1	1.57	0.468	△
7	Croscarmellose sodium	56.9	1.57	0.309	▽
8	Aspirin B-102	42.6	1.35	0.722	⦶

Therefore, the value of ψ_2 ranged from zero to 1 and its value decreased as the surface irregularity of particle increased. The particle density, ρ, was obtained using a helium-air pycnometer (Shimadzu-Micromeritics). Particles of crystalline cellulose and croscarmellose sodium were so porous that the mass of one particle was determined by measuring the number and mass of more than 10000 particles.

Substrates Slide glass for a microscope, polyvinyl chloride (PVC) sheet and stainless steel plate were used as substrates. To prepare the rough surface, these substrates were ground with alumina powder (48 μm). Glass substrates with various surface roughness were obtained by using three kinds of alumina powder with different particle diameters (3, 16, 48 μm) as grinding materials.

Method of Attaching Particles to Substrate Free Falling Method: Particles were deposited with negligible force by allowing them to free fall on a substrate.

Fluidized Method: The Air Jet Sieve (200 LS, Alpine) was used for attaching particles to a substrate in a fluidized state. 300 mg of sample powder was fed into a container having a capacity of 38.5 cm^3 (70 mm in diameter and 10 mm in depth). A substrate (18 mm in diameter and 2 mm in thickness) was fastened to the cover of the sieve with double adhesive tape, and fresh air was blown through the device for 1 min at a flow rate of 3.6 m^3/min as shown in Fig. 1. Thus, a single layer of particles could be obtained on the substrate. The operation was conducted at 25±1 °C with a relative humidity of 40±10%.

Measurement of Adhesive Force The adhesive force between particles and substrate was determined by the impact separation method.[1a)] Sample particles on the substrate were set in a measuring cell which was fixed to the impact hammer of a pendulum shock testing machine (Yoshida Seiki, PST-300). The hammer was motor-driven to a desired height and then allowed to fall to impact a shock-absorbing mat. The impact acceleration generated was measured with an accelerometer. Separation force, f, can be obtained from Eq. 2,

$$f=\frac{\pi}{6}\cdot\rho\cdot d^3\cdot\alpha \qquad (2)$$

where ρ is particle density, d is particle diameter, and α is impact acceleration. The percentage of particles adhering to the substrate was determined by counting the number of particles before and after impact by means of an image analyzer connected to a microscope. A plot of separation force *vs.* percentage of remaining particles on a logarithmic probability paper yielded the average adhesive force, f_{50}, which was defined as the separation force where 50% of the particles remained on the substrate after separation. The experiments were carried out at 25±1 °C with a relative humidity of 40±10%. The detaching measurement was performed after 10 min from the time particles attached to a substrate.

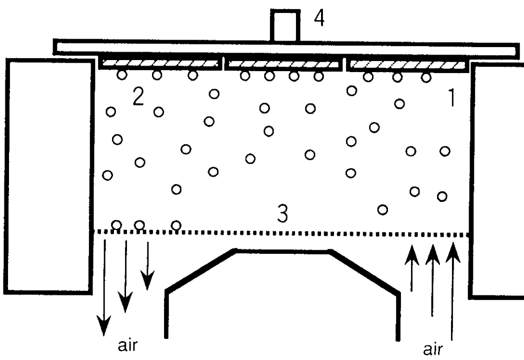

Fig. 1. Schematic Diagram of Apparatus for the Fluidized Method
1, substrate; 2, particles; 3, sieve; 4, cover.

Measurement of Surface Roughness of a Substrate For the glass substrates ground by different alumina powders, the surfaces were examined by scanning tunneling microscopy: STM (Kurasurf-101, Kurabo Co., Ltd.) which revealed the surface structure of the substrate without contact. The tunnel current and bias voltage were set at 1 nA and 1 V, respectively. The range of measurement in the z-direction was ±1 μm and the x and y-directions 10 μm × 10 μm. The resolution in the z-direction was 0.5 nm.

Measurement of Electric Potential of a Substrate Measurement of the electrostatic properties of the substrates was carried out using a vibrating reed electrometer (Statiron-DZ, Shishido Electrostatic, Ltd.). The surface electric potential of the substrate, V, was indicated directly at the point 22 mm apart from the substrate.

Results and Discussion

Adhesive Force by Means of the Free Falling Method

a) Effect of Surface Roughness of the Substrate and Particle Shape on the Adhesive Force The adhesive force between particles and smooth and rough surfaces of glass, PVC and stainless steel is shown in Fig. 2, where the values of average adhesive force, f_{50}, are plotted against particle shape index, ψ_2. When the surface was smooth, the adhesive force increased as the shape index increased in each of the substrates. It was supposed that the effective contact area between a particle and a substrate would become larger as the particle shape approached that of a sphere.[1c)] The adhesive forces for a rough surface were found to be less than those for smooth surface in each of the substrates. The degree of decrease was remarkable in those particles with higher sphericity. Namely, on a rough surface, the contribution of particle shape to the adhesive force can be ignored.

b) Effect of Degree of Surface Roughness of Substrate on the Adhesive Force In order to examine the contact state of particles on a substrate in further detail, four kinds of glass substrates with varying surface roughness were used. Figure 3 shows the surface condition of these glass substrates by STM topographic images. A is the original slide glass; B, C and D are glass plates whose surfaces were ground with alumina powder of different particle sizes. It was found that the degree of surface roughness inceased as

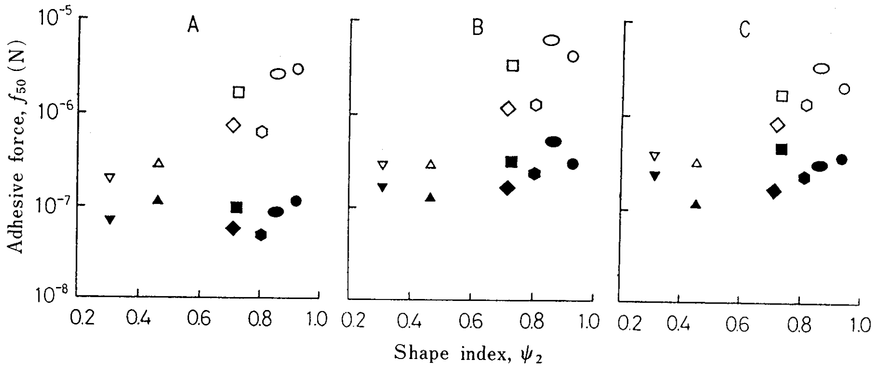

Fig. 2. Relationship between f_{50} and ψ_2 for Smooth Surface (Open Symbols) and Rough Surface (Closed Symbols)
A, glass; B, PVC; C, stainless steel. ○, glass beads; ◇, crushed glass; o, calcium carbonate P-70; ⬭, potato starch; □, sulfadimethoxine; △, crystalline cellulose; ▽, croscarmellose sodium.

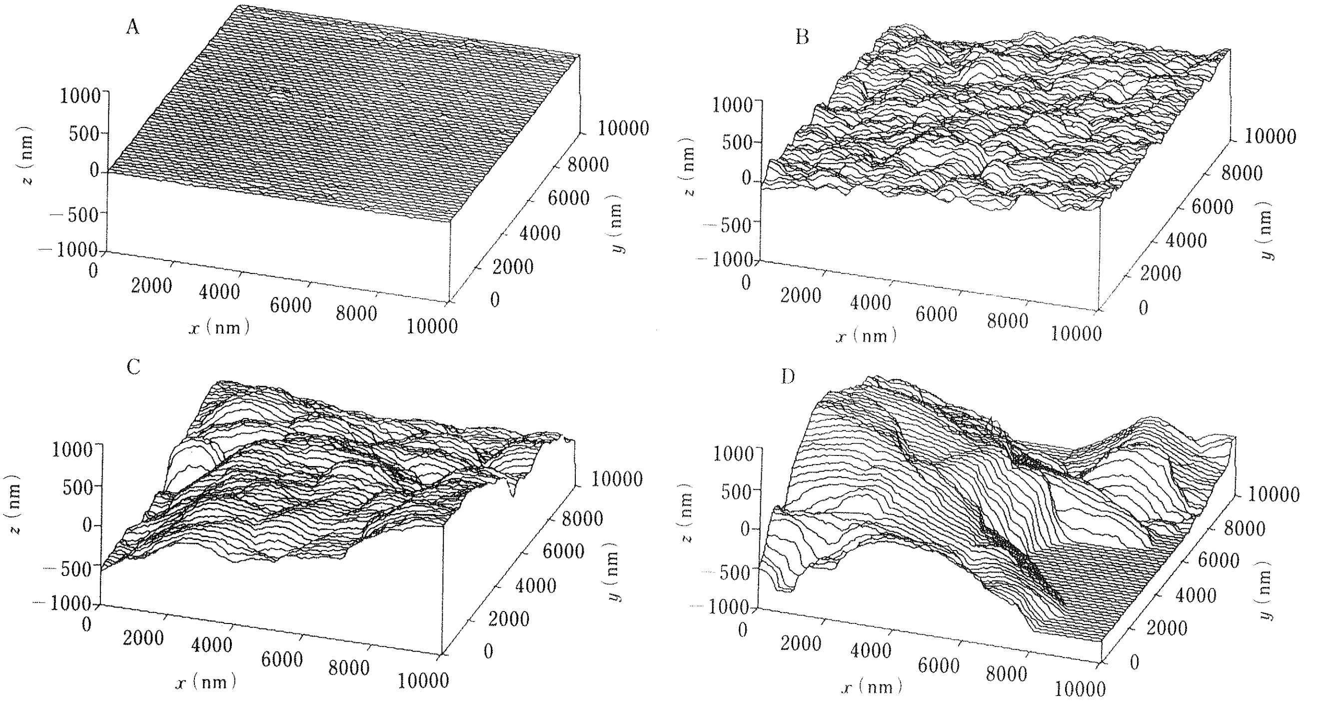

Fig. 3. Three Dimensional Diagram of Surface Roughness of Glass Substrates

A, smooth surface; B, C, and D rough surface ground with alumina powder having diameters of 3, 16 and 48 μm, respectively.

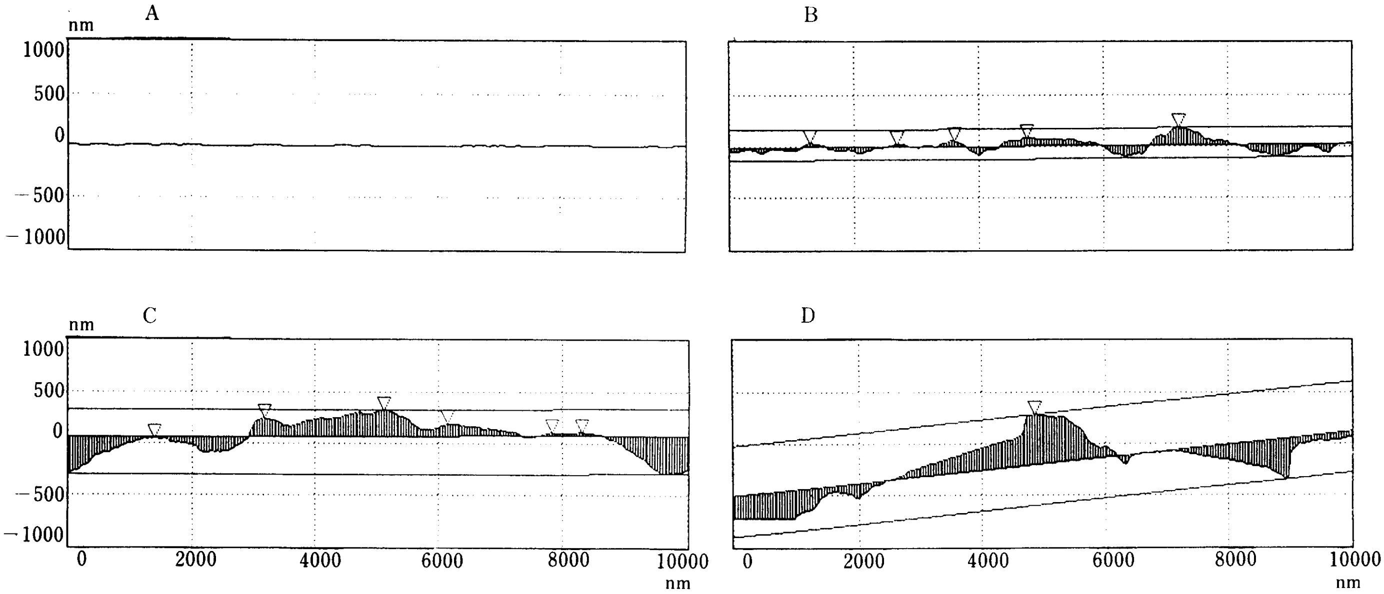

Fig. 4. Cross Sectional View of the Surface of Glass Substrate

A, smooth surface; B, C, and D rough surface ground with alumina powder having diameters of 3, 16 and 48 μm, respectively.

the size of alumina powder used increased.

Figure 4 shows a cross sectional view of each surface of glass substrate measured by STM. The arithmetic average surface roughness, Ra, based on the result of STM, was given as follows:

$$Ra = \frac{1}{l}\int_0^l |f(x)|\,dx \qquad (3)$$

where $f(x)$ is the vertical distance from the mean line in the x axis profile and l is the sampling length. Figure 5 shows the relationship between Ra and adhesive force for glass beads/glass substrate systems. Initially, the f_{50} value decreased rapidly with an increase in Ra, and it appeared to gradually approach the fixed value.

Assuming that the adhesion is caused by van der Waals force, F_{vdw}, the theoretical adhesive force between a sphere having the radius R and a plane surface is given by

$$F_{vdw} = \frac{\hbar\bar{\omega}}{8\pi z_0^2} R \qquad (4)$$

where $\hbar\bar{\omega}$ is the Lifshitz-van der Waals constant and z_0 the adhesional distance between a particle and a plane surface.

If the $\hbar\bar{\omega}$ value of 4.8×10^{-19} J for Pyrex glass[8)] and z_0 value of 0.4 nm[7)] are used, the van der Waals force between a glass sphere ($R=20\,\mu$m) and a smooth glass surface is calculated to be 2.4×10^{-6} N from Eq. 2. This value is in good agreement with that of the measured adhesive force of 2.9×10^{-6} N. As the surface roughness increases, it is supposed that the total effective particle/substrate contact area would become smaller than that of the particle/smooth surface, and the adhesive force would fall. When surface roughness is great enough, it is suggested that the glass sphere is supported with a small number of protuberances on the substrate (Fig. 6). Regarding the protuberance as a small sphere, the van der Waals force, F'_{vdw}, between two spheres is calculated by Eqs. 5 and 6.

$$F'_{vdw}=\frac{\hbar\bar{\omega}}{16\pi z_0^2}R' \tag{5}$$

$$R'=\frac{2\cdot R_1\cdot R_2}{R_1+R_2} \tag{6}$$

where R_1 is the radius of a large particle (20 μm) and R_2 is that of a small particle. If the value of R_2 was assumed to be 0.35 μm (the Ra value found for the substrate having the roughest surface) and 0.5 μm, which might be a possible value according to Figs. 4 and 6, the F'_{vdw} were calculated to be *ca.* 4×10^{-8} N and *ca.* 6×10^{-8} N, respectively. These values are in the same order of magnitude as the measured adhesive force in the high Ra region in Fig. 5. Thus, at Ra values of 0.5 μm or above, the adhesive force between a particle and a substrate with a rough surface may be adequately approximated by the model based on the adhesion between a large particle and a small particle.

Adhesive Force by Means of the Fluidized Method It is well known that organic powders are easily attached to a solid insulator. However, very little research data has been shown on the net adhesive force between a particle and a substrate. Kulvanich and Stewart[2c)] measured the total degree of adhesion of drug particle/carrier (glass beads coated with hydroxypropylmethylcellulose) systems, and the electrostatic charge was measured with an air stream Faraday cage. They described obtaining a good correlation

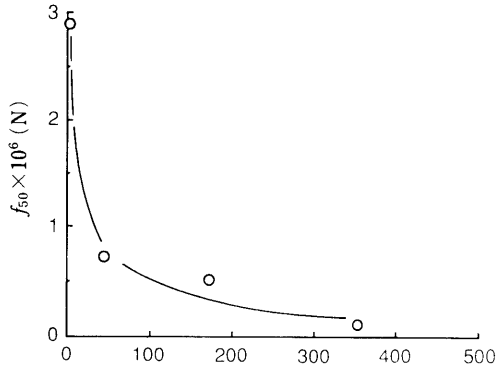

Fig. 5. Relationship between f_{50} and Ra for Glass Beads/Glass Substrate System

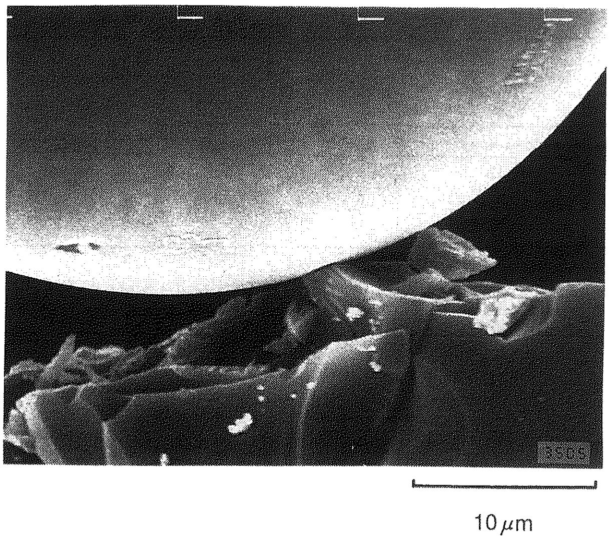

Fig. 6. Scanning Electron Micrograph of Glass Sphere Adhered on Glass Substrate

Glass substrate was ground with alumina powder having a diameter of 48 μm.

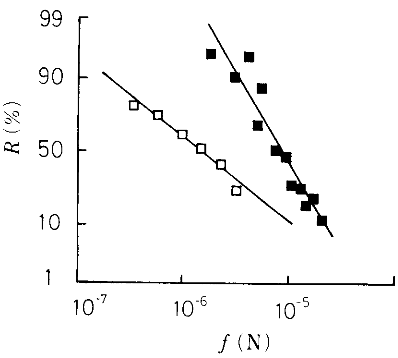

Fig. 7. Plots of Percentage of Remaining Particles, R, against Separation Force, f, on log-Probability Paper for Sulfadimethoxine/PVC System

□, free falling method; ■, fluidized method.

TABLE II. Average Adhesive Forces and Electric Potential ($n=10$)

Substrate		Sulfadimethoxine		Aspirin B-102		Potato starch	
		f_{50} (N)	V (kV)	f_{50} (N)	V (kV)	f_{50} (N)	V (kV)
PVC (Smooth)	Free falling	1.5×10^{-6}	-0.08	1.9×10^{-6}	-0.06	3.8×10^{-6}	-0.02
	Fluidized	8.8×10^{-6}	-2.6	7.8×10^{-6}	-1.1	6.7×10^{-6}	-0.50
PVC (Rough)	Free falling	3.7×10^{-7}	-0.02	1.7×10^{-7}	-0.01	—	—
	Fluidized	2.8×10^{-6}	-1.7	4.1×10^{-6}	-1.0	—	—
Glass	Free falling	2.1×10^{-6}	0.03	1.1×10^{-6}	0.01	2.7×10^{-6}	0.03
	Fluidized	1.8×10^{-6}	0.14	3.1×10^{-6}	-0.22	—	—
Stainless steel	Free falling	1.8×10^{-6}	0.02	9.2×10^{-7}	0.02	3.9×10^{-6}	0.01
	Fluidized	6.4×10^{-7}	-0.11	4.4×10^{-6}	-0.12	—	—

between the two. In the present work, using some organic powders, the effect of the type of substrate material on particle adhesion was investigated by the fluidized method, in which the particles are fluidized with a jet of air and attached to the substrate. The measurement of adhesive force was then carried out by the impact method. In Fig. 7 the results were compared with those of the free falling method. The value of f_{50} of the former was larger than that of the latter. The difference in adhesive force might be due to the electrostatic effect caused by particle collision and/or friction against the substrate. All the adhesion results obtained from the free falling method and fluidized method are shown in Table II, along with the surface electric potential of the substrate. Among these, sulfadimethoxine and aspirin attached on PVC by the fluidizing method showed extremely large values of f_{50} and electric potential. It is also interesting that, in the fluidized method, there seems to be no great difference in the adhesive property of PVC between smooth and rough surface. This finding implies that in these systems the effect of electrostatic force was superior to that of surface roughness on adhesion.

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References and Notes

1) *a*) A. Otsuka, K. Iida, K. Danjo, H. Sunada, *Chem. Pharm. Bull.*, **31**, 4483 (1983); *b*) *Idem*, *ibid.*, **33**, 4054 (1985); *c*) *Idem*, *ibid.*, **36**, 741 (1988); *d*) K. Iida, A. Otsuka, K. Danjo, H. Sunada, *ibid.*, **40**, 189 (1992).
2) *a*) P. Kulvanich, P. J. Stewart, *J. Pharm. Pharmacol.*, **40**, 453 (1988); *b*) *Idem*, *Intr. J. Pharmaceut.*, **36**, 243 (1987); *c*) *Idem*, *ibid.*, **39**, 51 (1987).
3) *a*) M. Corn, *J. Air Poll. Control Assoc.*, **11**, 566 (1961); *b*) M. Corn, F. Stein, *Am. Ind. Hyg. Assoc. J.*, **26**, 325 (1965).
4) A. D. Zimon, T. S. Volkova, *Colloid J. USSR*, **27**, 306 (1965).
5) J. Okada, Y. Matsuda, Y. Fukumori, *Yakugaku Zasshi*, **91**, 1207 (1971).
6) S. W. Booth, J. M. Newton, *J. Pharm. Pharmacol.*, **39**, 679 (1987).
7) H. Krupp, *Adv. Colloid Interface Sci.*, **1**, 111 (1967).
8) B. Dahneke, *J. Colloid Inter. Sci.*, **40**, 1 (1972).