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The Effects of Interfacial Physical Properties on the Cohesive Forces of Moist Powder in Air and in Liquid

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The tensile strength of a powder bed of calcium carbonate moistened with aqueous solutions of surface-active agents was measured in air and in carbon tetrachloride by a diametrical compression method. The cohesive force at the point of contact of particles was determined by means of the Rumpf equation. The cohesive force determined by the diametrical compression method was much stronger than that obtained by the traction table method in air. This finding suggests that the area of contact played an important role in determining the cohesive force. When the liquid saturation ratio was less than 20%, *i.e.* in the pendular region, the cohesive force increased with increasing saturation ratio in both air and liquid. The cohesive force also depended on the interfacial tension of the moistening liquid, the action of which was slightly different in liquid and in air. The cohesive force was drastically decreased by rendering the particles hydrophobic. It is suggested that the cohesive force at the point of contact in the pendular region can be represented qualitatively by equation (7) in the text.

$$H = \phi f(\gamma) f(S) f(\theta,\beta) \tag{7}$$

In the funicular region, where the liquid saturation ratio was larger than 20%, the cohesive force decreased with increasing saturation ratio. This might be due to the action of agglomerates formed in the powder bed. It was also found that the cohesive force increased with increasing interfacial tension of the moistening liquid.

Keywords——tensile strength; diametrical compression method; traction table method; cohesive force at point of contact; calcium carbonate; interfacial tension; surface treatment; measurement of cohesive force in air and in liquid

Recently much attention has been paid to measuring the adhesive or cohesive force of powders in the field of powder technology, since this parameter is extremely important in relation to efficient powder processing.[1] Most studies on this subject have been carried out under dry conditions in air rather than under moist conditions.[2] When handling moist powder in a liquid, *e.g.* wet spherical agglomeration,[3] as well as in air, it is necessary to measure the cohesive force exerted on the moist particles in the required environment. In the previous paper by the present authors[4] it was proved that a diametrical compression method[5] was useful to measure the cohesive force of moist powder as well as the traction table method, *i.e.*, the so-called Farley–Valentin method.[6] The diametrical compression technique is preferable in liquids compared to the traction table method due to its simplicity.

In the present study, the tensile strength of moist calcium carbonate particles was measured in carbon tetrachloride and in air by the diametrical compression method and the traction table method. The objective of the study was to clarify the effects of interfacial physical properties on the cohesive force of moist powder in liquid as well as in air. To change the interfacial chemical properties of the system, surface-active agents were added to the moistening liquid at various concentrations. The effect of surface treatment of powder on the cohesive force was also investigated in air. Finally we hoped to correlated qualitatively the cohesive force with parameters such as the surface tension, the liquid saturation ratio, *etc.*

Experimental

Preparation of Moist Powder——The test powder used was precipitated calcium carbonate (Nitto Funka Co.) having a volume surface mean diameter of 3.7 μm and a true density of 2.45 g/cm^3. The surface treatment of powder was conducted by adsorbing stearic acid on the powder. Calcium carbonate (100 g) was suspended in benzene solution saturated with stearic acid for 2 h by stirring, then the powder was separated and dried at 70°C. The contact angle of water against the solid was measured by the method of Heertjes, the so-called h-ε technique.[7] A large drop of water was placed on the surface of a tablet of calcium carbonate saturated with water. The contact angle was calculated by means of equation (1).

$$\cos\theta = -1 + \left(\frac{2}{3(1-\varepsilon)}\left(\frac{2}{Bh^2}-1\right)\right)^{1/2} \tag{1}$$

where h is the height of the droplet measured with a cathetometer, and $B=\rho g/2\gamma$, where γ is the surface tension of the liquid, ρ is the liquid density and ε is the tablet porosity. The contact angles against untreated powder and treated powder were $13\pm3°$ and $150\pm2°$ respectively. Aqueous solutions of sodium oleate (Kishida Chemical Co.), polyoxyethylene sorbitan monooleate (Tween 80, Kao Soap Co.) and perfluorooctanoic acid (PFOAA, Kao Soap Co.) were prepared at various concentrations. The surface tension values of the solutions, measured by the Wilhelmy method (surface tensiometer CBVP, Kyowa Kagaku Co.) at 20°C, are tabulated in Table I. Distilled water or an aqueous solution of surface-active agent (0.5 to 6.5 ml) was sprayed uniformly over the treated or untreated powder (30 g) spread thinly on a flat pan. During spraying, the powder was mixed well to ensure that it was uniformly moistened.

TABLE I. Surface Tension of Moistening Liquid and Interfacial Tension of Moistening Liquid/Carbon Tetrachloride

I) Surface tension

Moistening liquid	Surface tension (dyne/cm)
Water	71.4
Tween 80 (3.68×10^{-4} w/v%)	66.0
Tween 80 (0.1 w/v%)	41.4
Sodium Oleate (0.1 w/v%)	25.2
P.F.O.A.A. (0.1 w/v%)	47.2
P.F.O.A.A. (0.37 w/v%)	31.3
P.F.O.A.A. (2.0 w/v%)	19.3

II) Interfacial tension

Moistening liquid	Interfacial tension (dyne/cm)
Water	40.1
P.F.O.A.A. (0.1 w/v%)	32.1
P.F.O.A.A. (0.37 w/v%)	20.5
P.F.O.A.A. (2.0 w/v%)	less than 5.0

Measurement of Cohesive Force of Powder——Diametrical compression method: The moist powder was placed in a die with an internal diameter of 2 cm and was compressed by an oil press (Rikenseiki Co.) at 54 to 640 kg/cm^2 for 2 min. The resultant tablet was removed and placed in a stoppered weighing bottle to prevent the evaporation of water. It was left for 30 min to permit elastic deformation to occur. After measurement of the dimensions of the tablet, it was immediately mounted on the platform of a diametrically compressing tester (Reorobot KA 300, Kyowaseiko Co.). The porosity of the resultant tablet was found to be 0.2 to 0.4. The specimen was compressed diametrically by a flat platen moving down at 0.9 mm/sec. The load applied was monitored by a strain gauge attached to the platform. The maximum load recorded was taken as the stress causing fracture. When the fracture occurred along the diametrical plane joining the line of contact of the specimen and the platens, the tensile stress could be calculated by means of equation (2).[4,8]

$$\sigma = \frac{2F}{\pi Dl} \tag{2}$$

where F is the load at fracture, and D and l are the diameter and thickness of the tablet, respectively. Newton *et al.*[9] expressed the tensile strength corrected for fractional voidage (ε) in terms of equation (3).

$$\sigma = \frac{2F}{\pi Dl(1-\varepsilon)} \tag{3}$$

In the present study, the original equation (2) derived theoretically was used since it is generally accepted, as specified in JIS.[10] After the compression test, the fractured specimen was weighed and then dried at

70°C *in vacuo* for one day. The weight loss during drying corresponded to the water contained in the specimen. The liquid saturation ratio for water was determined by the use of equation (4).

$$\phi = \frac{v}{\varepsilon V} \tag{4}$$

where ϕ is the liquid saturation ratio, v is the volume of water determined from the weight loss and V is the volume of the specimen.

The compression test in liquid was carried out in carbon tetrachloride as described in the previous report.[4] A specimen containing the required moisture level was immersed in carbon tetrachloride and then the system was evacuated to remove air contained in the specimen. Without removing the specimen from carbon tetrachloride, the compression test was undertaken directly in the liquid.

Traction Table Method: The traction table used was a cylindrical cell made of aluminum, as shown in Fig. 1. The diameter and the height of the cell were both 4 cm. The moist test powder was placed in the cell and compacted by loading with 0.5 to 6.5 kg for 10 min. The porosity of the compacted powder bed was 0.5 to 0.71. One side of the cell was pulled horizontally at 3.99 cm/min until the powder bed in the cell fractured. The stress required to cause the failure was taken as the tensile strength of the powder bed. The liquid saturation ratio and the porosity of the powder bed were determined in the same ways as in the case of the diametrical compression test.

All of the tests were repeated 6 to 20 times. The data in the figures are average values. The experimental variations are indicated by the standard deviation bars in the figures.

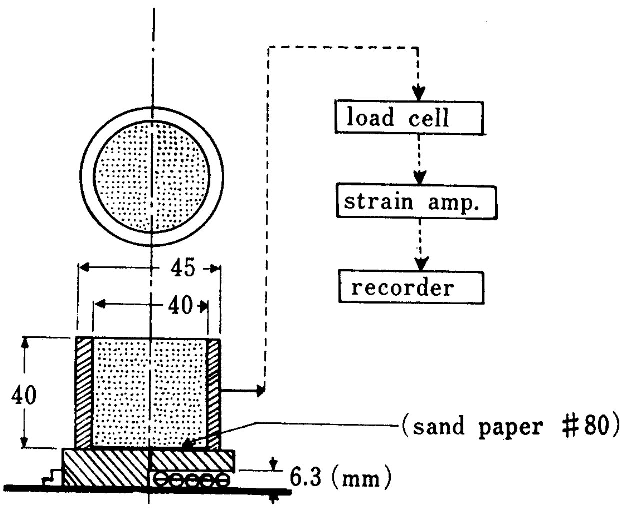

Fig. 1. Farley-Valentin Apparatus

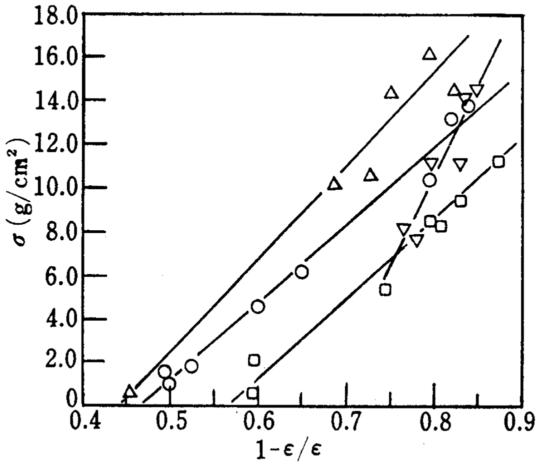

Fig. 2. Relationship between Tensile Strength (σ) and ($1-\varepsilon/\varepsilon$) (Farley-Valentin Method in Air)

Saturation ratio (%): ○, 3.1; △, 13.2; □, 26.7; ▽, 37.7.
Moistening liquid: 2.0% PFOAA.

Results and Discussion

Determination of Cohesive Force at the Point of Contact

Rumpf[11] proved that the tensile strength exerted on unit area of the fracture plane of a powder bed could be expressed by equation (5).

$$\sigma = \frac{1-\varepsilon}{\pi} k \frac{H}{d^2} \tag{5}$$

where σ is the tensile strength per unit area of the fracture plane, k is the coordination number, d is the diameter of the particles, ε is the porosity of the powder bed and H is the cohesive force at the point of contact. Assuming $k\varepsilon=\pi$, equation (6) was obtained.

$$\sigma = \frac{1-\varepsilon}{\varepsilon} \cdot \frac{H}{d^2} \tag{6}$$

The tensile strengths measured by the traction table method and the diametrical compression test were plotted as a function of $(1-\varepsilon)/\varepsilon$. All of the data obtained by both methods were con-

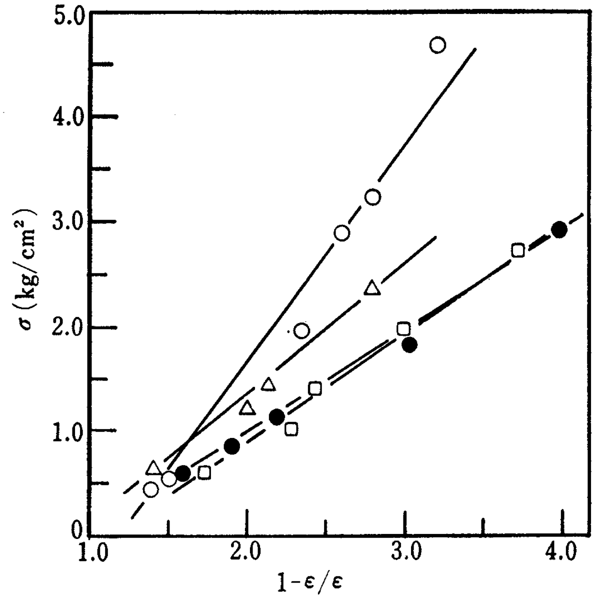

Fig. 3. Relationship between Tensile Strength (σ) and (1-ε/ε) in Carbon Tetrachloride

Saturation ratio (%): ○, 10.8; △, 17.0; □, 43.0; ●, 55.6
Moistening liquid: water.

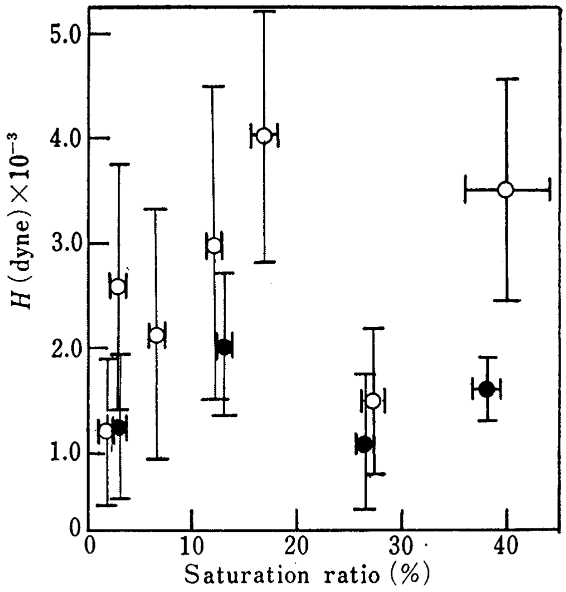

Fig. 4. Effect of Surface Tension on Cohesive Force at the Point of Contact (H) (Farley-Valentin Method in Air)

Moistening liquid: ○, water (71.4 dyne/cm);
●, 2.0% PFOAA (19.3 dyne/cm).

sistent with linear relationships between the tensile strength and $(1-\varepsilon)/\varepsilon$. Figs. 2 and 3 show representative data obtained in air and in liquid, respectively. The tensile strengths obtained by the traction table method were much smaller than those obtained by the diametrical compression method. This difference might be interpreted in terms of higher porosity of the powder bed in the traction cell as compared with that in the diametrical compression test. It was also found that slopes of the straight lines varied with the liquid saturation ratio of the powder bed with the moistening liquid. To rationalize these phenomena further, the cohesive force at the point of contact was determined by means of equation (6).

The Cohesive Force at the Point of Contact in Air

The cohesive force at the point of contact determined by the traction table method is illustrated as a function of the liquid saturation ratio in Fig. 4. The cohesive force increased with increasing saturation ratio when the saturation ratio was less than 20%. Above this point the cohesive force fluctuated. This fluctuation might be a result of an uneven distribution of moistening liquid in the powder bed. The cohesive force decreased when 2% solutions of PFOAA were used as a moistening liquid. The effect of PFOAA was confirmed at the 5% significance level by analysis of variance. This phenomenon was interpreted in terms of reduced surface tension of the moistening liquid, which might decrease the bridging force between the particles. It was impossible to measure the tensile strength when the saturation ratio was more than 40% due to the slippage between the powder bed and the traction table.

The relationship between the cohesive force at the point of contact as determined by the diametrical compression method and the saturation ratio is shown in Fig. 5. The cohesive force determined by the diametrical compression test was much greater than that obtained by the traction table method. It has been pointed out that the area of contact of particles in the powder bed plays an important role in relation to the cohesive force of the powder bed.$^{12)}$ The lower porosities of the specimens used with the diametrical compression method as compared to those in the traction table method (as described in the experimental section) suggested that deformation of the contact point of particles might have occurred. This deformation might enlarge the particle contact area, which could contribute to enhancing the cohesive force. When the saturation ratio was less than 20%, in the so-called pendular region, the cohesive force increased almost proportionally to the saturation ratio. When the saturation ratio exceeded 20%, the cohesive force decreased with increasing saturation ratio. This adverse effect of the saturation ratio could be explained by the formation of agglomerates. When the liquid saturation ratio is greater than 20%, the moistening liquid in the powder bed exists in a funicular state, in which liquid bridges and regions filled with liquid can coexist. The regions saturated with liquid should behave as an agglomerate. Thus, the apparent size in the powder bed should become heterogeneous, reducing the effective contact points contributing to the cohesion. The cohesive force tended to decrease with increasing concentration of surface-active agent added to the moistening liquid, but also depended on the liquid saturation ratio. When the liquid saturation ratio was less than 15%, the effect of surfactant on the cohesive force became complex.

The cohesive force could be correlated with the surface tension of the moistening liquid when the liquid saturation ratio was larger than 20%, as can be seen in Fig. 6. At 20% saturation ratio, the surface tension of the moistening liquid strongly affected the cohesive force. The cohesive force of powder that had been rendered hydrophobic drastically decreased when the liquid saturation ratio was less than 20%, as shown in Fig. 7. In addition, the effect of moistening liquid on the cohesive force was distinct, and the result was clearly different from that for the untreated powder. When the liquid saturation ratio was larger than 20%, the cohesive force increased with increasing liquid saturation ratio, and finally became larger than that of the untreated powder at 50%. However, this correlation in respect of the liquid saturation was only apparent, since the moistening liquid could hardly wet the treated powder due to the high contact angle (higher than 90°). To increase the liquid saturation ratio of such a hydrophobic powder bed, compression of the powder is the only alternative to adding liquid. The strong compaction increases the contact area of particles, leading to enhancement of the cohesive force.

The Cohesive Force at the Point of Contact in Liquid

The cohesive forces at the point of contact as determined by the diametrical compression method in carbon tetrachloride are plotted as a function of the liquid saturation in Fig. 8. The effects of liquid saturation and surface-active agent on the cohesive force were almost the same as those found in air. This finding suggested that in the funicular state some

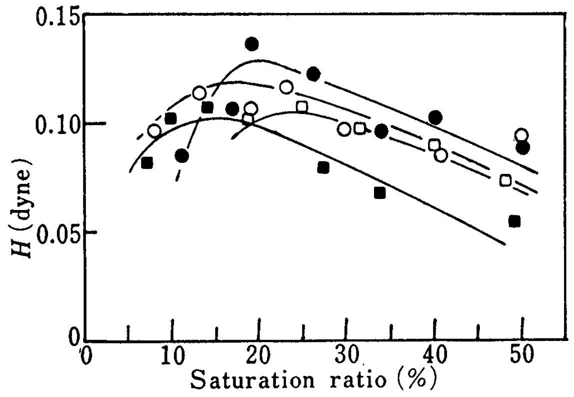

Fig. 5. Relationship between Cohesive Force at the Point of Contact (H) and Saturation Ratio (ψ) in Air

Symbol	Wetting agent	Surface tension
●	water	71.4 (dyne/cm)
○	PFOAA (0.1%)	47.2
□	PFOAA (0.37%)	31.3
■	PFOAA (2.0%)	19.3

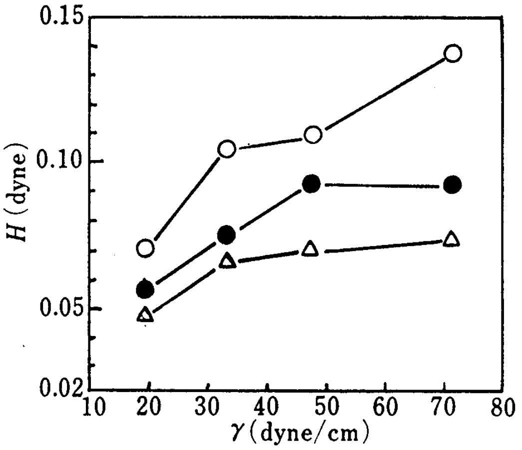

Fig. 6. Effect of Surface Tension (γ) on Cohesive Force at the Point Contact (H) in Air

Saturation ratio (%): ○, 19.3; ●, 49.3; △, 69.6.
Surfactant: PFOAA (conc., 0.1—2.0%).

agglomerates were formed in the powder bed. It was also found that the cohesive force in liquid depended on the interfacial tension between the moistening liquid and the medium. As expected, the cohesive force increased with increasing interfacial tension, as shown in Fig. 9. This effect was marked when the liquid saturation was 20%, as observed in air. The cohesive forces in the liquid were slightly stronger than in air, when compared at the same level of interfacial tension. This difference could be interpreted in terms of the liquid bridge geometry at the contact point in liquid. Rumpf and Schubert[13] reported that the liquid bridge geometry

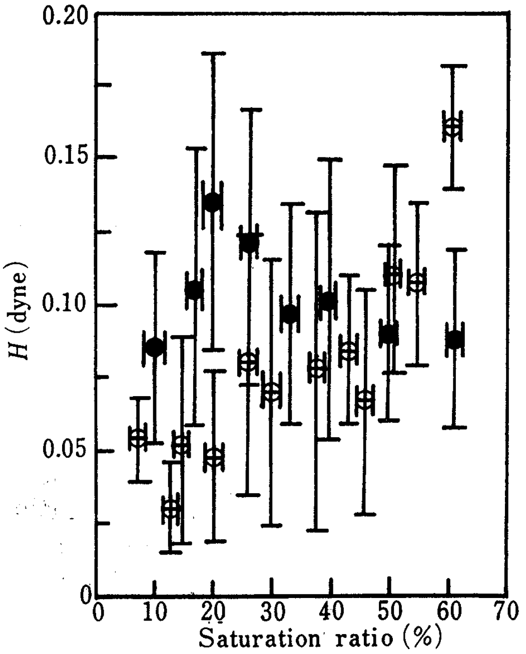

Fig. 7. Effect of Hydrophobization of Powder on Cohesive Force at the Point of Contact (H)

Specimen: ●, untreated; ○, hydrophobilized.
Moistening liquid: water.

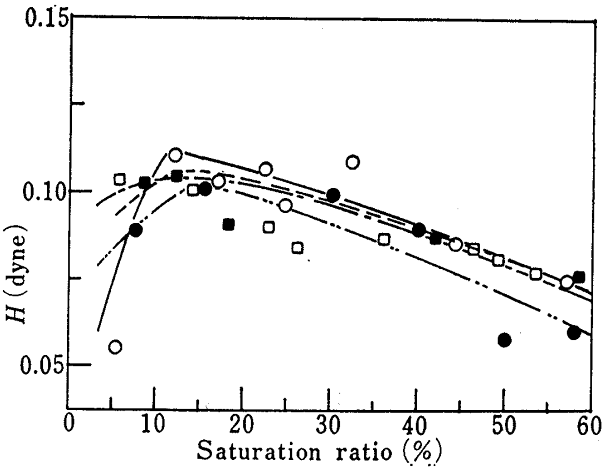

Fig. 8. Relationship between Cohesive Force at Point of Contact (H) and Saturation Ratio (ψ) in Carbon Tetrachloride

Symbol	Wetting agent	Interfacial tension
○	water	40.0 (dyne/cm)
■	PFOAA (0.1%)	32.1
□	PFOAA (0.37%)	20.5
●	PFOAA (2.0%)	<5.0

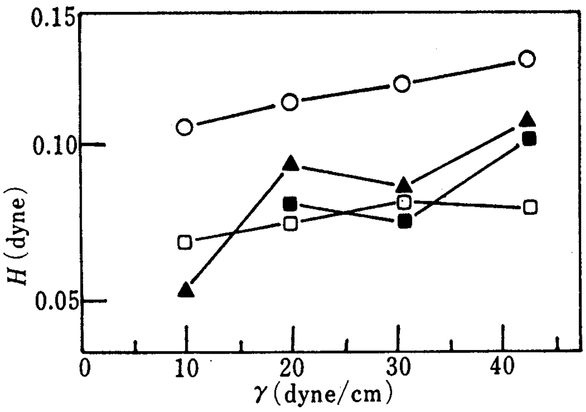

Fig. 9. Effect of Interfacial Tension (γ) on Cohesive Force at the Point of Contact (H) in Carbon Tetrachloride

Saturation ratio (%): ○, 12.4: △, 20.4; ■, 32.7
□, 45.9.
Surfactant: PFOAA (conc., 0.1—2.0%).

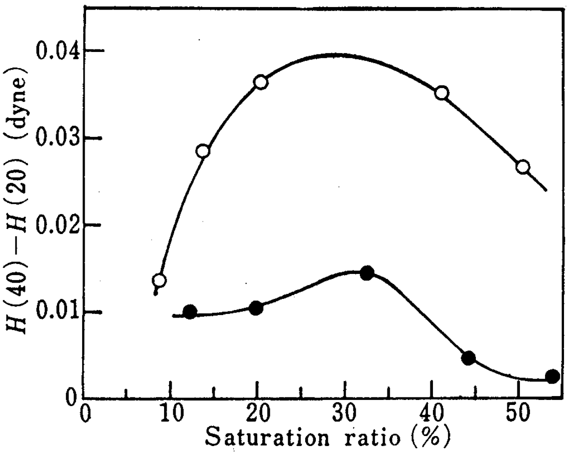

Fig. 10. Comparison of the Effect of Interfacial Tension on Cohesive Force at the Point of Contact (H) in Air and in Carbon Tetrachloride

○, in air; ●, in carbon tetrachloride.
Moistening liquid: water or PFOAA (conc., 0.1—2.0%).

is an important parameter determining the cohesive force of moist powder. The liquid bridge geometry depends on the contact angle as well as the filling angle of the liquid at the point of contact. The contact angle of moistening liquid in carbon tetrachloride should be different from that in air.[14] Thus, a change in the liquid bridge geometry results.

To compare the effect of interfacial tension on the cohesive force in liquid with that in air, the differences between the cohesive forces at interfacial tensions of 20 to 40 (dyne/cm) are plotted against the liquid saturation ratio in Fig. 10. Generally the effects of interfacial tension in air were stronger than in liquid. This result suggested that the surface tension had more effect on the geometry of the liquid bridge at the contact point in air than in liquid. This finding might be also interpreted in terms of a difference in the contact angles of liquid bridges with the particles in liquid and in air . The effect of interfacial tension was strongest in both air and liquid at 30% liquid saturation ratio. When the saturation ratio exceeded this value, the effect on interfacial tension in air decreased more rapidly than in the case of liquid. At present, it is difficult to suggest an explanation for this phenomenon.

Conclusion

The differences in the data obtained by the diametrical compression test and the traction table method (Figs. 4 and 5) indicate that the area of contact plays an important role in determining the cohesive force of powder. When the liquid saturation ratio was less than 20%, *i.e.* in the region of pendular state, the cohesive force increased with increasing liquid saturation ratio both in air and in liquid, but also depended upon the interfacial tension of the moistening liquid. The cohesive forces determined under the same conditions of liquid saturation ratio and interfacial tension of liquid bridges were different in liquid and air, as can be seen in Figs. 6 and 9. The surface treatment of powder also affected the cohesive force, as shown in Fig. 7. In conclusion, it appears that the cohesive force exerting at the contact point of moist particles in the pendular state can be expressed by equation (7).

$$H = \phi f(\gamma) f(S) f(\beta,\theta) \tag{7}$$

where H is the cohesive force at the point of contact, $f(\gamma)$ is a function of interfacial tension, ϕ is the liquid saturation ratio, $f(S)$ is a function of the area of contact and $f(\beta,\theta)$ is a function of liquid bridge geometry, determined by the contact angle (θ) and filling angle of liquid (β).

When the liquid saturation ratio became larger than 20%, *i.e.* in the funicular state, the cohesive force decreased with increasing saturation ratio as shown in Figs. 5 and 8, both in liquid and air. This finding can be interpreted in terms of the formation of some agglomerates in the powder bed, reducing the effective contact among particles. A linear relation was found between the cohesive force and the interfacial tension of liquid bridges.

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