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Penetration of Outer Layered Particles of Agglomerate into Inner Intersticies of Agglomerate during Spherical Agglomeration in Liquid

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Layering agglomeration of aluminum lake particles, *i.e.* a fine reddish pigment, was conducted by depositing them on a cored agglomerate of lactose prepared by the wet spherical agglomeration technique with a bridging liquid, *i.e.* water, in a dispersing medium, *i.e.* chloroform, under agitation. The layered agglomerates were spheronized and compacted during agglomeration. The processes of layering agglomeration and compaction are as described by the selective coalescence mechanism proposed by Kapur and a modified Kawakita's equation. It was newly found that the aluminium lake particles layered on the surface of a core agglomerate penetrated gradually into the inside of core agglomerates during agglomeration. The penetration behaviors of aluminum lake particles were represented by their relative movement coefficients, found by measuring their distributions in the agglomerate with a color measuring system. The mechanism of penetration of aluminum lake particles was discussed by referring to the tapping processes of aluminum lake and lactose powders in liquid and air.

Key words fine particle penetration; layering agglomeration; compaction process; internal structure change; agglomeration mechanism; spherical agglomeration

A wet spherical agglomeration technique has been accepted as an attractive method for agglomerating fine particles dispersed in liquid. The particles are agglomerated spherically with a bridging liquid, which is immiscible with a dispersing medium and preferentially wets the particles.[1]

This technique has been widely employed for agglomeration in various fields, *e.g.* metallurgical,[2] environmental[3] and pharmaceutical industries. Many studies on it application to pharmaceuticals have been carried out, such as the preparation of wax microspheres,[4] agglomeration of proteins as an alternative to lyophilization[5] and continuous processes of agglomeration and microencapsulation.[6]

Many fundamental works on agglomeration mechanisms[7] have shown that the agglomeration process follows first order kinetics. This behavior is explained by the restricted movements of particles in space due to the particle interaction, such as the layering agglomeration of fine particles on a coarse particle. However, little work has focused on the surface structure of layering agglomeration.

In the present study, fabrications of the surface structure of layering agglomeration were investigated with aluminum lake, *i.e.* tracer particles, and lactose, *i.e.* core particles, in a dispersing liquid system. During the agglomeration, it was found, surprisingly, that the aluminum lake particles were deposited on the surface of the core lactose particles submerged in the agglomerate particles. The factors promoting those interesting phenomena were investigated and the mechanisms of this process were discussed.

Experimental

Materials As core particles for agglomeration, lactose powders fractionated with two different diameters, *i.e.* 74—105 μm and 177—250 μm, and a particle density of 1.53 g/cm^3 were employed. Food yellow No. 5 aluminum lake powders (Benifuji Chemicals), 2.3—8.6 μm in diameter and with a particle density of 1.89 g/cm^3, were used as layering particles. Distilled water and chloroform (Nacalai Tesque reagent grade) saturated with distilled water were used as the bridging liquid and dispersing medium, respectively.

Layering Agglomeration in Liquid System Lactose particles (5.76 g) were dispersed in 300 ml of chloroform introduced in a round bottomed vessel (500 ml) under stirring with a turbine type agitator at 400 rpm or 500 rpm, as shown in Fig. 1.

The whole system was thermostatically controlled at 20 °C. The bridging liquid, *i.e.* distilled water (1.38 or 1.50 ml), was introduced into the lactose dispersions to produce core agglomerates under agitation for 5 min. Then, aluminum lake particles (0.5 g) were added into the system for layering agglomeration with the resultant core agglomerates of lactose. After layering agglomeration continued for a required time (5, 10, 20, 30, 40, 50 or 60 min), the agglomerates were removed and dried at ambient temperature under a vacuum. It was confirmed that the drying process did not affect the penetration of aluminum lake.

Measurement of Physicochemical Properties of Agglomerates Heywood diameters (D) of the agglomerates were measured by a photographic counting method with a particle size analyzer (TGZ-3, Carl Zeiss). Porosity (e_a) of the agglomerates was determined by Eq. 1.

$$e_a = 1 - 6W/\rho\sum\pi D^3 \qquad (1)$$

where W is the weight of agglomerates (g), ρ is the mean true density of composed particles (g/cm^3) and D is the particle diameter of the agglomerates (cm). The compaction ratio (C_a) of the agglomerates was calculated by Eq. 2.

$$C_a = (e_{a0} - e_a)/e_a \qquad (2)$$

where e_a is the porosity of the agglomerates, and e_{a0} is the porosity of the core agglomerate (agglomeration time = 0).

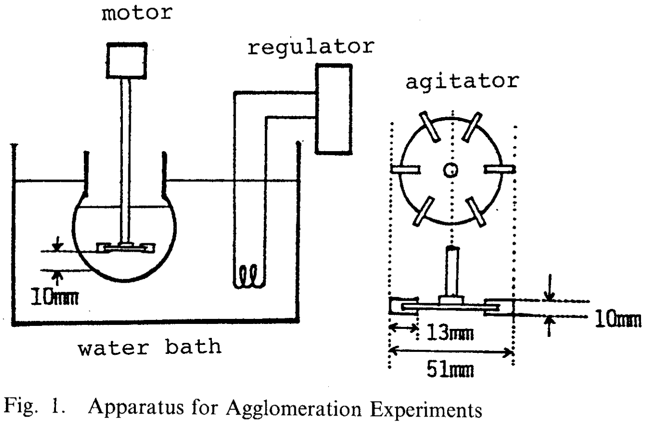

Fig. 1. Apparatus for Agglomeration Experiments

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Determination of Coefficient of Movement of Aluminum Lake Particles Penetrating into Agglomerate The degree of relative movement of aluminum lake particles which penetrated into the agglomerate (relative movement of aluminum lake particles, C_m) is represented by Eq. 3.

$$C_m = (M_1 + M_2)/2D \qquad (3)$$

where M_1 and M_2 are the distances between the most localized layer of aluminum lake particles, and the outer surface of the agglomerate and D is the diameter of the agglomerate, as illustrated in Fig. 2.

The distribution of the concentration of aluminum lake particles in the agglomerate was found by detecting that of a reddish color density of aluminum lake particles in the color photograph of a cross-section of the agglomerates using a color measuring system (Nippon Denshoku Industry), as shown in Fig. 2.

Compaction of Powder Bed Layers of Lactose and Aluminum Lake Particles by Tapping Aluminum lake particles (0.2 g) were first placed on the bottom of a measuring cylinder through a funnel. Then, lactose particles (2.0 g) were layered carefully on the aluminum lake powder bed to avoid mixing. Finally, more aluminum lake particles (0.2 g) were placed on the lactose layer in a similar way. This powder bed system was tapped with a tapping apparatus (Konishi Iryou Instrument) (tapping test A). Another compaction test of the same powder bed placed in a liquid medium contained in the measuring cylinder was conducted by tapping (tapping test B), as illustrated in Fig. 3. The relative movement of aluminum lake particles (C_{mt}) in the lactose particles is represented by Eq. 4.

$$C_{mt} = (B_n + C_n)/2A_n \qquad (4)$$

where B_n and C_n are the thicknesses of the aluminium lake powders and A_n is the thickness of whole powder bed, as shown in Fig. 3.

The compaction ratio of the tapped powder bed (C_t) was determined by Eq. 5.

$$C_t = (e_0 - e)/e_0 \qquad (5)$$

where e_0 is the porosity of the powder bed at the initial state before tapping and e is the porosity after tapping.

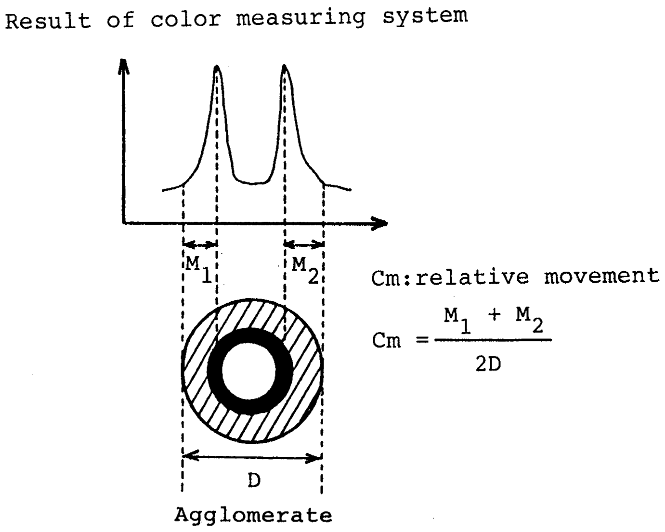

Fig. 2. Calculation Method of Relative Movement of Aluminum Lake Particles (C_m)

Results and Discussion

Agglomeration Behaviors Agglomeration processes are shown in Fig. 4. At the initial stage of agglomeration to prepare core particles in 5 min, the particle size of the agglomerates rapidly increased due to the random coalescence of lactose particles.

The growth rate of the agglomerates was enhanced by reducing the agitation speed, decreasing the particle size of lactose and increasing the amount of bridging liquid used, as predicted by the previous report.[7] When the layering agglomeration of aluminum lake particles with core agglomerates of lactose began, the agglomeration rate decreased rapidly. The available bridging liquid which adhered on the surface of the core agglomerate for agglomeration should be preferentially utilized to agglomerate aluminum lake particles. The coating layer of aluminum lake particles on the core agglomerate might prevent further coalescence of the core agglomerates, although a few coalesced agglomerates were found. The process of layering agglomeration was represented by a straight line on the logarithmic diagram in Fig. 5. This finding suggested that the agglomeration process was

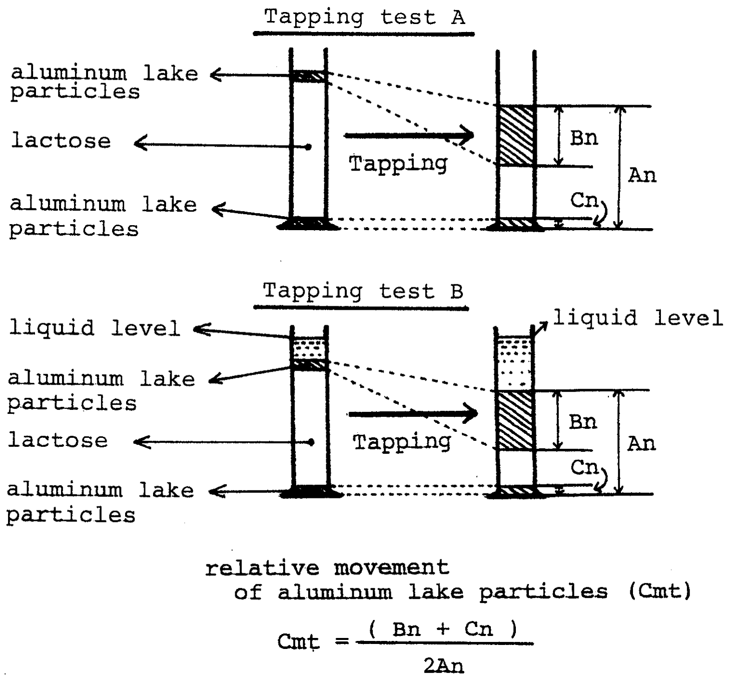

Fig. 3. Calculation Method of Relative Movement of Aluminum Lake Particles by Tapping Experiment (C_{mt})

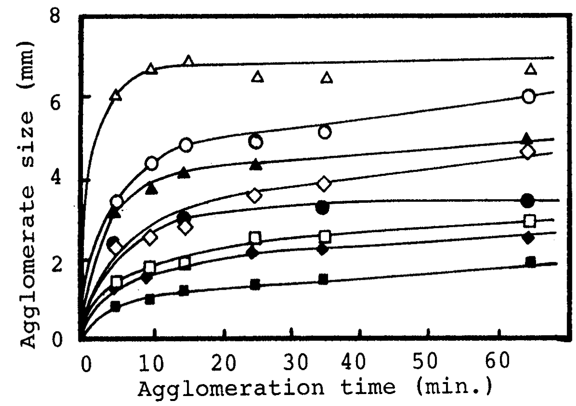

Fig. 4. Agglomeration Processes

Key	Lactose size (μm)	Amount of bridging liquid (ml)	Agitation speed (rpm)
○	74—105	1.38	400
△	74—105	1.50	400
□	177—250	1.38	400
◇	177—250	1.50	400
●	74—105	1.38	600
▲	74—105	1.50	600
■	177—250	1.38	600
◆	177—250	1.50	600

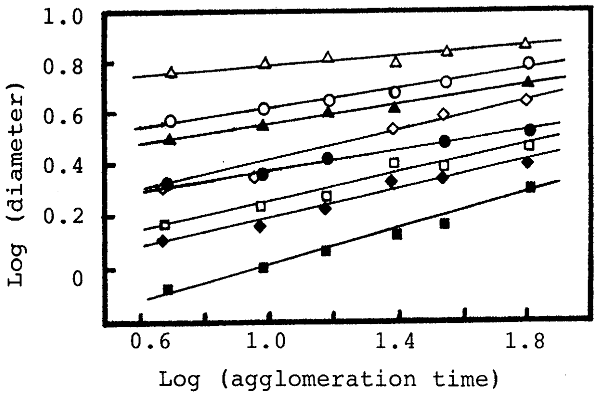

Fig. 5. Process of Layering Agglomeration

All keys are the same as in Fig. 4.

described by a selective coalescence mechanism proposed by Kapur.[8] The kinetic equation is expressed by Eq. 6.

$$\log d = C_3 \log t + C_4(\lambda) \tag{6}$$

where d is the diameter of the agglomerates (mm), t is agglomeration time (min), $C_4(\lambda)$ is a function of the coalescence rate (λ) and C_3 is the constant.

During agglomeration, the agglomerates were spheronized and compacted. The compaction process of agglomerates was represented by the changes in porosity of the agglomerates with agglomeration time, as shown in Fig. 6. The agglomerates were more easily compacted by increasing the agitation speed and the amount of bridging liquid, because of the subsequent increase in the shear force applied to the agglomerates and the plasticities of agglomerates, respectively. It was found that the compaction processes of the agglomerates were described by a modified Kawakita's equation (Eq. 7),[9] as shown in Fig. 7.

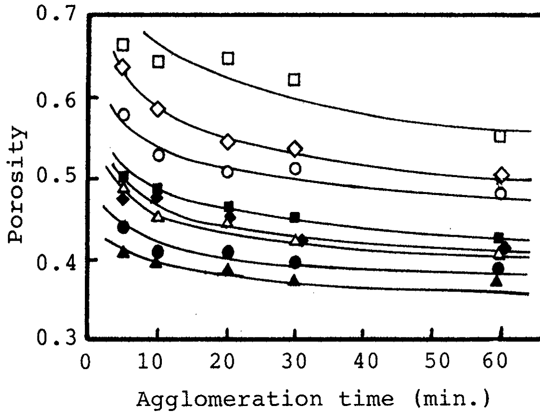

Fig. 6. Compaction Process of Agglomerates by Porosity Change

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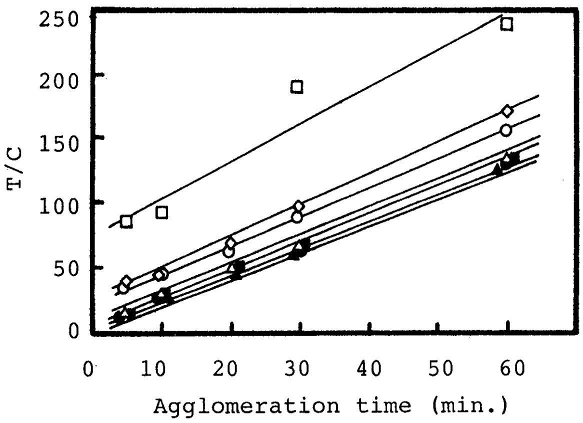

Fig. 7. Compaction Processes of Agglomerates Tested by Modified Kawakita's Equation

All keys are the same as in Fig. 4.

$$T/C = 1/ab + T/a$$
$$C = (e_{a0} - e_a)/(1 - e_a) \tag{7}$$

where T is the agglomeration time and a, b are constants. This finding indicated that the agglomerates were continuously compacted in the stirred vessel and the compaction processes were mainly dependent on applied pressure brought about by external forces, such as collision and shear forces under agitation.

Penetration of Layered Aluminum Lake Particles into Core Agglomerate It was found that the aluminum lake particles layered on the surface of the core agglomerate submerged gradually into the agglomerate during agglomeration. In Fig. 8, microphotographs of a typical cross-section of agglomerates are shown. At the initial stage, *e.g.* agglomeration time = 5 min, aluminum lake particles were localized on the outer surface of the agglomerate. At the later stage, *e.g.* agglomeration time = 60 min, aluminum lake particles penetrated into the agglomerate, and a circular layer of aluminum lake particles appeared in the agglomerate. The relative movement of aluminum lake particles into the agglomerate were plotted with agglomeration time as a function of agitation speed, the amount of bridging liquid and the particle size of lactose in Fig. 9. The relative movement of aluminum lake particles increased with increasing

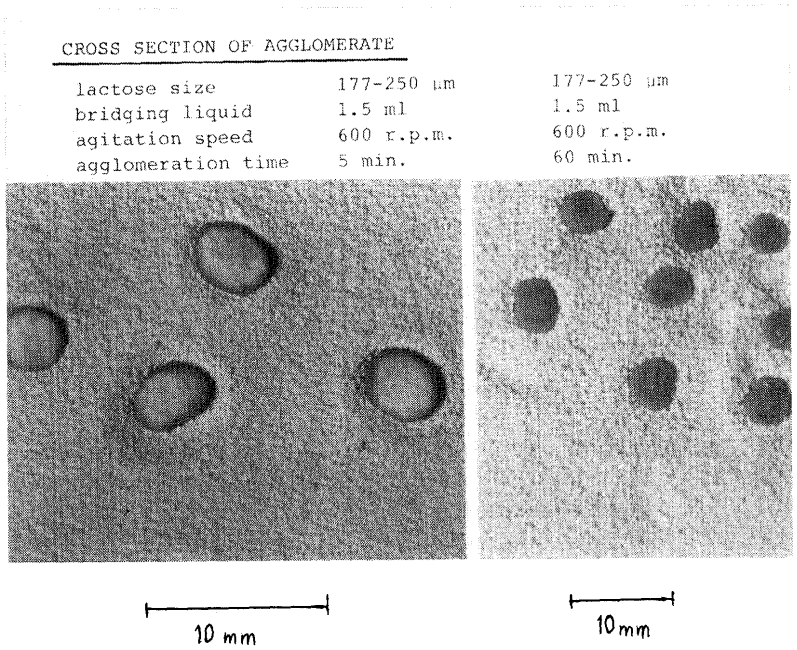

Fig. 8. Cross-Section of Agglomerate

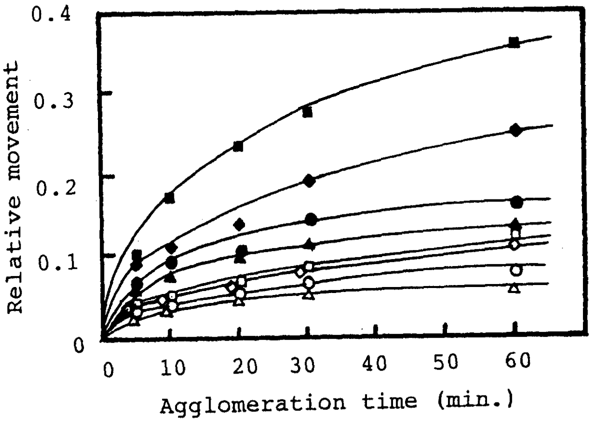

Fig. 9. Relative Movement of Aluminum Lake Particles into Agglomerates

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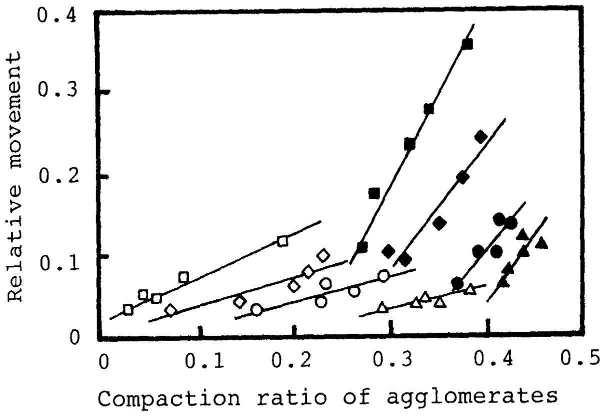

Fig. 10. Correlations between the Relative Movement of Aluminum Lake Particles and the Compaction Ratio of Agglomerates

All keys are the same as in Fig. 4.

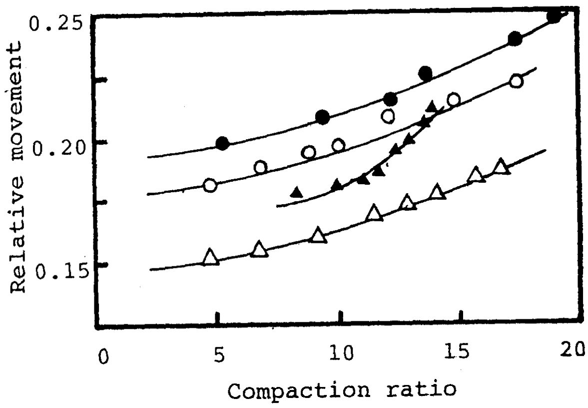

Fig. 11. Relative Movement of Aluminum Lake Particles by Tapping Test of the Powder Bed

△, lactose size 74—105 μm tested in air medium; ▲, lactose size 177—250 μm tested in air medium; ○, lactose size 74—105 μm tested in liquid medium; ●, lactose size 177—250 μm tested in liquid medium.

agitation speed and particle size of lactose, and with decreasing the amount of bridging liquid used. Linear correlations between the relative movement of aluminum lake particles and the compaction ratio of agglomerates were found, as shown in Fig. 10. The agitation speed was a predominant parameter for enhancing the relative movement and compaction ratio of the agglomerates. In the previous report,[10] it was found that the outer surface of the agglomerate was more closely compacted compared to the inside of the agglomerate. Therefore, it was assumed that the aluminum lake particles might be forced to migrate into the looser interstices inside the agglomerate. The pore diameter between coarse lactose particles should be larger than that between fine lactose particles in the agglomerate, if the packing structure is the same. When the amount of bridging liquid was small, the interstices between lactose particles were partially filled with the bridging liquid. Upon compaction of the agglomerate, the bridging liquid was squeezed into more tightly spaced interstices inside the agglomerate. This fluid dynamic force might enhance the movement of fine aluminum lake particles in the interstices between coarse lactose particles. This mechanism resembled the penetration phenomena of silicone carbide powders into an aluminum–lithium alloy when mixed in a high sheared mill.[11] Satoh explained this phenomenon in terms of superplasticity.

The bridging liquid or dispersing medium phase formed around the particles might reduce the internal friction between the particles when moved under shear force. This speculation was proved by a tapping test of the powder bed in liquid and air, as shown in Fig. 11. Dispersion rate (relative movement) of the aluminum lake particles in lactose particles in a liquid medium was higher than in air. It was also found that the relative movement in a coarse powder bed was higher than in a fine powder bed in a liquid medium.

Conclusion

Fine particles deposited on the core agglomerate submerge in the interstices of cored particles during layering agglomeration in a liquid medium under agitation. Superficial compaction of the agglomerate squeezes the bridging liquid into the more tightly spaced inside of the agglomerate. This fluid movement induces the migration of fine particles into the inside of the agglomerate. Therefore, the fluid dynamic force and the shear force applied during agglomeration should play important roles in the penetration of fine particles inside the agglomerate. This finding confirmed that even the internal structure of an agglomerate changes during layering agglomeration of fine particles by their being deposited on the core agglomerate. It was also suggested that a new particle design technique might be devised using this phenomenon.

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