1,1'-Dibenzylidene-4,4'-alkylene-bis(thiosemicarbazides) (IX to XXXI)——A solution of arylaldehyde (2 mole) in DMF was added to a solution of 4,4'-alkylene-bis(thiosemicarbazides) (1 mole) in DMF, and the mixture was warmed at 40—50° for 2—5 hr. The resulting precipitate was collected by filtration and recrystallized from a suitable solvent (see Table II).

1,1'-Diaroyl-4,4'-hexamethylene-bis(thiosemicarbazides) (XXXII to XXXVIII)——A solution of aroyl chloride (2 mole) in DMF was added to a solution of VI (2 mole) in DMF at 0°, the mixture was warmed at 40—45° for 1—3 hr, and concentrated under reduced pressure. The residue obtained was recrystallized from a suitable solvent (see Table III).

1,1'-Dialkyl- or 1,1'-Diaryl-6,6'-alkylene-bis(bithioureas) (XXXIX to LXI)——To a solution of 0.1 mole of 4,4'-alkylene-bis(thiosemicarbazides) dissolved in 50 ml of DMF, 0.2 mole of alkyl or aryl isothiocyanates was added under ice-cooling and the mixture was kept at room temperature for 24—48 hr. The solvent was removed by distillation under reduced pressure and the residue was recrystallized from an appropriate solvent (see Table IV).

N,N'-Hexamethylene-bis[2-amino-5-(2-methoxyphenyl)thiadiazole] (LXII)——To a solution of 1.1 g (0.025 mole) of XXI in 50 ml of THF and 10 ml of H_2O solution of 0.9 g (0.075 mole) of $FeCl_3$ in 20 ml of EtOH was added. The reaction mixture was heated at 70° for 1 hr, concentrated, and the resulting precipitate collected by filtration was recrystallized from EtOH to light yellow prisms, mp 180—181°. Yield, 0.7 g (57.8 %). *Anal.* Calcd. for $C_{24}H_{28}O_2N_6S_2$: C, 58.03; H, 5.58; N, 16.92. Found: C, 57.83; H, 5.85; N, 16.58.

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Caking of δ-D-Gluconolactone Powder

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The sorption of water vapor and the caking behavior of δ-D-gluconolactone (DGL) have been studied. Severe caking of DGL was observed only when both the humidifying and the subsequent drying procedure were taken on it. The crushing strength of the cake increased with an increase in the amount of water evaporated in the drying process. These results may prove the conception that caking is mainly caused by solid bridges formed by the crystallization of dissolved DGL. The caking of DGL was influenced by the compaction state of powder beds. The crushing strength showed a trend to increase with decreasing porosity. It may be due to the increase in the number of total contact points between powder particles.

Powdered materials often exhibit to become caked during storage, reducing their commercial value. In the case of inorganic salts, sugar, feritilizers, *etc.*, it has been considered that caking is mainly caused by crystallization of dissolved substances from the saturated solutions formed on the surface of powder particles due to moisture sorption.[2] Factors known to affect caking of powders include moisture content, temperature, particle size, pressure under which the material is stored and time of storage. The effect of these factors on the extent of caking varies with materials. In addition, the actual caking phenomena are

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[1] Location: *a) Tempaku-cho, Tempaku-ku, Nagoya*; *b) Kashima-cho, Higashiyodogawa-ku, Osaka.*

[2] *e.g.* R.R. Irani, C.F. Callis, and T. Lin, *Ind. Eng. Chem.*, **51**, 1285 (1959); W.B. Pietsch, *Trans. Am. Soc. Mech. Eng., Ser. b.* (*J. Eng. Ind.*) **91**, 435; Y. Peleg and C.H. Mannheim, *J. Food Technol.*, **4**, 157 (1969).

often related to two or more variables above mentioned simultaneously. Therefore, in the investigation on caking behavior of powders, it is desirable that the moisture sorption characteristics of the materials to be caked are clarified and that the conditions of humidifying and drying are defined precisely. In most studies published in past, however, it seems that less consideration has been taken in these respects.

In the present work, δ-D-gluconolactone (DGL) was employed as a testing material and the effect of caking conditions on the crushing strength of cakes was examined. Accelerated caking tests were performed either at a constant temperature with humidity variation or at a constant water vapor pressure with temperature variation. The sorption of moisture by DGL at 25° was also determined.

Experimental

Material——DGL was prepared by Fujisawa Pharmaceutical Co., Ltd. The surface area determined by the air permeability method (Shimadzu SS-100 Powder Surface Area Determinator) was 0.16 m^2/g.

Moisture Sorption Measurement——1) About 1 g of the sample was spread in a Petri dish, which was placed in a desiccator. The desiccator was set in a constant temperature incubator of 25° and was left for 10 days. Desired relative humidity (R.H.) in the desiccator was acquired by choice from a series of H_2SO_4–H_2O mixture. The values of R.H. and water vapor pressure can be found by reference[3] to the literature. After humidification the sample was removed from the desiccator and the moisture content of the sample was determined by Karl Fischer method. The measurement was done in a room in which the temperature and the R.H. were controlled. 2) About 2 g of the sample was placed in a quartz pan and the sorption of water vapor was determined by means of a quartz spring balance housed in the sorption apparatus (Sibata-Type P-850S). The sample was dried at 100° and 10^{-4} mmHg pressure prior to the sorption measurement until no change in weight was observed.

Caking Procedure——1) About 60 g of powder packed in a cylindrical container 6.5 cm in diamecter and 7 cm in height was tapped until it attained a required porosity. The sample was placed in a desiccator with a given R.H. at 25° and allowed to stand for 10 days. Then, the container was transfered into another desiccator with less R.H. at the same temperature and the sample was dried for 10 days. 2) The samples humidified at 25° in a similar way as 1) were dried at 30°, 35°, or 40° for 10 days in the desiccators where the vapor pressure of water was maintained at the same as in the humidification.

Crushing Strength Measurement——Crushing strength measurements were made using 1 cm cubes of cake under a given temperature and humidity, the apparatus for which is shown in Fig. 1. The sample to be tested, 1, is placed on a L-shaped holder, 2. A metal rod of 4.2 mm in diameter, 3, is moved in the direction of the arrow at the speed of 6.8 cm/min. The load measured by the strain gauge, 4, fixed on the metal rod is led through a strain meter, 5, to a recorder, 6. One of the typical records is shown in Fig. 2. Measurements have been made three times on each sample caked under given conditions, and the average values of crushing load were taken.

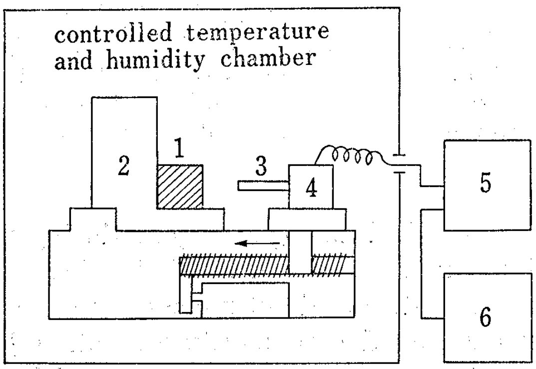

Fig. 1. Apparatus for Measurement of Crushing Strength

1: sample cake
2: holder fixed to base
3: metal rod
4: strain gauge
5: strain meter
6: recorder

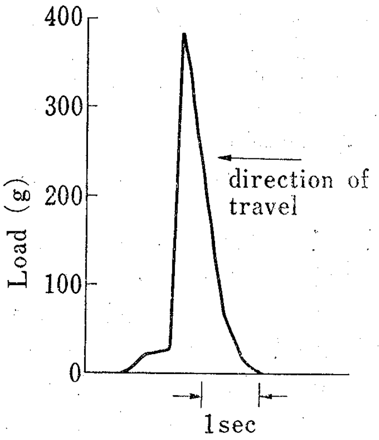

Fig. 2. Typical Record of Crushing Strength Measurement

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3) C.H. Greenewalt, *Ind. Eng. Chem.*, 17, 522 (1925).

Results and Discussion

Moistuer Sorption Isotherm

The moisture sorption isotherm of DGL at 25° is presented in Fig. 3, the scale of the ordinate being magnified in the upper figure. The isotherm indicates physical adsorption up to around 75% R.H., whereas the amount of water sorbed increases markedly above the critical relative humidity (C.R.H.). Within the region where physical adsorption is assumed, the sorption amounts were found to be much larger than those expected from the specific surface area determined by the air permeability method. This may be explained by either or both of the following two mechanisms. (1) In the case of the air permeability measurements the flow area calculated from Kozeny-Carman equation is found to be less than the area measured by the BET gas adsorption method when the powder particles to be tested have micropores and internal surfaces. (2) In the sorption of water vapor by hydrophilic substances, the diffusion of water molecules into powder particles is accompanied with a simple physical adsorption. That is, since DGL has a strong affinity for water vapor, not only the surfaces of the particles achieve a more stable solvated state but also this stabilizing effect may extend to the lower cohesive energy regions in the particles. Kanazawa and others[4] reported that the surface areas of some water-soluble fertilizers obtained by water vapor sorption measurements were extremely high compared with those by N_2 adsorption at low temperature. They mentioned that above phenomena may be explained by the diffusion of water molecules into particles, considering the values of isosteric heats of adsorption of water vapor for these materials.

From our experiments here, it is unfortunately difficult to conclude which mechanism is more adequate for the explanation of the results. However, considering the facts that the surface area of DGL by means of N_2 adsorption at low temperature was actually too small (<0.3 m^2/g) to determine with a sufficient accuracy, and that DGL is a highly hydrophillic substance as expected from its structural formula and from its high solubility in water, it can be said that there is quite a possibility of mechanism (2).

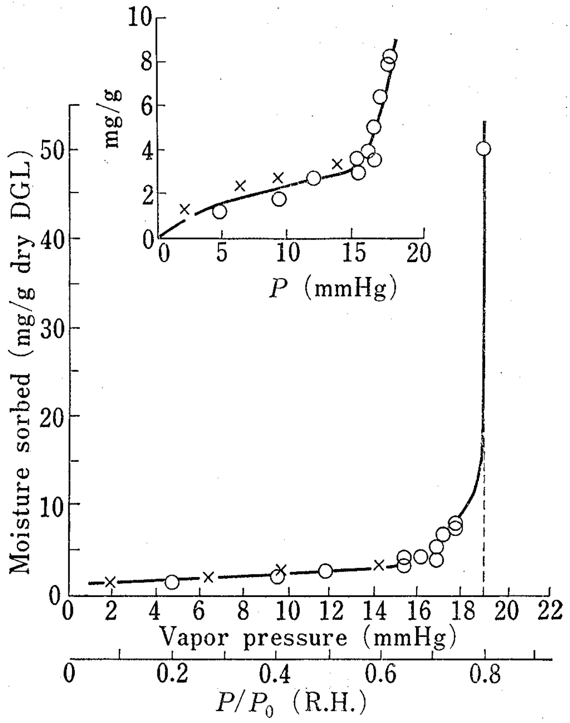

Fig. 3. Moisture Sorption by DGL at 25°

○: Karl Fischer method
×: spring balance method

Effect of Caking Conditions on Crushing Strength of Cakes

Table I shows the caking conditions and the crushing strengths of cakes as well as the amounts of moisture evaporated during the drying process. The crushing strength increased with an increase in the amount of water evaporated. Particularly, when the released moisture exceeded 5 mg per 1 g dry DGL severe caking was observed.

Although it has been generally said that moisture sorption makes hygroscopic substances caked, moisture evaporation from the humidified powder due to some environmental changes

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[4] T. Kanazawa, M. Chikazawa, and M. Kaiho, *Kogyo Kagaku Zasshi*, 73, 1654 (1970).

TABLE I. Experimental Conditions and Results

Experimental number	Porosity of powder bed	Conditions of moisture sorption		Conditions of drying		Amount of moisture evaporated (mg/gDGL)	Crushing load (g)
		Temperature	Vapor pressure of water (mmHg)	Temperature	Vapor pressure of water (mmHg)		
1	0.612	25	15.4	25	11.9	0.87	65
2	0.612	25	16.2	25	11.9	1.31	82
3	0.612	25	16.6	25	11.9	2.68	110
4	0.612	25	17.1	25	11.9	3.86	277
5	0.612	25	17.8	25	11.9	5.30	1401
6	0.573	25	15.4	35	15.4	0.01	159
7	0.573	25	16.6	35	16.6	0.65	181
8	0.573	25	17.8	30	17.8	5.04	2154
9	0.573	25	17.8	35	17.8	5.21	2335
10	0.573	25	17.8	40	17.8	5.57	5045

seems to be necessary for caking, as Moss and others[5] already pointed out. In our experiments, caking did not take place even when the humidification was carried out near the C.R.H. unless the subsequent drying procedure was taken. This may prove the conception that caking is mainly caused by solid bridges formed by the crystallization of dissolved DGL.

Kanazawa and others[6] stated that, in the case of NaCl powder, migration of Na^+ and Cl^- through the adsorbed layers occurred even in the region not exceeding bimolecular layer. They also found that NaCl particles began to agglomerate when the amount adsorbed exceeded three layers. Since humidification was carried out near the C.R.H. in most of our experiments, it can be undoubted that the state of sorbed water is close to that of the liquid water into which DGL can be dissolved easily. Then, evaporation of water from the solution on the surface of particles may cause severe caking.

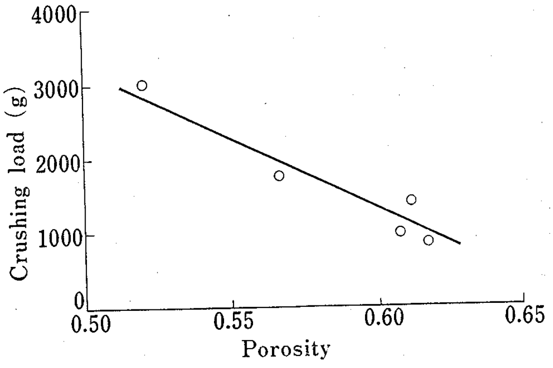

Fig. 4. Relation between Porosity and Crushing Strength

Caking conditions are the same as those of Ex. 5 in Table I.

Effect of Porosity

Fig. 4 shows the relation between porosity and crushing strength. The caking conditions are identical with the experimental number 5 in Table I, and porosity is controlled by the variation of tapping height. Crushing strength has a trend to increase with decreasing porosity. It is generally considered that crystallization of dissolved substances occurs preferably in the contact region between particles. Thus, the effect of decreasing porosity on caking strength can be attributed to the increase in the number of total contact points in a powder bed.

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5) H.V. Moss, T.W. Schilb, and W.G. Warning, *Ind. Eng. Chem.*, **25**, 142 (1933).
6) M. Kaiho, M. Chikazawa, and T. Kanazawa, *Nippon Kagaku Zasshi*, **1974**, 233.