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A Modified Penetration Rate Method for Measuring the Wettability of Magnesium Oxide Powders

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A modified penetration rate method was used successfully to evaluate the wetting properties of magnesium oxide powders.

The Washburn equation was employed for analysing experimental data on the assumption that penetrating liquids rise in large number of capillaries formed by particles in the powder bed.

The particle size dependency of penetration rate and $r \cdot \cos\theta$ was discussed based on the results obtained.

Generally, contact angle measurement is made to evaluate the wettability of powders. Although there exist static[2)] and dynamic methods for measuring contact angle, the penetration rate method is one of the dynamic methods.

Most of previous studies on the wetting rate and the contact angle by this method were concerned with fibers[3—5)] and few with powders.[6,7)] With regard to the apparatuses used, they were not of automatic recording type and the time of reaching of a penetrating liquid at a suitable height was measured by a stop-watch.[7,8)]

In this study, therefore, an attempt was made to introduce a balance type recording penetration rate measuring apparatus so that we can measure the penetration rate more easily and accurately than ever before. Magnesium oxide powders which are frequently used in medicines as an antacid were selected as the samples, and the wettability with lower alcohols of beds of the powders was examined by this method. The particle size dependency of penetration rate and contact angle was discussed based on the results obtained.

Experimental

Materials——Powder samples used for measurement of penetration rate in this study were of magnesium oxide (Kyowa Chemical Industry Co., Ltd.), which were obtained by calcinating the starting material, magnesium hydroxide or magnesium carbonate, in a Siliconit Furnace (Siliconit Konetsu Kogyo Co., Ltd., Tokyo, BM-3550 box type) at 800, 900, 1000, 1100, or 1200° for three hours, and had the characteristics given in Table I. All of the calcinated samples were numbered according as the starting material and represented by the corresponding abbreviations as shown in Table I.

Liquids used for penetration into powder bed were methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl alcohols, all of which were of reagent grade.

Methods——Measurement of Penetration Rate: A) Preparation of Powder Bed: A glass tube of about 1 cm in i.d. and about 15 cm in length was covered at one end with a No. 7 filter paper and the paper was

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1) Location: *a) 12 Funagawara-machi, Ichigaya, Shinjuku-ku, Tokyo; b) 4035 Hayashida-machi, Sakaide-city, Kagawa.*

2) T. Sasaki, "Jikken Kagaku Koza. Vol. 7, Kaimen Kagaku," 3rd ed., Maruzen, Tokyo, 1956, pp. 75—83.

3) H. Matsumaru, *Yakugaku Zasshi*, **79**, 67 (1959).

4) H. Kuno and R. Abe, *Kogyo Kagaku Zasshi*, **61**, 57 (1958).

5) S. Chwastiak, *J. Colloid Interface Sci.*, **42**, 298 (1973).

6) R.W. Rance, *J. Soc. Cosmet. Chem.*, **24**, 501 (1973).

7) H. Hasegawa, *Yakugaku Zasshi*, **80**, 1179 (1960).

8) R.L. Peek, Jr. and D.A. Mclean, *Ind. Eng. Chem.*, **6**, 83 (1934).

TABLE I. Characteristics of Magnesium Oxide prepared from Magnesium Hydroxide or Magnesium Carbonate

Starting material: $Mg(OH)_2$

Calcination temp. (°C)	800 A-1	900 A-2	1000 A-3	1100 A-4	1200 A-5
MgO content (%)	95.81	96.65	97.25	97.45	97.50
Citric acid-test (sec)$^{a)}$	25.4	62.4	105.2	405.4	998.4
BET (m^2/g)	51.0	19.0	12.0	3.0	0.5
(200) X-ray diameter (μ)	0.0198	0.0480	0.0666	0.1240	0.2330
Porosity$^{b)}$	0.875	0.851	0.840	0.776	0.718

Starting material: $MgCO_3$

Calcination temp. (°C)	800 B-1	900 B-2	1000 B-3	1100 B-4	1200 B-5
MgO content (%)	95.53	96.29	96.97	97.82	98.01
Citric acid-test (sec)$^{a)}$	17.6	22.6	62.0	246.4	672.8
BET (m^2/g)	62.0	41.0	21.0	9.0	2.0
(200) X-ray diameter (μ)	0.0170	0.0274	0.0630	0.1050	0.2440
Porosity$^{b)}$	0.882	0.889	0.873	0.837	0.753

a) A beaker containing 100 ml of 0.4N citric acid solution was placed in a magnetic mixer thermostated at 30°. After temperature of the solution attained 30°, 2 g of a sample powder was introduced into the beaker and a stop-watch was allowed to start working at the same time. After 10 seconds, stirring of the solution and continuous reading of pH by a pH meter (Hitachi-Horiba Seisakujo, Tokyo, M-5 type) were started, and then the stop-watch was stopped at the time when the pH of the solution became 8.0 and the time was read.

b) Mean value for 10 runs of powder packing in glass tube.

TABLE II. Times of Tapping

	A-group powders					B-group powders				
	A-1	A-2	A-3	A-4	A-5	B-1	B-2	B-3	B-4	B-5
Times of tapping	400	300	300	250	130	400	320	300	250	130

tied up with cotton thread. A sample powder, previously dried at 105° for one hour by an Infrared-moisturemeter (Kett Electric Laboratory Co., Ltd., Tokyo, Kett 2A type) and passed through a 32 mesh sieve, was introduced into the glass tube by using a funnel to form a powder bed. Then the glass tube was tapped by a packing-density measurement apparatus (Toyo Kagakusangyo Co., Ltd., Osaka, TSP-D type) until the height of the powder bed became constant. In this way, as shown in Table II numbers were given to the times of tapping required to make the height of the powder bed constant.

Another glass tube was filled partly with molten solid paraffin at its bottom part, and it was covered with a No. 7 filter paper after cooling. This was used as the blank.

B) Measurement of Penetration Rate: A balance type recording penetration rate measuring apparatus is shown in Fig. 1. The measurement was made in the atmosphere at 25° in the following way; two glass vessels containing a liquid for penetration measurement of almost the same weight were placed on the both balance plates. Evaporation of a liquid seems to be compensated each other between these

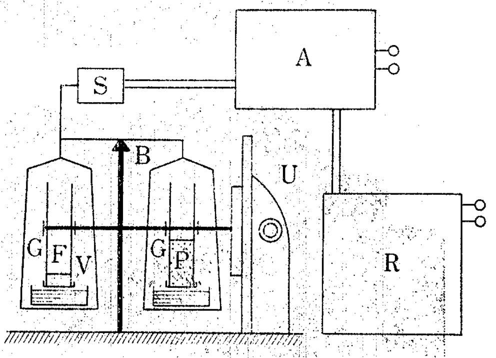

Fig. 1. Apparatus for Penetration Rate Measurement

A) stabilizer B) chemical balance F) paraffin G) glass tube P) sample powder R) recorder S) strain gauge U) up-down slider V) solvent vessel vessels. The powder packed glass tube and the blank glass tube were attached to the up-down slider at the same height. Then, the balance was operated, and the up-down slider was moved down very carefully after the balance reached a steady state so that the bottoms of the both glass tubes entered into the liquid at the same time. The penetration of the liquid started immediately, and the balance of the plates was broken owing to the difference in weight. This difference was transformed into electric current by a strain gauge and continuously followed by a records at a constant chart speed.

Measurements of Properties of Powders——Specific gravity of powder in each of the liquid was measured by a picnometer in a thermostat controlled at 25°.

Surface tension of liquid was measured at 25° by Du Noüy tensiometer (Rigosha Mfg., Co., Ltd., Tokyo).

Viscosity values were taken from literatures.[9,10]

Results and Discussion

The powders had different mean diameters depending on the calcination temperature and they are shown in Table I, Fig. 2-a, and b. This is due to the fact that the degree of sintering increases with increasing calcination temperature.

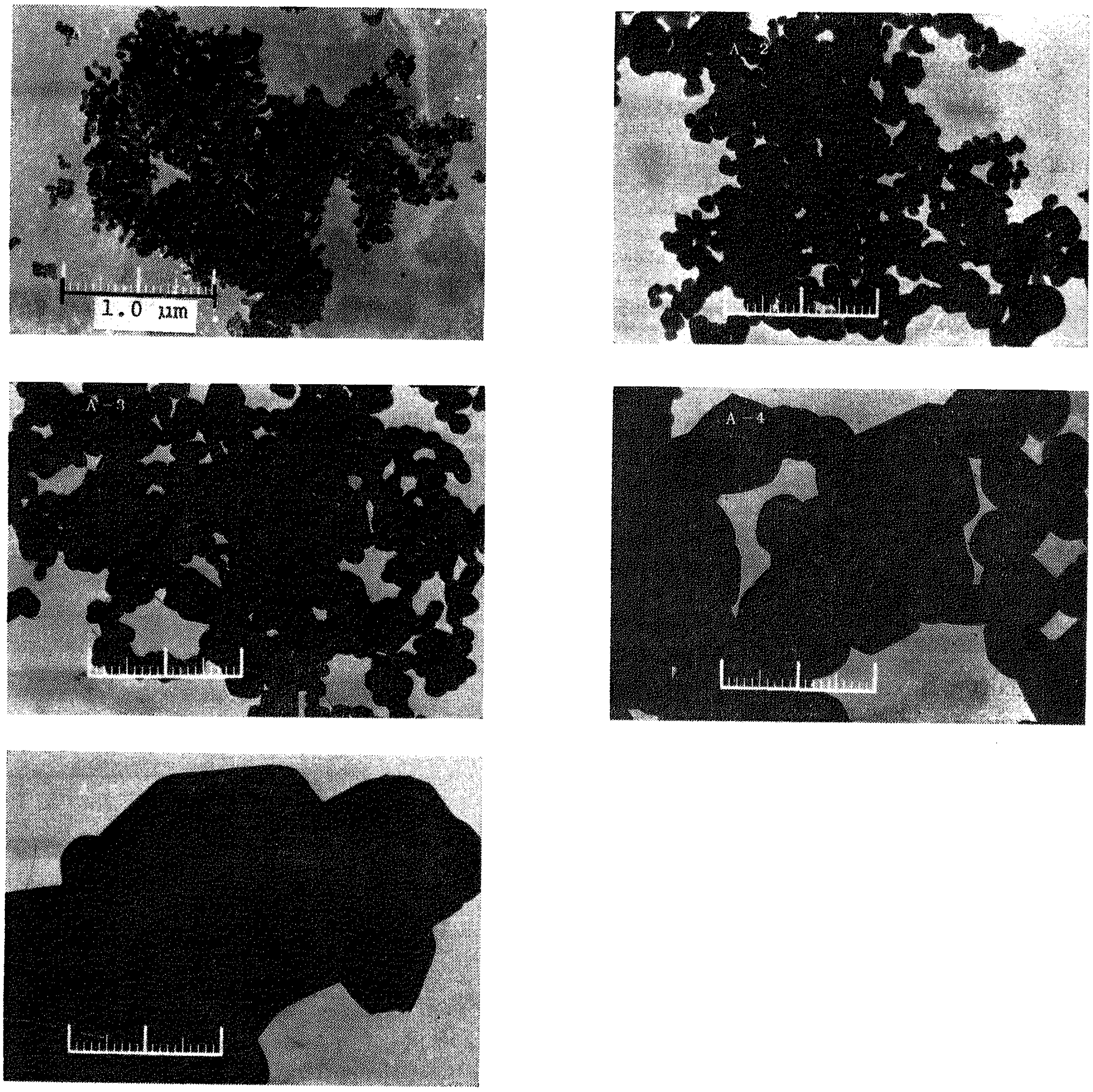

Fig. 2-a. Electronmicrographs of A-group Powders

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9) J.A. Riddick and W.B. Bunger, "Organic Solvents," 3rd ed., John Wiley and Sons. Inc., New York, N. Y., 1970.

10) Nihon Kagakukai ed., "Kagaku Binran, Kisohen (II)," 5th ed., Maruzen, Tokyo, 1966.

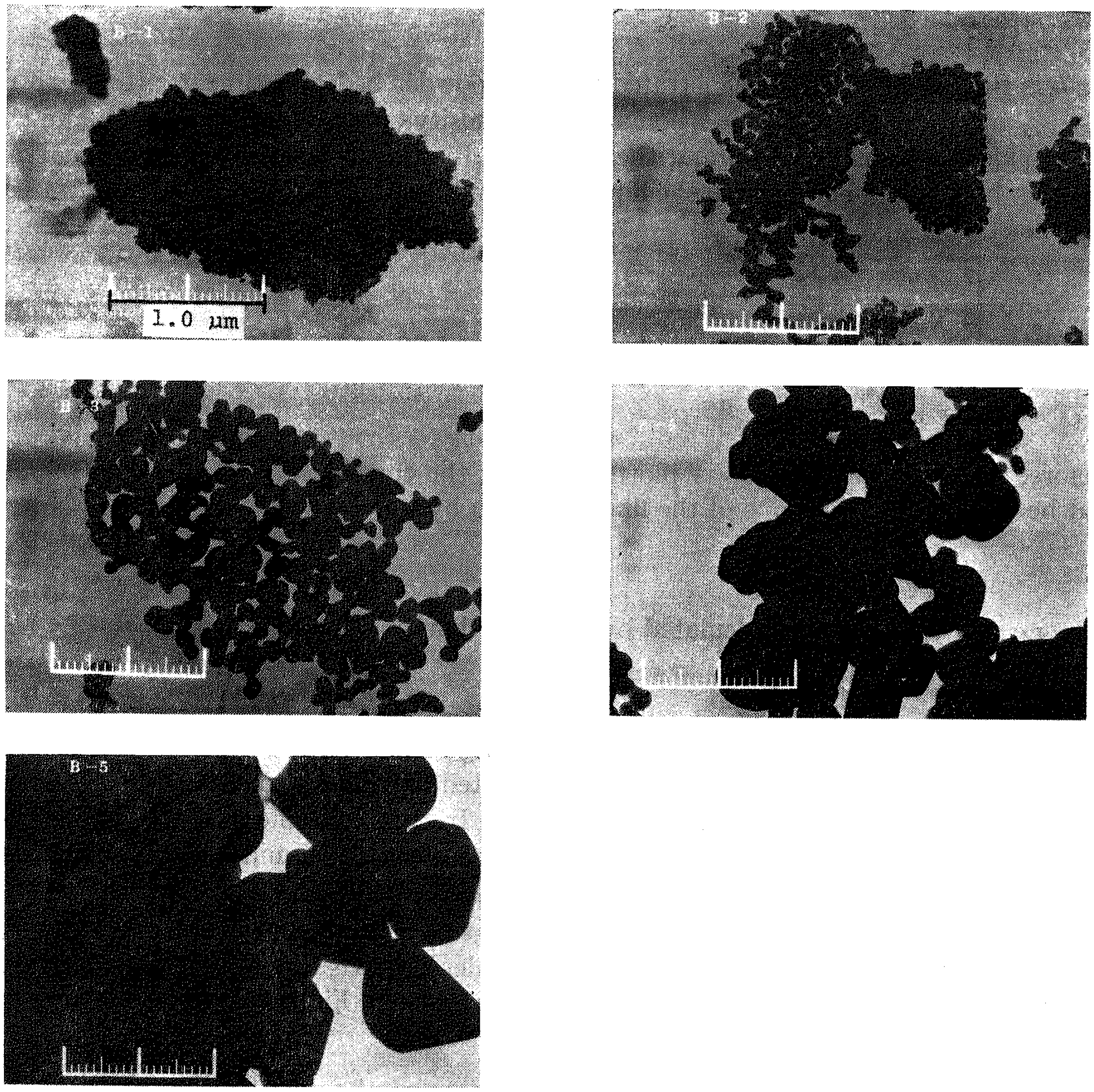

Fig. 2-b. Electronmicrographs of B-group Powders

The mean diameters of the powders were determined by an X-ray diffractometer (Rigaku Denki Co., Ltd., Tokyo, Geiger Flex D-S type) with copper K-α radiation using the line broadening method. In this method the X-ray diameter D_{hkl} at $2\theta=42.8°$, (200), was calculated by the usual equation.11)

The effect of particle size on porosity, ε, is shown in Fig. 3 for the powders packed in glass tubes. In Fig. 3, (1-ε) on the vertical axis represents the net powder volume ratio in the bed. Each line was determined by the least squares method. Fig. 3 suggests that $\sqrt[3]{1-\varepsilon}$ is proportional to the particle size within the same group of powders.

Though both of surface tension and gravitation are expected to be closely related to the rate of liquid rise in capillary, if the radius of capillary is extremely small, the influence of gravitation is negligible.12) Hence, assuming that the void formed by powder particles in a powder bed as shown in Fig. 1 consists of a large number of capillaries which have a mean radius r and that liquid rises in the capillary system in the process of penetration, the following equation is obtained.

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11) N. Ueda, "Funtai, Riron To Oyo," 3rd ed., ed. by T. Kubo, E. Suito, Y. Nakagawa, and S. Hayakawa, Maruzen, Tokyo, 1962.

12) T. Sasaki, "Jikken Kagaku Koza. Vol. 7, Kaimen Kagaku," 3rd ed., Maruzen, Tokyo, 1956, p. 84.

$$h^2 = \frac{r\gamma_l \cos\theta}{2\eta_l} t, \tag{1}$$

where h is the height of liquid penetrated into the powder bed at a time, t, after penetration starts. γ_l and η_l are the surface tension and the viscosity of a liquid, respectively, and θ is the contact angle between the liquid and the powder. In addition, if the cross sectional area of the powder bed is A, the density of the liquid is ρ_l, and the weight of the liquid penetrated into the powder bed is w, then

$$h = \frac{w}{A\varepsilon\rho_l}. \tag{2}$$

Substituting Eq. (2) into Eq. (1) and rearranging we obtain

$$\frac{w}{A} = \left(\frac{\varepsilon^2\rho_l^2 r\gamma_l \cos\theta}{2\eta_l}\right)^{1/2} t^{1/2}. \tag{3}$$

Therefore, when the value w/A is plotted against the corresponding $\sqrt{t}$, a linear relation should be obtained. The slope of the line α is given by

$$\alpha = \left(\frac{\varepsilon^2\rho_l^2\gamma_l r\cdot\cos\theta}{2\eta_l}\right)^{1/2} \tag{4}$$

and the $r\cdot\cos\theta$ value can be calculated by the equation

$$r\cdot\cos\theta = \alpha^2\cdot\frac{2\eta_l}{\rho_l^2\gamma_l}\cdot\frac{1}{\varepsilon^2}. \tag{5}$$

Now, the required w at any time can be read from the recorded curve by the penetration measuring apparatus because the weight of penetrated liquid is automatically registered continuously on a chart as soon as penetration starts. In this experiment, the capillary systems appear to be saturated by the penetrating liquid vapor with any liquids, and the liquids not to react with the powders.[13] When several values of w are read from the curve and the corresponding values of w/A are plotted against $\sqrt{t}$, a linear relation holds between w/A and $\sqrt{t}$ in the region I where the liquid rises steadily in the powder bed as is seen in Fig. 4. This insures the applicability of Eq. (3) to the region I. The plateau region in Fig. 4 indicates that penetration

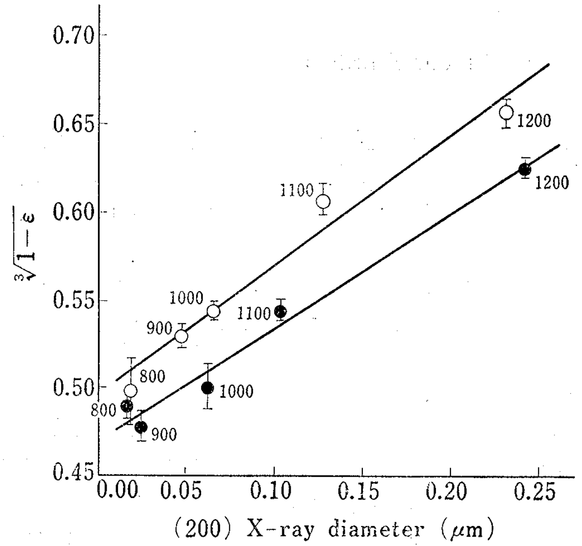

Fig. 3. Effect of Particle Size on Porosity[a)]

a) Mean value of 10 runs was plotted. Each subscript shows calcination temperature. A-group powders (○), B-group powders (●)

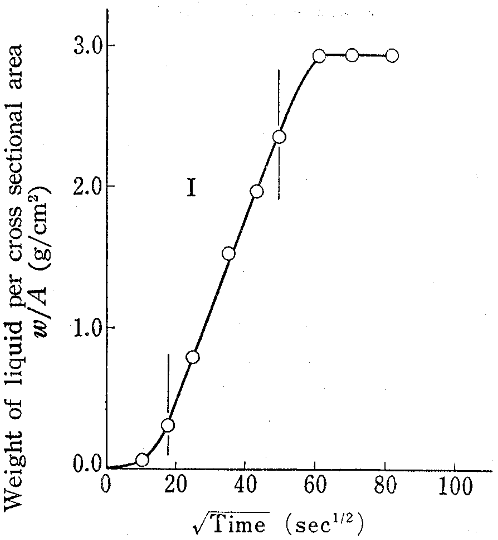

Fig. 4. Change in Weight of Penetrating Liquid with Time for Combination of A-1 and n-Propyl Alcohol

tapping times: 400, porosity: 0.883

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[13] H. Utsugi, *Funtai To Kogyo*, 6, No. 12, 61 (1974).

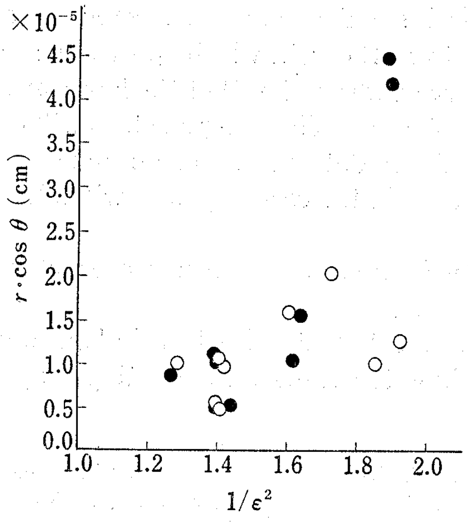

Fig. 5-a. Plots of $r\cdot\cos\theta$ *vs.* $1/\varepsilon^2$ for A-group Powders

methyl alcohol (○), ethyl alcohol (●)

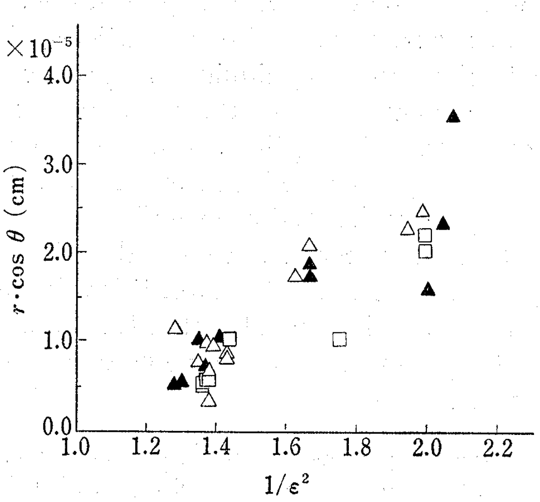

Fig. 5-b. Plots of $r\cdot\cos\theta$ *vs.* $1/\varepsilon^2$ for A-group Powders

n-propyl alcohol (△), *n*-butyl alcohol (▲), *n*-amyl alcohol (□)

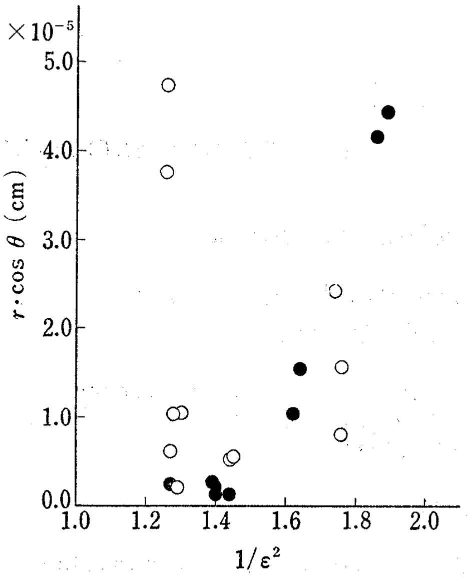

Fig. 6-a. Plots of $r\cdot\cos\theta$ *vs.* $1/\varepsilon^2$ for B-group Powders

methyl alcohol (○), ethyl alcohol (●)

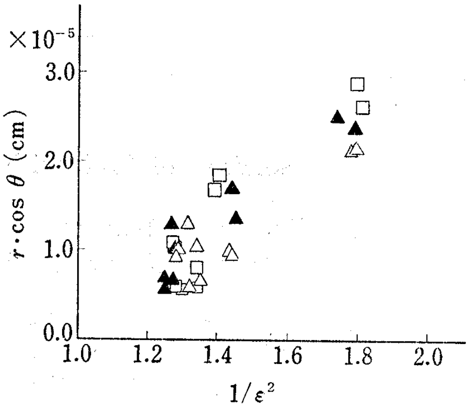

Fig. 6-b. Plots of $r\cdot\cos\theta$ *vs.* $1/\varepsilon^2$ for B-group Powders

n-propyl alcohol (△), *n*-butyl alcohol (▲), *n*-amyl alcohol (□)

ceases. The value of w at the point where the plateau starts gives the absorbed liquid volume. However, this will not be discussed here. The slope, α, which is equivalent to the rate of penetration, increases, in most cases, with increasing particle size. From Eq. (5), $2\eta_l/\rho^2{}_l\gamma_l$ should be constant when the same liquid is used. On the other hand, ε decreases with increasing particle size as is seen from Fig. 3. Therefore, the product of α^2 and $1/\varepsilon^2$ contributes to the increment in $r\cdot\cos\theta$ as is clear from Eq. (5). In Fig. 5-a, b, 6-a, and b are plotted $r\cdot\cos\theta$ as a function of $1/\varepsilon^2$ for each of the liquid used. Fig. 5-a and 6-a are for methyl and ethyl alcohols, while Fig. 5-b and 6-b are for n–propyl, n–butyl, and n–amyl alcohols. Although there is a tendency of $r\cdot\cos\theta$ to increase with $1/\varepsilon^2$ in Fig. 5-b and 6-b, such tendency is not evident in Fig. 5-a and 6-a, because the vapor pressures of methyl and ethyl alcohols at 25° are much higher than the other alcohols and adsorbed[14] layers of these alcohol molecules are formed on

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[14] D. Nicholson and J.H. Petropoulos, *J. Colloid Interface Sci.*, **45**, 459 (1973).

the walls of capillaries prior to penetration. Further, if r is small enough as expected especially for powder beds made of small particles, air expulsion from the void will be prevented in the penetration process by liquid plugs produced by capillary condensation[15] of the lower alcohols on the capillary wall, and the rate of penetration will be slower. The other alcohols will not be adsorbed onto the capillary wall so much as methyl and ethyl alcohols. The presence or absence of such adsorbed layers and the degree of absorption on the capillary wall will affect the rate of penetration and $r\cdot\cos\theta$.[16]

Then, it is necessity to see if there is a relation between $r\cdot\cos\theta$ and surface characteristics of powder particles. However, this will not discussed here.

Finally, it is concluded that the modified penetration rate method is fast, independent of operator judgment, and can be used as a simple technique to evaluate the wetting properties of powders.

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[15] H. Matsumaru, *Yakugaku Zasshi*, **78**, 1205 (1958).

[16] R.J. Good, *J. Colloid Interface Sci.*, **42**, 475 (1973).

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Isolation of Pretazettine from *Narcissus tazetta* L.

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(Received May 24, 1975)

Reinvestigation of the alkaloidal constituents of *Narcissus tazetta* L. revealed that the main alkaloid was pretazettine, although the main alkaloid of this plant had been reported to be tazettine and also provided a convenient and efficient scheme for isolation of pretazettine.

In 1967, one of us (W.C.W.) reported isolation of a novel alkaloid pretazettine (I) from *Sprekelia formosissima* L. and suggested that tazettine (II) which was one of the abundant alkaloids of the Amaryllidaceae was an artifact produced by a rearrangement of pretazettine during the course of usual isolation procedure for alkaloids.[2] Based on the above finding and antileukemic activity[3] of the alkaloidal extract of *Narcissus tazetta* L., we carried out a reinvestigation of the constituents of this plant, the main alkaloid of which was reported to be tazettine.[4]

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[1] Location: *a) 3675 Kilauea Ave. Honolulu, Hawaii 96816*; *b) Yoshida, Sakyo-ku, Kyoto*; *c) Ames, Iowa 50010.*

[2] W.C. Wildman and D.T. Bailey, *J. Am. Chem. Soc.*, **89**, 5514 (1967); *idem*, *J. Org. Chem.*, **33**, 3749 (1968).

[3] E. Furusawa, N. Suzuki, S. Tani, S. Furusawa, G.Y. Ishioka, and J. Motobu, *Proc. Soc. Exp. Biol. and Med.*, **143**, 33 (1973).

[4] E. Späth and L. Kahovec, *Ber.*, **67**, 1501 (1934).