

Some physical properties of lactose and magnesia

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Anomalies in some of the physical properties of spray dried lactose and granulated magnesium oxide have been traced to the presence of fines. These are strongly adsorbed onto particles of about 1,000 μ diameter, being held in position by van der Waals' and electrostatic forces. Although they are not displaced during sieving, they can be removed by washing the powders with organic solvents.

THERE has been relatively little systematic work done on the effect of particle size on the physical properties of powders. The equations for angle of friction (Cremer, Conrad & Kraus, 1952; Fowler & Chodziesner, 1959), angle of repose (Fowler & Wyatt 1960; Brown 1961a), density and rate of flow through orifices (Fowler & Glastonbury, 1959; Rose & Tanaka, 1959; Brown & Richards, 1960) have been derived from data relating to a large number of different materials. This has been necessary in order to cover a reasonable range of particle sizes, but the materials involved have often differed considerably in the shape, density and roughness of the particles, all of which would be expected to affect the results.

With the availability of granulated powders in which the shape, density and roughness of the particles remains sensibly constant over a wide range of sizes, it has become possible to eliminate the effects of some of these variables. Nevertheless there remain certain anomalies in the graphs obtained by plotting properties such as angle of repose, density and flow rate against particle size.

The purpose of the present work has been to investigate these anomalies for two materials, magnesia and lactose, in some detail and to attempt to explain their occurrence.

Experimental

MATERIALS

Granulated magnesium oxide from the Washington Chemical Co. was dried at 800° for 2 hr. Spray dried lactose from McKesson & Robbins Limited was granulated in a dish granulator and dried at 120°. Both materials were sieved into narrow fractions on an Alpine Airjet Sieve, using 20 g portions, and were stored in dry screw-capped bottles.

It should be emphasised that the properties of both materials varied from batch to batch. For this reason it was necessary to obtain a large stock of each material and make all the measurements on the one batch.

MEASUREMENTS

The sizes of particles in the range 40 to 2,000 μ were obtained by sieving. For material below 40 μ diameter the Andreasen pipette method was employed, using 500 ml of a 2% dispersion in toluene or carbon

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tetrachloride (Martin, 1960) and withdrawing eight 10 ml samples over a period of 2 hr and calculating the particle diameter from Stoke's Law.

Particle densities over the size range 50 to 1500 μ were measured at 22° in toluene or benzene by the specific gravity bottle method using the equation:

$$\text{Specific gravity} = \frac{S(W_2 - W_1)}{SV - (W_3 - W_2)} \quad \dots \quad (1)$$

where S = specific gravity of toluene; W_1 = weight of the bottle; W_2 = weight of bottle plus powder; W_3 = weight of bottle plus powder plus toluene; V = volume of bottle.

The bulk density of each sieve fraction was obtained in the Heywood bulk density apparatus.

Tap densities were determined as described in British Standard (1948). The densities of compacts of the magnesia were determined in the apparatus shown in Fig. 1 by filling it with 25 g of the powder and then compressing at 168 kg cm⁻² between the platens of an Avery Tensile Tester, and measuring the resulting thickness of the compact on the dial micrometer.

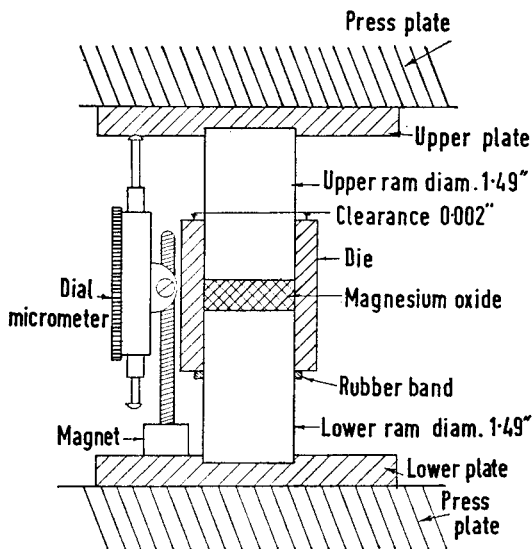


FIG. 1. Apparatus for compaction of magnesia.

A few granules from each sieve fraction were placed on a clean glass slide, one end of which was slowly raised until the granules started to slide. The elevation of the slide then yielded the angle of friction (Fowler & Chodziesner, 1959). Angles of repose of the different fractions were measured by a static method (Pilpel, 1964).

Rates of flow were measured from a 60° tapered glass separating funnel of maximum diameter 5 cm which was fitted with a sliding shutter to give interchangeable orifices having diameters between 0.47 and 1.70 cm.

Finally a representative number of particles from each sieve fraction were viewed under the microscope at magnifications of 200x and 60x to determine approximately the size and amount of fine material that was adhering to their surfaces.

A batch of the 1,000 μ material was then freed as completely as possible from fines by washing it with chloroform, and its angle of friction and angle of repose were measured. The size range of the displaced fines was also determined by sedimentation.

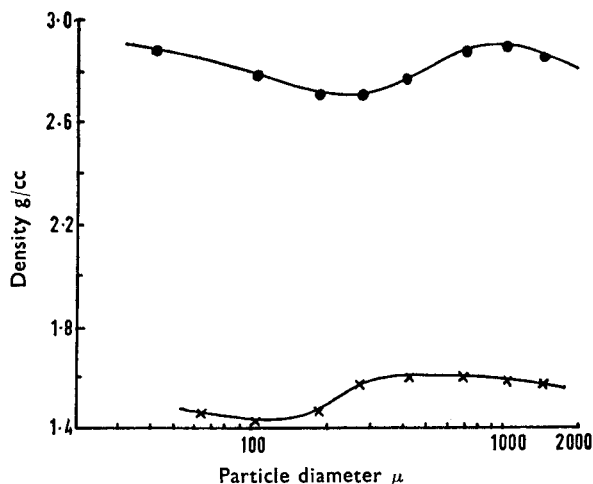


FIG. 2. Effect of particle diameter on particle density at 22° C. ● = Magnesia. × = Lactose.

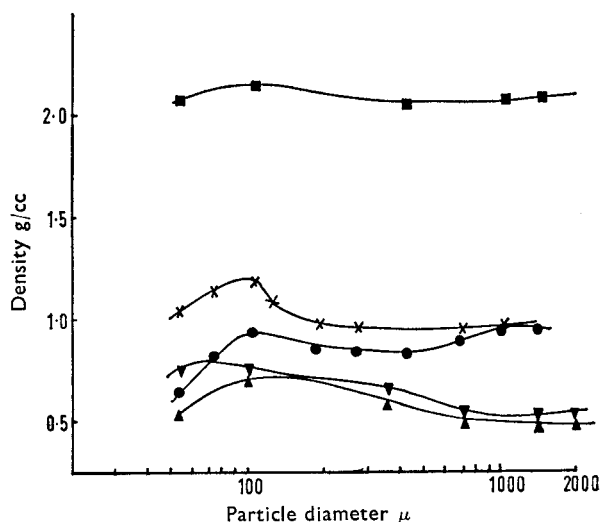


FIG. 3. Effect of particle diameter on powder density. ● = Bulk density of magnesia. × = Tap density of magnesia. ■ = Compacted density of magnesia at 160 kg/cm². ▲ = Bulk density of lactose. ▼ = Tap density of lactose.

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Results

The graph relating the particle density to the particle size is given in Fig. 2. Fig. 3 shows the variation of bulk, tap and compacted densities with particle size. Fig. 4 relates the sizes of the particles to the elevation of the glass slide when sliding commenced.

The graphs of angle of repose versus particle size for narrow sieve cuts are given in Fig. 5, which also includes some literature results on sulphathiazole (Nelson, 1955) and silica sand (Brown, 1961a). Rates of flow

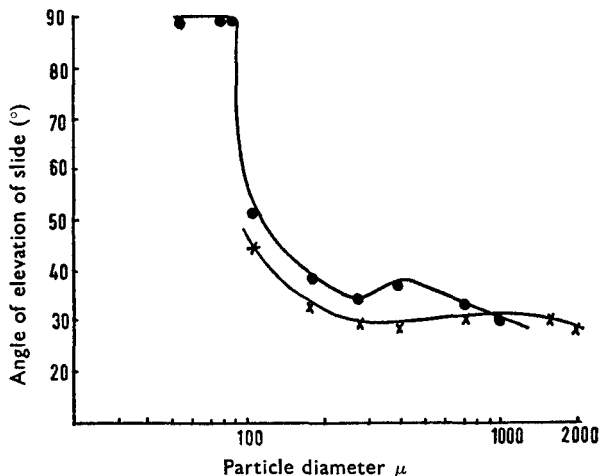


FIG. 4. Effect of particle diameter on angle of friction. ● = Magnesia. × = Lactose.

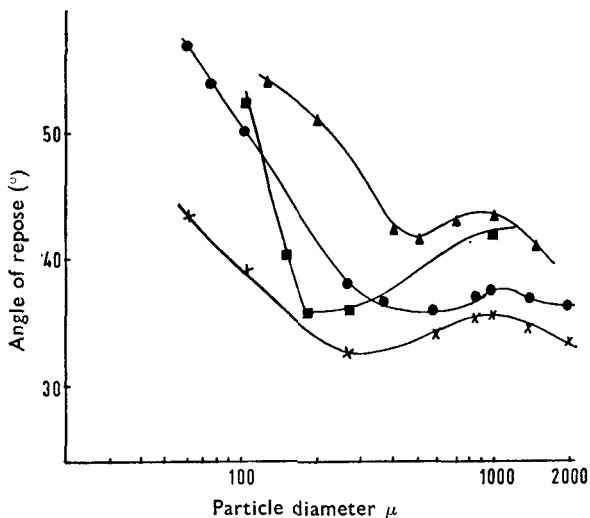


FIG. 5. Effect of particle diameter on angle of repose. ● = Magnesia. × = Lactose. ■ = Silica sand. ▲ = Sulphathiazole.

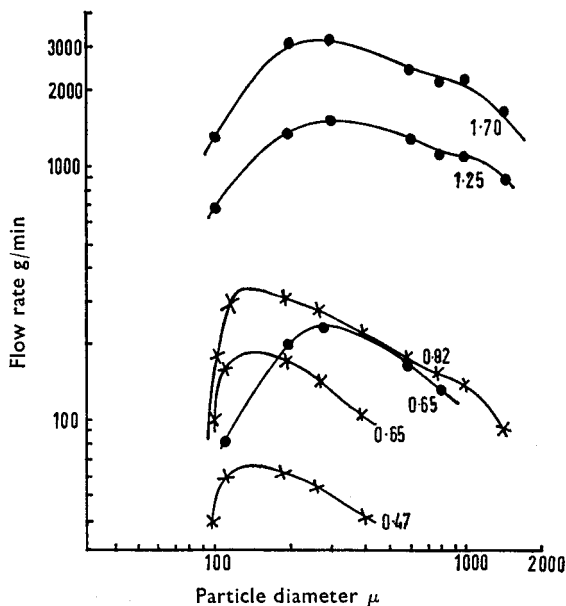


FIG. 6. Effect of orifice and particle diameter on rate of flow. ● = Magnesia. × = Lactose. Figures on the curves are the orifice diameters in cm.

through five different sized orifices are plotted in Fig. 6. All measurements were made in duplicate or triplicate and the limits of reproducibility were as follows: particle, bulk, tap and compacted densities ± 0.02 g/cc; angles of friction and repose, $\pm 0.3^\circ$; rates of flow, $\pm 7\%$.

Figs 2-6 show that over the size range 600-1,200 μ the physical properties of all the powders under investigation exhibit anomalies. The granule densities of magnesia and lactose pass through slight maxima, the bulk, tap and compaction densities rise to maxima at about 100 μ (when cohesion between particles becomes negligible) and fall to minimal values near 800 μ .

Regarding the angle of friction and the angle of repose, Figs 4 and 5 both show maxima and minima between 300 and 1,000 μ . The flow curves in Fig. 6 have the general shape expected (Rose & Tanaka, 1959) though between 700 and 1,000 μ some of the curves exhibit points of inflexion. The graphs of log flow rate versus log orifice diameter are practically linear for each size of particle and their slopes lie between 2.5 and 3.2 (see Franklin & Johanson, 1955).

As a result of washing the powders in chloroform, the angles of friction and of repose of the 1,000 μ magnesia and lactose were reduced as were kinks in the flow curves. Typical data before and after washing are given in Table 1. However, more fines were formed during handling of the powders; it was difficult to check the effect that their removal had had on the other physical properties. Sedimentation showed that about 80% of the displaced fines were in the size range 10-50 μ .

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TABLE 1. EFFECT OF FINES BEFORE AND AFTER WASHING

Material				Angle of friction°		Angle of repose°		Flow rate g/min	
				Before	After	Before	After	Before	After
Magnesia	400 μ	37.5	36.0	36.5	36.5	—	—
"	1,000 μ	31.0	31.5	37.5	36.5	1,150	1,050
"	1,400 μ	—	—	37.0	36.5	—	—
Lactose	500 μ	—	—	34.0	34.0	—	—
"	1,000 μ	31.5	30.5	35.5	34.5	150	130

Discussion

It has been noted by many workers that fine particles in powders profoundly affect their properties. This is due to an enhancement of the van der Waals cohesive forces which operate between neighbouring particles. For example, an added weight fraction P₁, of fines with diameter D₁, increases the angle of repose θ of coarser magnesia (denoted by a subscript₂), the relevant equation being (Pilpel, 1964):

$$\left(\frac{\sin \theta}{\tan \theta_{lim}} - \cos \theta \right) = \frac{k D_1^{n-2}}{g \delta_2 X_2} \left[\frac{P_1}{(\delta/\delta_2 - P_2)} \right]^{2/3} \dots \dots (2)$$

where θ_{lim} is the limiting angle of repose of the coarse particles, k, n and X₂ are geometrical constants and δ is the particle density.

For magnesia and spray dried lactose, the cohesive forces become comparable to the weights of the particles when they are about 50 μ in diameter.

Particles of this size or below tend to be adsorbed on the surfaces of coarser particles forming a coating which may or may not be continuous. While cement particles apparently form a continuous coating on the balls used for grinding cement clinker (Bond, 1940), with the present materials, microscopic examination shows that particles 1,000 μ in diameter are only partially covered by adsorbed fines. These adhere sufficiently tenaciously to the surface not to be displaced during sieving. They can, however, be partially removed by washing the powders with chloroform.

By measuring their sedimentation rate in the Andreasen pipette apparatus, it has been found that about 80% of the fines fall in the size range 10–50 μ. There appear to be about 0.1 g of these fine particles associated with each gram of the 1,000 μ material.

Let it be assumed that the average radius of the adsorbed particles is r and that, on average, they cover a fraction, φ, of the surface of the larger particles, radius R. If the small particles are close packed in an hexagonal arrangement, then the number present on the surface of each large particle is $\frac{4\pi(R+r)^2\phi}{2r^2\sqrt{3}}$. Since the densities of the large and small

particles are similar (Fig. 2), it follows that $\frac{2\pi r(R+r)^2\phi}{R^3\sqrt{3}}$ g of fines are associated with each g of the larger sized particles. Thus

$$\frac{2\pi r(R+r)^2\phi}{R^3\sqrt{3}} = 0.1 \dots \dots (3)$$

and substituting $R = 500 \mu$ and $r = 15 \mu$, ϕ works out at approximately 0.4. This accords satisfactorily with the visual observation of the $1,000 \mu$ particles under the microscope: a representative sample of 200 of these had approximately one-third of their total surface area covered by fines.

The presence of adsorbed fines is not restricted to particles of $1,000 \mu$. Both coarser ($>2,000 \mu$) and finer ($200\text{--}300 \mu$) particles exhibit some adsorption. But on these sizes, the fines seem to adhere less tenaciously and the majority are therefore displaced during the preliminary sieving.

The marked adsorption of $10\text{--}50 \mu$ material onto approximately $1,000 \mu$ particles suggests that these larger particles have surface irregularities $10\text{--}50 \mu$ in diameter into which the smaller particles can fit. They are assumed to be held in position both by adhesive forces and by electrostatic forces of attraction (Harper, 1961). Considering first the adhesive forces F , if it is assumed that there is perfect contact between particles (Krupp & Sperling, 1964)

$$F = 2\pi r \Gamma \left(1 + \frac{\Gamma}{ZY} \right) \text{ dynes} \quad \dots \quad (4)$$

where Γ , the free adhesional energy is 1.5 times the free surface energy of the material, Y is its yield pressure and Z is approximately 4 \AA . For the granulated magnesia, the yield pressure, derived from the Vickers hardness tester (Bowden & Tabor, 1964) is of the order of 5 kg mm^{-2} and the surface energy is about 10^3 erg cm^{-2} (Gregg 1961). Taking r as 15μ , F works out at about 2×10^3 dynes.

This figure is based on the assumption that the particles are perfectly smooth and that the real area of contact is of the order of magnitude of r^2 . In fact, the *real* area of contact between the particles at normal pressures probably does not exceed $r^2 \times 10^{-6}$ (Bowden & Tabor, 1958) and the force between the particles is therefore substantially less, i.e. about 10^{-3} dynes (Kitchener, 1961). This force is of the same order of magnitude as the weights of the particles involved.

Now the fact that the fines are displaced when the $1,000 \mu$ material is immersed in an organic solvent, indicates that electrostatic attractive forces must also be playing some part, because the free surface energy of magnesia in chloroform is less than its free surface energy in air by only 27 ergs cm^{-2} (the surface tension of chloroform) and such a reduction would not significantly alter the value of F . Although it has not been possible to measure the magnitude of the electrostatic forces in the present work, one estimate (Harper, 1961) suggests that they might be as high as 10^{-3} dynes/particle. They are reduced in the presence of chloroform by a factor of 4.8, the dielectric constant of chloroform, and this results in partial detachment of the fines.

It has been considered of interest to compare some of the results in Fig. 6 with those predicted for powders flowing from a 60° funnel, by the minimum energy theorem (Brown, 1961b). The dimensionless quantity, γ , given by

$$\gamma = \frac{4Q}{\rho\pi(D_0 - k)^2\{g(D_0 - k)\}^{1/2}} \quad \dots \quad (5)$$

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where Q is the flow rate in g/sec, ρ is the bulk density of the powder, D_0 is the orifice diameter and k is a measure of the *vena contracta*, has been calculated from the measured values of Q and D_0 . Allowing for the fact that the different orifices unavoidably had slightly different geometries, the values, given in Table 2, are seen to agree very satisfactorily with the predicted value of 0.62.

TABLE 2. FLOW OF LACTOSE AND MAGNESIA

Material	Bulk density g/cc	k cm	Orifice diameter cm	Observed
Magnesia 550 μ	0.85	0.10	1.70	0.65
" "	"	"	1.25	0.75
" "	"	"	0.65	0.65
Lactose 550 μ	0.55	"	0.82	0.54
" 400 μ	"	0.09*	0.65	0.58
" "	"	"	0.47	0.58
Mean				0.62

*Estimated.

CONCLUSION

The hypothesis that adsorbed fines contribute in part to the anomalous behaviour of lactose, magnesia and other powders is consistent with the data in Figs. 2-6. Their presence increases the diameters of particles in the region of 1,000 μ and therefore cause displacement of the points along the abscissae. The fines also affect the frictional, cohesive and packing properties of the particles, causing displacements of the experimental points on the ordinates. The hypothesis is consistent with the observation that when the fines are displaced by washing the powder with chloroform, or alternatively, when there are relatively few fines present, as for example in a partially sintered grade of magnesia with a Vickers hardness of about 10 kg mm⁻², the anomalies are diminished.

The same hypothesis explains the fact that in many powders there are fewer fines than would be expected on the basis of the Rosin Rammler distribution law (Herdan, 1960).

$$\text{viz:} \quad \log \left(\log \frac{100}{R} \right) = \text{Constant} + n \log x \quad \dots \quad (6)$$

where R is the percentage by weight of particles bigger than a particular size, x , and n is a constant. While some fines are undoubtedly lost by air entrainment during the milling of powders, the present findings indicate that a significant fraction of material, less than about 50 μ in diameter, can also appear to be lost by adsorption on the surface of coarser particles.

Acknowledgement. The authors wish to thank Mr. E. Segovia for providing some of the data on spray dried lactose.

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