J. Pharm. Pharmacol., 1964, **16**, 705–716 Received June 12, 1964

Research Papers

The flow properties of magnesia

N. PILPEL

A study has been made of the effect of particle size and particle size distribution on the angle of repose of granulated magnesium oxide. Particles smaller than about 100 μ diameter produce a substantial increase in the angle of repose: this has been explained in terms of frictional and van der Waal's cohesive forces.

MEASUREMENT of the angle of repose of a powder yields information on how it flows in comparison with other powders. Angles of 30° or below usually indicate that the flow is "free," angles of 40° or above that it is broken and that the phenomenon of "balling" may occur (Neumann, 1953). Brown (1960), Train (1958), Craik (1958), Miller (1958) and Dallavalle (1948) have shown that the value of the angle of repose that is obtained depends not only on the way in which the cone of powder is produced, but also on the nature of the powder, how it has been prepared, on the size of the particles and on their size distribution. But relatively little work of a quantitative nature has been done to correlate the measured angles of repose with these variables.

A simple new technique has now been developed for forming prepared mixtures of granulated magnesium oxide into cones. A study has been made of the effect of particle size and particle size distribution on the angle of repose and equations have been developed from first principles to explain the observed results in terms of frictional and cohesive forces that act between neighbouring particles.

Experimental

PREPARATION OF SIEVE FRACTIONS

Granulated magnesium oxide, obtained from the Washington Chemical Company, was dried at 800° for 2 hr in the oven. It was separated into narrow fractions by sieving on an Alpine Airjet sieve (Lavino 1964) using 50 g portions and sieving for a standard period of 2 min. The various fractions were stored before use in dry screw-capped bottles and mixtures of the different sized powders were made up by weight.

ANGLE OF REPOSE

(*a*) A few granules from each sieve fraction were placed in turn on a clean, dry glass slide, one end of which was then slowly raised until the granules started to slide. At this point, the elevation of the slide to the horizontal was measured.

The microscopic appearance of the different granules at a magnification of $\times 100$ was noted to see whether there was any significant change in their shape with size.

From the School of Pharmacy, Chelsea College of Science and Technology, Manresa Road, London, S.W.3.

The densities of the different sized granules were also determined by the specific gravity bottle method, using toluene and a light mineral oil as the fluids.

(*b*) Preliminary measurements of the angle of repose, in which a fixed volume of powder was allowed to flow through a funnel to form a conical heap, gave variable results. This was due to the occurrence of non-uniform "broken" flow which, in several instances, produced damage to the apex of the cone.

A static method of measurement was therefore devised. A fixed volume of powder was poured into an open brass tube, 1·5 inch in diameter and 2 inches high, standing on a 2 inch diameter brass base. On slowly raising the tube the powder flowed out to form a conical heap on the base. The height, h, of the cone was measured and the angle of repose θ, calculated from the expression

$$\theta = \tan^{-1} \frac{h}{r}$$

where r is the radius of the base.

Since values of θ varying by up to 2° could be produced by using tubes and bases of different sizes, it was necessary to use one apparatus for all the measurements. These were made in sextuplicate, individual determinations were found to be reproducible to $\pm$ 1°, the error in the mean of the six determinations being, therefore, $\pm$0·2°.

Results

The graph relating the size of the particles to the elevation of the slide when sliding commences is given in Fig. 1.

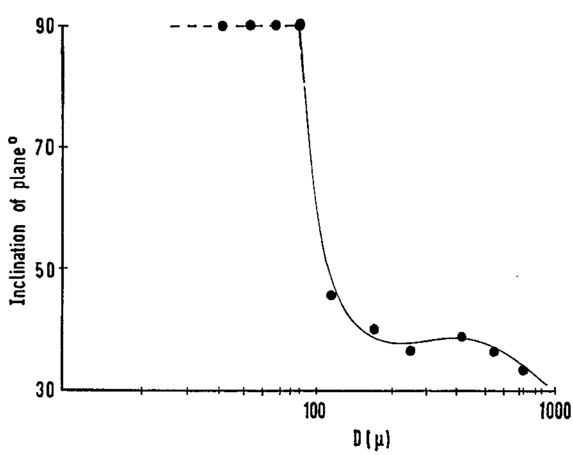

FIG. 1. Inclination of plane (degrees) when sliding of different sized particles commences.

Fig. 2 shows the variation of angle of repose with particle size for narrow sieve cuts.

Fig. 3 shows the effect on the angle of repose of adding various amounts of smaller particles ("fines") to a particular sieve cut, 400 μ in diameter.

Figs 4 (a) and (b) give the corresponding results for the ternary systems.

Examination of Fig. 1 shows that small particles slide less easily down an inclined plane than large ones, sliding ceasing altogether when the particles are less than 90 μ in diameter. There is a slight upward trend in the curve between 350 and 450 μ which may be due to the particular influence of very fine material trapped on the surfaces of particles of this size.

Below the critical size of 90 μ it appears that the weight of a particle of MgO is being completely supported by the force of adhesion which acts between it and the surface of the glass. The effect of particle shape can be discounted since under the microscope the shapes of all the particles in the size range 53 to 725 μ were essentially similar.

Now the density of granular magnesium oxide 90 μ in diameter is about 3 g/cm^3. Its real, as opposed to its apparent area of contact with the glass is probably between 10^{-8} and 10^{-10} times its total surface area (Bowden & Tabor, 1954) implying contact along a line between 10^{-6} and 10^{-7} cm long. Calling γ ergs cm^{-2} the interfacial energy and assuming that the coefficient of friction between the granule and the glass is unity, γ is found to lie between 10^2 and 10^3 erg cm^{-2}. This is in reasonable agreement with the figures given by Gregg (1961) for the surface energies of glass and of magnesia.

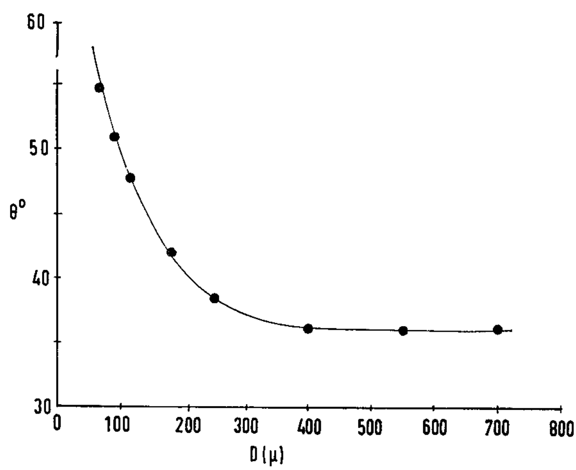

FIG. 2. Angles of repose for different sieve cuts.

Fig. 2 shows that for a powder comprising a narrow sieve cut, the angle of repose is inversely proportional to the size of the powder particles, the relationship being of the form

$$\theta = AD^{-1} + B$$

where D is the particle mean diameter in μ and A and B are constants whose values depend on the nature of the powder and on the suface shape, roughness and so on of the particles. With the present material A = 18×10^3 and B = 32·2.

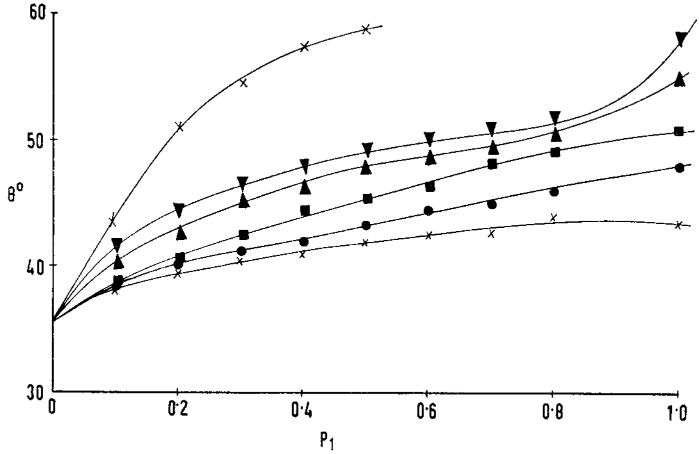

FIG. 3. Effect of fines on powder 400 μ diameter.
× = 180μ; ● = 125μ; ■ = 90μ; ▲ = 68μ; ▼ = 53μ; upper curve × = 30μ (average).

Fig. 3 shows that for mixtures of two sieve cuts of which one—designated fines has particles <150 μ in diameter, the angle of repose is inversely

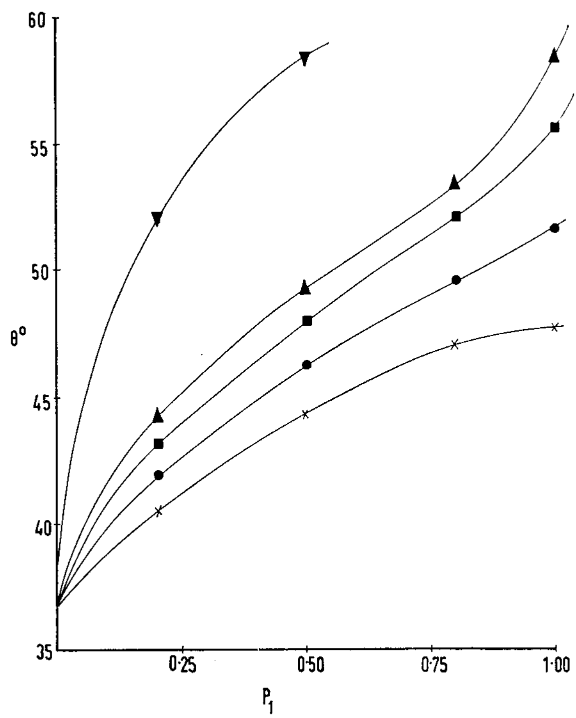

FIG. 4 (a). Effect of fines on mixtures of powder. 20 parts 250μ diameter, 80 parts 725μ diameter.
× = 125μ; ● = 90μ; ■ = 68μ; ▲ = 53μ; ▼ = 30μ (average).

proportional to the size of the fine particles, but directly proportional to the weight fraction of them present.

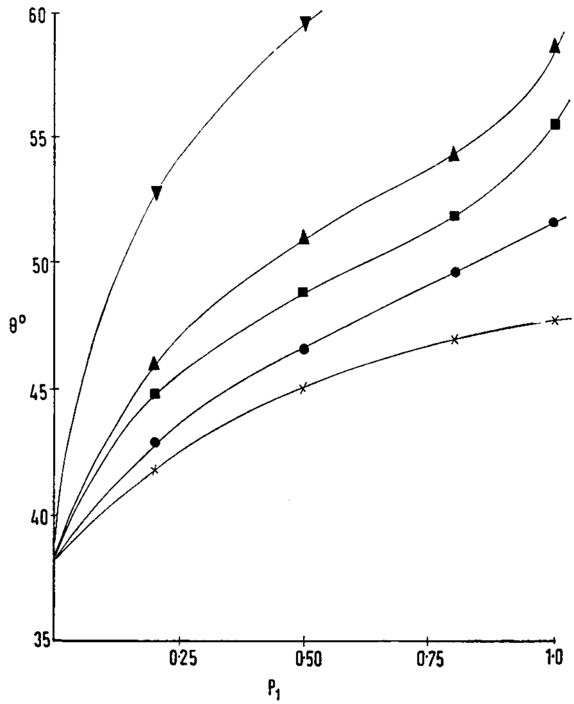

FIG. 4 (b). Effect of fines on mixtures of powder. 50 parts 250μ diameter 50 parts 725 μ diameter. Key as Fig. 4 (a).

Figs 4 (a) and (b) show that for mixtures of three sizes of powder in which at least one has particles less than 150 μ in diameter the angle of repose is a function of the ratio of the linear dimensions D_1, D_2, D_3 of each size of particle, and also a function of their weight fractions P_1, P_2, P_3.

$$\text{i.e. } \theta = f(D_1 : D_2 : D_3, P_1 : P_2 : P_3)$$

Discussion

It is well known that the presence of fines can have a considerable effect on the angle of repose of a powder and in the present systems as little as 0·05 weight fraction increases θ by between 2 and 5°. This can be presumed to be due to the enhancement of the forces that normally operate between the particles concerned.

Five types of force may be postulated as acting between particles in a powder. Firstly, the force of friction. Secondly, surface tension forces due to the possible presence on the particles of adsorbed films of gas and/or moisture (Gregg, 1961) in spite of the precautions taken in their preparation. Thirdly, mechanical forces caused by interlocking of particles of irregular shape. Fourthly, electrostatic forces which arise from friction between particles (Green & Lane, 1957). Fifthly, cohesive or van der Waal's forces which operate between neighbouring molecules (Green & Lane, 1957).

But of these the surface tension and mechanical forces are probably small since it is known that spherical particles often exhibit greater cohesion than irregular particles both before and after degassing. The electrostatic forces are forces of repulsion which, even for particles in the size range 1 to 10 μ do not exceed about $D_1 \times 10^{-8}$ dynes per particle (Kunkel, 1950) and which, for larger particles of MgO with a density circa 3·2 g/cm^3 become negligible in comparison with their weight.

There remain friction and the van der Waal's forces of cohesion.

Bradley (1936), Hamaker (1937) and Jordan (1954) have considered the magnitude of the van der Waal's forces for powders of different materials, making allowance for the fact that the particles may be non-spherical in shape and have appreciable surface irregularities. For magnesium oxide they appear to be of the order $D \times 10^{-6}$ dynes per particle, i.e. large in comparison with any electrostatic forces and when the particles are about 30 μ in diameter the cohesive forces become comparable to their weight.

Let it therefore be assumed that it is friction and the van der Waal's forces which predominate and which are primarily responsible for the effects produced by fines on the angle of repose of magnesia powder.

In the simplest instance of a particle of MgO of mass m starting to slide down the inclined surface of a cone of identical particles

$$mg \sin \theta = \mu (mg \cos \theta + F)$$

or

$$F/mg = \left(\frac{\sin \theta}{\mu} - \cos \theta\right) \quad \ldots \quad (1)$$

Where θ is the elevation of the cone (angle of repose).

μ is the coefficient of friction

and F is the cohesive force between the particle and its neighbours.

For large particles F becomes negligible in comparison with mg and

$$\mu = \tan \theta_{\lim} \quad \ldots \quad (2)$$

Where $\theta_{\lim}$ is the angle of repose of coarse particles.

Substituting into equation (1)

$$F/mg = \left(\frac{\sin \theta}{\tan \theta_{\lim}} - \cos \theta\right) \quad \ldots \quad (3)$$

Now consider the cone to be composed of particles of M different sizes, their linear dimensions $D_1, D_2, D_3 \ldots D_r \ldots D_M$ being such that

$$D_1 << D_2 << \ldots D_r << \ldots D_M$$

For convenience the particles are assumed to be small cubes. An r-sized particle (designated an r-particle) is pictured as occupying a cell (an r-cell) having the shape of a rectangular parallelopiped whose dimensions $a_r \times a_r \times X_r$ are relatively large in comparison with D_r. Each r-particle is surrounded by a number n_r (r–1) cells measuring $a_{r-1} \times a_{r-1} \times X_{r-1}$, each of which in turn contains an (r–1) particle and n_{r-2} (r–2)-cells. The smallest cell is a 2-cell, the smallest particle is a 1-particle and $D_1 << D_2, a_2 << \ldots D_r, a_r << \ldots D_M, a_M$.

It is possible to derive expressions relating the angle of the cone to the friction and the cohesive forces exerted by the 1-particles in it.

Let P_r be the weight fraction of r-particles

δ_r the apparent density of powder in an r-cell

m_r the mass of powder in an r-cell

n_r the number of r-cells in an (r + 1)-cell

D_r the linear dimension of an r-particle, so that its volume is D_r^3

δ the density of any particle.

The mass of powder in an r-cell is given by

$$m_r = a_r^2 \times X_r \delta_r = (D_r^3 + n_{r-1} m_{r-1}) \qquad \ldots \quad \ldots \quad (4)$$

and

$$\frac{P_r}{\sum_{i=1}^{r-1} P_i} = \frac{D_r^3 \delta}{n_{r-1} m_{r-1}} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

from equations (4) and (5) it follows that

$$m_r = \frac{D_r^3 \delta}{P_r} \sum_{i=1}^{r} P_i \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

Now in an r-cell of volume $a_r^3 X_r$ there is one r particle with a volume of D_r^3 and n_{r-1} (r–1)-cells. So the average volume of an (r–1)-cell is $\frac{1}{n_{r-1}} (a_r^2 X_r - D_r^3)$. But only those (r–1)-cells that are situated on the base of the r-cell come into contact with the r-cell below which is supporting it on the inclined plane. The number N_r of (r–1)-cells contributing to cohesion between two adjacent r-cells is thus

$$N_r = \frac{a_r^2}{\left[\frac{1}{n_{r-1}} (a_r^2 X_r - D_r^3)\right]^{\frac{2}{3}}} \qquad \ldots \quad \ldots \quad \ldots \quad (7)$$

Employing equations (4) and (6) this can be rewritten

$$N_r = \frac{a_r^2}{\left[\frac{1}{n_{r-1}} D_r^3 \left(\frac{\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - 1}{P_r}\right)\right]^{\frac{2}{3}}}$$

$$= \frac{D_r^3 \delta}{P_r X_r \delta_r \left[\frac{1}{n_{r-1}} D_r^3 \left(\frac{\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - 1}{P_r}\right)\right]^{\frac{2}{3}}}$$

$$= \frac{\delta D_r \sum_{i=1}^{r} P_i}{X_r \delta_r P_r} \left[\frac{1}{n_{r-1}} \left(\frac{\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - 1}{P_r}\right)\right]^{-\frac{2}{3}}$$

But from equation (5) and using equation (6)

$$\frac{1}{n_{r-1}} = \frac{P_r}{\sum\limits_{i=1}^{r-1} P_i} \frac{m_{r-1}}{D_r^3 \delta} = \frac{P_r D_{r-1}^3}{P_{r-1} D_r^3}$$

Thus

$$N_r = \frac{\delta D_r^3 \sum\limits_{i=1}^{r} P_i}{\delta_r P_r X_r D_{r-1}^2} \left[\frac{1}{P_{r-1}} \left(\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - P_r \right) \right]^{-\frac{2}{3}} \quad \ldots (8)$$

The number, N, of smallest particles, i.e. 1-particles contributing to the cohesive force between an M-cell face and the inclined plane is

$$N = N_2 N_3 N_4 \ldots N_M \quad \ldots \quad \ldots \quad \ldots (9)$$

Hence

$$N = \delta \prod_{r=2}^{M} \frac{D_r^3 \sum\limits_{i=1}^{r} P_i}{\delta_r P_r X_r D_{r-1}^2} \left[\frac{1}{P_r} \left(\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - P_r \right) \right]^{-\frac{2}{3}} \quad (10)$$

These particles produce a total cohesive force F which is known to be proportional to their linear dimension and which can be assumed to be proportional to the number of them, n, present in each 2-cell. Writing this in the form

$$\frac{F}{mg} = \frac{kND_1^n}{m_M g} \quad \ldots \quad \ldots \quad \ldots \quad \ldots (11)$$

where k is a constant and employing equations (6) and (10) it follows that

$$\frac{F}{mg} = \frac{k}{g} \frac{P_M D_1^n}{D_M^3} \prod_{r=2}^{M} \frac{D_r^3 \sum\limits_{i=1}^{r} P_i}{\delta_r P_r X_r D_{r-1}^2} \left[\frac{1}{P_{r-1}} \left(\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - P_r \right) \right]^{-\frac{2}{3}} \quad (12)$$

This is the general equation relating friction and the cohesive force to the numbers and sizes of the different particles in the powder. Substituting from equation (3) in order to introduce the measured angle of repose it follows that

$$\left(\frac{\sin\theta}{\tan\theta_{lim}} - \cos\theta \right) = \phi = \frac{k}{g} \frac{P_M D_1^n}{D_M^3} \prod_{r=2}^{M} \frac{D_r^3 \sum\limits_{i=1}^{r} P_i}{\delta_r P_r X_r D_{r-1}^2} \left[\frac{1}{P_{r-1}} \left(\frac{\delta}{\delta_r} \sum_{i=1}^{r} P_i - P_r \right) \right]^{-\frac{2}{3}} \quad \ldots (13)$$

We can now consider several special cases.

(a) Powder containing only one size of particle

Here $M = 1$ $P_1 = 1$. Although it does not follow formally from equation (3) it is apparent that

$$\phi = \frac{k}{g} D_1^{n-3} \quad \ldots \quad \ldots \quad \ldots \quad \ldots (14)$$

which may be compared to the empirical expression for θ already obtained.

(*b*) *Powder containing "fines" and one other particle size*

Here M = 2, $P_1 + P_2 = 1$ and equation (13) reduces to

$$\phi = \frac{k}{g} \frac{D_1^{n-2}}{\delta_2 X_2} \left[\frac{P_1}{(\delta/\delta_2 - P_2)}\right]^{\frac{2}{3}} \quad .. \quad .. \quad .. (15)$$

(*c*) *Powder containing "fines" and two other particle sizes* $D_1 << D_2 << D_3$

Here M = 3, $P_1 + P_2 + P_3 = 1$ and equation (13) becomes

$$\phi = \frac{k}{g} \frac{P_3 D_1^n}{D_3^3} \left\{ \frac{D_2^3(1 - P_3)}{\delta_2 P_2 X_2 D_1^2} \left[\frac{P_1}{\delta/\delta_2(1 - P_3) - P_2}\right]^{\frac{2}{3}} \right\} \left\{ \frac{D_3^3}{\delta_3 P_3 X_3 D_2^2} \left[\frac{P_2}{\delta/\delta_3 - P_3}\right]^{\frac{2}{3}} \right\}$$

$$= \frac{k}{g} \frac{D_1^{n-2} D_2 (1 - P_3)(P_1 P_2)^{\frac{2}{3}}}{\delta_2 \delta_3 X_2 X_3 P_2 \left[\delta/\delta_2(1 - P_3) - P_2\right]^{\frac{2}{3}} \left[\frac{\delta}{\delta_3} - P_3\right]^{\frac{2}{3}}} \quad .. (16)$$

(*d*) *Powder containing "fines" and two other particle sizes* $D_1 << D_2 < D_3$

Here a weighted mean size is taken for D_2 and D_3 and the problem then reduces to case (*b*) above.

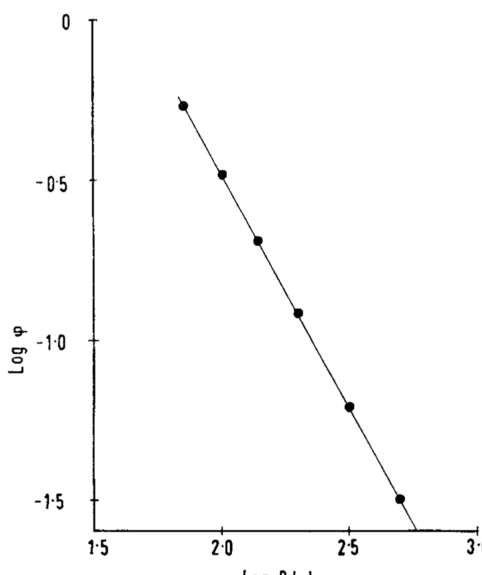

FIG. 5. Single component system. Log ϕ versus log D.

It is seen that in case (*a*) ϕ should be proportional to D_1^{n-3}, in all the other cases to D_1^{n-2}. (Considerations of symmetry show that ϕ should remain proportional to D_1^{n-2} for higher values of M also, although an increasing correction will now be required to allow for density differences of the powder in the different sized cells.) It follows that straight line graphs should be obtained when log ϕ is plotted against log D_1, the slopes of the lines yielding values for n. This prediction has been tested in Figs. 5–8 for the data on the single component system (contained in Fig. 2) for the data on the binary system (contained in Fig. 3) and for the data on the ternary systems (contained in Figs 4 (a) and (b).) It is seen that in all instances the agreement with prediction is very good.

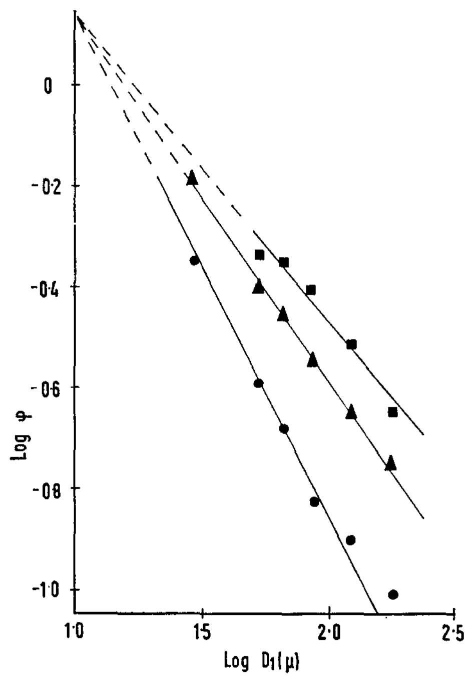

FIG. 6. Binary systems. Log ϕ versus log D_1.
■ $P_1 = 0{\cdot}8$; $n = 1{\cdot}39$ ▲ $P_1 = 0{\cdot}5$; $n = 1{\cdot}28$ ● $P_1 = 0{\cdot}2$; $n = 1{\cdot}00$.

As the weight fraction of fines in a binary or a ternary system is increased, so the value of n increases, the relationship being of the form

$$n = c \log P_1$$

where c is a constant and P_1 as before is the weight fraction of fines. This results in divergence of the plots of log ϕ versus log D_1 from a virtual common origin for each system.

The ordinate of the origin yields a value for ϕ and since $\theta_{\lim}$ for the system is known, θ at this point can be calculated. The values turn out to be exactly 90° both for the binary systems and for the ternary systems.

Theoretically, therefore, the origins may be pictured as representing idealised combinations of particle sizes when the angle of repose should become 90° and the powder ceases to flow (for the binary systems this would be when the fines were 10·5 μ in diameter, for the ternary systems

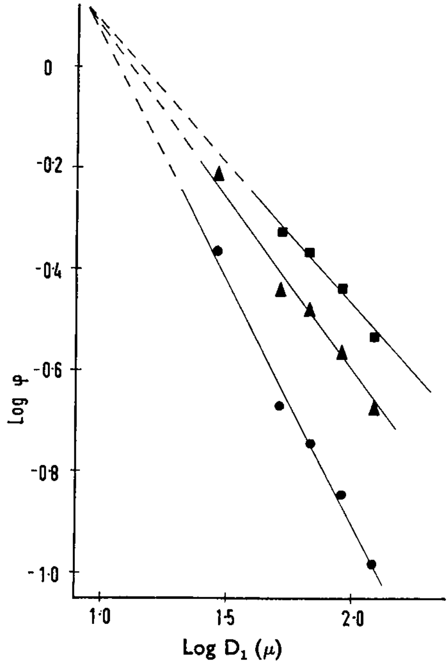

FIG. 7. Ternary systems. (20/80 mixture). Log ϕ versus log D_1.
■ $P_1 = 0{\cdot}8$; $n = 1{\cdot}44$ ▲ $P_1 = 0{\cdot}5$; $n = 1{\cdot}32$ ● $P_1 = 0{\cdot}2$; $n = 1{\cdot}04$.

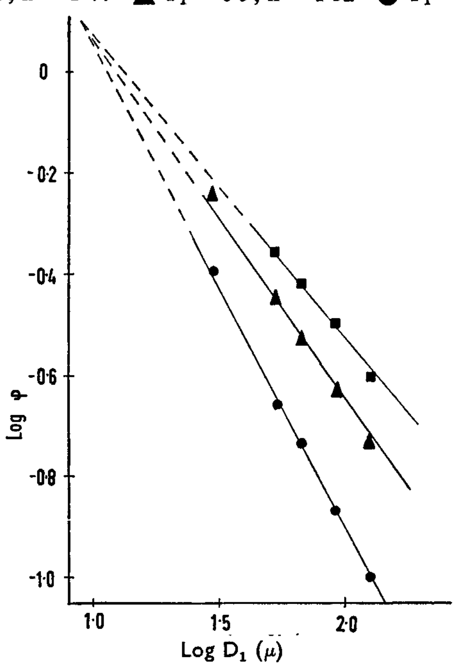

FIG. 8. Ternary systems. (50/50 mixture). Log ϕ versus log D_1.
■ $P_1 = 0{\cdot}8$; $n = 1{\cdot}41$ ▲ $P_1 = 0{\cdot}5$; $n = 1{\cdot}28$ ● $P_1 = 0{\cdot}2$; $n = 1{\cdot}05$.

when they were 8·9 μ in diameter, the total mass of powder in each system being small in comparison with the cohesive forces).

For real systems, however, where the mass of powder must be large in comparison with the cohesive forces if the angle of repose is to be measured, this idealized situation does not occur. The powder continues to flow, albeit in a broken column, and the plots of log ϕ versus log D_1 in Figs 6–8 must therefore depart from linearity when the values of D_1 are made very small.

It is hoped to be able to test this prediction in due course.

Going back to the general equation (13) relating friction and the cohesive force to the number and sizes of the different particles in the powder, it is seen that the intercept on the ordinate of the graph of log ϕ versus log D_1 should yield a value for the sum of the logarithms of all the other terms in the equation. If the values of P_r, δ_r and X_r, etc. were known, this would enable k, the force constant, to be calculated.

However, it is more convenient to determine k from equation (14) which contains no other unknown quantities. From the intercept on the ordinate of Fig. 5, k is found to have the numerical value of 2·14 when D is measured in cm and g is 981 cm sec^{-2}.

Acknowledgements. The author wishes to thank Mr. M. Solomons for making some of the measurements and Mr. P. Heyda for mathematical assistance.

References

Bradley R. S. (1936). *Trans. Faraday Soc.*, **32**, 1088–1090.
Brown, R. L. (1960). Paper presented at the Symposium on Powders in Industry. Society of Chemical Industry—Surface Activity Group. London.
Craik, D. J. (1958). *J. Pharm. Pharmacol.*, **10**, 73–79.
Craik, D. J. & Miller, B. F. (1958). *Ibid.*, **10**, *Suppl.* 136*T*–143*T*.
Dallavalle, J. M. (1948). *Micromeritics—The Technology of Fine Particles.* London: Pitman.
Green, H. L. & Lane, W. R. (1957). *Particulate Clouds, Dusts, Smokes and Mists.* Chaps 2 and 3. London: E. & F. N. Spon.
Gregg, S. J. (1961). *Surface Chemistry of Solids.* Chaps 2 and 3. London: Chapman & Hall.
Hamaker, H. C. (1937). *Physica*, **4**, 1058–1061.
Jordan, D. W. (1954). *Brit. J. Appl. Phys.*, **5** Suppl. 3, S194–S197.
Neumann, B. S. (1953). *Flow Properties of Disperse Systems.* Editor, Hermans, J. J. Chap 10. Amsterdam: North Holland.
Lavino (London) Ltd. (1964). *The Alpine Airjet Sieve.*
Train, D. (1958). *J. Pharm. Pharmacol.*, **10**, *Suppl.* 127*T*–135*T*.