THE FLOW PROPERTIES OF POWDERS UNDER HUMID CONDITIONS

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The flow properties of different types of powder, with varying moisture contents, and the effects of adding small quantities of magnesium oxide, were measured. An explanation of the results in terms of adhesion by intermolecular forces and by the surface tension of moisture films is suggested.

THE flow properties of starch powders, and of mixtures of starch with light magnesium oxide and other very finely divided powders, were recently investigated using the angle of repose method[1]. The electron microscope demonstrated the adsorption of the very fine powders on to the surfaces of the larger particles and it was considered that the greatly improved flow properties of the mixtures were due to the reduction of the adhesion between the particles. These investigations were made in the conditions prevailing in the laboratory and no account was taken of the moisture content of the starch.

A high moisture content is known to reduce the ease of flow of some powders, an effect which may be very pronounced with soluble crystalline powders. Experiments were designed, therefore, to measure the flow properties of powders with varying moisture contents, and to determine to what extent the addition of magnesium oxide might affect the properties under these conditions. Some commercial preparations contain additives presumably intended to counteract the effects of an appreciable moisture content on the ease of flow.

EXPERIMENTAL

Measurement of the angle of repose of a powder gives a reproducible numerical value for the flow properties so long as the conditions of the measurement remain constant. In these experiments the angle of repose was measured by pouring the powder through a funnel on to a horizontal sheet of graph paper, until the tip of the heap so formed reached the stem of the funnel. The diameter of the base was then read and the angle of slope of the side of the cone calculated. The end of the stem of the funnel was ground flat and was 3 mm. in diameter and 1·5 cm. above the plane of the paper. The accuracy of the measurement depends upon the kind of material measured. When the angle of repose is low the values are reproducible within 5 per cent, but when the angle is very large an irregular heap is formed and the variation of subsequent readings may be as much as 10 to 20 per cent.

Three very different kinds of material were examined; an organic amorphous powder, maize starch, an organic crystalline powder, sucrose, and an inorganic crystalline powder, sodium chloride. The samples of

sucrose and of sodium chloride were each of two different particle diameters of approximately 100 μ and 10 μ, called "coarse" and "fine", making a total of five samples. Six batches of 5 g. of each were prepared and 0, 0·25, 0·5, 1·0, 2·0 and 4·0 per cent of light magnesium oxide were added to each.

To obtain different values of the moisture content, the powders were placed in open jars, 4 cm. in diameter, in which they formed a layer less than 1 cm. deep, in a cabinet in which a controlled temperature and humidity could be maintained. The air in the cabinet was constantly circulated and from the work of Browne[2] on sucrose, and of Yee[3] on sodium nitrate, it was to be expected that the crystalline powders would attain equilibrium with the atmosphere in one, or two hours. Twenty-four hours was chosen as a convenient interval for exposure to any one humidity. Accurately weighed quantities of the five powders were also placed in open weighing bottles in the cabinet, and these were weighed whenever the angle of repose was measured so as to infer the moisture content of the samples. Weighing the samples on which the measurements were made would not have been significant owing to the slight loss of material incurred. The depth of the powder in the weighing bottles was equal to that in the jars.

The humidity in the cabinet was controlled by phosphorus pentoxide or saturated salt solutions[4], and measured by the dew point method; the temperature was maintained at 30°C. The cabinet was equipped with a Perspex front through which rubber gloves were sealed so that the angle of repose could be measured without removing the powders from the appropriate atmosphere.

RESULTS

For the sake of clarity only those results obtained at four well-spaced humidity values will be considered, at 0 (nominally, actually less than 4 per cent), 42, 65, and 81 per cent relative humidity (R.H.). Results obtained at other humidities generally fitted in well between these. At 42 and 65 per cent R.H. the sugar and salt appeared to achieve equilibrium with the atmosphere within 24 hours shown by weighing the controls at intermediate times. At 81 per cent R.H. equilibrium had not been attained but measurements were taken at the end of 24 hours after which the powders continued to absorb moisture until they became too moist for measurement. At humidities above 81 per cent both the soluble powders deliquesced rapidly. In Table I the moisture contents are

TABLE I

MOISTURE CONTENT (PER CENT) AFTER 24 HOURS EXPOSURE TO THE HUMIDITIES INDICATED. THE VALUES CORRESPONDING TO 81 PER CENT R.H. DO NOT REPRESENT EQUILIBRIUM

Humidity (per cent)	Starch (per cent)	Sucrose 100 μ (per cent)	Sucrose 10 μ (per cent)	NaCl 100 μ (per cent)	NaCl 10 μ (per cent)
42	5·5	0·03	0·07	0·01	0·03
65	8·6	0·08	0·14	0·03	0·06
81	10·7	0·12	0·20	0·09	0·14

expressed as percentages on the assumption that the powders were dry after 60 hours over phosphorus pentoxide.

Graphs of the angle of repose against the concentration of added magnesium oxide for the five powders at four different humidity values, and corresponding water contents, are shown in Figures 1 to 5. Each set of curves shows different characteristics. The curve for starch at 42 per cent R.H. (Fig. 1) is similar to that previously obtained[1]. The effect of the variation of moisture content is regular over the whole range of concentrations, the shape of the curves not being appreciably altered.
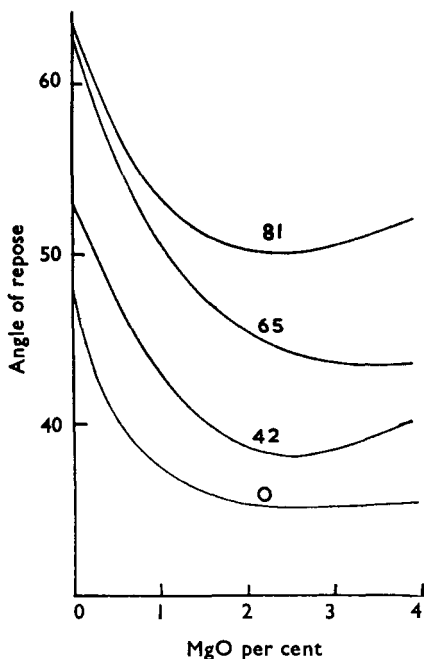

FIG. 1. The angle of repose of starch and mixtures with light magnesium oxide after 24 hours exposure to atmospheres of 0, 42, 65 and 81 per cent humidity at 30°.
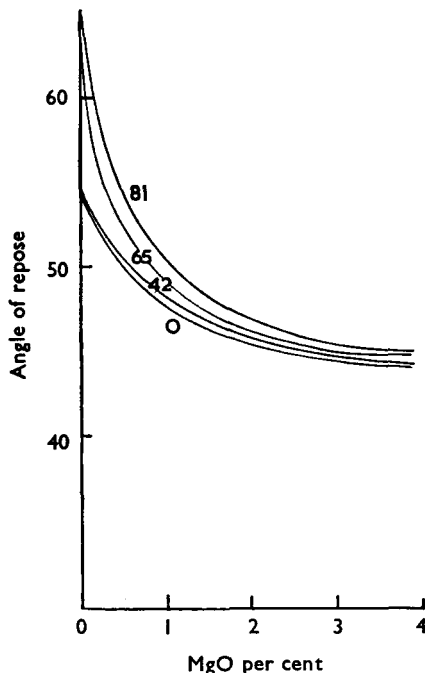
FIG. 2. The angle of repose of sucrose (10 μ) and mixtures with magnesium oxide at relative humidities of 0, 42, 65 and 81 per cent.

The graphs for the fine sugar (Fig. 2) show that at moderate humidities the effect of the added magnesium oxide is similar to that for starch, the angle of repose being reduced by approximately 12° for the 1 to 2 per cent mixture. When the humidity is raised the angle of repose of the fine sugar alone is increased but the mixture flows nearly as easily as before. The close spacing of the curves above 0·5 per cent magnesium oxide contrasts with those for starch.

The main difference in the behaviour of the coarse sugar (Fig. 3), compared with that above, is that when it is dry or at intermediate humidities (42 per cent), the addition of magnesium oxide does not reduce the angle and may even increase it slightly. When the humidity is raised to

81 per cent, however, and the moisture content is 0·12 per cent, the coarse sugar mixtures show the most striking effect of all, the angle being reduced from a high value to that typical of the dry powder.
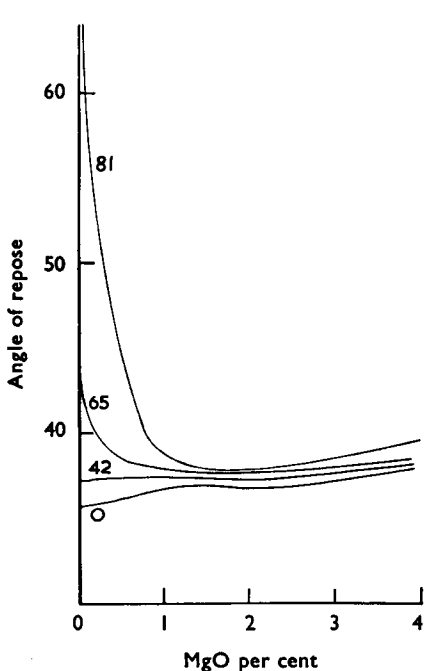

FIG. 3. The angle of repose of sucrose (100 μ) and mixtures with magnesium oxide at relative humidities of 0, 42, 65 and 81 per cent.
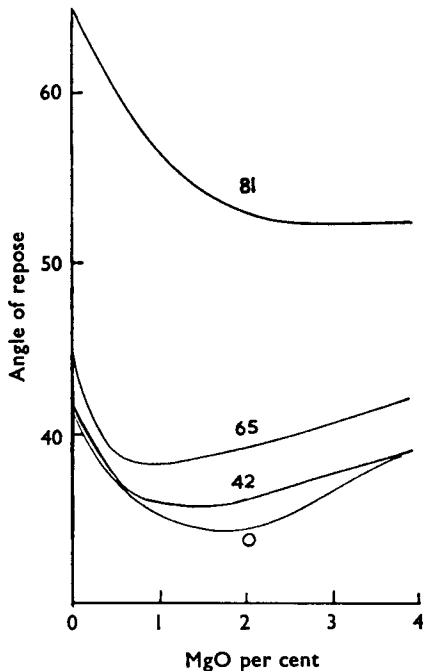
FIG. 4. The angle of repose of sodium chloride (10 μ) and mixtures with magnesium oxide at relative humidities of 0, 42, 65 and 81 per cent.

At low humidities the fine salt is affected in a similar way (Fig. 4), but to a lesser extent than the starch. At high humidities (81 per cent), the effect becomes much more pronounced but, unlike the fine sugar, the flow properties are not completely restored, this curve being well above the others.

The effect of the varying humidity on the coarse salt is similar to that for the coarse sugar (Fig. 5). The added magnesium oxide has a negligible effect on the angle of repose at low humidities but a great effect at higher humidities. The difference in appearance was striking in these conditions, the normal material being aggregated in large irregular clumps and sticking to the sides of the jar while the mixture generally appeared identical with the dry material.

Whether the powders had become caked on exposure to the various humidities was noted. The starch was only slightly caked at the highest humidities and the caking was suppressed by the addition of 0·25 to 0·5 per cent of magnesium oxide. The fine sugar caked considerably at 81, 70 and 65 per cent R.H. The caking was suppressed by the admixture of 1 per cent magnesium oxide at 81 per cent R.H., 0·5 per cent magnesium oxide at 70 per cent R.H., and 0·25 per cent magnesium oxide at

65 per cent R.H. The coarse sugar also caked at high humidities and this was suppressed by 0·5 per cent magnesium oxide at 81 per cent R.H., and 0·25 per cent magnesium oxide at 70 per cent R.H. Similarly, caking of the fine salt was suppressed by 0·5 per cent magnesium oxide at 81 per cent and 70 per cent R.H., and of the coarse salt by 0·25 per cent magnesium oxide at 70 per cent and 81 per cent R.H. For the purpose of these observations caking was considered to have occurred when the powder could not be moved by vigorously shaking or tapping the jar.
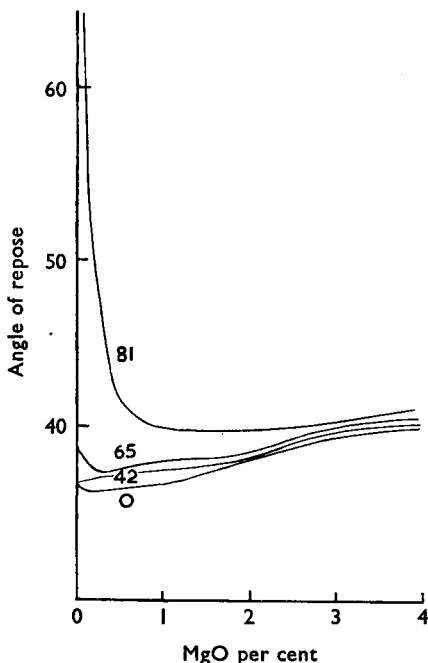
In addition to the effects on the flow properties of the powders, the addition of the magnesium oxide substantially diminishes the tendency to set or cake, more of the additive being necessary to achieve this result at higher humidities, and at the lower particle sizes.

Replicas, for examination in the electron microscope, of samples of the sugar and salt, and mixtures with magnesium oxide, were prepared by evaporating carbon on to the particles on a Formvar film and subsequently dissolving away the film and the particles. It was necessary to keep the sugar samples a considerable distance from the carbon rods to avoid melting. The carbon film containing the particles was floated on the surface of distilled water for about an hour to remove the salt or sugar. This treatment did not remove the magnesium oxide which remained attached to the carbon replica. The magnesium oxide was adsorbed on the surfaces of the sugar and salt particles to a considerable extent. When the concentration was low all the magnesium oxide was adsorbed, none being found on the intervening areas of the film. The surfaces of the crystals were never completely covered; when the concentration of the magnesium oxide was high, a large number of separate aggregates remained unadsorbed. The magnesium oxide was identified by taking selected area diffraction patterns.

FIG. 5. The angle of repose of sodium chloride (100 μ) and mixtures with magnesium oxide at relative humidities of 0, 42, 65 and 81 per cent.

DISCUSSION

Both sucrose and sodium chloride are deliquescent when exposed to humidities in excess of those at which the vapour pressure of the moisture in the atmosphere is equal to the vapour pressure of their saturated

solutions[5]. Thus, sodium chloride is deliquescent above 75 per cent R.H. at 30°C.[4], and sucrose above approximately 80 per cent R.H.[6] Below these points both these materials absorb very small amounts of moisture depending on the humidity, while above the critical points the moisture contents continue to increase with the time of exposure, no true equilibrium being attained until complete solution has occurred. This investigation, therefore, concerns the material either below the critical humidity, or a little above it before the absorption has proceeded very far. Starch is hygroscopic and absorbs much greater amounts of moisture at corresponding humidities with no tendency to go into solution.

To analyse the results, some quantitative relations concerning the angle of repose must be quoted, although a fuller discussion of the factors concerned and of the factors governing the flow of a powder must be reserved for a separate publication. The angle of repose corresponds qualitatively to the flow properties of a powder. A high angle (e.g., 50° to 60°) is obtained for powders which form large aggregates and can be caused to flow only with difficulty, while a low angle (30° to 40°) is obtained for powders which acquire a smooth surface and flow easily. Since the method gives a reproducible numerical value, it is reasonable to adopt it as a measurement of the flow properties.

It may be calculated that a powder consisting of spherical non-adhering particles will always have the same angle of repose, of approximately 30°, so long as the heap formed is stable. All particles tend to adhere, regardless of variable factors such as electrostatic charging[7], but the relative effect of this adhesion compared with the gravitational force on the particles, or to their momenta, depends upon the particle size. Using an approximate model it may be calculated that, for the materials here investigated, adhesion will be significant when the particle size is less than 100μ. The source of this adhesion may be considered to lie in the short-range intermolecular forces which vary inversely with the seventh power of the separation of the molecules[8,9], while a theory of the attraction of macroscopic bodies, which did not make use of assumptions concerning the interaction of individual atoms or molecules, was developed by Lifshitz in terms of electromagnetic theory and this showed the force to be inversely proportional to the third or fourth power of the separation. When adhesion is significant the angle of repose is increased, and it may also be increased by extreme variation of the shape of the particles from the spherical, but this is not significant here.

The variation in the angle of repose of dry starch may then be considered to represent the conversion of an adhering powder to a non-adhering powder, by the presence of the adsorbed magnesium oxide. The adhesion is overcome because of the short range of the forces compared with the size of the magnesium oxide particles. The dry fine sugar is similarly affected by the addition of magnesium oxide, although the adhesion is not reduced to such a great extent by any concentration of the magnesium oxide. The particle sizes of both the starch and the fine sugar (approximately 10μ) are well within the calculated limits for adhesion.

The particle sizes of the coarse sugar and salt are ten times as great and these are effectively non-adhering powders, when dry, having an angle of repose approaching 30°. It is thus to be expected that the angle of repose is not further reduced by the addition of magnesium oxide. When the moisture content is increased these powders show an increasing adhesion, which is largely overcome by small concentrations of magnesium oxide. The amount of water involved is very small.

These effects can be explained if it is assumed that the moisture is adsorbed as a surface layer on the crystals. The adhesional force, due to the surface tension in a liquid film, between two spherical particles can be calculated to be $2\pi a \left(\dfrac{2m}{300}\right)^{\frac{1}{2}}$ T dynes, where a is the particle radius (cm.), T is the surface tension of the liquid in dynes/cm. and the moisture content is m per cent. Comparing this with the gravitational force on the particles, the critical radius below which the particles adhere is approximately $500\,\mu$ when m = 0·1 per cent. Since this is greater than the radius of any of the crystalline samples examined, this postulated liquid film introduces forces of sufficient magnitude to account for the adhesion.

The thickness of the moisture film, when a = $100\,\mu$ and m = 0·1 per cent is $0·03\,\mu$. The particles of the magnesium oxide are approximately $0·05\,\mu$ in diameter, and since the crystals are always separated by twice this distance, the moisture film will only be continuous over a few very small regions, and the forces due to surface tension will be greatly reduced.

Thus, if it can be assumed that the absorbed water resides on the surface of the crystal, a quantitative explanation can be given of both the effects of moisture on the flow properties of the crystalline powders, and the effects of the added magnesium oxide in maintaining the ease of flow of moist powders.

APPENDIX

To obtain independent evidence of the existence of the moisture films on which the above theory depends, the resistance of approximately 1 cm. cube of sodium chloride powder was measured and found to be 200, 120, 8, 4 and 2 megohms when the moisture content was 0, 0·02, 0·05, 0·1 and 0·2 per cent, respectively. If the moisture remained on the surface of the crystals a large drop in the resistance would be expected, since the conducting solution would carry the current. If the moisture entered the crystals, however, it would be necessary to assume that it could cause the formation of a large number of lattice vacancies, to increase the conductivity to such a great extent[11]. Since this would require a considerable amount of energy, it is unlikely to occur, and thus the conductivity measurements appear to verify the existence of the moisture films although they may not, at this stage, be regarded as a conclusive proof.

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DISCUSSION

The Papers were presented by DR. D. TRAIN and MR. D. J. CRAIK respectively.

THE CHAIRMAN. In Mr. Craik's paper, were the powders mixed with the magnesium oxide before placing in the humidity cabinets?

MR. N. J. VAN ABBÉ (Loughborough). Mr. Craik had found that there was a limiting concentration of magnesium oxide for optimal flow properties, but not so with talc, in contradiction to the work of Nelson. Could angle of repose indicate flow properties which would result in ready dispersibility in mixing?

MR. D. W. HUDSON (Hove). Would the results found explain the troublesome problem of layering seen with coloured talcs in filling machines? Was the specific gravity of the powder of importance?

MR. J. H. OAKLEY (London). Why did Dr. Train sieve his sand wet, dry it and then sieve it again? He could not correlate the two methods for obtaining angle of repose because Table I referred to 100/120 mesh and Table II to 14/16 mesh. What was the method of levelling, and how was the end point determined? Was the impacting a feature in the apparent divergence due to dimensions of the table?

MR. H. D. C. RAPSON (Betchworth). In Mr. Craik's paper, why did 10μ particles of sodium chloride appear to be less strongly adherent than 10μ particles of sucrose, which was contrary to argument based on van der Waal's forces. If sodium chloride were absolutely dry one would expect a resistance of 100 or 1000 times the 200 megohms reported for the apparently dry samples. The sodium chloride and sucrose were, therefore, not absolutely dry and the results might be explained by the film of surface water on the particles. Table I showed that the water content of the 10μ sucrose particles was higher than that of the sodium chloride and this would point to a slightly thicker water layer on the former and would probably explain its apparent higher adhesion in the angle of repose measurements. These water molecules between the surfaces must be considered in the interpretation of any adhesion between small particles.

DR. L. SAUNDERS (London). Was the surface tension mentioned on page *142 T* of Mr. Craik's paper that of a bulk salt solution?

DR. TRAIN replied. Nelson had used talc as an example of the effect of a lubricant on the angle of repose. He did not think that angle of repose would be a useful test to show efficiency of mixing in powders. Layering was associated with density as shown by Maĩtra and Coulson *Trans. Chem. Eng. Soc. Imp. Coll. Lond.*, 1948, **4**, 135. A shape factor was also

concerned.   Wet sieving was more efficient than dry sieving and the final sieving was to insure that all aggregates had been broken up.   Other size ranges than those shown in the Tables had been covered and there was no significant difference.   The surface of the bed using a tilting table was standardised by sliding a steel rule from the right (Fig. 2); if pushed the other way, the powder tended to impact.   In a small length bed the size of the particle which was just within and parallel to the surface was significant.   This factor tended to have less effect as the bed length increased.   The revolving cylinder was put in the jaws of a chuck on a lathe with a ruler aligned on the diametrical plane and both were turned together.   When the bed collapsed the ruler was held stationary and this maximum angle achieved for this surface was checked by moving the cylinder again.   The results were consistent and the method the easiest.

MR. CRAIK replied.   The mixtures had been made up before exposure to the humid atmospheres.   Water did not have considerable physical effect on the magnesium oxide particles since he postulated their effect to be purely as mechanical spacers.   The authors were trying to measure the thickness of the water layers.   A solid lubricant had a layer lattice structure which cleaved easily along the plane, and then slid easily. Magnesium oxide had a cubic crystal structure and would not cleave easily.   A dye adsorbed on talc particles would effect the surface, and so the rate of flow.   He could not explain the anomaly of the relatively free flow of sodium chloride which would almost certainly have a monolayer of water on the particles.   Intermolecular forces would come into play whenever particles were closer than 0.1 μ.   In some recently published work it was shown that when the separation increased to about 1 μ the attractive forces dropped off very rapidly and this fitted in with the separation of particles by a layer of magnesium oxide particles of 0.05 μ diameter.   A layer of water molecules should make no significant difference to the intermolecular forces and any additional effect of the layer calculated from the surface tension would be infinitesimal.