RESEARCH PAPERS

THE FLOW PROPERTIES OF STARCH POWDERS AND MIXTURES

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The addition of small proportions of fine powders, particularly magnesium oxide, to maize starch, alters its flow properties in a manner which is contrary to the generally observed effects for fine powders. A measure of this effect is obtained by the angle of repose method and the disposition of the two components of the mixture is observed by the electron microscope. An explanation of this effect in terms of adhesion by Van der Waals' and valency forces is put forward.

POWDERS possess special physical properties in addition to those of the bulk material. One of these, of considerable interest in the field of pharmacy is the extent to which a powder will flow freely or, conversely, aggregate into a mass which flows with difficulty. The flow properties of powders vary considerably between those of dry sand which will flow smoothly and continuously through a small orifice, and those of a fibrous powder like asbestos which forms fluffy masses and will not maintain an even flow under any circumstances. Starch can be considered as a fairly sticky powder forming large loose aggregates on shaking, and flowing with difficulty, but when as little as 0·5 per cent of light magnesium oxide is added the mixture flows much more freely and tends to acquire a smooth flat surface on shaking in the same way as it had been reported that the admixture of various substances with sulphonilamide will alter the properties of the powder[1,2]. This effect is in contrast to the observation that, in general, fine powders flow less freely than coarse ones, and that the presence in a powder of a considerable proportion of fine particles reduces the ease with which it flows[3]. In order to elucidate this phenomenon the electron microscope was used to study the relation between the two components of the mixture, and of mixtures of starch with other fine powders. It was first necessary, however, to obtain a numerical measurement of the effect.

Viscosity governs the flow of a liquid but there is no such fundamental property of a dispersed solid. Instead a number of tests exist which separately give reproducible comparative results[4]. These have no specific relation to each other and are not necessarily influenced by the same factors. One test consists of measuring the rate of flow of a powder through a tube or orifice[5]. Since the effect under study is concerned with movement of the powders, a dynamic method of measurement like this would have been preferred but it was found that, while the mixture would flow quite readily, the starch on its own could not be induced to sustain a continuous and reproducible flow. However, measurement of the angle of repose gave reproducible results, which appeared to give a measure

of the effect of the added powders on the flow properties of the starch, and this method of measurement was adopted.

The powder was formed into a conical heap by dropping it through a glass funnel supported at a fixed distance above a horizontal plate. When the tip of the cone just reached the funnel the diameter of the base was measured in several directions and, knowing the height, the angle of slope of the side of the cone was calculated. Sticky powders give a steep cone with a large angle, while free-flowing powders give a wider cone having a smaller angle of repose. Though it is not clear to what physical properties this angle corresponds it is useful as an index.

The manner in which the powder falls on to the heap affects the results. When the particles arrive more or less singly their velocity is low and they do not have sufficient momentum to disturb the heap which has already

TABLE I

ANGLE OF REPOSE OF STARCH POWDER' AND MIXTURES

Substance added	Per cent	Angle°*	Substance added	Per cent	Angle°*	Substance added	Per cent	Angle°*
(Control)	—	53	Zinc oxide ..	0·5	58	Mag. oxid. (heavy)	0·5	53
Mag. oxid. (light)	0·05	51	Titanium dioxide..	0·5	58	Chromium trioxide	0·5	53
,, ,, ,,	0·1	50	Sulphur	0·5	56	Calcium oxide ..	0·5	51
,, ,, ,,	0·3	40	Talc	0·5	56	Mag. trisilicate ..	0·5	47
,, ,, ,,	0·5	38	Talc	5·0	54	Alumina	0·5	46
,, ,, ,,	1·0	37	Zinc stearate ..	0·5	54	Mag. trisilicate ..	1·0	45
,, ,, ,,	3·0	42	Silica ppt. ..	0·5	54	Carbon black ..	0·5	43
,, ,, ,,	5·0	46	(Control)	—	53	Mag. oxide (light-		
,, ,, ,,	100	54				est grade) ..	0·5	42

* The average of 5 determinations.

formed; they take up stable positions after rolling down the sides of the cone. When a large aggregate or a solid stream of particles falls from the funnel, however, its momentum is sufficient to cause flow to take place in the bulk of the heap, which is consequently deformed. These two effects were involved in each determination, and to obtain reproducible results the powder had to be added in as uniform a way as possible. This was achieved by attaching an electrical vibrator at 50 c.p.s. to the funnel, and adding the powder slowly from a spatula. The results then obtained were reproducible to within 5 per cent.

Since the absorption of water from the atmosphere is likely to affect the properties of the powders, all the samples were prepared from the same batch of maize starch and kept under identical conditions. A second factor which could influence the measurement is the previous packing of the sample. For example, if the mixture of starch and magnesium oxide is shaken vigorously, then a gentle horizontal movement will cause the surface to flow. If the container is then tapped on the bench this mobility is completely suppressed. However, by the time the powder has passed through the funnel any difference in the degree of packing will have been destroyed, an advantage of the method employed.

The results are given in Table I. They include mixtures of starch with different proportions of magnesium oxide and also mixtures with other fine powders. Each figure for the angle of repose is the average of five determinations.

The results for magnesium oxide of varying concentration are plotted in Figure 1. The variation of the angle has a flat minimum, at approximately 1 per cent after which a gradual rise takes place presumably approaching the value for magnesium oxide alone.

Light magnesium oxide being a very fine powder cannot be examined by optical microscopy, while starch grains are very large on the scale of the electron microscope, and are opaque to the electron beam so that direct observation gives only an outline of the grains. For this reason a replica technique was adopted to show the full surfaces of the starch grains and reveal the disposition of the fine particles in the mixtures. The starch powder or mixture was applied to a collodion film, on a specimen grid, by touching the filmed surface of the grid on to the powder surface. The grids with the specimens uppermost were then placed in a vacuum chamber and a layer of carbon was applied by passing a heavy current through a pair of carbon rods situated above them, one of which
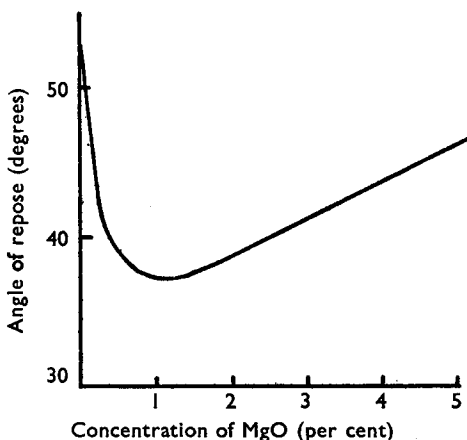

FIG. 1. Graph of the angle of repose of mixtures of starch powder and light magnesium oxide in varying proportions.

was turned down to a small diameter at the point of contact, a method of evaporation developed by Bradley[6]. It was found to be necessary to apply a thicker layer than is used for the highest resolution replicas, or the final specimens broke due to the comparatively large size of the starch grains; the evaporation proceeded until the film on the slide was dark brown by transmitted light. The specimen grids were then placed on curved strips of stainless steel mesh under which amyl acetate was run to remove the collodion film. The starch could be dissolved completely by strong hydrochloric acid. To remove the starch without displacing the carbon film, the grids were placed on to the surface of a bath of 50 per cent hydrochloric acid at a temperature of 60° so that they floated while the specimen was dissolved. After twenty minutes the grids were lifted on bent strips of steel mesh and floated on distilled water for an hour to wash thoroughly and then they were once more picked up in the same way and left to dry. The replica then consisted of a thin transparent shell following the contours of the original specimen. If the other material present was soluble in the acid it also appeared as a shell, but if not then the original particles appeared superimposed on the replica. Magnesium oxide powder was also examined as a shadowed specimen, prepared in the usual way.

Light magnesium oxide exists as large aggregates, visible in the optical microscope, which are seen with the electron microscope, to consist of

very closely packed sheets of much smaller particles, as in Figure 2. That these are distinct particles and not just a surface texture, is demonstrated by selected area electron diffract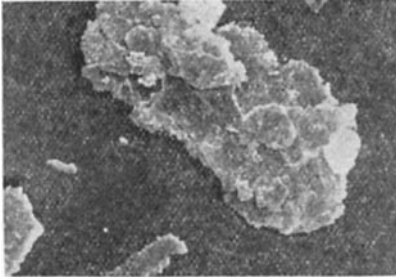ion; a field such as that shown in Figure 2 gives rise to a pattern of continuous rings as opposed to the pattern of spots which would be given by a single crystal. The diameter of the particles is approximately $0.05\ \mu$ and, since the starch grains are $5\ \mu$ or more in diameter the small amount of magnesium oxide which is needed to produce an obvious effect is less remarkable. Thus, considering the relative densities, the mixture containing 0.5 per cent magnesium oxide contains approximately 1000 times as many particles of magnesium oxide as of starch.

FIG. 2. Carbon replica of an aggregate of light magnesium oxide × 5,000.

Figure 3 is an electron micrograph of a replica of a whole starch grain and is typical of the sample except that the grains occur mostly in the form
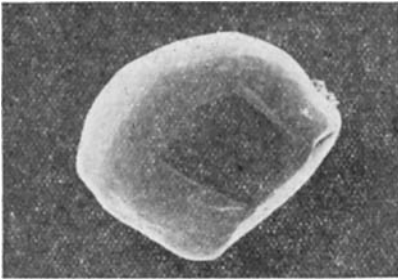
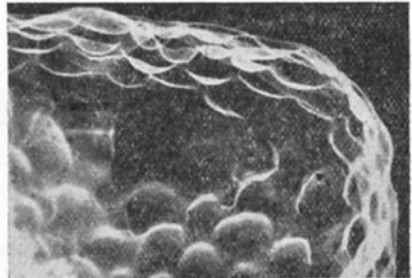

FIG. 3. Carbon replica of a typical starch grain × 6,600.

FIG. 4. Carbon replica of a part of a starch grain with an unusual surface pattern × 6,600.
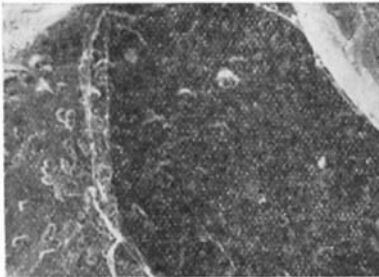

FIG. 5. Carbon replica of part of a starch grain from a mixture with 0·5 per cent light magnesium oxide showing fine particles dispersed over the surface × 20,000.

FIG. 6. Carbon replica of a starch grain from a mixture with 0·5 per cent light magnesium oxide showing the fine particles attached to the surface in aggregates × 6,600.

of aggregates. The interesting pattern on part of a starch grain shown in Figure 4 is of rarer occurrence, but is not unique. Where aggregates had existed the replica was usually shattered but the fragments were similarly smooth. Examination of a mixture, with 0·5 per cent magnesium oxide revealed the absence of any separate aggregates of magnesium oxide, and showed that the replicas of the large starch grains were covered with a regular pattern of protuberances representing the position of the magnesium oxide particles before their removal by the acid treatment (Fig. 5). Comparison of Figure 5 with the preceding micrographs thus indicates that the aggregates of the magnesium oxide particles are broken up on mixing with the starch, and that the particles are wholly adsorbed on the surfaces of the starch grains. Usually these particles were evenly spread out over the surfaces in the form of small aggregates or single particles but occasionally, as in Figure 6, larger aggregates were adsorbed.

By examining carbon replicas of other mixtures it was seen that finely divided alumina was similarly adsorbed, carbon black was partially adsorbed, a small amount from a 0·5 per cent mixture being seen separate from the starch grains, and that titanium dioxide was also strongly adsorbed. Finely divided calcium oxide was not adsorbed at all but left the grains smooth. No other powder examined produced such a uniform covering as did the magnesium oxide. A mixture with 5 per cent magnesium oxide contained a considerable amount of unadsorbed magnesium oxide in the form of aggregates.

Discussion

The effect of the magnesium oxide on the flowing properties of the starch does not appear to conform to the usual principles of solid lubrication[7]. A solid lubricant, such as talc, depends for its effect on its layer-lattice structure, with very low bond strength between the layers which thus slip easily over each other. Magnesium oxide has an unrelated cubic structure and would not be expected to act as a solid lubricant. Also the reduction of the effect which occurs when more than a certain small amount is added (Fig. 1), would not be expected to occur as a result of lubrication.

The fact that the magnesium oxide is adsorbed on to the starch provides an interpretation of the graph. Thus, the electron microscope studies show that over the range where the angle falls rapidly all the magnesium oxide is being adsorbed, and a practically continuous layer exists where the angle of repose is at its minimum. At higher concentrations the additional magnesium oxide is no longer adsorbed but persists as large aggregates mixed with the starch grains in which form it begins to increase the angle of repose once more. Thus, the dip in the curve represents a saturation effect.

Surface roughness is not a major factor governing the flow of the starch since the adsorbtion produces a rougher surface, which should give an opposite effect to that which is observed. Thus, it appears that the natural adhesion of the starch is of major importance, and that the effect of the magnesium oxide is to reduce this adhesion. It was pointed out

by Beilby[8] that small particles have a tendency to adhere to each other, or to a solid surface, which is independent of such external influences as electrostatic charging or the presence of contaminating grease films. The forces which induce this adhesion, and lead to the existence of aggregation in most fine powders will be the same as those responsible for the cohesion of crystals or amorphous bodies and can be roughly classified as polar or apolar forces. The first exist in ionic crystals and represent primary bonds of high energy, while the weaker apolar forces correspond to the secondary bonds between unionised molecules, in crystals or amorphous materials. These forces are of very short range, the Van der Waals' attractive forces, of the second type, decreasing as the seventh power of the separation of the bodies involved. But these will be effective whenever such close contact is formed that neighbouring particles are separated by a distance which is of the order of the atomic or molecular spacing.

Thus, when the starch grains are prevented from approaching each other by less than 1000 Å, by the presence of the magnesium oxide layers, the Van der Waals' forces will be greatly reduced, probably to insignificance. If it is considered that the corresponding forces between the magnesium oxide particles are less effective owing to the particles having smaller areas of true contact, then this would explain the reduced adhesion. Since these particles are crystalline, however, there is the possibility that polar forces are involved due to the existence of unsaturated valencies in the crystal faces. If the particles were oriented in such a way that faces having the same type of residual valency were always directed outwards, then this would result in a strong repulsive force between the particles which would greatly reduce the adhesion of the grains. The effect would be analogous to the peptisation of a precipitate by the mutual repulsion of adsorbed ions.

The crystals of magnesium oxide have a cubic structure of the NaCl type[9] in which magnesium and oxygen ions alternate along the principal axes. Thus, a cubic (100) face consists of a chequerboard array of the two ions and, since the ions on the surface are not surrounded by the normal number of neighbours, a corresponding pattern of unsaturated valencies exists. In this case the valence charges give a zero resultant at a little distance from the surface, the two types being equal in number. A dodecahedral or (110) face consists of alternate lines of the two types of ion and the resultant is again zero, but an octahedral (111) face contains only one type of ion and thus represents a sheet of unsaturated valencies of the same sign. The fact that the magnesium oxide particles are plate-shaped suggests that the principle faces are octahedral faces. If the starch grains have on their surface a small unsaturated valency density this would cause the magnesium oxide particles to be oriented on the surface in such a way as to present sheets of valency charge of a uniform sign to the exterior, and thus they would have the effect of greatly increasing the charge density and the mutual repulsion of the surfaces. This would also explain the great mobility of the surface layer of a mass of the powder since it is near the surface that the repulsive forces would have their

greatest effect, while further down in the body of the powder they would be overcome by the gravitational forces of the superimposed material.

CONCLUSION

The addition of magnesium oxide to starch does not produce a simple mixture in which the two components remain independent of each other. The strong adsorption which takes place gives a powder having properties which, in one respect at least, are quite different from those of either of the components, while other properties involving the surfaces of the particles would be expected to be altered. To this extent the process resembles a chemical reaction or, more closely, the interaction of macromolecules in solution or suspension, which is considered to involve coulombic forces[10] and in which the structural identity of the molecules is maintained. The difference is in the size of the particles involved, and the fact that the interaction occurs in the dry state.

Although the discussion has been confined to starch and magnesium oxide it has been shown that similar effects are produced by mixtures of starch with some other fine powders, and it seems likely that many other combinations of powders may give similar results.

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