

Review Article

Powders: Particle-Particle Interactions

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BECAUSE nearly all medicaments exist as powders at some stage in their manufacture, it is not considered necessary to justify an interest in powders.

Many difficulties are associated with the study of the powdered state of solids. Even today technological advances have not produced satisfactory quantitative methods for describing their properties. However, it is possible to define more precisely the problems associated with characterizing powders and to discuss in a qualitative manner the factors that determine their physical properties. Because much of the work pertinent to the subject is scattered throughout the literature and has been done outside of the pharmaceutical field, it seems worthwhile to attempt to organize this material into a review article.

The emphasis of this discussion will be on the properties of solids that determine the magnitude of the forces acting between the particles when they are in contact. These are predominately surface properties. If the particles have been compressed enough to produce plastic deformation or crushing of the particle, the mechanical properties become very important also. Since compressed tablets compose the largest volume of pharmaceutical products sold, it is tempting to extend the discussion to include the compression of particles into aggregates. However, in the inter-

est of brevity, the scope of this review will be limited to particulate solids under compression forces of a much smaller nature than used in tableting. For example, forces such as might be exerted by the weight of the powder bed on the particles at the bottom of the bed or the forces imposed by an auger in moving the material. The theoretical discussion will describe the properties of solid surfaces. The discussion of experimental methods will emphasize methods of measuring the cohesion and adhesion of powder particles.

Definition of the Problem.—The bulk density of a powder bed is not uniform. Therefore, the physical properties of the bed are not uniform either. The properties of a powder bed depend on the cumulative effect of the previous history of all the portions of the bulk being considered. Isolated regions of shear, vibration, or compaction may have produced high bulk density regions. These may remain intact in subsequent flow of the powder or may fragment into macroscopic regions mixed throughout the less dense bed. The forces acting on the top of a bed may be quite different from those at the bottom of the bed. Therefore, a thermodynamic treatment of a powder bed as a homogeneous mass is not possible. This discussion will try to develop, qualitatively, the factors that contribute to the interaction of solids. The following are considered the main topics of interest.

(a) The interaction between two particles is

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dependent upon the surface to interfacial energy change that occurs when the solids come into contact. The surface energy of a solid rarely is homogeneous. Therefore, the energy change at the true areas of contact will not be a single function of the true area of contact but will vary with the nature of the exact portions of the two solid surfaces in contact.

(b) The area of true contact between individual particles is dependent on the particle shape, size distribution, roughness, the compressive force at the interface, the shear to which the sample has been subjected, and the mechanical properties of the particles. Also, the number of nearest neighbors, *i.e.*, the coordination number, will be a function of these same factors.

(c) Most organic solids are insulators. Unless their surface is made conducting by contaminants such as surfactants or water (especially under high humidity conditions), the solids will charge on contact. The resulting electrostatic attraction may be large.

GENERAL BULK PROPERTIES OF SOLIDS

When the forces acting between molecules are strong enough to overcome the translational motion of the molecules and to compensate for necessary entropy changes, the molecules associate as a solid mass. If the association is in a predominately orderly manner, the solid is said to be crystalline. The crystalline solid is not necessarily the permanent, fixed arrangement often implied in elementary texts. Entropy *versus* temperature curves may provide evidence of nonisothermal changes in addition to the isothermal changes that occur when there is a change in crystal structure (1). Globular solids are said to be the antipode of liquid crystals (2). In globular solids, rotational freedom apparently occurs at lower temperature than the translational freedom of the molecules, whereas in liquid crystals, translational motion occurs prior to rotational freedom. These phenomena suggest that the properties of all crystalline solids are not the same and that the physical properties are not a single entity for a given solid substance but may be strongly temperature-dependent.

The order within the crystal always is much less than perfect. Solids often consist of numerous intimately associated grains. Crystal lattice continuity does not exist across these grain boundaries. Within the grains, numerous crystal dislocations, both screw and edge type, exist (3). The mechanical properties of solids are determined by the freedom of these dislocations to move. If they move readily, the solid will be

plastic. If they cannot move, the solid will be brittle (4). The mechanical strength of brittle solids will vary with the presence or absence of surface cracks (5). Also, the mechanical properties are influenced by the surface energy. The mechanical properties of solids are a principal factor in determining the true area of contact between solid materials under pressure.

The mechanical properties of organic solids have had only limited attention and our knowledge of the role of dislocations must, for the most part, be extrapolated from the studies on metals, semiconductors, and a few inorganic materials. However, dislocations in organic crystals do exist (6).

Some grain boundaries and dislocations extend to the surface of crystals and provide one source of heterogeneity on the surface. Adsorption of impurities result in additional sources of surface heterogeneity.

Because our primary interest is the forces of interaction between two surfaces brought into contact, the bulk properties will not be discussed in greater detail. However, it is necessary that one recognize that both the bulk and surface properties of a given substance may vary significantly and particle-particle interactions may be influenced by these variations. Furthermore, plastic flow is known to occur in many organic solids. Globular solids are sometimes called "plastic crystals." Some nonglobular solids may be tableted directly. This would not be possible unless plastic flow occurred to relieve elastic stresses.

THE "ADSORPTION" THEORY OF PARTICLE-PARTICLE INTERACTIONS

The Minimum Work of Fracture.—The minimum work required for the separation of two surfaces and, therefore, the energy bonding them together is equal to the difference in free energy after separation and the free energy before separation, *i.e.*, for materials *C* and *D*, the work of adhesion, W_a , is given by:

$$W_a = A (\gamma_c + \gamma_D - \gamma_{CD})$$

where

- A = the area produced by the separation,
- γ_c = the free energy of the surface per unit area of the solid *C* in air,
- γ_D = the free energy of the surface per unit area of the solid *D* in air, and
- γ_{CD} = the free energy of the *C*-*D* interface per unit area.

Similarly, for the fracture of a single material, for

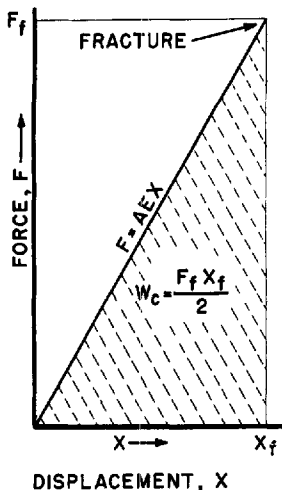


Fig. 1.—The minimum work of fracture of an ideal elastic body.

example, substance *C*, the work of cohesion, W_c , is given by:

$$W_c = 2A \gamma_c$$

If substance *C* obeys Hooke's law until it fractures, then the stress-strain diagram is as shown in Fig. 1. The equation for the line is $F = AEX$, where E is Young's modulus, F is the tensile force, and X is the displacement. The minimum work done in fracturing the solid, *i.e.*, the work of cohesion, is the area under the line, $W_c = F_f X_f / 2$; where F_f is F at fracture and X_f is the displacement at fracture.

Eliminating X_f from the work equation gives $W_c = F_f^2 / 2AE$. Replacing W_c with the surface energy from our earlier equation, one obtains on rearrangement:¹

$$F_f = 2A \sqrt{\gamma_c E}$$

The analogous equation for W_a is:

$$F_f = 2A \sqrt{\frac{E_C + E_D}{E_C E_D} (\gamma_c + \gamma_D - \gamma_{CD})}$$

The notion that the cohesion of solids is related to the surface energy is not new. Bradley (8), in 1932, discussed the role of dispersion forces in surface energy and in the cohesion of solids. Morgan (9) and Rumpf (10) have considered the strength of attraction between solids in a similar way. Recently Krupp and Sperling (11) have developed a model for the interaction of powder particles that involves the surface energy.

¹ Note the similarity of this equation to the fundamental equation of the Griffith crack theory of the strength of brittle solids (5, 7) which is:

$$F = K \sqrt{\frac{\gamma C}{E}}$$

where K is a proportionality constant and $2C$ is the crack length.

The Surface Energy of a Solid.—The argument in the preceding paragraphs has demonstrated that the surface energy of a solid is an important term in the strength of attraction between two substances. Therefore, the factors contributing to surface energy must be explored if even a qualitative concept is to be obtained. Part of the information may be inferred from our knowledge of liquids. First, let us consider the differences between solid surfaces and liquid surfaces.

Obviously, the relative immobility at room temperatures of the molecules of a solid account for the differences between the solid and liquid. For example, the chemical potential is the same in both the surface and bulk of a liquid phase, even when more than one component is present. However, for the solid, the surface usually is impure and the surface layer cannot equilibrate with the bulk in any reasonable length of time. Therefore, the chemical potential of a component on the surface may be quite different from that in the bulk.

The surface layer of a liquid has a lower density of molecules than the bulk. Since these molecules are free to move in the surface plane, they tend to undergo a two-dimensional "condensation," which results in a tension force in the surface plane. Because of random fluctuations, this process is never completed; the "condensed" molecules disappear into the bulk and are replaced randomly by other molecules. Gurney (12) discusses the thermodynamics of surfaces and concludes that equilibrium can exist only when the surface molecules are under a tension stress.

The tension component in the surface of liquids depends on the mobility of the surface layer. A solid surface cannot produce a tension component unless its surface molecules are mobile also. However, the unbalance of forces acting at the surface does result in a significant surface energy. Often the terms surface tension and specific surface free energy of a solid are carefully defined mathematically but the molecular model is not discussed. A recent review of the surface tension of solids (13) is of interest and illustrates this point. In this review, reference will be made only to the specific free energy of solids.

Attraction Forces Between Molecules at Interfaces.—There is an oft-stated observation that oil repels water. This useful though inexact statement could induce careless thinking. Only differences in magnitude of attraction are involved, not repulsion. All electrically neutral materials attract one another by dispersion

forces except when the spacing between them is so small that electron orbitals overlap. Attraction forces of greater magnitude than the dispersion forces often exist. The only repulsion force known that acts over a long distance is the electrostatic repulsion of like charges. Water is attracted to paraffin. A small droplet of water will cling to the underside of a paraffin surface. However, when the size of the drop is increased, enough gravitational force exists to overcome the attraction of the water for the paraffin and it falls off. Each water molecule has greater attraction for the other water molecules than for the paraffin; therefore, the entire drop falls away.

The origin of the attractive forces between two different solids in contact should not be a mystery to anyone since they are the same forces that act to hold all solids together. The one whose magnitude is most commonly underestimated is the London-van der Waals' force or the dispersion forces. Too often, the dispersion forces are described as "those weak interactions such as between hydrogen molecules, which explains it being a gas." However, these same forces cause many materials to be a solid at room temperature, *e.g.*, the longer chain aliphatic hydrocarbons. Unfortunately, theoretical treatments such as those given by Rowlinson (14), Debye (15), and de Boer (16) often do not leave the reader with an intuitive feel for their magnitude. Consequently, we shall look at some experimental evidence that indicates the relative importance of various forces.

Solubility Parameters.—The development of the solubility parameter concept provided considerable insight into the interactions between unlike molecules. However, the primary reason for including the solubility parameter in this discussion is to show the relationship of surface tension to the cohesion energy density. The term "cohesive energy density" is the square of the solubility parameter δ . Solubility parameters are intended only for "regular solutions" (17-20), *i.e.*, nonpolar substances. This parameter has been identified with the heat of vaporization:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2}$$

where ΔE is the energy of vaporization to a gas at zero pressure and V is the molal volume of the liquid. Also, $\delta \simeq 1.2 a^{1/2}/V$, where a is van der Waals' gas constant.

Note that all the above mathematical relations are measures of the cohesion of the individual liquids. Hildebrand gives for mixing components 1 and 2:

$$\frac{\Delta H_m}{V_m \phi_1 \phi_2} = (\delta_1 - \delta_2)^2$$

where ΔH_m is the heat of mixing, V_m is the total volume of the mixture, ϕ_1 and ϕ_2 are the volume fractions of the respective component in the mixture.

Thus, the square of the differences in the square roots of the cohesion energy densities gives the heat of mixing if corrected for volume effects. Solubility results when the difference $\delta_1 - \delta_2$ is small, *i.e.*, the heat of mixing does not dominate the entropy contribution to the free energy change of the solution process.

Another interesting relationship is $\delta = 4.1 (\gamma/V^{1/3})^{0.43}$,² where γ is the surface tension. The experimental verification of this relationship is evidence that the surface tension results from the attraction between molecules. Each of these equations express the interaction of molecules with each other.

Interfacial Tension Method of Evaluating Interactions.—A more recent approach to describing the forces between unlike molecules is given by Fowkes (21-23). He has obtained, by a systematic use of interfacial tension values, a measure of the contribution made by dispersion forces and the other types of forces acting at interfaces. His model makes use of the fact that the surface tension in air is a measure of the attraction due to all intermolecular forces in the liquid. Also, he assumes that the dispersion forces at the interface between two substances produce an interaction between unlike molecules. The interaction from dispersion forces is equal to the square root of the product of the dispersion component for each. He writes two equations—one for the contribution of each material to the interfacial tension. Since each equation describes only one liquid at the interface, let us call it the 1/2-interface equation. If the surface tension of *C* in air is γ_C and of *D* is γ_D , and provided only dispersion forces produce an interaction between *C* and *D*, the 1/2-interface equation for component *C* is:

$$\gamma_{C^{1/2}} = \gamma_C - \sqrt{\gamma_C^d \gamma_D^d}$$

where γ_C^d and γ_D^d are the respective contributions to surface tension produced by the dispersion forces.

For component *D* the 1/2-interface equation is:

$$\gamma_{D^{1/2}} = \gamma_D - \sqrt{\gamma_C^d \gamma_D^d}$$

The sum of the two yield the interfacial tension between *C* and *D*:

² This is an empirical relationship that gives more accurate results than the dimensionally homogeneous form $\delta \propto (\gamma/V^{1/3})^{0.5}$.

$$\gamma_{CD} = \gamma_C + \gamma_D - 2\sqrt{\gamma_C^d \gamma_D^d}$$

Since γ_{CD} , γ_C , and γ_D each can be determined by an independent experiment, it is necessary to know only either γ_C^d or γ_D^d before the other can be calculated. In the special case of a liquid such as an aliphatic hydrocarbon whose molecular interactions are due only to dispersion forces, $\gamma = \gamma^d$. For example, the surface tension of benzene is about 29 dynes/cm. and is due entirely to dispersion forces. Furthermore, in contact with mercury, only dispersion forces act between benzene and mercury. If benzene is called *C*, then $\gamma_C = \gamma_C^d = 28.85$ dynes/cm. Mercury is liquid *D*, so $\gamma_D = 484$ dynes/cm. γ_{CD} is measured and is 363 dynes/cm. Substituting into the equation and calculating γ_D^d , one obtains $\gamma_D^d = 194$ dynes/cm. Then one may calculate $\gamma_{C1/2}$ which turns out to be about -47 dynes/cm. The negative sign results because the mercury attracts the benzene stronger than the benzene attracts itself. Similarly, $\gamma_{D1/2} = 408$. Fowkes finds as average values for the mercury-air interface about 284 dynes/cm. is due to the metallic bond and 200 dynes/cm. from the dispersion forces of the mercury.

Similarly, Fowkes shows that the dispersion forces for water account for 21.8 dynes/cm. of its 72.8 dynes/cm. total surface tension. This value comes from interfacial tension data taken at a water-straight chain hydrocarbon interface. However, for the water-benzene case the assumption of only dispersion force interactions between water and benzene is not valid. About 13-16 dynes/cm. come from other forces (perhaps π bonds).

The metallic bond of mercury and the hydrogen bond in water should not interact at the water-mercury interface. However, it was questioned whether the permanent dipole of water might induce an image dipole in the mercury to produce a net attraction. Theory predicts this to be negligible and the measurements made by Fowkes confirm the prediction.

Fowkes has extended his studies to solid-liquid interfaces. Table I lists a few values for the dispersion forces of solids.

TABLE I.— γ^d VALUES FOR SOLIDS^a

Solid	γ^d (ergs/cm. ²)
Paraffin wax	25.5
Polytetrafluoroethylene	19.5
Polyethylene	35.0
Graphite	120-132
Copper	60.0
Lead	99.0
Silica	78.0

Data from Reference 22.

TABLE II.— γ_c VALUES FOR POLYMERIC SOLIDS^a

Solid	γ_c (dynes/Gm.)
Polyhexafluoropropylene	16.2
Polytrifluoroethylene	22.0
Polyethylene	31.0
Polymethyl methacrylate	39.0
Polyhexamethylene adipamide	46.0

^a Data from Reference 25.

Critical Surface Tension.—Zisman and co-workers (24-26) have used the equilibrium contact angle method to assign an average surface energy value to the solid surface. A homologous series of liquids is placed on the surface of the solid and their respective contact angles are observed. A plot is made of $\cos \theta$ versus γ_{lv} where γ_{lv} is the liquid surface tension of liquid in equilibrium with its saturated vapor in air. This plot is extrapolated to zero contact angle, and the value of the surface tension at this point noted. This surface tension at zero contact angle is called the critical surface tension, γ_c . The critical surface tension is assumed equal to the specific surface energy of the solid (23).

The technique sounds easy, but only when homologous liquids are used does one obtain a straight line. Otherwise, scatter and/or curvature exists. The experimental problems are many because of the difference between advancing and receding contact angles that often are observed. Also, contamination and roughness of the surfaces may vary and influence the results. Nevertheless, the critical surface tension has been identified within a narrow range on some solids. The γ_c values of some of these are given in Table II.

Friction and Adhesion.—In this discussion, the consideration of the forces between molecules has progressed from studies of liquid-liquid to solid-liquid interfaces. Studies of friction and adhesion of solids focuses the attention directly on the solid-solid interface. Here, for the first time, one must consider the important problem of determining the area of true contact. Since the true contact area is unknown in nearly all cases, it is most difficult to evaluate solid-solid interactions on a quantitative basis.

Friction sometimes is defined as the shear force required to break the adhesion "bonds" that form when solids are in contact, and the adhesional force is the tensile strength of the same bonds. This is the position taken in the classic work of Bowden and Tabor (27-30). They claim that the friction manifestation of adhesion is readily observed with large objects because all the "bonds" are sheared simultaneously in a friction measurement. However,

the tensile strength manifestation of adhesion usually is not observed because the elastic energy stored in the touching asperities is released gradually on separation, *i.e.*, the asperities have different lengths so that the separation does not occur simultaneously.

The classical, empirical laws of friction state that the frictional resistance to movement is independent of the apparent geometrical area of contact. It depends directly on the normal load. In the modern concept, if all unit areas of true contact have equal shear strength, then the true area of contact must be identical for a given normal load independent of the apparent geometrical contact area. Actually, exceptions to this law are readily found. However, the rarity of exceptions to the classical laws is remarkable when one considers the vast variety of surfaces that may be in contact.

The importance of the true area of contact has led to a study of adhesion and friction under very special conditions. Some of these illustrate the importance of the mechanical properties of solids and account for the author's brief treatment of the mechanical properties in an earlier part of the discussion.

A steel ball pressed into freshly scraped indium exhibits very large adhesive forces. When removed, the steel surface is covered with indium showing adhesion to be stronger than the cohesion of the indium (27). Obviously, the choice of indium is because of the low yield value that must be overcome to produce plastic flow. In plastic flow the elastic energy is reduced to a very small value, and the area of intimate contact becomes very large. Hence, the mechanical properties of indium make it possible to observe the adhesional force in a tension measurement.

The importance of a clean metallic surface, as in the freshly scraped indium above, is demonstrated in another experiment. Two clean iron surfaces, cleaned by outgassing under vacuum at high temperature, were pressed together with an initial load of only a few grams. Yet, over 500 Gm. was required to pull them apart. The metallic junction area was estimated and found to have the bulk strength of iron (29). Stepwise addition of traces of oxygen reduced the cohesion stepwise. Even H_2 and He will prevent gross seizure. The surface contamination apparently prevents the cold welding of the metals. Metallic bonding is much stronger than dispersion forces and the adsorbed contaminants prevent the stronger metallic bond from forming. The contaminants, thereby, reduce the energy of interaction.

The influence of a monolayer of lauric acid on the adhesion between two metallic surfaces has been measured (28). The monolayer was spread on the plastic surface of indium. The indentation produced by the steel ball pressed into the indium surface caused an increase of surface area so that some uncoated area of indium was formed at the indium-steel interface. The direct contact of metallic surfaces at the uncoated areas permitted metallic bonding to occur and produced high adhesion, in proportion to the area of metal-metal contact area.

Friction studies have not been limited to metals. Bowden (30) has reviewed adhesion and friction for various materials. Polymers represent a plastic material that deforms readily under load. He concludes that organic polymers under light loads exhibit friction forces that follow the same variation with load as the area of contact. Also, it appears that many polymers adhere strongly to metals and the shearing plane is in the polymer and not at the interface. Thus, transfer or wear occurs. With polytetrafluoroethylene (Teflon), the adhesion is small, slip occurs at the interface, and wear is minimal.

Also, it is of interest to consider elastic materials. Bowden (30) discusses the friction of diamond on diamond. Because diamond is a highly elastic material, the real area of contact is not expected to be proportional to the load but to the load to the $2/3$ power. As expected, the friction coefficient decreases as the load increases. Removing gas films from diamond causes the friction coefficient to increase markedly, apparently due to the stronger forces of interaction at uncontaminated diamond interfaces. Estimates of the true area of contact indicate that for clean diamond sliding over clean diamond *in vacuo*, the effective shear strength of the regions of true contact is comparable to the bulk strength of diamond.

Another interesting series of studies on the interaction between solid surfaces involve molecularly flat surfaces of mica. Freshly cleaved but uncontaminated mica surfaces can be put back together with very little loss in strength. However, if the sheets are separated and coated with a monomolecular layer of a fluorinated fatty acid and then placed together, the work required to separate them is reduced. The reduction is believed to be in proportion to the surface energy, *i.e.*, to the work necessary to create the new area of solid-air interface. The shear strength of freshly cleaved mica surfaces in contact was very high and the surface damage from sliding was great. However, monomolecular layers of cal-

cium stearate placed on the sheets reduced the shear strength markedly and left the surface undamaged by the shearing process. Obviously, the shearing plane remained in the interface when contaminants reduced the energy of interaction. These studies are mentioned by Bowden (30). Much of the work is that of Bailey, some of which is reported in *References 31 and 32*.

In a later section of this review, it will become evident that much of the experimental effort to study powders has been by friction measurements. Hence, the above information from some of the general studies of friction will be useful later. Furthermore, it is one of the few fields of study in which an extensive literature of solid-solid adhesion exists. Of course, adhesives, soldering, and welding also contribute some pertinent experimental observations.

All of these studies show the significance of the surface energy and the importance of the kinds of bonds that act across the interface. Obviously, the metal-metal bond is much stronger than the van der Waals' forces for the organic monomolecular layers. Similarly, the carbon-carbon bond in diamond is much stronger than between the contaminants. The mica experiments produce similar results.

Adhesives.—Adhesion in relation to friction has been discussed. Studies in the field of adhesives confirm all of the observations that have been discussed, but also point out one additional factor that has not been considered—*viz.*, the electrostatic term due to charge transfer at an interface.

There are said to be three theories of adhesives, *viz.*, the adsorption theory (33), the electrostatic theory (34, 35), and the diffusion theory (36). All of these have two factors in common: (a) a very large area of true contact must be established between the adhesive and the solid; and (b) to assure that the air is displaced from the interface, a low contact angle is needed. The differences among the theories are in the emphasis placed on the origin of the bond strength. The adsorption theory considers the bond strength to be determined by the changes in interfacial energy necessary to remove the adhesive from the solid (provided the adhesive itself is not split at an even lower energy). The electrostatic theory assumes that an electric double layer is established in the fluid adhesive and removal requires doing work to separate this double layer. The diffusional theory assumes that the macromolecules of the adhesive diffuse into the solid surface sufficiently to add an entanglement factor to the strength of the bond. Probably all three factors are, at least in some cases, important. However,

the diffusional aspect could be important for solid-solid interfaces only when contact exists for extended periods or when a solid has a very mobile surface layer.

Usually, adhesives are applied as a liquid phase in order to develop the high true area of contact. The solid-solid interactions exist after the adhesive "sets." This may be a drying by evaporational or diffusional loss of "solvent" or a chemical change such as occurs in the epoxy resins. A strong bond remains only when the setting occurs without excessive loss of true area of contact and without the development of significant elastic stresses resulting from dimensional changes of the adhesive. Again the important roles of a high true area of contact and of the mechanical properties are demonstrated.

Wear.—The process of wear has been studied in some detail (37). Although there are several classifications of types of wear, only the adhesional wear process is considered pertinent to this discussion. Adhesional wear occurs when surfaces slide over each other, and adhesion of small regions develop because of intimate contact. The adhesion is strong enough to pull fragments out from one of the solids. The size of wear particles is found to be remarkably uniform. Archard (38) has described a model for wear for which corresponding equations have been derived. Rabinowicz (39) gives the following equation for the condition of loose particle formation:

$$d = 60 \times 10^3 \frac{W_{ab}}{p}$$

where d is the diameter of the particle, W_{ab} is the work of adhesion, and p is the hardness of the surface yielding the particle. Note this is not a rate equation but only relates the size of the particles to the properties of the solid when wear occurs. Nonmetals and metals have been studied and reasonable correlation exists. One very important difference between wear and friction arises because only a few of the adhesional bonds produce wear, but all adhesional bonds contribute to friction.

Since W_{ab} appears in this equation, there is additional evidence that the surface energy is the important property determining solid-solid interactions. Although an oversimplification, boundary lubrication may be considered the technology of reducing wear by reducing W_{ab} to such a small magnitude that the wear rate is reduced to a negligible or very small value.

The "adsorption" theory of the particle-particle interaction of powders is only an ex-

tension of the "adsorption or adhesion" theories of friction, wear, and adhesives. Our interest in the forces of interaction between molecules at surfaces has been shown to be germane to a study of solid particles in contact.

Adsorption and Heats of Immersion.—Now let us look at evidence that suggests a nearly universal, heterogeneous nature for solid surfaces. We have learned already that grain boundaries and dislocations extend to the surface so that some heterogeneity results from these high energy regions. The best available evidence for the heterogeneity of a surface is found as before in reactions involving the interaction of the solid with individual molecules either from the gaseous or the liquid state. Adsorption and the related catalysis studies are of much interest.

Champion and Halsey (40) have shown that the formation of multilayers on a *homogeneous surface* must give rise to "stepped" adsorption isotherms. Apparently, the steps correspond to the formation of a new layer, each 1 molecule thick. However, the adsorption isotherms usually observed are not stepped; instead, they start off at high slope and gradually, but in a continuous manner, change to a curve of low slope. This suggests that most solid surfaces are heterogeneous, as expected. Classically, adsorption isotherms have been considered as belonging to one of five types (41). All of these show the gradual curvature characteristic of a heterogeneous surface.

Zettlemoyer and co-workers (42, 43) have used differential heats of immersion studies to characterize the heterogeneity of surfaces of solids. The derivative of the heat of immersion curve provides a differential heat curve, and the differential of the latter curve yields, when inverted, an approximate site energy distribution (43, 44). These workers have shown that the van der Waals' interaction energy between a polar adsorbent and a polar adsorbate consists of three parts, *viz.*, a nonpolar dispersion force, E_D ; the force of interaction of the electrostatic field of the surface and the dipole moment of the adsorbate molecules, E_0 ; and a force term arising from the polarization of the adsorbate by the surface, E_I . For alcohol on rutile, the distribution is about 68% E_0 , 6% E_I , and 26% E_D ; for hydrocarbons on the same surface, it is 67% E_D and 33% E_I , and for polar or nonpolar liquids on graphon, it is 100% E_D (45). These results predate the data of Fowkes. Both show the importance of the dispersion forces.

Studies of catalysts have led to a more detailed understanding of chemisorption. A brief review of this type of reaction has been given by Dowden

(46). Another interesting review is by Emmett (47). Both articles discuss the formation of bonds with surface atoms. Some may be electron donors and others electron acceptors. Active centers of catalysts often are classified as acid or basic. Apparently it is not clear whether a proton switching or an electron-pair switching mechanism is involved, *i.e.*, the Brønsted or the Lewis mechanisms.

Chemical interactions between particulate solids have been studied also. Specific solid-solid surface interactions of pharmaceuticals have been reported by Lach and co-workers (48).

Electrostatic Attraction.—It appears that solids are rarely separated without also separating a charge. The charge transfer becomes evident at separation of the surfaces. Richards (49) reports that by wringing together optically flat pieces of glass a charge is developed that is independent of the amount of frictional work but is proportional to the area of contact. As long as the plates remained in contact, an X-ray beam would not diminish the charge. Jefimenko (50) demonstrated that only contact and not friction is essential to electrification. A glass rod dipped into mercury or a paraffin rod dipped into water produced the same characteristic charge for the respective couple independent of the amount of work done. The kinetics of charging are not a factor in the last case because high true area of contact exists between a liquid and a solid. These experiments have established that charge transfer may result at areas of true contact between solids. Work must be done to separate the transferred charge and this is a part of the energy causing solid surfaces to attract. The amount of the charge and the direction of charge transfer will depend on the specific properties of the surfaces in contact.

Kunkel (51) dispersed dusts of homogeneous composition from containers lined with the same material. In all such cases, the total dust cloud was essentially neutral but practically all the particles were charged. If homogeneous clouds are blown so that they make and break contact with a different solid surface, the separation of the heterogeneous interface may impose an asymmetry on the relative members of positive and negative particles. The average charge increases somewhat more slowly than the surface of the particles, so particle size is important.

Nash *et al.* (52) observed the charges on powders after they passed through a copper funnel. They observed that the fraction of the sample that was charged could be altered by treating them with different surface-active agents. However, they did not distinguish between ag-

glomerates that were composed of equal numbers of oppositely charged particles and truly neutral particles or agglomerates.

Kordecki *et al.* (53) used centrifugal force to expel particles from solid surfaces. They found that glass spheres were much more difficult to remove from a Teflon surface when in a very dry atmosphere than when in a 50% relative humidity atmosphere even in the presence of a weak α -emitting radioactive source. However, the radiation from radium-D, a more powerful source, reduced the measured adhesion in a 10% relative humidity environment. They do not claim that the electrostatic component was completely removed from the adhesion by the ionization of the atmosphere. Richards' (49) work would suggest that it would not be completely removed.

Deryagin and Zimon (54) have observed the charges on individual particles torn from a flat surface. They found that both the adhesion and charge increased with residence time on the surface. [Deryagin has contributed, also, to the electrostatic theory of adhesives (55, 56).] These experiments demonstrate the importance of the electrostatic effect in the attraction between solids.

To discuss the kinetics of charging one really discusses the accumulation of charge by repeated contacts of one solid with another. This is the common way of observing friction and accounts for the term "frictional electricity." If one of the solids is a metal grounded to earth, the charge on the metal may be neutralized as soon as the separation reduces the inductive effect. Ciborowski and Wlodarski (57) observed the effect of grounding a conductor by repeatedly passing particles of a fluidized bed over a surface. They observed the charge on the powder by placing in the fluidized powder a small metal electrode connected to an electrometer. They state, "The highest electrode potentials, of a range of several thousand volts, were observed in equipment (a) when, apart from the electrode, other metal elements were also introduced into the fluidized bed and connected to earth. If there were no such elements, or else when they were not connected to earth, the electrode potential was generally considerably lower, of a range of a hundred volts at the utmost." Their equipment (a) used a glass tube to contain the fluidized bed. The grounded metal behaved as a very large body that did not change charge. All the difference in charge resulted from charge changes on the particles. Because of the grounded metal probe, the charge transfer could continue until all the powder particles were highly charged. Also, agglomeration of insulating particles was ob-

served. This suggested that the particles were not all highly charged with the same sign. Many particles stuck to the metal probes and to the walls of the container. Furthermore, a lowering of electrode potential was produced by applying a grounded conductor to the glass wall of the equipment.

Another interesting experiment with powders was reported by Gill and Alfrey (58). Cubes of ebonite or a volume of sand slid down a grounded metal plate into a cup connected to an electrometer. Approximately 1 cm. above this plane, an insulated, parallel metal plate was positioned, and a source of potential was placed between the two plates. When the top plate had no charge, the particles became negative as they slid over the plate. When the top plate was positive the magnitude of the negative charge on the particle increased. When the top plate was negative the charge on the particles decreased; if sufficiently negative, the particles had a reversed sign of charge. The following equation fits their data:

$$Q = AX - Q_0$$

where

- Q = the charge for a potential on the plate of X volts,
- Q_0 = the charge when sliding in zero field,
- A = a constant, and
- X = taken as positive when the upper plate is at positive potential with respect to the lower one.

This experiment suggests that the charge transfer will occur until some definite potential difference exists between the particles and the surface. Perhaps most important is the observation that the particles could be made to have zero charge with respect to ground when the potential difference between the plates was chosen correctly.

The mechanism of charging of metals and semiconductors is adequately treated by the band theory of solids. Perfect insulators would not charge in this manner. However, it is not clear to what extent the charging of insulators is dependent on the electrons associated with surface states. Harper (59, 60) states that the actual transfer of ions may account for the charging of insulators. For additional discussion of the mechanism of charging, several articles about static electrification may be consulted: Montgomery (61), Loeb (62), Rose and Ward (63). Skinner (64) has treated the case of insulators from the thermodynamic viewpoint.

By now it should be clear that when a solid is in contact with another solid a difference in charge

will develop. The only sure cure for the accumulation of charge is to make the nonconductor a conductor. High humidity often provides enough surface conductivity to reduce the accumulation of charge significantly. Also, anti-static agents may be used on the surface. These function by increasing the surface conductivity. Surfactants (detergents) are commonly used for this purpose. Several patents have been obtained on combinations involving zinc soaps (65). Another approach has been demonstrated by the work of Gill and Alfrey (58) discussed earlier. This requires the presence of a highly charged surface and could result in some hazardous conditions if used indiscriminately.

Grinding and Agglomeration.—*Agglomeration During Grinding.*—Ball mills of either the rotating or vibrating type seem to be superior to air mills for producing very fine particles. Also, they produce, at least in some cases, an interesting reversal of grinding, *i.e.*, they produce compact aggregates. Khodakov and Rebinder (66) have studied the disintegration of quartz in various media. They describe their mill as a laboratory eccentric vibromill but do not elaborate further. However, in a separate study they describe a vibromill operating at 50 c.p.s. with amplitudes of 3 to 5 mm., and mention steel balls in the grinding. Perhaps it is the same mill. They found that quartz ground in air did not show the very large specific surface area of quartz ground in water (determined by nitrogen adsorption). In air the surface area reached a maximum and further grinding produced agglomeration. The agglomerates were so compact that the bonding between particles reduced the surface available to nitrogen gas. After 16 min. of grinding the specific surface was 6.5 M.²/Gm. and had decreased to 5.9 M.²/Gm. after 32 min. of grinding. When ground in water, the specific surface was 42 M.²/Gm. after 16 min. and 73 M.²/Gm. after 32 min. Evidence that grinding in air produced a high degree of agglomeration was obtained when water was added to the quartz ground in air. A very sharp increase of specific area was obtained with only 40 sec. of additional grinding after adding water. Furthermore, powder obtained by grinding in water when dried and then reground in air produced a decrease in specific surface during the air grinding.

Another interesting case, described by Gregg (67), shows the change with grinding time of specific surface (by N₂ adsorption) and the change in dissolution rate of kaolin in acid solution. The dissolution rate continues to increase even when the specific surface is decreasing by

agglomeration. Apparently a high energy kaolin is produced. The evidence that a new state of kaolin is produced by grinding is obtained by thermogravimetric analysis. After many hours of grinding, most of the solid has changed to a new form, the form that dissolves more rapidly.

In Khodakov and Rebinder's work with quartz, other liquids, such as benzene, acetone, and alcohol, influenced the grinding, but only a slight improvement over air grinding was observed. This is somewhat surprising since the heats of wetting for all the liquids are similar to that for water. (If the Rebinder effect, adsorptional-strength-lowering, were the only determining factor, the specific surface values for grinding in these media should be nearly the same.) The product of grinding in these liquids was similar to the air-ground material, *i.e.*, very short periods of additional grinding in water yielded higher specific surfaces. Dried, water-ground materials, reground in the other liquids, agglomerated to give decreased surface areas. Only small amounts of liquids were required to produce significant effects on the amount of "amorphous" material produced. These authors studied, in addition to quartz, calcite, corundum, talc, rutile, alumina, silicate glass, quartz glass, and cement. In most cases the results were similar. Of course, the effects of hydration of cement prevented a complete study of it.

The influence of the grinding medium on the agglomeration process demonstrates that the bonding of solid particles involves a surface phenomenon. The unavailability of the "internal" surface of the agglomerates to nitrogen is evidence that the bonding involves a high true area of contact between the individual particles of the agglomerate.

Disturbed Surface Layers Produced Mechanically.—In the preceding paragraphs, the surface material produced by grinding has been referred to as high energy material and "amorphous" material. Khodakov (68) has reviewed the influence of fine grinding on the properties of solids. Rieck and Koopmans (69) have investigated wet ground quartz particles of 3 μM. diameter.³ They have concluded that the quartz particles are coated by a disturbed layer that is about 0.4-μM. in thickness.

Bacon (70) used line width of X-ray data to follow the change in crystallinity of graphite during grinding in a mill for a period exceeding 60 hr. The deterioration of crystallinity continued throughout this period. Gundermann (71) reports that materials, such as sugar and

³ 1 μM. = 1 × 10⁻⁶ M.

cellulose, also exhibit amorphization of the surface on prolonged grinding. He reports that the heat of solution of sugar appears to be increased by grinding; in fact, it changed from negative to positive.

The above evidence suggests that powder surfaces may have unusual properties because of a disturbed layer. Consequently, the electrostatic properties, the surface energy, and the mechanical properties may be different from the bulk properties of the same material.

Capillary Condensation Between Particles.—Moisture may influence the force of interaction between solid particles in at least three ways—namely, (a) it may adsorb on the surface and influence the surface energy, (b) it may alter the surface conductivity and, therefore, the electrostatic charging of the particles, and (c) it may condense in the capillary regions contiguous to the true areas of contact. Previous sections of this paper have discussed the first two. Now, we shall consider the third.

Capillary condensation occurs at high relative humidities, usually in excess of 60%. Only small amounts of water need be involved. The phenomenon of adhesion produced by capillary condensation is the same as wet granulation using very small amounts of water. Small liquid bridges are formed between particles. The case of the wet granule has been treated quantitatively and will be used here to describe the attraction between powder particles produced by capillary condensation.

Rumpf (10, 72) considers three classes of wet granules. They are: (a) the case where the hollow spaces between particles are only partially filled with liquid, the liquid being held by capillary forces as "lens" at the point of particle-particle contact; (b) the internal voids are completely filled with liquid but the external or surface layer voids of the granule are not completely filled; and (c) the liquid completely envelopes the solid, and only the surface tension of the drop holds the particle together (this is really a drop of a suspension, not a granule). Newitt and Conway-Jones (73) also use three classifications. Corresponding to class (a) according to Rumpf is a state Newitt and Conway-Jones call the *pendular* state. When the moisture content is high enough that the liquid forms a continuous network throughout the internal surface of the granule, but air spaces still exist inside the granule, these authors call it the *funicular* state. It is a condition intermediate between the (a) and (b) classes of Rumpf. The third state, according to Newitt and Conway-Jones, is called the *capillary* state. This corresponds to Rumpf's class (b).

The strength of a wet granule depends on the surface tension of the liquid phase and the contact angle of the liquid with the solid. The following is essentially the Newitt-Conway-Jones treatment. Consider an ideal case of two hard identical spheres of radius r in contact. About the point of contact, a small droplet of liquid would form, in the plane tangent to the two spheres, a circle of radius b . The case is simplified further by neglecting the force of gravity and by assuming the contact angle of the liquid on the solid is zero. For a small amount of liquid between the two spheres, the liquid would form a concave surface approximating the arc of a circle of radius c if viewed in a plane passing through the centers of the two spheres. The tensile force, f_1 , of attraction between the two spheres produced by the surface tension at this concave surface would be:

$$f_1 = 2 \pi b \gamma$$

where γ is the surface tension. Also, the surface tension is causing the pressure inside the liquid phase to be reduced so that there is a hydrostatic "suction" pressure holding the particles together. This is given by the Laplace equation for two curvature capillary pressure and is:

$$f_2 = \pi b^2 \gamma \left(\frac{1}{c} - \frac{1}{b} \right)$$

The total force holding the particles together is:

$$f_1 + f_2 = 2 \pi b \gamma + \pi b^2 \gamma \left(\frac{1}{c} - \frac{1}{b} \right)$$

To obtain the strength of a granule it is necessary to correct this for the number of particle-particle contacts, *i.e.*, the packing. However, the above will suffice to explain the origin of the granule strength under a static condition. In powder beds, it explains the attraction produced by capillary condensation between each pair of particles. Mason and Clark (74) have eliminated the influence of gravity by studying liquid bridges between particles dispersed in liquid vehicles. They report that the maximum values agree with the calculations of Fisher (75).

A dynamic term may be added to f_2 . If the liquid between the particles has a high viscosity, separation of the particles must overcome the resistance to deformation of the viscous liquid. This produces a change of the "suction" pressure that increases with the rate of particle separation. Consequently, viscous liquids add a shock resistance to the strength of the liquid "bond."

Among the classes of granules discussed by Rumpf and by Newitt *et al.*, the capillary state is the strongest. However, the amount of water condensed into the capillary regions surrounding the contact regions of powders usually would be

much less than that required to produce a high-strength granule.

Even small amounts of water deposited from the atmosphere by capillary condensation may increase the adhesion throughout the bed. If some solubility of the powder occurs in the liquid, caking may result, especially when alternating high-low humidity cycles exist. Ertle (76) used a penetrometer to detect caking in stored fertilizer. Whynes and Dee (77) have used a procedure adapted from the study of soil stability. It measures the crushing strength of a cylinder of the preconditioned powder held in a rubber sleeve.

As the liquid evaporates from the capillary region, any dissolved materials deposit at the points of particle-particle contact. If no material were dissolved in the liquid phase there would be no increase in dry strength produced by the wet-dry cycle. Newitt *et al.* report that solutions of ammonium sulfate were used to granulate fine sand. They state, "... as total dryness is approached, the strength may exceed some fifty times the original moist strength."

THE TRUE AREA OF CONTACT BETWEEN SOLIDS

This section will be limited to a discussion of the areas of true contact established between macroscopic solid objects because the author is unaware of any work done to measure the true area of contact between small particles. Worthwhile perspective on the problem is gained by considering the evidence available for the macroscopic case.

The importance of the true area of contact is obvious from the previous discussion. The surface interactions are nearly all from short-range forces. Electrostatic charging occurs at actual contact points and elastic and plastic displacement require true contact. All of these are important factors in determining the tensile strength between particles in contact.

Again the source of much of the information is from the studies of friction and wear. Earlier in this review mention has been made of the extensive contributions of Bowden and Tabor (27-29). In addition to their work, some recent reviews of studies of the true areas of contact between solids (78, 79) have been translated from the Russian language. None of the experimental methods used are free from error. However, many of the results are worthy of consideration. Among the methods used are (a) changes in electrical conductivity with pressure, (b) transfer of very thin layers of paint (both luminous phosphors and radioactive isotopes have been used with this method), and (c) optical

methods, suitable for use only when one or both solids are transparent. These depend on light reflection or transmission, respectively, at points of contact and light scattering at regions of no contact. The optical method permits contact area measurements to be made during sliding. Theoretical calculations based on specific models have been made. These models include: (a) elastic contact involving hemispherical asperities in contact with a plane, (b) elastic contact of two surfaces involving an assembly of rods, (c) contacts between surfaces with randomly distributed asperities, and (d) elastic-plastic contacts of asperities with a rigid plane and without work hardening of the solid.

The following general conclusions are based on a large amount of experimental data and are taken from *Reference 79*.

(a) "The actual contact area is determined to a large degree by the original microgeometry of the compressible bodies."

(b) "The microgeometric shape of the surface varies during compression."

(c) "The contact area is directly proportional to a power smaller than one of the applied load."

(d) "The contact area depends on the physico-mechanical properties of the surface layer of the compressed body."

(e) "The area of a single contact zone is almost completely independent of the applied load."

(f) "The deformation of a compressed surface is elastic."

A series of plots of the real area of contact versus the applied pressure is given in *Reference 78* for different metals. Only a slight curvature is apparent in most of the plots. Therefore, the deviation from linearity, referred to in (c) above, is not large for these specific materials. From simultaneous measurements of both the static frictional force and the true area of contact, the real specific frictional force in Kg./cm.² and the real pressure in Kg./cm.² were obtained. The results for polymethyl methacrylate and for silver chloride (apparently against a very smooth glass surface) are given. The specific frictional force was not constant. For both cases, the force appeared to increase with increase in pressure. The increase was more rapid with polymethyl methacrylate than with silver chloride. The author states that this is consistent with the known property of work hardening of this polymeric solid.

If true areas of contact are established through strong asperities, then plastic flow may occur in the bulk of the solid below the asperities. This would not lead to establishing high areas of true contact; but it would result in the storage of

some energy in the elastic displacement of the asperities. This would be necessary to exceed the yield value and produce plastic flow. Consequently, the cohesion of such a solid would be very small.

Bowden and Tabor (83) have discussed the persistence of work-hardened asperities. They have made gross indentations in bulk copper without producing extensive deformation of preformed microscopic work-hardened ridges. Herring and Galt (81) have pointed out that whiskers (growth around a single screw dislocation) of tin are many times stronger than the bulk metal. Beams *et al.* (82) have demonstrated the very large strength of thin films. The explanation is believed to be that plastic flow does not occur where sections are so small that crystal dislocations are either not present or where they cannot move to generate new dislocations.

Since none of the reported studies involve typical pharmaceutical, organic solids, it is possible only to speculate on whether these results are applicable. Probably the mechanisms are the same, but the relative occurrence or importance of various mechanisms may be different. There are important unknowns concerning the true nature of the surface regions of an organic solid. How rough is the surface of a powder particle? What is the distribution of asperities? Are the asperities whiskers? How readily do dislocations move in complex organic crystalline solids? Only further study will resolve these problems.

It is common knowledge that many powders become "sticky," *i.e.*, exhibit high cohesive forces, when the size range includes many particles of less than 10 μ diameter. However, other materials may not become "sticky" even when in a much smaller size range. Possibly the structure of the surface varies; those powders with smooth enough surfaces to readily produce high true areas of contact, even at low contact pressure, would be expected to be sticky. Those with a very rough surface and a low true contact area would be less sticky. Electron photomicrographs such as those made of polyethylene glycol 6000⁴ by Nash *et al.* (52, 80) suggest that some solids may have relatively flat surfaces. Nevertheless, the resolution of these photomicrographs is not sufficient to provide evidence of the degree of roughness at molecular levels.

EXPERIMENTAL EVALUATION OF COHESION AND ADHESION OF POWDER PARTICLES

Numerous other reviews have been written

⁴ Marketed as Carbowax 6000 by Union Carbide Corp., New York, N. Y.

that discuss both the methods and the results of measuring cohesion and adhesion of powders. Therefore, the author has chosen to treat this section relatively briefly and leave it to the reader to consult some of the other reviews or the original articles for more details. Other reports summarizing some of the studies are Böhme *et al.* (84), Lowes (85), Morgan (9), Patat and Schmid (86), and Brown (87).

Angle of Repose and the Angle of Internal Friction.—The earlier discussion of friction has indicated the significance of friction measurements in relation to particle-particle interactions. Numerous methods have been employed to obtain friction values. The simplest of these is the angle of repose. Train (88) has compared the results from four different methods and reports that the value obtained depends on the method used. The four methods he compared are: (a) fixed funnel, free standing cone, (b) fixed bed cone, (c) tilting box, and (d) revolving cylinder. Zenz and Othmer (89, 90) conclude that there are two different types of angles of repose. One is obtained when a pile is formed and the other when a hollow cone is formed by draining through an orifice. (These authors define other related angular properties of solids, *viz.*, angle of internal friction, angle of wall friction, angle of rupture, and angle of slide.) Taylor (91) points out that the angle of repose represents, at best, a crude approximation to the angle of internal friction. The angle of repose differs from the angle of internal friction because it is determined by the least stable particles. The particles on the surface can be stable only when the least stable grains are in equilibrium. The internal friction depends on the average condition for all grains. Perhaps internal friction would correlate more closely with flow properties. Dalla Valle (92) equates the tangent of the angle of repose to the coefficient of friction. However, general application of this formula may lead to serious error because the derivation assumes no cohesion between particles. When cohesion is present the normal force, σ , on a pile would be:

$$\sigma = mg \cos \theta + C$$

where m is mass, g is gravitational constant, θ is the angle of repose, and C is the cohesion force. The tangential force, τ , is:

$$\tau = mg \sin \theta$$

and the friction equation is:

$$\tau = \mu \sigma$$

or

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

In this equation, μ and C are both unknowns

and cannot be evaluated from an angle of repose measurement. Usually, C is ignored, and μ is calculated as if C equals zero.

In this laboratory, the arbitrary assignment of $C = 0$ has been overcome by adding a centrifugal component to the pile. This is accomplished by forming the pile on a rotating horizontal disk. It is called the "spinning disk" technique. The corresponding equations are:

$$\begin{aligned}\sigma &= mg \cos \phi_r + C - mr\omega^2 \sin \phi_r \\ \tau &= mg \sin \phi_r + mr\omega^2 \cos \phi_r\end{aligned}$$

and the friction equation is:

$$\begin{aligned}g \sin \phi_r + r\omega^2 \cos \phi_r \\ = \mu \left(g \cos \phi_r + \frac{C}{m} - r\omega^2 \sin \phi_r \right)\end{aligned}$$

where ϕ_r is the slope of the profile of the pile at radius, r , *i.e.*, the angle between the horizontal and a tangent to the surface of the pile at radius, r , $\omega = 2\pi$ (rev./sec.).

Values of ϕ_r for various r values are obtained by sifting as much powder as possible onto an 11-cm. diameter disk covered with sandpaper. A small lip on the edge of the disk helps during the starting of the pile. The completed pile is photographed on transparency film and then projected. From the projected profile of the pile, corresponding values of r and ϕ_r are obtained by drawing tangents to the surface of the pile. By plotting the corresponding values of τ/m versus $\frac{\sigma}{m} - \frac{C}{m}$ and then calculating the least squares line, it is determined whether $C = 0$, *i.e.*, it is determined whether the plot goes through the origin. The slope of the line is μ . Often the plot is not linear when $C > 0$; and the method fails. Attempts to use this method to obtain both μ and C/m when $C > 0$ usually have been unsuccessful. However, the fact that one obtains an indication whether C is or is not zero is an important improvement over a simple angle of repose measurement. The accuracy and precision of a value obtained from a least squares line was found far superior to the single point method of an ordinary angle of repose pile. Of course, constant humidity conditions are essential for precision of any method.

Figure 2 shows the apparatus and Fig. 3 dramatically shows the cohesion existing in a pile of sticky powder.⁵ To form this pile the powder was sifted gently onto the disk, no compaction was used to make the pile stick. The relative humidity was 50%. The surface of the pile was

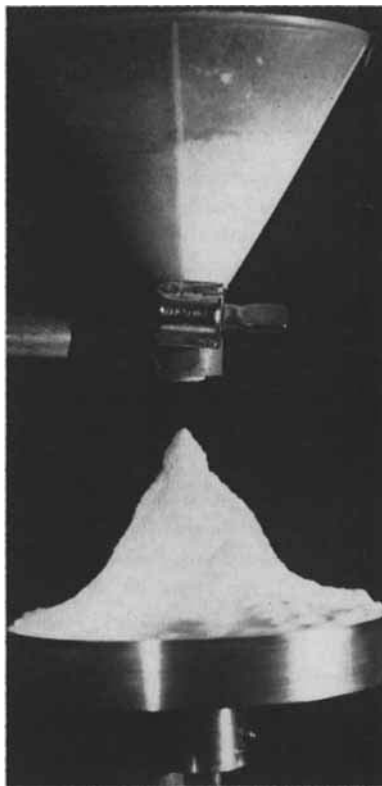


Fig. 2.—Forming of a powder pile on a spinning disk. Powder is lidocaine base.

exposed to radiation from a polonium source to remove the accumulated charge. (Of course, this did not remove the electrostatic component of adhesion at points of true contact.) The pile was inverted immediately after forming; only the tip fell off.

Variations of the angle of repose method have been used to obtain cohesion values. This is useful only when the powder bed behaves as a plastic body. A preformed bed may be tilted very slowly until a shear plane develops and a mass of the powder slides off. The angle of

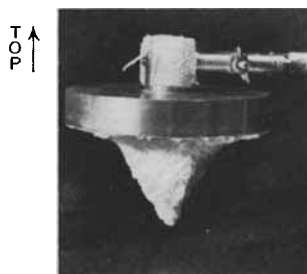


Fig. 3.—Lidocaine base pile formed in 50% R.H. air has sufficient cohesion and adhesion to remain intact when inverted.

⁵ Lidocaine. Marketed as Xylocaïne Base by Astra Pharmaceutical Products, Inc., Worcester, Mass.

slide observed is assumed to be the angle of internal friction. Hayashi and Minami (93) varied the length of a tilted box filled with powder to obtain variable forces and angles so that the cohesion could be calculated. Lowes (85) and Lowes and Perry (94) describe a similar method based on the tilting of a preformed cone until a shear plane develops.

Studies in which the cohesion was not evaluated are very numerous. Possibly the angle of repose is the most common method of obtaining an index of flow, in spite of its limitations. A few of these reports will be mentioned here to provide a starting point for the reader interested in pursuing the subject further. A complete list is prohibitively long.

Studies of the influence of particle size and size distribution on the angle of repose have been reported by Krishna and Rao (95), Train (88), Nelson (96), Pilpel (97), and Nakajima *et al.* (98). The influence of additives has been studied by Craik (99), Nelson (96), Awada *et al.* (100), and Nash *et al.* (52, 80). Awada *et al.* report the use of glass beads as a diluent to sticky powders. They estimate the angle of repose for the pure powder by varying the composition and extrapolating to 100%. The influence of moisture content has been reported by Fowler and Wyatt (101), Lowes and Perry (94), and Craik and Miller (102). Fonner *et al.* (103) attribute to surface roughness of granules a strong influence on the angle of repose. Other reports and discussions of interest are those of Dawes (104) and Carr (105). In general, these studies indicate that the presence of fines increase the angle of repose. Diluents alter the flow properties; diluents that are themselves free flowing usually decrease the angle of repose and vice versa of the mixture. It is clear that the angle of repose increases at high relative humidities, presumably as a result of capillary condensation in the regions of true contact.

Tilted Plane Method.—If small amounts of powder are placed on a flat surface and then the surface is tilted at an ever-increasing angle until the powder slides off, the process may be described by the same equations as before. The friction equation used is:

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

A is the adhesion of the powder to the plate when the shear plane is between the powder and the plate, *i.e.*, the powder slides off as a single clump. Cremer *et al.* (106) obtained plots of τ versus σ by varying the size of the powder layer to change the mass. She used the equation in the form:

$$mg \sin \theta = \mu mg \cos \theta + H$$

Her H values correspond to μA above. Böhme *et al.* (84) discusses the work of Patat and Schmid (86) in which they concluded that the complicated nature of the sliding process prevents this from being a satisfactory method. For example, it sometimes produced negative values for H . (The same complication was observed by the author with sticky powders when using the spinning disk.) Zimon (107) reports good results with the method but points out that it is not a true measure of adhesion of individual particles because of the mechanism of sliding. Many others have used it, *viz.*, Pecht (108), Batel (109), Krishna and Rao (95), and Hayashi and Minami (93). Pecht, Batel, and Patat and Schmid used a vacuum arrangement so that the influence of different atmospheric conditions could be explored. Pecht studied relatively narrow size distributions and found that sometimes the adhesion decreased with increase in size distribution.

The above method is designed to measure friction and adhesion to the surface. However, it is not always possible to maintain the shear plane at the powder-substrate interface. Sometimes the particles may adhere to the substrate and the shear plane develops in the powder bed. Also, the particles may move as individuals. In either case the method fails.

The Shear Cell Method.—The intentional development of a shear plane in a powder bed provides another method of using the friction equations to measure cohesion. Dawes (104) used two types of shear cells. One of these assured that the shear plane was in the powder by having vertical vanes on both the upper and lower plate. The powder bed was just thick enough to prevent the vanes from striking each other. His alternate cell used only sandpaper on the bottom of the top plate. He compared the values of σ and τ for both methods; and he found, for a given powder, that the values obtained in the two cells were slightly different. In his study both μ and C were somewhat lower when the sandpaper-covered plate was used.

Jenike (110, 111) has used a shear cell that is packed with powder. The cell is split so that the shear plane is in the powder. Since the powder is packed into the cell, the true area of contact between powder particles and the test results may be influenced by the packing. Jenike has used data from his apparatus to design hoppers. Ashton *et al.* (112) have attempted to control the bulk density in a Jenike-type cell and have obtained a series of isodensity curves for various powders. These authors find that the equation

$$(\tau/C)^n = \frac{\sigma}{T} + 1$$

describes the "yield loci" at

constant bulk density of many powders; n is a constant for a given powder of a given particle size and size distribution. It is independent of bulk density and usually is between 1 and 2. C' is equivalent to μC in the earlier equations. T is the tensile strength of the powder measured in a special apparatus described by Ashton *et al.* (113); it is a modification of an apparatus described by Dawes (114). The cohesion apparatus will be discussed under *Tensile Strength of Powder Beds*. Apparently the tensile strength measured in this manner is always less than the value of C obtained by extrapolation of the shear cell data, *i.e.*, the τ versus $\sigma - C$ plots.

The results of Ashton *et al.* show the effect of the bulk density changes. These results confirm many of the general conclusions stated in the sections dealing with the theoretical considerations.

The Jenike method of describing powder flow and of hopper design using the shear cell data is discussed by Williams (115). Additional discussion of the shear cell and its uses can be found in several papers in a single issue of *Rheologica Acta* (116).

Other workers have used a shear cell method in evaluating powders. Taneya (117)⁶ has compared the results of the shear cell technique with another based on a modified Couette viscometer (discussed below). The two methods do not always produce the same results. Okada and Abe (118) report results using an apparatus they attribute to Deryagin and Lasarev (119).

A simplified apparatus is described by Nash *et al.* (52, 80). This simple shear cell has been used in these laboratories. The force required to shear a thin layer of powder between two emery paper-coated surfaces is observed. The author has modified the apparatus to permit the top plate to be suspended on a long thread from a balance so that normal loads less than the weight of the top element may be applied. A laboratory jack is used to raise the powder bed gently up and under the top plate, stopping at the null point of the balance. Because of the simplicity of the apparatus, it is readily used inside a constant humidity chamber.

It is difficult to assess the merits of the various shear cell designs and methods of using them. However, the choice of the simple cell described by Nash *et al.* is not determined only by its convenience in use. Because it uses a very thin layer of powder, it was felt that the sample density will be more uniform throughout; also, that its bulk density will be determined by the

load applied instead of by the method of prepacking of the cell. Tests indicate that the bed thickness used, $1/8$ in., is sufficient that the magnitude of τ is not affected by changes in thickness. The powder bed is formed by gentle sifting to minimize the packing. However, the screen size through which the powder passes and previous handling may determine the agglomerate size and influence the density of beds of a cohesive powder. Certainly these factors can influence the results.

Certain powders do not yield straight line plots of τ versus $\sigma - C$. Often these same powders form nearly spherical compact aggregates when handled, often called pilling. The author's experience has been that these are very cohesive powders of fine particle size. Also, qualitatively a low plastic yield value for beds of these powders has been observed. Under the heavier loads, *e.g.*, about 20 Gm./cm.², they form a sufficiently strong wafer that it must be peeled off the sandpaper. Also, a few cohesive powders yield negative values of C . Hence, the assumed model on which the simple friction law is based is not sufficient to describe all powders.

Several investigators have used coaxial cylinders in an arrangement similar to a Couette viscometer to measure the friction coefficient and the cohesion. Matheson *et al.* (120) used a Stormer type viscometer with a flat paddle as the moving element. It was suspended in a fluidized bed. They classified the flow into three types, *viz.*, (a) cohesive, (b) aggregative with good fluidization, and (c) slugging. Type (a) was observed with small particles, usually less than 40 μ diameter. Slugging occurred with high air velocities. Meaningful results were obtained only with type (b) flow. Quantitative values for the cohesion are not possible with this arrangement. Benarie (121), Taneya (122), and Kuno and Kurihara (123) have used the "viscometer" arrangement to produce a cylindrical shear region in a powder bed. This permits calculation of μ and C if the radius of the effective cylinder can be determined. It was found that this experimental approach is limited to relatively noncohesive powders. The powders must flow freely into any voids formed by the motion in the shear plane. Cohesive powders that have a low bulk density first undergo forced packing in the vicinity of the shear plane and then form a cylindrical void region. The shear region becomes an air gap and no measurement is obtained. Taneya and also Benarie report surprisingly large cohesion values for the coarse particles they studied. Possibly this technique is a more sensitive method than the direct tensile strength test procedure to be described next.

⁶ Refers to description of apparatus in Taneya, S., and Sone, T., *Oyo Butsuri*, 31, 286(1962).

Tensile Strength of Powder Beds.—Reference has been made previously to the Tideswell-Tallyfield apparatus described by Dawes (114). An improved model is described by Thouzeau and Taylor (124); also, a similar apparatus used by Ashton *et al.* (113) already has been mentioned. These apparatus are split containers with one-half fixed and the other movable. They are arranged so that the powder bed breaks into two halves either by tilting the apparatus so the movable half moves away (104) or by using the apparatus in a horizontal position and applying a force on the movable half of the cell (113) to pull it away and break the powder bed. Obviously, this method cannot be used unless the powder is cohesive enough to provide a clean break. Otherwise, the powder would slide into the space between the two halves of the cell as they separate.

The true area of the break plane is not easily calculated since the fracture results in an irregular surface. Furthermore, the concentration of stresses at local regions usually cause tensile strength tests of brittle solids to measure a low cohesion value. It seems reasonable to assume that in this test the powders would behave similar to a brittle solid. However, McKee (125) has measured very weak, sintered compacts in a modified Tideswell apparatus, and he claims that the Griffith crack mechanism is not a significant factor in the breaking mechanism of these compacts.

Farley and Valentin (126) have combined data from the equipment described by Ashton *et al.* with data from a Jenike-type shear cell. The observed cohesion is less than the intercept value, C , from the shear cell data. Eisner *et al.* (127) have studied the increase in tensile strength of powder beds on exposure to humid air. Increases continued for up to 8 hr. Thouzeau and Taylor (124) observed differences in raw materials supposedly supplied from the same source. In both studies (124, 127), a decreased cohesion value was observed after the powder had been "waterproofed," *i.e.*, coated to alter its surface energy. Shotton and Harb (128) studied various starches and observed various patterns of change in cohesion with changes in moisture content of the powder.

Another device for evaluating the cohesion of powders has been described by Nash *et al.* (52, 80). Two coaxial cylinders of the same diameter are placed end to end. Powder is placed in the cylinders; and it is compressed at low load. The force required to separate the cylinders and to fracture the powder bed is observed. For a given compression load, the bulk tensile strength

is an exponential function of the length of the column in the cylinders. By using different amounts of powder to change the column length and then plotting the observed cohesion values on semilog paper, an extrapolation to zero column height may be made. This zero height value varies with compression load. A plot of zero column length cohesion values *versus* the respective compressive loads yields an approximately linear relationship over the range studied by these investigators.

So far the methods considered for evaluating powders have been concerned only with a powder bed, not the individual particles. Another very interesting body of experimental data has been obtained on individual particles. The normal force required to pull a particle off a surface is a tensile strength test of the individual particle "bond" to the surface. These studies are most interesting. They reveal a very broad range of forces for similar particles and the maximum force between a particle and a solid surface is surprisingly large.

The Centrifugal Method.—Kordecki *et al.* (53, 129) used a centrifuge in studies of the adhesion of particles to a flat surface. Determinations were made of the size distribution of the particles initially sprinkled on a slide and of the size distributions of those remaining after subsection in discrete steps to successively higher fields of force. The maximum acceleration applied was in excess of 8 g. At maximum acceleration, nearly all of the largest particles and a significant fraction of the smallest particles were removed.

Böhme *et al.* (84, 130-132) also have used the ultracentrifuge, one of them capable of producing forces in excess of 10^6 g. Because they used a very narrow size range of particles, they plotted their results differently. They compared the per cent of particles adhering *versus* the applied force (dynes) and found that the variation of force with particle size was small. Apparently the larger acceleration required for small particles is a consequence of their small mass. Also, these authors have gathered some data on the influence of surface composition and texture on the adhesion of particles to the surface. Their results are consistent with the concepts developed in the early paragraphs of this review. Krupp and Sperling (11) have developed a theory of the adhesion of small particles using the concepts of deformability of solids, surface roughness, and surface energy.

Zimon and Volkova (133) have used the centrifuge method to study the effect of surface roughness. Their conclusions are in agreement

with others, *i.e.*, the adhesion is highest on very smooth surfaces. Zimon (134) has studied the influence of capillary condensation on the adhesion of individual particles. The observed adhesion force was smaller than his calculated values.

Deryagin *et al.* (135) have used centrifugal fields providing up to 300,000 g. They did not succeed in removing all 5- μ diameter glass particles from a polished steel rotor. They used, also, an impact method but give no details. They state that they completely removed glass particles using an impact. The experiments were performed at relatively high velocities of the bullet.

The Vibrating Plate Method.—Deryagin and Zimon (54) used ultrasonic vibration of a metal support surface to measure the force required to remove particles from the metal. Accelerations up to 24,000 g were possible with this unit. Because the forces required to hold individual mono-sized particles covers such a broad range, the representative force used in making comparisons was chosen as the force required to remove 50% of the particles. They found that to remove small particles a larger force was required than for large particles. In this paper, these authors report also the electrical charge observed on particles being blown off the surface of a solid. A broad range of charges was observed. The charge on the particles increased with time in a manner similar to the rate of the increase in adhesional force with time. Consequently, these authors propose that the electrostatic charging process makes an important contribution to the adhesional force.

Impingement and/or Dispersibility of Powders in an Air Stream.—Both the dispersibility in an air stream and the adhesion on impingement of powder in an air stream are used to evaluate the stickiness of powder. Dawes *et al.* (104, 136, 137) have studied the dispersibility of a powder bed in an air blast. In general, two types of behavior are observed. Noncohesive powders allow a gradual erosion process to occur. Cohesive powders denude suddenly by the tearing away of large chunks.

Pecht (138) measured the loss in an air stream of powder from the surface of a granular substrate. From this he developed a relative stickiness factor. Jordan (139) used the air velocities required to remove various percentages of the particles from a plate for making comparisons. Larsen (140) and Corn and Silverman (141) have studied removal by air streams of solid particles from filters. The relationship between adhesion and adherence on impingement

has been discussed by Jordan (139). Adherence on impingement has been studied both in connection with the air filtration problem and in connection with the impactor as a sampler of dust in air.

The cascade-impactor is used in the particle size analysis of aerosols. It depends on the size selective impingement (with adhesion) of particles from successively higher velocity air streams. Several factors that influence collection efficiency in impactors have been discussed by Stern *et al.* (142). Aerosol sampling has been reviewed briefly by Whitby and Liu (143).

In addition to the relatively sophisticated approaches, some very empirical methods have been used to provide indexes of dispersibility. Drop tests have been described by Neumann (144) and by Carr (105).

The Weight Method.—Böhme *et al.* (84) reviewed the older efforts to measure directly by weighing the adhesion of relatively large particles or fibers. A more recent study is reported by Corn (145) in which the adhesional force of micron-sized particles to solid surfaces were measured using a microbalance. The pendulum technique was used by Howe *et al.* (146) for measuring adhesion of a large bead (0.5 mm. or larger) to a surface measures adhesion directly but is not suitable for very small particles.

SUMMARY

It would be encouraging if from all of the studies considered in this review one could summarize the results in a simple quantitative manner. However, the only generalizations possible seem to be statements of the variations observed. The observed cohesion varies with the experimental method used to measure it. Some powder beds seem to exhibit negligible cohesion. Yet, individual particles may require accelerations approaching 1,000,000 g to remove them. At low humidities, the electrostatic component may be large. Theoretical considerations of the electrostatic charging of insulators is not sufficiently developed to be of any help in predicting the behavior of most organic powders. Surface energy and topography are seldom known. Mechanical properties of individual particles vary and have been explored insufficiently to permit any quantitative consideration.

In this review the author has attempted to discuss experimental evidence that indicates the types of forces that act between solids in contact. That powder particles attract is not surprising. Also, the relationship of the mechanical properties and topography to the areas of true con-

tact have been considered. The final section reviewed the methods used by various investigators to obtain either numerical values or rank order classifications of the forces of attraction between solids, powders, and/or particles. The complexity of the problem of developing a quantitative, universal theory for the interaction of powder particles with solids makes such a result appear to be remote indeed. However, from a qualitative understanding, it often is possible to determine a systematic approach to our formulation problems; some call it guided empiricism.

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