was about equal to the volume of the hydrocarbon boil up rate. The following data were obtained:

Time,hr	Overhead composition, %EtBn	Stillpot composition, %EtBn	Rel. vol.
1	75.30	20.48	1.18
2	81.08	20.64	1.21
3	83.14	20.47	1.22

Again, it will be noted that it takes about 2 hr for this equipment to attain equilibrium and that this extractive agent raises the relative volatility from 1.06 to 1.22.

In order for extractive distillation to be economically attractive, the agents must be chemically stable and capable of continual recycle. The combinations of agents shown in Table 2 were allowed to boil at atmospheric pressure in the equilibrium still for periods of time ranging from 24 to 96 hr with no evidence of decomposition.

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Influence of Condensable Vapor on Strength of Powders

Diametrically different influences of small moisture contents upon strength are often measured in beds of different kinds of particles. Here we explain such opposing trends in terms of capillary forces exerted by condensed liquid rings at the points of particle contact. The effects of such rings are opposite for different particle shapes at the point of contact, namely, at spherical or at sharp angular contact points. In addition to the theoretical development, data are given for two different illustrative types of particles.

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Increasing moisture content of beds of powders influences their strength in diverse ways, depending on the nature of the particulate powders. In some instances, strength increases, and in some it decreases as moisture concentration grows. Such converse behavior has been a theoretical problem for years; we propose a possible resolution of this difficulty. Haines (1925) laid down the early theoretical foundations for such effects of moisture by considering the capillary forces acting upon nonporous, insoluble, identical spherical particles as a result of liquid (water) condensed in the form of rings at the points of contact of the spheres. Following Haines (1925), Fisher (1926) was the first to deduce theoretically that both the tension in the air-liquid interface and the pressure deficiency in the capillary condensed liquid rings must be considered together in computing the net force effect. This theory predicts a monotonic decrease in strength with increasing liquid content, a behavior actually observed in practice only for some nonporous insoluble powders. Other powders can behave very differently.

More recently, Dietl and Coughlin (1976) presented a simplified one-dimensional model based on capillary condensation at points of particle contact that was used to explain quantitatively the bizarre influence of humidity on the electrical conductivity of flyash; this model relied upon the conduction pathway provided by the capillary condensed liquid and did not consider the capillary forces which are very sensitive to the curvature of the liquid surface.

According to the spherical model, and assuming the solid is perfectly wet by the liquid (liquid-solid contact angle = 0 deg), we can approximate the air-liquid interface (before coalescence of the liquid rings) as having two radii of circular curvature t_0 and y as shown in Figure 1. With respect to radius t_0, the liquid surface is concave, whereas with respect to radius y, it is convex. The curvature of the liquid surface is such as to decrease the internal pressure of the liquid by an amount $\gamma(1/t_0 - 1/y)$. In addition to this hydrostatic suction, the liquid surface will exert a tension also tending to hold the particles together. The total force acting to hold the spheres together is readily computed at the plane tangent to each sphere at the point of contact; the intersection of this plane with the liquid surface is the circle of circumference $2\pi y$ at which the surface tension force $2\pi y\gamma$ acts, whereas the capillary suction force within the liquid at this plane acts across the surface area πy^2. The total force is

$$F_{\text{tot}} = \pi y^2\gamma\left(\frac{1}{t_o} - \frac{1}{y}\right) + 2\pi y\gamma = \pi y\gamma\left(\frac{y + t_o}{t_o}\right) \qquad (1)$$

The foregoing expression can also be written in terms of the central angle ϕ, as illustrated in Figure 1, by expressing y and t_o in terms of ϕ and substituting them into the above equation. It can be shown that t_o and y are given by

$$t_o = r\,\tan\phi\tan\frac{\phi}{2} \qquad (2a)$$

and

$$y = r\,\tan\phi\left[1 - \tan\frac{\phi}{2}\right] \qquad (2b)$$

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Accordingly, the expression for the total force becomes

$$F_{\text{tot}} = \frac{2\pi r\gamma}{1 + \tan\phi/2} \tag{3}$$

For very small liquid rings (or as ϕ approaches zero), the above expression predicts the limiting value of $2\pi r\gamma$. Because the theory of capillarity becomes invalid as t_o and y approach molecular orders of magnitude, the limit $2\pi r\gamma$ has a physical meaning only for sufficiently large ϕ (for example, $\phi > 100\text{A}°/r$). Therefore, the interparticle force due to the liquid must fall in some undefined way from a value of about $2\pi r\gamma$ to zero as the liquid content approaches zero. If, on the other hand, the liquid content increases, then the size of the liquid ring increases until a limiting value is reached at $\phi = 53.13$ deg and $y = t_o = 2r/3$, for which $F_{\text{tot}} = 4\pi r\gamma/3$. This limit corresponds physically to the situation where the hydrostatic suction force in the liquid vanishes upon coalescence of the liquid rings associated with either hexagonal close packing or cubic packing of spheres. Thus, as ϕ increases, the interparticle force falls from almost $2\pi r\gamma$ to $4\pi r\gamma/3$ owing to the changing curvature of the liquid-vapor surface.

Although Carr (1967) accepted Fisher's prediction of increasing strength with decreasing moisture content as characteristic of spherical particles, Douglas (1967) rejected it on the grounds that it was contrary to experimental observations for real agglomerates. On the other hand, Cross and Picknett (1963) have confirmed Fisher's predictions experimentally by using very smooth spheres and delicate torsion balances. Rumpf (1962) measured the tensile strength of limestone pellets, and Carr (1967) measured the tensile strength of various coal fractions; they found that as the moisture content decreased, so did the strength, contrary to the theory of Fisher. Pietsch and Rumpf (1967) showed that if equal spheres were separated by a liquid bridge at least 1/100 of the sphere diameter in thickness, an increase in ϕ produced an increase in the attractive forces, thus exhibiting the same trend for tensile strength as real agglomerates. At any percentage of liquid saturation, the touching spheres yielded the greatest force.

At this stage we introduce the concept that a point of contact between particles of a powder will experience different trends in capillary force due to condensed liquid, depending on the geometry and surface curvature of the solid particles in the region near the contact point. Accordingly, the influence of capillary forces due to liquid condensed at the contact of two perfectly smooth spheres will be different from that at a contact point between the sharp asperities supposed to be present on rough surfaces. Because every real surface has asperities when viewed with sufficiently great magnification or size resolution, it must be emphasized that our distinction between the types of contact points is relative. Accordingly, the contact may be viewed as that between asperities when the size scale of the asperities is of the same order as that of the particles; when the asperities are very much smaller than the scale of the particle, then they will be completely submerged within the domain of any condensed liquid ring sufficiently large to influence interparticle forces, and such asperities will therefore make an essentially negligible individual contribution to capillary forces. In other words, particles that seem to have a relatively smooth spherical surface when viewed with magnification no larger than that necessary to resolve the particles will behave differently than particles that appear to have angular surface asperities when viewed with similar relative magnification. Thus, from the standpoint of capillary condensed liquid rings at points of particle contact, we distinguish between the surface curvature and geometry of the smooth, spherical contact points, treated theoretically by Fisher, and the angular or conical contact points to be considered next. Figure 2 depicts the liquid at a contact point between two conical asperities; the capillary force will depend on the surface tension, cone half angle α, cone size, as well as t_o and y, the principal radii of the vapor-liquid interface which is assumed to be spherical. From trigonometry we have

$$\cos\alpha = \frac{t_o}{t_o + y} \tag{4}$$

Rearranging the above equation, we get

$$y = t_o\left(\frac{1 - \cos\alpha}{\cos\alpha}\right) \tag{5}$$

t_o can be expressed in terms of length of the wetted side of the cone a and cone half angle α as

$$t_o = a\,\frac{1}{\tan\alpha} \tag{6}$$

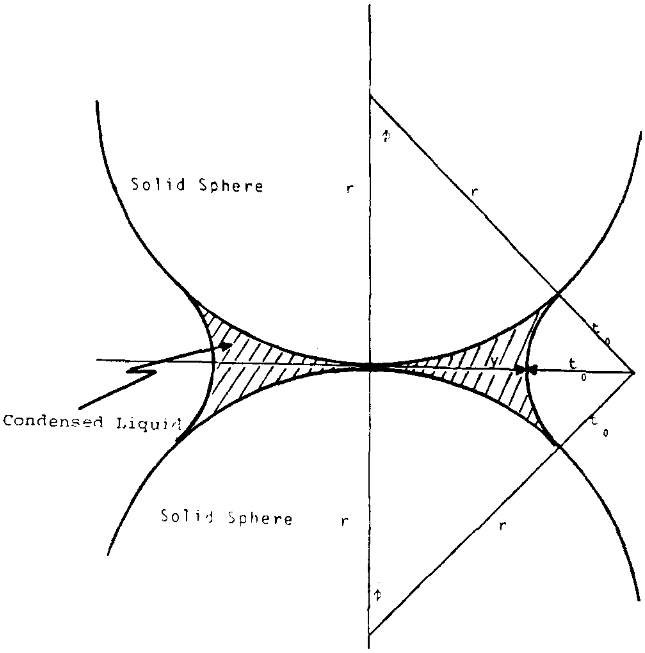

Figure 1. Condensed liquid ring at the point of contact between two solid spheres; contact angle = 0.

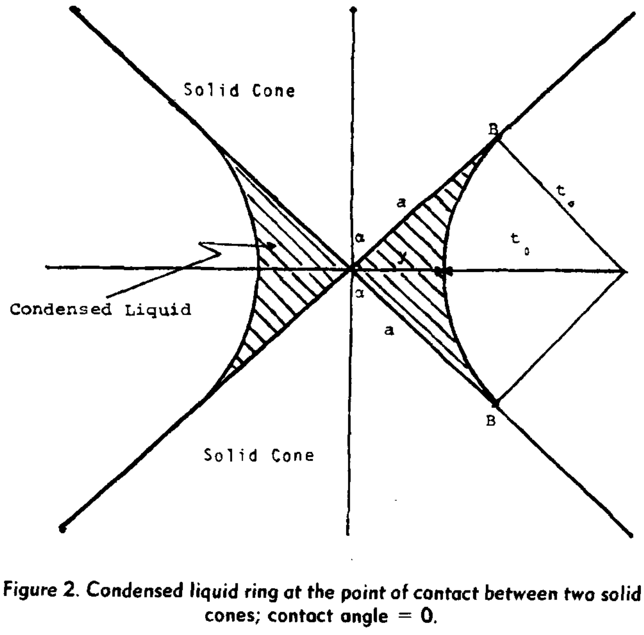

Figure 2. Condensed liquid ring at the point of contact between two solid cones; contact angle = 0.

Substituting Equation (6) into Equation (5) and after simplification, we get

$$y = a \tan (\alpha/2) \tag{7}$$

The total force at the neck can be calculated as before by substituting Equations (4) and (7) into Equation (1). This yields, for the total force

$$F_{\text{tot}} = \pi a \gamma \frac{\tan \alpha/2}{\cos \alpha} \tag{8}$$

Equation (8) predicts that the total force for conical asperities increases with a, which is a measure of the size of the meniscus, and the effect of increasing α is to increase the interparticle force. It is clear that the theory of capillary forces predicts a strikingly different effect of moisture content for conical asperities in contrast to Fisher's theory for smooth particles.

Analysis of the contact point between a sphere and a flat plane predicts the same behavior as for the two-sphere case. Similarly, the point of contact between a cone apex and a flat plane shows no essential departure in capillary force behavior from that predicted by the foregoing analysis for the contact point between the apexes of two cones.

The divergent influence of capillary condensed liquid at the two different kinds of contact points is illustrated by Figure 3, which shows the different effects of increasing relative humidity, and thus the equilibrium moisture content, on measured shear strength for different types of particles under various normal loads in a simplified shear cell, similar to the one used by Hiestand et al. (1973) and by Hiestand and Wells (1977). The strength of the powders was assessed by measuring their shear strength rather than their tensile strength because for the moisture contents employed, it was impossible to carry out tensile experiments for fine powders. Moreover, tensile strength is related to shear failure which involves rupturing the liquid bridges. Figure 3*a* is for nonporous alumina for which the accompanying scanning electronphotomicrograph, Figure 3*b*, reveals relatively smooth, gently curved surfaces which might be supposed to form contact points to which Fisher's spherical model would apply. At 60% relative humidity, the amount of water condensed by capillary condensation was found to be 4.6% w/w on a dry basis. Figure 3*c* is for surface treated, amorphous, nonporous silica particles (IMSIL A-10S) which have many irregular asperities as shown by the scanning electronphotomicrograph of Figure 3d. The equilibrium moisture content of water in IMSIL A-10S at 90% relative humidity was found to be 0.11% w/w, which implies that water at the particle contact points is still in the ring form state. At low moisture contents, for which unfused liquid rings are expected to be capillary condensed at the points of contact, it is evident that the particles revealed by the electronphotomicrographs to have two different kinds of contact points display correspondingly opposite response of shear strength to change in moisture content. For low moisture contents, shear strength decreases with humidity, as shown in Figure 3*a*, for the particles of gentle surface curvature shown in Fibure 3*b*; opposite behavior is evident in Figure 3*c* for the particles with sharp surface asperities depicted in Figure 3*d*.

The different behaviors of spherical and conical contact points reside only in the capillary force contribution, namely, $\pi y^2 \gamma \,(1/t_o - 1/y)$. As the liquid ring grows by condensation at the point of contact, t_o and y are affected in different ways for the two kinds of contact points. Whatever the geometry, increasing t_o makes the exposed liquid surface less concave and thereby lowers the internal pressure and the attractive force. Similarly, increasing y makes the exposed liquid surface more convex and also decreases thereby the internal pressure, but the net effect on force due to increasing y is the opposite because increasing y also tends to increase the area (πy^2) over which the capillary pressure is exerted. With reference to Figures 1 and 2, it is clear that as the liquid ring increases in size, spherical contact points place a greater limitation on the corresponding growth of y than is the case for conical contact points. Expressed more precisely, the relative increase of y with respect to t_o is constant for cones but is always lower for spheres and tends to decrease for spheres as the liquid rings grow. This underlies the strikingly different behavior trends evident in Figure 3. Further and more precise elucidation of this behavior will be given in a forthcoming publication.

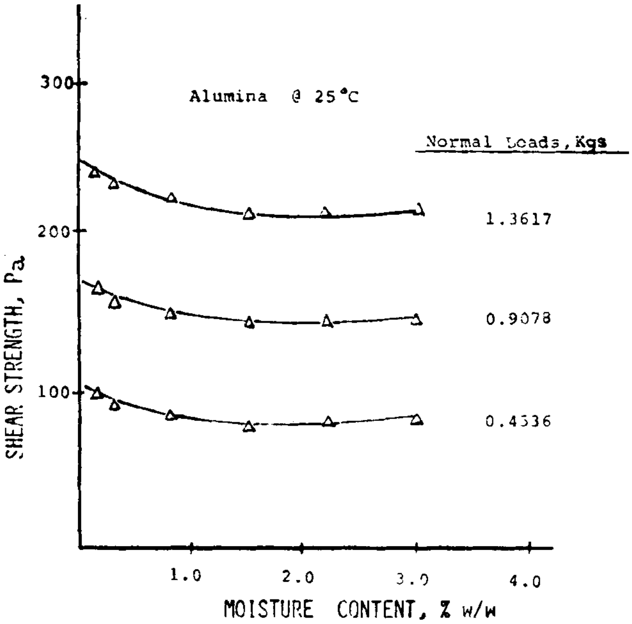

Figure 3*a*. Shear strength vs. moisture content for alumina at 25° C.

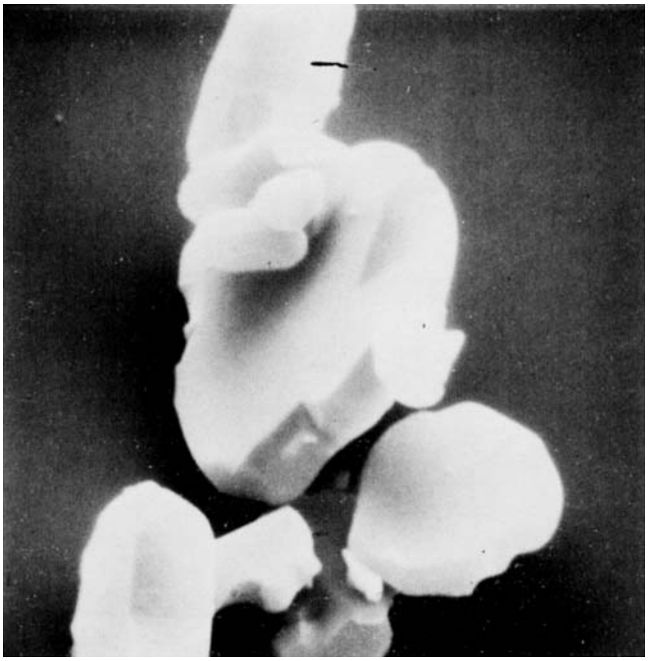

Figure 3*b*. Scanning electrophotomicrograph for alumina particles at 6 000X.

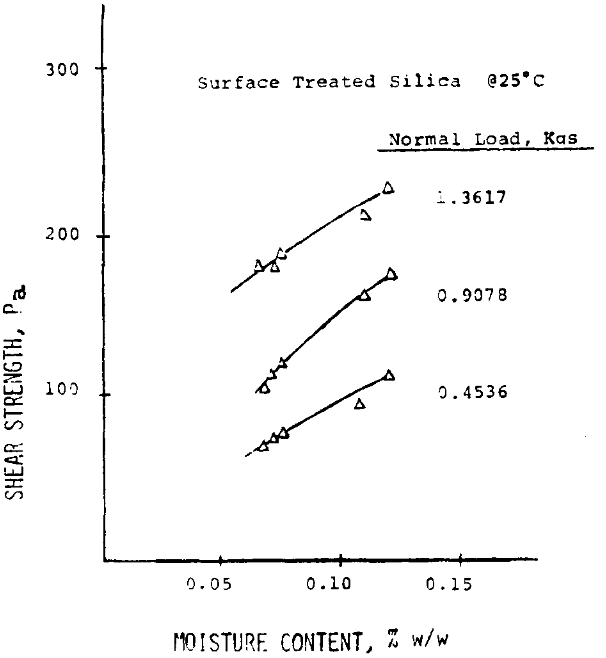

Figure 3c. Shear strength vs. moisture content for nonporous surface treated silica @ 25°C.

Conical contact points have been analyzed before. For example, Schubert (1974) computed numerically the capillary forces resulting from liquid bridges for particles possessing rotational symmetry. Adorjan (1977) determined the tensile strength of agglomerate models by computing the exact vapor-liquid surface profiles for cones attached to cube faces in cubic packing to represent angular particle agglomerates. The simpler approximate analytical development we have presented above is not only more convenient but, most important, it affords a ready analytical, intuitive understanding of why the different types of contact points behave so differently regarding the effect of moisture on their strength. It seems that although these very different theoretical predictions provide a ready explanation for the different trends actually observed in practice, the utility of this approach has not heretofore been recognized as a basis for resolving the difficulties of the past regarding failure of the theory of perfect spheres to predict the different trends actually observed in practice. A model based solely on spherical particles for agglomerates is inadequate to explain the behavior of angular or surface irregular particles for which a conical model for contact points predicts qualitatively the experimentally observed influence of moisture on strength.

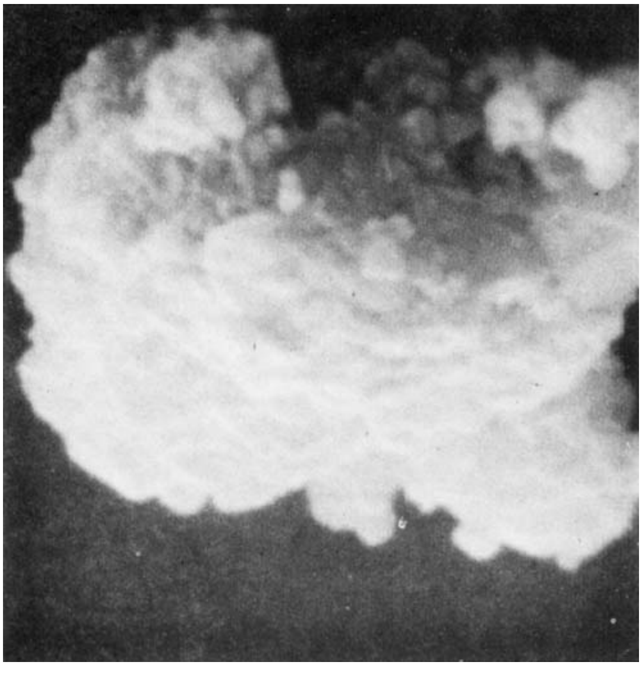

Figure 3*d*. Scanning electrophotomicrograph for nonporous surface treated silica at 12 000X.

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NOTATION

a = length of wetted side of cone
F_{tot} = total force at the neck
r = radius of spherical particles
t_o = radius of curvature of concave surface
y = radius of curvature of convex surface
α = cone half angle
ϕ = central angle of spherical particles
γ = surface tension of liquid

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