3. We have qualitatively shown that under experimental conditions, sulfur trioxide is not formed by catalytic action of the vessel walls.

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THE MANIFESTATION OF INTERFACIAL FORCES IN DISPERSED SYSTEMS

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For the present purpose, a definition of heterogeneity will be confined to that degree of this state lying outside of the molecular or ionic and will therefore comprise colloidal dispersions. As an introduction, it will be briefly recalled that heterogeneous dispersates differ from the homogeneous in their behavior under capillary shear.[1] While homogeneous fluids within certain fairly wide limits of applied stress (pressure) conform to Poiseuille's equation in capillary shear, heterogeneous systems depart from this and Hooke's law in yielding parabolic P/V relationships according to the proximate equation

$$P/V^{\phi} = \text{constant} \qquad \text{(A)}$$

where ϕ is fractional and less than unity. A further difference between homogeneous and heterogeneous systems lies in the fact that many if not all of the latter show a property of static rigidity which is exponentially variable with the applied stress.[2] The complete equation defining the behavior of a plastic on shearing through a capillary has been shown[3] to be

$$\pi R^4 g(P - fe^{-PR/2l})/8V^{\phi}l = \eta \qquad \text{(B)}$$

where the static rigidity or elasticity ("yield value") at infinite rest is denoted by f, e = log base, and the negative exponent in the numerator corresponds to the stress applied under the conditions defined. It will be noted that f remains constant under all conditions of stress, but the entire exponential term in the numerator, which may be denoted as F the elasticity or yield value under any condition, diminishes as the stress

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[1] de Waele, *J. Oil Colour Chem. Assoc.*, **6**, 33 (1923).

[2] de Waele, *Kolloid-Z.*, **36**, 332 (1925).

[3] Criticisms have been advanced as to the dimensional validity of Equation B on the score of the exponent of V in the denominator. Consideration of the underlying principles of the mechanism of the extrusion of heterogeneous dispersates to be found in the last reference will show that of the two variables, that corresponding to V or the volume in cc. per sec. cannot in itself have the identity demanded by the definition of viscosity, since it does not correspond with an efflux volume that has been extruded under a continuous velocity gradient, but comprises both sheared and slipping zones. The equation may be written in the form $\pi r^4(P - fe^{-PR/2l})/8\eta l = V^{\phi} = Q$. Thus, of the total efflux extruded as a mixed regime, that fraction only corresponding to V^{ϕ} or Q has accounted for the loss of hydrostatic pressure applied as shear. The application of the exponent ϕ then must be regarded as being merely equivalent to the use of a factor.

across the face of the capillary exceeds a certain limit from the wall to the center axis of flow.[4]

The exponent ϕ in the denominator has been further shown to correspond to the volume proportion of *shearable* viscous phase in the system, while $(1-\phi)$ corresponds to the ratio of indeformable phase. This is to be distinguished from the volume ratio of, for example, mere solid nucleus in a solid/solid dispersion in that this solid nucleus carries around it an attached layer under certain conditions. It is in regard to the condition of adhesion of this layer that the following remarks apply.

The relationship between surface energy and cohesion may be exhibited in a simple manner by the consideration of a liquid bar of unit cross section. If the bar be pulled apart along a transverse plane, the work done against the cohesive forces (W_c) is utilized in the formation of the two unit surfaces at the plane of rupture, or $W_c = 2T$, or the work done against the cohesive forces is numerically equal to twice the free surface energy.

If the bar consists of two bars of dissimilar liquids s and l joined at an interface sl, the work of separation or adhesion, W_a, is utilized in producing a unit surface of both liquid s and liquid l, but it is aided by the energy set free when unit area of the interface ls disappears, thus: $W_a = T_s + T_l - T_{ls}$, wherein T_l, T_s and T_{ls} refer to the tensions of the liquids s, l, and of the interface ls, respectively, it being remembered that the term on the left-hand side of the equation has been defined as work per unit cross section.[5]

A liquid will spread over another if its work of surface cohesion W_c is less, and will not spread if its work of surface cohesion is greater, than its work of adhesion W_a with respect to the surface of the other liquid (or solid if such be under consideration) upon which the spreading is to occur. The *spreading coefficient,* which under the conditions specified gives a measure of the tendency to spread, is defined[6] as $E = W_a - W_c$.

The free-energy decrease which occurs in spreading when unit areas are considered is obviously given by the expression

$$E = T_s - (T_l + T_{ls}) \tag{1}$$

The work of adhesion, W_a, or the work necessary to pull apart 1 square cm. of the interface ls, is given by Dupré as

$$W_a = T_s + T_l - T_{ls} \tag{2}$$

The work of cohesion has been shown to be

$$W_c = 2T_l \tag{3}$$

wherein T_l refers to the surface tension of the spreading phase or that of the lower surface tension.

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[4] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, **1922**, p. 223.

[5] W. D. Harkins, "Colloidal Behavior," Bogue, McGraw-Hill Book Co., Inc., New York, **1924**, vol. 1, p. 147.

[6] Harkins and Feldman, THIS JOURNAL, **43**, 2665 (1921).

Combining 1, 2 and 3 gives

$$E = W_a - W_c \tag{3a}$$

which exhibits the simple relationship that spreading occurs if the adhesion between the two liquids is greater than the cohesion in the liquid which is in the position for spreading, and vice versa.

The above criterion, which has been quoted practically verbatim from Harkins' article on "The Surface Energy of Colloid Systems," will next be applied to a criterion due to Edser[7] to determine the three possible states of dispersion of solid particles completely submerged in a liquid.

Taking into account the possible variation of E from a positive to a negative through a zero value, it can be shown that:

Case 1.—When E is positive $W_a > 2T_l$, or the adhesion is greater than the cohesion and the particles of disperse phase will repel one another.

Case 2.—When $E = 0$, $W_a = 2T_l$, the cohesion equals the adhesion, the normal angle of contact when one phase meets another equals 0° and a condition of equilibrium betokened neither by repulsion nor attraction of the dispersed particles to one another results. In other words, the positive force holding the liquid layer to the dispersed phase in Case 1 is absent in Case 2, although no positive force is actually tending to remove it.

Case 3.—E is negative and $W_a < 2T_l$, and the angle of contact lies between 0° and 90°. Here, attraction between dispersed particles results and this positive aggregating force leads to a condition in which no layer is present.

There is ample evidence for the existence of the layer in Cases 1 and 2, but little comment seems to have been made in the published literature as to its dimensions exceeding that of a unimolecular or bimolecular thickness.

By presenting, as it were, a liquid medium to a powder and determining the volume ratios necessary to form a paste in which the coherence is just complete but the wetting property of the mass to an external phase is absent ("the specific absorption of a powder"), figures are obtained with solid/liquid systems betokening critical layers 30–60 molecules deep.

TABLE I

SPECIFIC ABSORPTIONS OF SOME PIGMENTS FOR MINERAL OIL

Pigment	D.	Factor P
American carbon black	1.85	5.11
Potash (Prussian) blue	2.10	3.78
Zinc oxide	5.97	3.38
Violet lake (Alumina base)	1.76	1.44
Blue lake (Alumina base)	2.66	2.70

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[7] Edser, Fourth Colloid Report, "Flotation," H. M. Stationery Office, London, 1922, p. 308.

The ratios P = (volume of interstices)/(volume of nucleus) which should correspond to 0.325 and 0.910 for hexagonal and cubical piling, respectively, are shown as examples in Table I in which mineral oil has been used as a liquid medium.

We may conclude, therefore, that for at least the cases shown above mere piling in either of the two alternative manners indicated is not realized, and we are inevitably led to the conclusion that contact of solid to solid is not obtained.

Without entering into a discussion as to whether the small radius of curvature is accountable for the discrepancy between the formation of a uni- or bimolecular layer and the dimensions from the observed values, we will for the time being accept the actual magnitude of this critical layer as a fact. The relatively small effect of varying polarity of the liquid on the dimensions of the layer is shown in Table II.

TABLE II

EFFECT OF VARYING POLARITY OF MEDIUM ON SPECIFIC ABSORPTION OF CARBON BLACK

Medium	Factor P
"Straight" non-polar mineral oil	4.45
Aromatic base mineral oil (polar)	5.38
Mixture of 2 parts of the former to 1 part by volume of the latter	5.11

While the paste from the first cited system on further dilution became completely flocculated, the second and third pastes when diluted with the non-polar oil gave colloidal solutions which were not separable by filtration and in which the particles showed active Brownian motion.

As regards the mechanism of the attachment of this layer some references are to be found in the recent work of Hardy[8] on lubrication, but the following description of an experiment may prove illuminating.

A clean capillary tube of uniform bore was divided into three separate portions, thoroughly cleaned with the usual reagents and dried. Two of the tubes were packed with petroleum jelly and the third left clean. By careful manipulation the petroleum jelly in one of the two tubes was extruded at such a low velocity that no telescopic flow within the extruding mass took place, the jelly extruding as a solid plug with sharp edges. Coincidently with this particular régime of slow extrusion, the walls of the tube appeared to be perfectly clean, no monochromatic layer being visible. Thus it would appear as if complete slipping of the jelly had taken place just as in the case of a solid piston in a cylinder. The contents of the remaining tube of petroleum jelly were subjected to pressure in such a way as to comply with the tenets of telescopic flow in leaving a definite layer attached to the walls of the tube, that is, so that $v = 0$ at $r = R$. It may be mentioned that such a layer was in this case quite visible.

[8] Hardy and Bircumshaw, *Proc. Roy. Soc.*, **108A**, 1 (1925).

To determine whether the tube the contents of which were extruded at very low velocity did actually hold a layer of jelly on its walls or not, the capillary rise in the three tubes was determined under identical conditions. The results were as follows: in a clean tube the rise was 2.57 cm.; in the low-velocity tube, 2.49 cm.; in the high-velocity tube, 0.40 cm.

Taking the case of the visibly fouled tube, the result is in accordance with that anticipated, in that the high angle of contact of water to petroleum jelly has been realized as an adhesion considerably less than the cohesion, or a high interfacial tension.

The case of the tube with the invisible layer is interesting. The contact of the rising water indicates neither a perfectly clean tube nor yet one with a layer of jelly. We are thus inevitably led to the conclusion that when a phase A overlays a phase B, below a certain critical thickness of the former, it no longer displays the physical properties of A in bulk, that is, of the phase removed to an "infinite" distance from another phase. Below this critical thickness, the overlying phase approximates more and more in properties to that with which it is immediately in contact.

The conclusions to this experiment have been arrived at in a variety of ways by different experimenters, notably Hardy when investigating the problem of film lubrication on solid surfaces, although the latter appears to prefer to regard his investigated surface as that of the overlaid phase. There is, furthermore, considerable evidence to show that this critical thickness corresponds to considerably more than uni- or bimolecular dimensions.

This chain of reasoning begins to lead up to the reason why in determining specific absorptions of powders, the characteristic wetting property of the liquid employed is not displayed until quite a ponderable thickness of overlying liquid is present.

The mechanism of the physical change taking place when two phases are brought into contact may be illustrated as follows.

From the fact that the interfacial tension of two completely immiscible phases meeting each other normally at an angle of contact of zero equals the difference of the surface tensions of each phase taken separately, or $T_s - T_l = T_{sl}$, this equilibrium holding equally well for phases soluble to some slight degree in each other, if the surface tensions of the component phases saturated with regard to one another be considered,[9] it would appear that the component tensions T_s and T_l act, so far as they are able, in opposite directions to saturate free surface energies. Thus, experience seems to show that liquids of equal surface tensions are miscible, and no free interfacial tension is present. We may then depict the surface tensions of oppositely disposed phases as vectors proportional to the magnitude of the said tensions, the range of influence of the vectors being further in direct relationship to their magnitude. Fig. 1 illustrates the effect

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[9] Reynolds, *Trans. Chem. Soc.*, **119**, Pt. 1, 466 (1921).

obtained by overlaying a wedge-shaped section of liquid on a solid surface, which latter, in accordance with general acceptance, would be considered to possess the higher surface tension.

The figure illustrates that at the point A, that is, where the surface of the solid is not overlaid by liquid, the normal vector of surface tension due to the solid is completely unsaturated and manifests itself to its maximum value. At the point B on the surface of the liquid where the distance from the solid surface may be considered to correspond to "infinite" thickness of the former, the normal vector of surface tension due to the liquid is in its turn manifested. At the point C, however, vectors or lines of force of the two phases may be considered to have been directed against one another to effect saturation, the thickness of liquid overlying the solid just corresponding to a magnitude of the sum of the vectors. Thus at this point the thickness of the layer corresponds to a distance just beyond the range of the solid by reason of the neutralizing liquid phase, although the latter finds itself just robbed of its normally-existing free surface forces. At this point, the attraction exercised by the solid for the liquid has been just satisfied, leaving no free line of force or vector for the liquid surface to exhibit, for example, the property of wetting a third phase with which it might be brought into contact. This point C then corresponds to the condition of the bounding surface of the "absorbed" liquid at the critical point when determining specific absorption. At any point on the surface of the liquid to the right of C, the liquid will exhibit normal surface properties, while to the left of the point, the properties exhibited will be intermediate between those exhibited at A and at C. The whole conception is based on the known relief of energy obtained by contact of two phases having angles of contact below 180°, such relief for liquid thicknesses up to the "critical" being comprised by complete saturation of surface forces in the phase of lower surface tension (liquid in the case considered), and such partial relief in the solid surface as would correspond to the difference in the tensions of the two phases, the experimental evidence, however, suggesting that the residual surface energy is manifested in the overlying liquid surface.

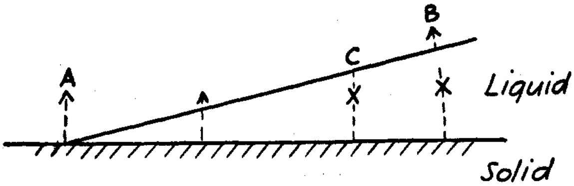

Fig. 1.

While Joshi[10] shows the surface tension of the continuous phase of a

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[10] Joshi, *Kolloid-Z.*, **34**, 197 (1924).

dilute emulsion to be equal to that of the continuous phase in bulk, Ostwald and Rath[11] show the surface tension of the layer immediately in contact with clay particles of a concentrated suspension to be higher than that of water.

A further proof as to the real existence of a definite layer surrounding a nucleus in certain systems will next be introduced. The specific absorption of American carbon black for a certain dispersing oil mainly composed of unsaturated mineral hydrocarbons corresponded to the critical layer, being just complete at a concentration of 28.7% by weight of solid in the total paste. Dilutions to concentrations of 20, 15, 10 and 5% by weight of carbon black were then made and the resulting pastes examined through the plastometer. It will be recalled that the factor ϕ which is the exponent of V in the P/V relationship in the shear of a disperse system has been theoretically deduced to correspond with the volume proportion of *free* (shearable) viscous phase. If, therefore, such theoretical deduction be fulfilled, and the medium beyond the boundary of the critical layer be present as viscous fluid in its *dynamic* behavior, then the volume ratios found by plastometric examination should correspond to those obtaining from simple calculation. The results, including that of the homogeneous oil medium, are shown in Table III.

TABLE III

OBSERVED AND CALCULATED ϕ VALUES OF CARBON BLACK IN POLAR MEDIUM

Concentration by wt.	ϕ determined	ϕ calcd.
0	1.00	1.00
5	0.836	0.826
10	.607	.652
15	.500	.478
20	.272	.304
28.7 (critical paste)	...	.0

The results, when plotted with concentrations as abscissas and ϕ determined as ordinates, show surprisingly good linearity (Fig. 2). It is thereby shown that the layer which forms up to the point of the critical paste is most rigidly held, or that the adhesion of solid for liquid is of a high order as it resists the effect of the surrounding velocity gradient set up during plastometric shear.

At dilutions with further medium, the critical paste when examined ultramicroscopically, showed no evidence of flocculation of the individual particles, Brownian movement being very marked and no tendency to settlement taking place. Furthermore, on filtration through filter paper, the filtrate still contained carbon held in colloidal suspension. It is to be noted that neither the "critical" paste nor any dilution of it possessing rigidity of shape showed any evidence of the continuous phase separating as a liquid.

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[11] Ostwald and Rath, *Kolloid-Z.*, **36**, 243 (1925).

By determining the specific absorption of the same carbon black for a medium showing in its composition no tendency to polarity or dispersing effect, namely, "straight" mineral oil of the type used as medicinal paraffin oil, the value obtained does not differ in any but a slight degree from that obtained with the highly polar dispersing medium (Table II). On attempting, however, to correlate ϕ plastometrically with that calculated from the spatial ratios, most unsatisfactory results are obtained, the log P/log V lines being discontinuous instead of straight, indicating non-uniform zones within the mass sheared. Further investigation of the cause of failure to obtain satisfactory plastometric readings showed that under the velocity gradient obtaining in the plastometer capillary, the layer surrounding the particles is removed to a great degree, some "seepage" or filtration of the viscous from the solid phase taking place. Such values of ϕ as could be approximately deduced from the readings obtained indicated values considerably higher than the calculated. Thus in the case under consideration, although a layer appears to be retained with close

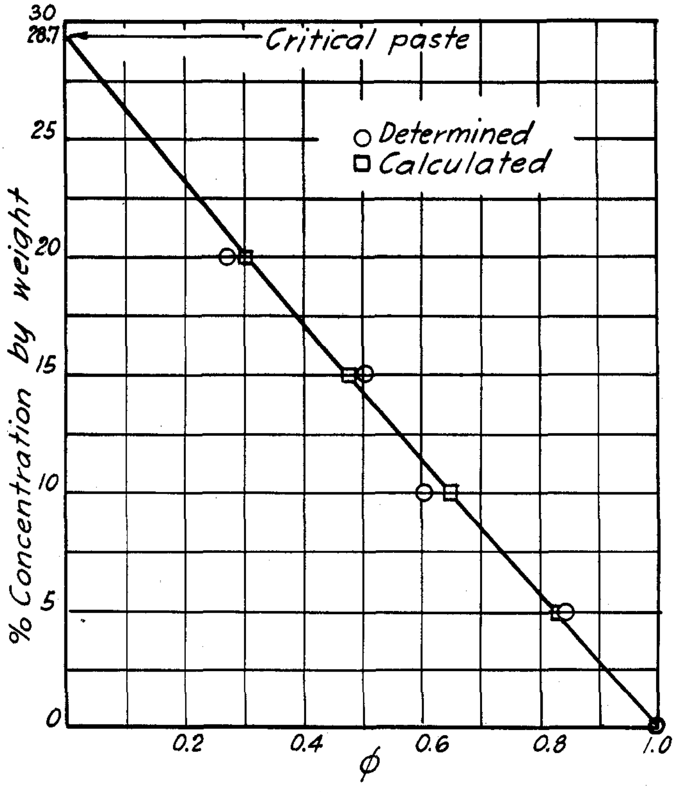

Fig. 2.

packing, disturbing conditions, such as shear, appear to be easily operative in removing it.

Further dilutions of the critical paste revealed that flocculation of the particles to bunches had taken place, the carbon being easily filterable, and settlement proceeding rapidly on standing. Dilutions of the critical paste to degrees wherein rigidity of shape was still manifest separated part of the continuous phase, on keeping. The comparative behavior of this last cited paste with that made from the dispersing medium in the respect of retention of the continuous phase indicates a behavior not dissimilar to syneresis. The rigidly held layer in the first of the two cases quoted would then appear to be characteristic of a layer characterizing solvation of the dispersed particles.

It might be mentioned in passing that zinc oxide in lithographic varnish (heat-thickened linseed oil) shows the behavior of the last cited case immediately after manufacture into a paste, the process of aging or maturing, however, decidedly showing a *tendency* for the system to change to one with a layer rigidly held under all conditions of shear, the other phenomena being also in keeping with the other states specified.

Returning to a consideration of the three states of dispersion previously referred to, Case 3 will be excluded as being one the treatment of which has been adequately dealt with in papers on flotation, but which otherwise presents no interest in dealing with any concepts of plasticity.

Cases 1 and 2 differ fundamentally in that the calculated and observed interfacial tensions, while showing divergence in the former, agree in the latter case. Thus,

$$\text{Case 1.}\quad W_a - E = W_c \quad (3a) \qquad \text{and}\quad T_s - T_l > T_{ls} \qquad (4)$$

$$\text{Case 2.}\quad W_a = W_c \quad (5) \qquad \text{and}\quad T_s - T_l = T_{ls} \qquad (6)$$

The force per unit surface E may then be interpreted as being of an electrical character, whereby the magnitude of T_s *on contact* with the other phase becomes diminished, since electrical charge tends to diminish surface tension.

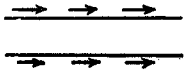

Fig. 3.—Apart.

The positive interfacial tension of a heterogeneous system should have a significance of its own in so far as the behavior of the system is concerned. By definition it corresponds to a force tending to separate the interface and so cause re-formation of the two component phases (flocculation), but the forces determining the equilibria of heterogeneous systems have been already dealt with and accounted for in Equations 1 to 3. If we consider that the forces of cohesion of a phase differ from the forces of adhesion from phase to phase in that the former are oriented in a direction parallel to the surface, while the latter are oriented transversely, we can diagrammatically express the meeting of the two phases to form an interface by Figs. 3 and 4.

Fig. 4.—Interface formed.

In Figs. 5 and 6, the numerical values corresponding to the respective surface tensions of the two approaching phases are shown vectorially as lines of force per unit of length, the solid phase being shown as possessing the higher surface tension.

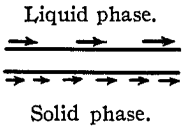

Fig. 5.—Apart.

In accordance with Equation 4, the adhesion has been shown to equal the cohesion, which in turn is equal to twice the surface tension of the liquid, so that for every line of force thrown across from one phase to the other, a similar line of force acts from the opposite to the first-named phase. We also see that the surface of the solid, while having lost some of its original cohesion, still retains a part equal in value to the expressed interfacial tension. The question next arises as to the disposition of this residual field of force. It is to be noted that although for simplicity of illustration, the surfaces of the phases have been shown as being at a distance from each other, they actually meet, and the range of the transversal mutually neutralized fields of force is limited by the critical layer. The residual interfacial fields of force on the solid may assume equilibrium either parallel to the solid surface as shown or, since they do not encounter any unsaturated oppositely disposed fields in the liquid within this critical layer, may orient themselves transversely and protrude through the critical layer. In such a case, the effect would be twofold; first, to confer such rigidity or comparative resistance to shear as is possessed by the critical layer itself to certain layers beyond it, and second to become active in saturating the field of cohesion of a similarly disposed system with which it may come in contact. The term "comparative resistance" is employed advisedly, as will be seen later.

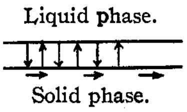

Fig. 6.

This reasoning being illustrative of Case 2, or a flocculated system, it will be readily grasped that Case 1, or a peptized system, differs from it in no way but in degree. In Case 1, the removal of the critical layer implies a certain output of energy, while the interfacial tension, being less than the difference of the surface tensions of the two phases, is generally low. While, however, the critical layer is shown thermodynamically to be held positively, no positive force can be found to affect the selective orientation of the residual interfacial field to a transversal more than to a longitudinal direction, and such residual field, although less in magnitude generally, is in no different condition from that in Case 2. It is interesting to suggest, by the way, that the observed difference between the calculated and realized interfacial tensions in Case 1 would be accounted for by imagining the transference of electrons from the higher to the lower field of force when the phases met, a behavior analogous to molecular formation, and consistent with the electrical charge generally known to be carried by a dispersed particle.

So far as the respective behaviors of the critical layers in the two Cases 1 and 2 are concerned, the hypothesis outlined is strictly in accord with the facts given earlier for the carbon-black dispersions in a peptizing and a flocculating medium. We have still to consider the effect of the residual interfacial tensions in the two cases.

The significance of the rigidly held layer on the surface of primary particles to the vitiation of results accruing from sedimentation velocities according to Stokes' law is to be noted, attention having already been drawn to this point by Williams.[12]

Now, while the sensible rigidity of the two critical pastes in question was found to be substantially the same, the two pastes behaved very differently on dilution beyond this stage. While the paste formed of the peptizing medium (Case 1) rapidly lost its rigidity of shape, the paste from the flocculating medium (Case 2) retained this rigidity to a far greater degree of dilution.

An indication as to the identity of this persistent rigidity, which will now be referred to as "yield value," with interfacial tension, was afforded by a comparison of two liquid/liquid emulsions. The one consisted of equal volumes of hydrous sulfonated cod oil and mineral spindle oil, while the other consisted of water dispersed in Yorkshire grease dissolved in the same spindle oil to the state of a fluid. The two emulsions as prepared consisted in the one case of mineral oil dispersed in sulfonated cod oil, and in the other of water dispersed in the oily medium. The surface-tension data were as follows.

TABLE IV

INTERFACIAL TENSION DATA OF EMULSIONS

Interfacial tension	Sul'd oil/mineral oil	Dil'd. Y. G./water
Observed	0.1	4.9
Calculated	4.4	38.0
Difference = E	4.3	33.1

The resulting emulsions showed degrees of rigidity or "yield value" in proportion to the values of interfacial tensions as determined. It may be mentioned that while the determined yield value of the grease/water emulsion approximated to 95 × 10^5 dynes per square cm., that of the sulfonated oil emulsion was so small as to be indeterminable under the conditions of the plastometric estimation.

Reverting once more to a correlation of interfacial tensions with behavior on shear, it will be realized that the elasticity term in the numerator of the plastic shear equation

$$F = fe^{-\text{stress}} \tag{7}$$

or for capillary shear

$$F = fe^{-PR/2l} \tag{8}$$

while

$$\mathrm{d}F/\mathrm{d}P = -FR/2l \tag{9}$$

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[12] Williams, *J. Oil Colour Chem. Assoc.*, **30,** 116 (1922).

By mere substitution to equivalent dimensions, the recovery of F on rest after release of stress can be shown to be

$$F = fe^{-\eta/t} \tag{10}$$

$$\text{and } \mathrm{d}F/\mathrm{d}t = f\eta/e^{\eta/t}t^2\text{, or taking } t \text{ as unity: } \mathrm{d}F/\mathrm{d}t = f\eta/e^{\eta} \tag{11}$$

from which it can be gathered that if the rate of loss of plasticity with applied stress be proportional to the elasticity present at the time and to the stress applied, the rate of recovery will be virtually an inverse exponential function of the viscosity.

While the first point has been capable of confirmation by experimental determination of the variation of the F term with varying stress applied, confirmation of the last-named equation has hitherto presented experimental difficulties precluding such. Nevertheless, qualitative confirmation as to the substantial validity of the recovery equation is not lacking. While the rate of regain of elasticity in a carbon black and kerosene paste is so high that its actual loss on shear can be recognized only by plastometric examination, a paste composed of carbon black and such a viscous medium as blown rape oil shows a quite perceptible recovery of rigidity after disturbance. The above indicates that the residual or interfacial tension may manifest itself as a force in either of two directions according to whether the system be at rest or under a tangential stress. Thus, at rest, this vectorial force will act along lines joining the centers of the dispersed phase and will manifest itself by thus orienting liquid molecules lying beyond the critical layer. During the application of tangential stress equal to or exceeding the yield value, such center-to-center orientation of the "free" liquid molecules is deflected to a direction parallel to the stress, whereby the force characteristic of interfacial tension in finding no other saturating field will then manifest itself as a force of cohesion within the disperse phase. Such alternative disposals of a force under alternative conditions of rest and stress show analogy with the retention or disposal of the "critical" layer in Case 2, wherein no positive force positively exhibiting itself to retain the layer is accounted for in the thermodynamic equation of Dupré.

This hypothesis may be applied to certain well-known phenomena in a few examples.

A "clean" solid left to itself attempts to relieve its stray field of force by attaching to itself a layer which wets it under the condition, $T_s - T_l - T_{ls} = E$, or in other words, losing potential energy on being wetted. Such a film, which may consist of moisture, condensed air, etc., is in accordance with the equation, rigidly held, and resists a definite pressure normal to the interface. When a sufficient stress is applied to overcome the force E, this layer is removed. By pressing two plane pieces of glass together, the layer may either be entirely removed and coalescence at the asperities of the glass surfaces take place, or the critical layer may be thinned down to a zone where the cohesion of the layer exceeds that of the glass itself, with the result that on traction of one plane over another, fracture takes place within the zone of lower cohesion, that is, within the glass. One illustration of such effect is the selective rupture within the body of the oppositely disposed phases of metal when soldered with a very thin layer, rupture of the solder itself, however, resulting when the joint is bounded by a layer the thickness of which is beyond the critical. The same applies also to glued joints. Another illustration is to be found in the mechanism of lubrication of bearings. A "poor" lubricant is one wherein the force of adhesion of the fluid to the bearing surfaces is less than that of the component of pressure tending to cause the approach of the metal surfaces. This would rather indicate that no lubrication whatever would be displayed by a metal/oil interface classifiable under Case 2, or where $T_s - T_l - T_{ls} = 0$, since the slightest force applied normal to the interfaces would remove the lubricating layer. However, the elementary principles of lubrication show that the mere viscosity of any fluid under shear results in the development of a "fugitive elasticity" opposing approach of the bearing surfaces.[13] The case is, however, very much more favorable to the retention of the oil film when the system is classifiable under Case 1. Under these conditions, we have present between journal and bearing an additional force of virtual repulsion tending to resist seizing of the bearing and journal. Modern lubricating practice has shown that the homogeneous, non-polar, poorly wetting oils represent the liquid in the first-named case, while the heterogeneous, polar, highly wetting oils constitute the good lubricants of the second class.

The process of Sherardizing is similarly explainable for its mechanism, and in the process of welding or sintering below the melting point of the phases to be united, the simultaneous desorption of the spontaneously saturated layer by raising the temperature and applying pressure exceeding the value E results in coalescence. Certain solids, for example, unvulcanized india rubber, oils solidified by heat treatment or oxidation, etc., do coalesce, and one is tempted to offer the explanation that the saturating adsorbed layer of oxygen normally inhibiting coalescence becomes chemically absorbed by the reducing substances.

In applying the hypothesis to the mechanism of the drying of printing ink on paper, it need hardly be recalled that in this case "drying" is but in exceptional cases a phenomenon of solidification of the oil by oxidation. As it would then appear mainly to be a question of absorption into the paper, we may determine the rate of penetration of the fluid ink into the capillary pores of the paper as follows.

The equation connecting the volume of liquid extruding through a

[13] Edser, "General Physics for Students," MacMillan and Co., Ltd., London, **1920**, p. 507.

capillary in unit time under a pressure P is

$$V = P\pi r^4 t/8\eta l \tag{12}$$

The linear rate of travel will be given as a differential coefficient and by dividing the numerator by πr^2

$$\mathrm{d}l/\mathrm{d}t = Pr^2/8\eta l \tag{13}$$

Since hydrostatic head of the deposited ink can hardly account for any but an infinitesimal driving force, capillary forces being the main source of stress determining travel along the capillaries, the latter may be substituted for P as

$$P = 2\sigma \cos \theta/r \tag{14}$$

From 13,

$$\mathrm{d}l/\mathrm{d}t = \sigma \cos \theta r/4\eta l \tag{15}$$

and since $\cos \theta$ is obviously equal to unity (if the printing ink be worthy of the name), $l\,\mathrm{d}l/\mathrm{d}t = \sigma r/4\eta$ and $\int l\,\mathrm{d}l = (\sigma r/4\eta) \int \mathrm{d}t$.
Integrating,

$$l^2 = \sigma rt/2\eta \quad \text{and} \quad l = \sqrt{r\sigma t/2\eta} \tag{16}$$

so that we conclude that the rate of drying is an inverse function of the square root of the viscosity. Why, then, does the printing-ink maker not employ raw linseed oil as a grinding medium in place of the more viscous lithographic varnish? The answer is to be sought in the fact that the system it is desired to absorb into the paper capillaries consists not of a liquid but of a heterogeneous dispersate. While a dispersion of carbon black in raw linseed oil represents a condition coming under Case 2, or $T_s - T_l - T_{ls} = 0$, the peptizing effect of lithographic varnish ensures a condition of dispersion corresponding to Case 1, wherein the right-hand side of the above equation is positive.

Absorption of *oil* actually would take place with raw linseed oil, but the pigment would remain behind virtually as a dry, non-coherent powder, showing the phenomenon technically known as "dry off-set," while with a dispersion in lithographic varnish, discrete particles consisting of nuclei of pigment surrounded by a critical layer of oil will enter the capillaries. The two cases differ in that capillary attraction is a sufficiently strong force to remove the layer from the solid particles in one case, but not in the other.

While expressing the mechanism of the process to a first approximation, a complicating fact is also present. It will be recalled that there exists the interfacial tension in a plastic body which manifests itself, not exactly as a cohesion from particle to particle, but as a resistance opposing a limiting tangential stress. When such resistance is overcome by the application of a sufficiently large tangential stress, the reappearance of the resistance manifests itself only gradually after release of the stress, to resume its original maximum value only after a period of "infinity." The conception of a static resistance to tangential shear without implying a force of attraction between the neighboring phases can be assumed to be of the nature of an orientation of the molecules of liquid phase lying between the particles of the unshearable phase, much in the same way as the bristles of two door-mats faced together would dispose themselves. The overcoming of the resistance-opposing tangential shear would then have for its mechanism the de-orientation of the said oriented liquid molecules from a position at right angles to the shearing plane to one parallel to the interface, a disposition then synonymous with that of the normally accepted vectorial forces characteristic of interfacial tension.

Thus, immediately after the shear resulting from application of the printed matter to the sheet, the erstwhile plastic behaves as if it possessed no yield value, and conforms to the law that the slightest stress results in a corresponding (but not proportional) strain. In other words, the F term in Equation B vanishes if a high value be assigned to the exponent (stress) in Equation 7,

$$P - fe^{-\text{stress}}/V^{\phi} \longrightarrow P/V^{\phi} = \text{constant} \qquad (17 \text{ and } 18)$$

We thus realize a condition of temporary deflocculation or non-interference of the composite particles, and these latter will then enter the capillary pores at a rate determined by Equation 16.

However, immediately after the release of the stress of the impression, yield value is progressively regained as shown by Equation 10, liquid molecules lying tangentially on the surface of the composite particles gradually orienting themselves at right angles to the tangent once more to show the "door-mat" effect and virtually unite. The rate of regain of F in Equation 10 is obtained as: $\mathrm{d}F/\mathrm{d}t = f\eta/e^{\eta/t}t^2$, or simplifying by taking t as unity, $\mathrm{d}F/\mathrm{d}t = f\eta/e^{\eta}$. (Equation 11.)

It will be immediately evident that, while viscosity apparently retards the rate of penetration into paper, and the rate of flocculation with stress is a function only of yield value (interfacial tension), the equally important factor of rate of recovery of yield value which should be a minimum to ensure efficient penetration is inversely proportional to an exponential power of the viscosity. In plain figures, of two systems with viscosities of 1.0 and 4.0, respectively, and possessing similar yield values, while the rates of penetration from Equation 12 are $1/\sqrt{1}$ and $1/\sqrt{4}$ or 1.0 and 0.5, respectively, the rates of reflocculation opposing the penetration are, according to Equation 14, $1/10^1$ and $1/10^4$, or 0.1 and 0.0001, respectively, that is in the ratio of 250 to 1.

The obvious applicability of these considerations to painting practice need hardly be enlarged upon beyond indicating that the flowing and brushing properties of paints are governed by a nice adjustment of the yield value and the rate of deflocculation under the brush together with the rate of recovery of yield value (reflocculation). By correct balancing of these factors, the subsidence of brush marks during the deflocculating régime can be made to coincide with a sufficient degree of recovery of yield value to inhibit undue flowing or "sagging" of the film.

The "feeding" of certain perfectly "inert" earth pigments in media is to be ascribed entirely to transient elasticity or yield value, a fact which may be confirmed by observing the loss of the same on shear and recovery on standing. The oft-quoted experiment of rendering fluid a paste of zinc oxide in non-polar Paraffinum Liquidum by addition of a few drops of oxidized linseed oil has none other for its explanation than that of reducing the residual interfacial tension automatically by addition of the polar fatty oil to change $T_s - T_l - T_{ls} = 0$, into $T_s - T_l - T_{ls} = E$, the values of T_l being virtually equal in the two cases.

The "wooliness" of certain pigments in oil paints and the fractionation of mixed colored pigments into a selectively colored layer at the surface, is explainable entirely by the dispersion in question either conforming to the condition of Case 2, or even of Case 3, $T_s - T_l - T_{ls} = 0$ or $-E$. Ultramarine in oil is a typical example. In certain cases, the magnitude of the excess cohesion of the vehicle over its adhesion to the pigment during drying may be such as to expel the latter to the surface as a film of higher concentration of pigment with resultant loss of gloss. These cases are often accompanied by excessive flow of the paint, in accordance with the absent (Case 3) or very loosely held layer (Case 2).

Summary

1. The dispersion of one phase s in another l may be defined by any of the systems $T_s - T_l - T_{ls} = +E$, 0 or $-E$, wherein the tensions of the component phases and interface are equated to change of energy per unit surface.

2. These correspond, respectively, to a condition of positive repulsion of the particles of the dispersed phase to one another, an equilibrium, and to an attraction between them.

3. The first of these cases is characterized by a positively held layer attached to the dispersed particles, the second by a loosely held layer, and the third by no layer at all.

4. The interfacial tension of a dispersed system manifests itself when the system is at rest as a force active at the boundary of the layer surrounding the particles in orienting the molecules of the free continuous phase normally to the interface.

5. On tangential shear, the transversal orientation is disturbed to a direction tangential to the surface of the dispersed particles, the rate of this orientation being determined by the applied stress.

6. The rate of re-orientation of the lines of force at rest after application of stress to a transversal direction is an inverse function of the viscosity of the continuous phase.

7. The significance of the presence or absence of the layer attached to the dispersed particles in a system has been discussed in respect of its bearing on the mechanism of well-known processes involving adhesion.

8. The reversible fugitive rigidity of plastic systems on shear has been discussed in its application to the mechanism of the "drying" of ink in the printing process.

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OPTICAL ROTATION AND ATOMIC DIMENSION. VI

BY D. H. BRAUNS

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The preparation of crystalline fluoro-hepta-acetyl cellobiose previously reported[1] necessitated the revision of the data for the other halogen-acetyl derivatives of this sugar. A careful purification of these *biose* derivatives and measurement of their rotations as recorded in the present paper led to the conclusion that they show a *deviation* from the regular relationship observed for the corresponding derivatives of the *monose sugars* (Table I). Thus it became interesting to compare the series of halogen derivatives of other *bioses*. As only an amorphous[2] fluoro-acetyl lactose could be obtained and the fluoro derivative is a characteristic value in the relationship, other bioses were investigated. Both maltose and gentiobiose octo-acetate gave crystalline fluoro-acetyl derivatives, but no crystalline bromo or iodo derivative could be obtained from maltose. Experiments for preparing the needed derivatives of gentiobiose, as well as of melibiose, will be conducted as soon as larger amounts of the octo-acetates of these sugars have been prepared.

The further study of fluorating acetyl derivatives[3] of sugars, however,

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[1] Brauns, THIS JOURNAL, **45**, 834 (1923).

[2] The fluoro-acetyl derivatives of mannose and galactose also could not be obtained in a crystalline condition. Rhamnose, the only readily available monose sugar left, will be investigated in the near future.

[3] Helferich and co-workers [*Ann.*, **447**, 27 (1926)] have published an interesting synthesis of gentiobiose taking fluoro-acetyl glucose as a starting material and using particular properties of the fluoro derivatives for performing the synthesis. The possibility of splitting off the acetyl groups and preparing the fluoro sugars were known to the author when the first article of this series was written, as a saponification for analysis was first performed by shaking at 0° with 0.1 N sodium hydroxide solution and titration with sulfuric acid after the compound had dissolved, which showed that the acetyl groups were split off. Only traces of sodium fluoride were found to be present in the solution, however. Hence the saponification with boiling 0.25 N sulfuric acid was used for the analysis as has been described and it was intended to study the observed peculiarity. The author did not realize that this behavior could advantageously be used for syntheses, but thought it to be of value for the study of the structure of complicated carbohydrates.