SOAP FILMS IN FLOTATION, DISPERSION, AND LUBRICATION

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I. INTRODUCTION

Unimolecular films of metal soaps play a fundamental role in many processes of great technological importance.

In froth flotation, valuable minerals are separated from unwanted rock or gangue by forming soap films on the surfaces of selected species. Water-soluble soaps impart hydrophilic properties; soaps of heavy metals, formed *in situ* by chemical reaction, make the surfaces of particles hydrophobic. When an aqueous slurry of the ore is aerated, the latter become attached to air bubbles, rise to the surface, and are subsequently recovered from the froth.

Soaps are widely employed in industry for dispersing solids in liquids, and typical examples are in the manufacture of paint, the washing and dyeing of textiles, and the preparation of lubricating greases. Water-soluble anionic and non-ionic soaps generally promote dispersions in aqueous media by making the surfaces of solids hydrophilic. Cationics and the soaps of heavy metals, on the other hand, produce hydrophobic surfaces and thus favor dispersions in nonaqueous media. However, it must be emphasized that dispersion in industry is still very much an art. It is affected by numerous variables—the quality and purity of the materials, the details of the operating procedure, the type of equipment—and these are often difficult to reproduce on model systems in the laboratory.

The third aspect of soap films which will be considered in the present review is the effect on the frictional properties of metal and other surfaces. It is well established that boundary lubrication involves physical and chemical adsorption of particular species onto the moving surfaces. In many instances it has been possible to demonstrate that the films actually consist of metal soaps. Recent work has been concerned with correlating the mechanical properties of the films with their efficiency in reducing friction and preventing abrasion between surfaces.

II. FROTH FLOTATION

A. MECHANISM OF ADSORPTION

The employment of intermediate and long-chain fatty acids, carboxylates, oleates, naphthenates, petroleum sulfonates, and similar materials as collectors for various mineral species dates back to the turn of the century (56, 129, 131). It is only within the last two decades, however, that serious study has been made of the mechanisms by which they are adsorbed onto solid surfaces. It is now clear that, in addition to physical adsorption, chemisorption plays an important role. In many instances collection involves the formation of a unimolecular soap film on the surface of the mineral. This may consist of a true chemical compound, capable of existing in the bulk state, or it may be a surface compound which cannot be isolated. To be effective, it should be essentially hydrophobic in nature, *i.e.*, containing an alkali earth or heavy metal. Films containing alkali metal or ammonium soaps are usually hydrophilic and thus tend to inhibit flotation.

However, the terms hydrophobic and hydrophilic require careful definition. It is incorrect to assume that all parts of the surface of a particular mineral species are equally available for adsorption. Many experiments on ionic crystals, oxides, etc. (2, 4, 7, 104), have shown that crystal edges, steps, dislocation, and fractures all adsorb collectors to different extents, with the result that the surfaces of most minerals are, in fact, essentially inhomogeneous.

Derjaguin and his collaborators (35, 38) have examined the factors controlling hydrophilicity and hydrophobicity of surfaces. Consideration of the electrostatic and dispersion forces often enables a prediction to be made about whether particles of a particular size and shape will attach themselves to air bubbles and rise to the surface. But other factors are clearly important. There is the work required to displace adsorbed water molecules from different parts of the surface (17). This is probably linked to the relative proportions of residual ionic and non-ionic bonds that are present (59). Both are temperature dependent (25, 73).

The chemisorption of collectors from aqueous media at the solid–liquid interface has been the subject of numerous investigations (89). Cooke, Iwasaki, and Choi (25), for example, find that temperature has little effect on the amounts of saturated and unsaturated fatty acids adsorbed onto hematite, but that on calcium-activated quartz, the amount of adsorption decreases with temperature. On the other hand, the recovery of hematite increases with temperature, whereas that of calcium-activated quartz decreases.

A case which is often considered involves an α liquid phase saturated with the solid and containing the collector, a β-phase of pure solid, and an interfacial phase, σ, of adsorbed soap. This is formed by double decomposition and in the example of sodium palmitate adsorbed on finely divided lead chromate, the surface reaction can be written

$$\mathrm{PbCrO_4 + 2C_{15}H_{31}CO_2Na \rightleftarrows Pb(O_2CC_{15}H_{31})_2 + Na_2CrO_4} \qquad \text{(Eq. 1)}$$

The relevant form of the Gibbs–Guggenheim equation (64) is then

$$\mathrm{d}\gamma = -\Gamma_{\mathrm{PbP_2}}{}^{(1)}\mathrm{d}\mu_{\mathrm{PbP_2}}{}^{\sigma} - \Gamma_{\mathrm{Na}}{}^{(1)}\mathrm{d}\mu_{\mathrm{Na}}{}^{\sigma} - \Gamma_{\mathrm{P}}{}^{(1)}\mathrm{d}\mu_{\mathrm{P}}{}^{\sigma} - \Gamma_{\mathrm{CrO_4}}{}^{(1)}\mathrm{d}\mu_{\mathrm{CrO_4}}{}^{\sigma} \qquad \text{(Eq. 2)}$$

(for brevity, the palmitate group is denoted by P) and from the postulated equilibria and the condition of electrical neutrality of each phase

$$\frac{\mathrm{d}\gamma}{\mathrm{d}\bar{n}^{\alpha}} = -(\Gamma_{\mathrm{PbP_2}}{}^{(1)} + \Gamma_{\mathrm{P}}{}^{(1)})\,\frac{\mathrm{d}\mu_{\mathrm{PbP_2}}}{\mathrm{d}\bar{n}^{\alpha}} - (\Gamma_{\mathrm{P}}{}^{(1)} + \Gamma_{\mathrm{CrO_4}}{}^{(1)})\,\frac{\mathrm{d}(\mu_{\mathrm{Na}} + \mu_{\mathrm{CrO_4}})}{\mathrm{d}\bar{n}^{\alpha}} \qquad \text{(Eq. 3)}$$

where $\bar{n}^{\alpha}$ is the total amount of the palmitate radical which is present in the α-phase.

Thermodynamic stability of this phase demands that $\mathrm{d}\mu_{\mathrm{w}}/\mathrm{d}\bar{n}^{\alpha}$ be negative, where w denotes water. In this event either $\mathrm{d}\mu_{\mathrm{PbP_2}}/\mathrm{d}\bar{n}^{\alpha}$ must be negative and $\mathrm{d}(\mu_{\mathrm{Na}} + \mu_{\mathrm{CrO_4}})/\mathrm{d}\bar{n}^{\alpha}$ positive, or both must be positive. The latter is by far the commoner. But there are undoubtedly situations, *e.g.*, at concentrations above the critical micelle concentration, when $\mathrm{d}\mu_{\mathrm{PbP_2}}/\mathrm{d}\bar{n}^{\alpha}$ becomes negative, and further adsorption of collector would produce a decrease in the tension at the solid–liquid interface.

Secondary mechanisms, therefore, come into operation. There may be a phase transition in which lead palmitate associates with water to form a hydroxy soap or it may start to desorb from the interface. Desorption, resulting in the occurrence of distinct maxima in the adsorption isotherms, has, in fact, been observed by several investigators.

Fava and Eyring (49), for example, followed the adsorption of radioactive sodium dodecylbenzenesulfonate onto lead and nickel surfaces. At the critical micelle concentration, there is a pronounced upward inflexion in the curve of adsorption *vs.* concentration, followed by a maximum. At higher concentrations the adsorption falls rapidly, and the rate of fall is accelerated by adding 0.01 N NaCl or HCl to the system. Vold and Phansalkar (140) have explained the results on the assumption that at a certain concentration the molecules of collector aggregate into micelles or, more accurately, into hemispherical micelles, in the surface layer.

Assuming that the molecules (here sodium palmitate which is denoted by NaP) can be present in the α-phase (water) and in the interfacial layer, σ, as both single molecules and as micelles, in the water

$$m\mathrm{Na}^{+} + n\mathrm{P}^{-} \rightleftarrows \mathrm{M}^{(n-m)-} \qquad \text{with } n > m \qquad \text{(Eq. 4)}$$

and that in the σ-phase

$$q\mathrm{Na}^{+} + r\mathrm{P}^{-} \rightleftarrows \mathrm{X}^{(r-q)-} \qquad \text{with } r > q \qquad \text{(Eq. 5)}$$

The Gibbs–Duhem equation for the α-phase is

$$n_{\mathrm{w}}{}^{\sigma}\mathrm{d}\mu_{\mathrm{w}}{}^{\alpha} + n_{\mathrm{Na}}{}^{\alpha}\mathrm{d}\mu_{\mathrm{Na}}{}^{\alpha} + n_{\mathrm{P}}{}^{\alpha}\mathrm{d}\mu_{\mathrm{P}}{}^{\alpha} + n_{\mathrm{M}}{}^{\alpha}\mathrm{d}\mu_{\mathrm{M}}{}^{\alpha} = 0 \qquad \text{(Eq. 6)}$$

This phase is electrically neutral; the system is in equilibrium and $\bar{n}^{\alpha}$ is the total number of gram-moles of NaP present in all its forms. It follows that

$$n_{\mathrm{w}}^{\alpha}\mathrm{d}\mu_{\mathrm{w}}^{\alpha} + \bar{n}^{\alpha}\mathrm{d}(\mu_{\mathrm{Na}}^{\alpha} + \mu_{\mathrm{P}}^{\alpha}) = 0 \quad \text{(Eq. 7)}$$

Similarly for the σ-phase

$$n_{\mathrm{w}}^{\sigma}\mathrm{d}\mu_{\mathrm{w}}^{\sigma} + n_{\mathrm{Na}}^{\sigma}\mathrm{d}\mu_{\mathrm{Na}}^{\sigma} + n_{\mathrm{P}}^{\sigma}\mathrm{d}\mu_{\mathrm{P}}^{\sigma} + n_{\mathrm{X}}^{\sigma}\mathrm{d}\mu_{\mathrm{X}}^{\sigma} = -A\mathrm{d}\gamma \quad \text{(Eq. 8)}$$

which, for similar reasons, reduces to

$$n_{\mathrm{w}}^{\sigma}\mathrm{d}\mu_{\mathrm{w}}^{\sigma} + \bar{n}^{\sigma}\mathrm{d}(\mu_{\mathrm{Na}}^{\sigma} + \mu_{\mathrm{P}}^{\sigma}) = -A\mathrm{d}\gamma \quad \text{(Eq. 9)}$$

Now the α- and σ-phases are in equilibrium and combination of Eq. 7 and 9 therefore gives

$$\Gamma_{\mathrm{NaP}}^{(1)}\,\frac{\mathrm{d}(\mu_{\mathrm{Na}} + \mu_{\mathrm{P}})}{\mathrm{d}\bar{n}^{\alpha}} = -\frac{\mathrm{d}\gamma}{\mathrm{d}\bar{n}^{\alpha}} \quad \text{(Eq. 10)}$$

But the α-phase is stable; hence, $\mathrm{d}(\mu_{\mathrm{Na}} + \mu_{\mathrm{P}})/\mathrm{d}\bar{n}^{\alpha}$ is positive. Since $\Gamma_{\mathrm{NaP}}^{(1)}$ is positive, $\mathrm{d}\gamma/\mathrm{d}\bar{n}^{\alpha}$ must be negative, but this requires that $\mathrm{d}(\mu_{\mathrm{Na}} + \mu_{\mathrm{P}})/\mathrm{d}\bar{n}^{\sigma}$ be negative, implying metastability of the σ-phase. A slight fluctuation in its composition causes it to disappear spontaneously, and this could explain the sharp fall in the adsorption curve that is observed after the maximum has been passed.

Not all isotherms exhibit these maxima. Sodium dodecyl sulfate is adsorbed on alumina, titania, barium sulfate, and calcium fluoride, forming the corresponding heavy metal soaps. But there are no maxima, the curves simply flattening out as the concentration of reagent approaches the c.m.c. It has been suggested that for these systems the adsorption occurs in two stages: a unimolecular film of orientated sulfate molecules is first chemisorbed on the surface; this is then partly penetrated by a second, physically adsorbed layer in which the orientation of the molecules is reversed (29, 132).

Certainly this mechanism could account for the stability of dispersions of barium sulfate in aqueous dodecyl sulfates and for the effects produced by the addition of electrolytes (29). It also provides an explanation for the well-known phenomenon of rewetting of solids, which occurs at high concentrations of adsorbate (89).

B. STATE OF ADSORBED FILM

The close connection between the state of the adsorbed collector film and the floatability of different mineral species has been the subject of a series of important papers.

Schulman and Smith (118), for example, measured the adsorption of sodium dodecyl sulfate on copper and zinc powders and on carefully ground samples of chalcopyrite, bornite, pyrite, galena, and carrolite, of known particle size. Cuming and Schulman (29) used both natural and synthetic barite. Peck (98) employed oleic acid and sodium oleate with fluorite, calcite, and barite.

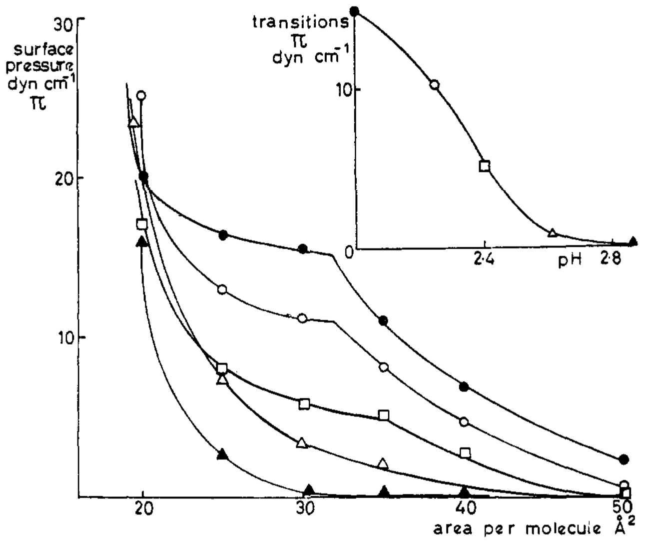

Figure 1.—Surface pressure *vs.* surface area for myristic acid on $5 \times 10^{-5}\,M$ $\mathrm{Th(NO_3)_4}$ (ref. 1): ●, pH 2.0 at 19°; ○, pH 2.26 at 22°; □, pH 2.41 at 17°; △, pH 2.61 at 20°; ▲, pH 2.85 at 20°.

A widely used technique in these studies has been to spread collectors, or their closely related homologs, at the air–water interface and adjust the composition of the substrate until the conditions approximate those obtained during a flotation process (40, 116, 123, 134, 145).

The interaction between the collector and the metal is followed by observing the changes produced in the force–area characteristics of the film, its surface potential, surface viscosity, and compression modulus.

It is found that interaction is controlled by a number of variables. These include the pH of the substrate (which determines the amount of ionization and dissociation of the molecules in the monolayer and also whether basic or complex metal soaps are formed), the cross-sectional area of the metal ion in the substrate and of the basic or complex metal ions, and the cross-sectional area of the hydrophobic portion of the monolayer molecules and of their polar groups. The effects of these variables have been discussed in detail elsewhere (80).

A particular example is afforded by the work of Spink and Sanders (123). These authors define σ_0 as the area per molecule at which the surface pressure π first starts to rise steeply when a monolayer of stearic acid is compressed on a substrate containing heavy metal ions. On copper, zinc, and iron chlorides, σ_0 decreases with increasing pH and passes through a minimum, which corresponds with the formation of the disoaps. Thereafter the film starts to expand, and this is ascribed to the conversion of the disoap into the monosoap, *e.g.* (St = stearate)

$$\mathrm{CuSt_2} + \mathrm{Cu^{+2}} + 2\mathrm{OH^-} \xrightleftharpoons{\text{pH 5–6}} 2\mathrm{Cu(OH)St} \quad \text{(Eq. 11)}$$

There is no minimum with $\mathrm{Ca^{+2}}$ in the substrate since basic calcium stearate is not formed. With $\mathrm{Al^{+3}}$ the

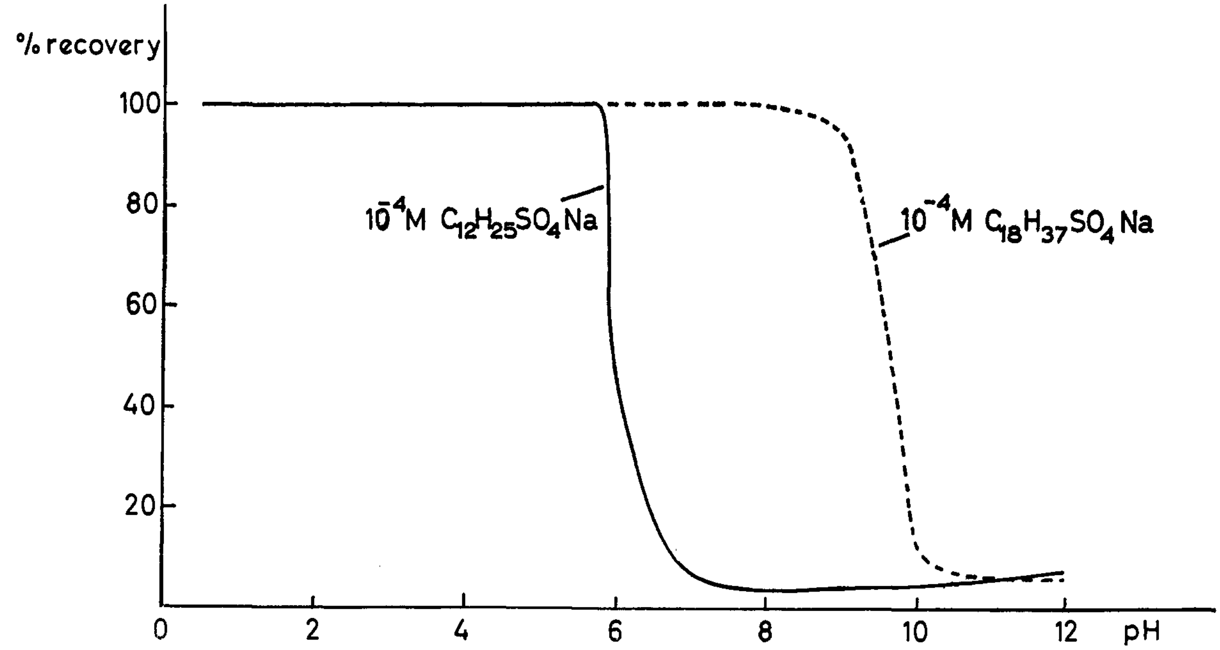

Figure 2.—Flotation of hematite (ref. 25).

behavior is also exceptional. There are two minima in the σ_0 *vs.* pH curve, due, apparently, to the well-known ability of aluminium to form complex and mixed soaps with the general formula $Al(OH)_m(O_2CR)_n$ (101).

Abramson and Ottewill (1) have extended this work on complex soap formation by spreading myristic acid on substrates containing lanthanum and thorium ions. The pressure at which the film solidifies on 5×10^{-5} *M* thorium nitrate falls considerably as the pH is raised from 2.0 to 2.85 (Figure 1). Thereafter it hardly changes up to a pH of 5.4. Over the same range of pH, *i.e.*, 2 to 3, neither dilute hydrochloric acid nor 10^{-4} *M* lanthanum nitrate produce solidification. At pH values between 2 and 3, myristic acid is un-ionized and is, therefore, unable to react with ions. But at pH 2.85, thorium ions become hydrolyzed as follows (76)

$$\begin{aligned} Th^{+4} + 4H_2O &\rightleftarrows Th(OH)_2^{+2} + 2H_3^+O \\ 2Th^{+4} + 4H_2O &\rightleftarrows Th_2(OH)_2^{+6} + 2H_3^+O \end{aligned} \qquad \text{(Eq. 12)}$$

the equilibrium constants of the reactions being, respectively, 3.4×10^{-8} and 2.6×10^{-5}. The basic ions are capable of interacting with undissociated myristic acid, probably *via* hydrogen bonding, and this produces considerable solidification in the monolayer, which retains the characteristics of a condensed film up to about 25 Å.²/molecule.

C. FACTORS AFFECTING FLOTATION

To correlate the results of metal–monolayer interactions at the air-water interface with actual flotation behavior has been singularly difficult. It is necessary to consider, *inter alia*, factors such as the amount of collector that has been adsorbed and the changes produced in the contact angle and the ζ-potential of the particles. In addition, penetration of the collector film by molecules of the frothing agent, coagulation, co-adsorption of metal, collector, and frother ions all play a considerable part. Despite these complications, useful progress has been made recently in several directions.

It has been found that flotation involving soap films on the surface of particles proceeds best when the fractional coverage, θ, is less than unity (80). Indeed flotation begins to decrease when $\theta > 0.2$ and generally ceases when a multilayer of collector has been adsorbed.

Sodium dodecyl sulfate and sulfonate, for example (70), give high recoveries of goethite at low concentrations, the contact angle remaining > 90° at pH values above 7. On the basis of ζ-potential and coagulation measurements, Ottewill and Watanabe (94–96) have shown that anionic collectors are adsorbed on positive sites on a surface. The number of these sites, as distinct from the amount of collector adsorbed, is characteristic of the collector's polar head group, but is independent of the length of its hydrocarbon tail. By contrast, the energy involved during adsorption is a function of the length of the tail group, but is almost independent of the nature of the head group.

The marked effect that the pH has on the collection process (Figure 2) (25) is almost certainly due to changes produced in the chemical processes by which the collector is adsorbed. Thus between pH 8 and 9 oleic acid appears to be adsorbed onto barite (98) by an ion-exchange mechanism which can be written (23, 79)

$$\vdots\mathrm{Ba(OH)^-} + \mathrm{RCOO^-} \rightleftarrows \vdots\mathrm{Ba(O_2CR)^-} + \mathrm{OH^-} \qquad \text{(Eq. 13)}$$

with an equilibrium constant

$$K_1 = \left(\frac{\theta}{1-\theta}\right)\left(\frac{\mathrm{OH^-}}{\mathrm{RCOO^-}}\right) = \left(\frac{\theta}{1-\theta}\right)\frac{K_w}{K_a(\mathrm{RCOOH})} \qquad \text{(Eq. 14)}$$

At pH values greater than 9.5, however, there is evidence that the adsorbed layer contains both individual molecules and soap micelles. This implies that there has been a change to a neutral molecular mechanism which can be written

$$\vdots\mathrm{BaOH} + \mathrm{RCOOH} \rightleftarrows \vdots\mathrm{Ba(O_2CR)} + \mathrm{H_2O} \qquad \text{(Eq. 15)}$$

with an equilibrium constant

$$K_2 = \left(\frac{\theta}{1-\theta}\right)\left(\frac{1}{\mathrm{RCOOH}}\right) \qquad \text{(Eq. 16)}$$

K_w and K_a are the equilibrium constant for water and the dissociation constant of oleic acid, and θ, the fractional coverage, varies between about 0.05 and 0.2 for flotation. Either of these equations gives a curve compatible with the data, and, if K_1 and K_2 are known, ΔF_1 and ΔF_2, the respective adsorption potentials, can be calculated from the expressions

$$\begin{aligned} K_1 &= e^{-\Delta F_1/RT} \\ K_2 &= e^{-\Delta F_2/RT} \end{aligned} \qquad \text{(Eq. 17)}$$

These range from about +5 to about −5 kcal. and from −5 to −20 kcal., respectively, for many of the minerals which are amenable to collection by fatty acids and soaps.

The relevance of the ζ-potential to flotation behavior has been studied by a number of authors (3, 4, 38, 53, 124).

Fuerstenau and Modi (54, 55, 87) were able to obtain good correlations between the changes in ζ-potential produced by altering the pH and the recovery of corundum by various cationic collectors, but were unable to show correlations when anionic collectors were used. This may have been because the ζ-potential of a mineral does not necessarily relate to its electrokinetic charge density. Adsorption of ions can produce large changes in the latter without significantly affecting the former (45, 91), if, at the same time, they alter the thickness of the compact solvated layer which surrounds each particle.

The ζ-potential of scheelite and the adsorption onto it of anionic collectors and inorganic activating agents has been studied by O'Connor (91). Table I gives typical values for its ζ-potential in conductivity water after having been treated in various ways.

Considering the effect of $\mathrm{Ca(NO_3)_2}$, Figure 3 shows that there is a steady decrease in the magnitude of the negative potential and that it becomes positive when the electrolyte concentration is 3.3×10^{-5} N. This is ascribed to preferential adsorption of $\mathrm{Ca^{+2}}$ into the compact layer with corresponding adsorption of $\mathrm{NO_3^-}$ into the diffuse layer. At higher concentrations, $\mathrm{Ca^{+2}}$ and $\mathrm{NO_3^-}$ appear to be simultaneously adsorbed on the surface. There is a decrease in the thickness of the diffuse double layer, which tends to counterbalance the change in the ζ-potential. This reaches a limiting value of about +10 mv.

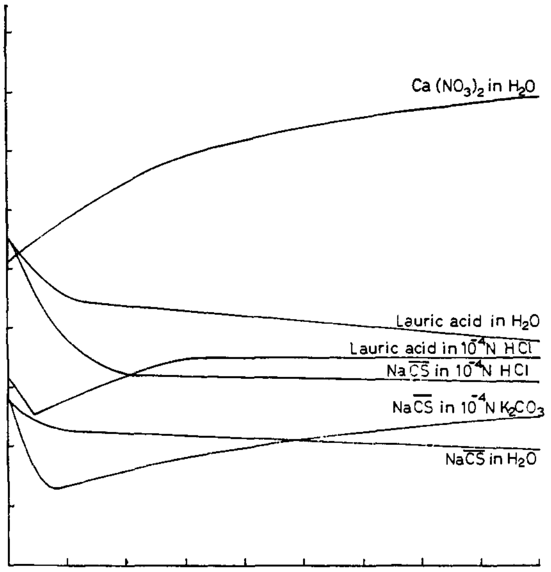

Figure 3.—ζ-Potential of scheelite (ref. 91).

TABLE I

ζ-POTENTIAL OF SCHEELITE

Treatment	ζ-Potential, mv.
Initial value	−19.0
After treating with	
$\mathrm{Ca(NO_3)_2}$	−26.7
$\mathrm{K_2CrO_4}$	−43.8
Sodium cetyl sulfate in water	−31.6
Sodium cetyl sulfate in 10^{-4} N $\mathrm{K_2CO_3}$	−54.7
Sodium cetyl sulfate in 10^{-4} N HCl	−48.5
Lauric acid in water	−34.6
Lauric acid in 10^{-4} N HCl	−47.6
Sodium oleate in water	−55.8
Sodium oleate in 10^{-4} N HCl	−67.5

The effects of sodium cetyl sulfate and lauric acid in water and in 10^{-4} N HCl and 10^{-4} N $\mathrm{K_2CO_3}$ are included in Figure 3. It is seen that the soap is only slightly adsorbed from acid and neutral media. This is consistent with the observation (60) that alkyl sulfates and sulfonates are not, on the whole, good collectors for scheelite. On the other hand, lauric acid is adsorbed into the compact layer at pH 4 by an ion–dipole mechanism and, like its homologs, capric and myristic acids, is thus usefully employed in practice as a collector for this mineral.

The adsorption of a soap profoundly affects the contact angle of a solid. The contact angle of barium sulfate rises from 0 to nearly 180° as sodium oleate

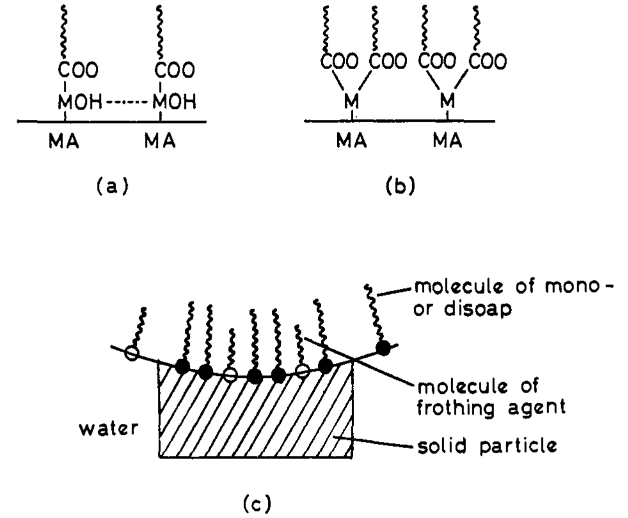

Figure 4.—Adsorption of collectors (schematic): (a) monosoap; (b) disoap; (c) solid surface during flotation.

is adsorbed onto the surface, forming a film of insoluble barium oleate (117). Carboxylic acids and alkyl sulfates and sulfonates produce similar effects, the value of the contact angle depending on the pH of the medium and on the hydrocarbon chain length of the collector employed. While doubt has been cast recently on the validity of many contact angle measurements on minerals (6, 111), investigations continue on the relationship between the contact angle and the attachment of particles to air bubbles during flotation.

Thus Robinson (113) has established reasonable correlations between the contact angle, the collector concentration, and the recovery achieved during batch flotations in a cell where provision was made to control the sizes of the bubbles in the pulp.

Klassen and Tikhonov (74) used an adhesion tension method to study the way in which fluorite and barite adhered to air bubbles when an oleate collector was employed. As the time elapsing before the bubbles in the liquid come into contact with the mineral is increased, so their adhesion decreases. This results in a decrease in flotation. The effect is independent of the age of the pulp and is thought to be due to armoring of the bubbles by an oriented layer of soap molecules. The same effect can be produced if there are excessive amounts of soaps present in the form of frothing agents, *e.g.*, alkyl aryl sulfonates.

In the light of the mechanism of monolayer penetration (81) whereby one surface-active species is able to penetrate a monolayer of another, the attachment of mineral particles to air bubbles has been visualized as the penetration of a diffuse film of the collector adhering to the solid by a very diffuse monolayer of the frothing agent (80). The collector may be present either as a monosoap with isolated hydrocarbon chains (Figure 4a), M being a divalent metal ion and A a divalent cation, or in the form of isolated patches of a condensed disoap (Figure 4b). The surface of the solid adhering to an air bubble when flotation occurs may then be pictured as in Figure 4c.

D. SOME PRACTICAL EXAMPLES

This section gives a summary of recent technological work in which it appears that soap films formed on the surfaces of the mineral particles are contributing to the flotation process.

Cooke and co-workers (24, 26) have shown that physical effects can completely outweigh ionic effects in the flotation of iron ores with fatty acids and resin acids. When the collector has a carbon chain greater than 12 atoms, and particularly when it is saturated, it becomes remarkably insensitive to the ore's surface charge. In fact, palmitic acid, stearic acid, and aromatic resin acids behave more like cationic than like anionic collectors and are more effective at high pH values than at low ones. These effects are due to the formation of metal soaps on the surfaces of the ore particles (16, 42) which can be identified by infrared spectroscopy (43, 72).

The adsorption of tridecylic acid on hematite and cassiterite (105–107) occurs uniformly on the former mineral, though on the latter only about 20% of the surface is covered. In both cases the adsorption is essentially ionic in nature, which accounts for the large losses of collector which occur when the minerals are subsequently washed and dried.

The action of sodium silicate as a depressant for calcite in the presence of fluorite, using oleic acid as the collector, appears to be due to hydration of the calcite surface and the formation of the hydroxy soap (44). The extent of depression depends on the ratio of Na_2O to SiO_2 in the sodium silicate (122), and a ratio of 2.9:1 produces more depression than one of 3.2:1 at pH 10.

The employment of mineral oils containing petroleum sulfonates and fatty acids as collectors has been reviewed recently by Falconer (48).

Heavy metal ions in the pulp leads to activation and depression of different species. Thus Gaudin and Fuerstenau (57) have shown that the adsorption of Ba^{+2} and Al^{+3} onto silica surfaces produces a reversal of surface charge which permits flotation by laurate ions at pH values where normally this would not occur. Adsorption of traces of Ca^{+2} and Mg^{+2} from water containing only 8 p.p.m. of these ions inhibits the separation of phosphates from silica with an oleic acid collector (128) presumably because calcium and magnesium oleates are formed on the surface. But other mechanisms operate during activation and depression with heavy metal ions. Eigeles (44) postulates surface hydration and the complexing of multivalent ions in solution. Gaudin and others (18, 58) have satisfactorily explained the activation of zinc ores by copper in terms of copper ion adsorption into the zinc lattice.

Dolomite, $Ca(MgFeMn)(CO_3)_2$, acts as a depressant in the flotation of malachite, $Cu_2(OH)_2CO_3$, and azurite, $Cu_3(OH)_2(CO_3)_2$, with fatty acids, because it preferentially adsorbs them to form calcium and magnesium soaps.

Other slime and gangue depressants such as sodium fluoride and lignin sulfonate (employed with sodium oleate in the flotation of spodumene, $LiAlSi_2O_6$) or fatty acid emulsions (used with carboxylic acids and alkali metal sulfonates in the flotation of alkaline earth oxygen minerals) operate by many different mechanisms. These include: the sequestration of activating or depressing ions; the precipitation or complex of activating ions; the prevention of collector adsorption by protective colloid action; the control of potential-determining ions to promote or inhibit the action of protective colloids; and the control of potential-determining ions to assist or retard collector adsorption (71).

III. SOAP FILMS IN DISPERSION

A. GENERAL

All disperse systems in which interfacial tension exists between the solid, s, and liquid, l, phases are thermodynamically unstable. The Gibbs free energy, G, is given by the expression

$$\gamma_{sl} = \left(\frac{\partial G}{\partial A}\right) \qquad \text{(Eq. 18)}$$

where γ_{sl} is the interfacial tension and A is the interfacial area. When a soap film is adsorbed onto the solid surface, the interfacial tension falls and this tends to increase the stability of the dispersion.

But if the particles are to remain dispersed over a long period, mechanisms other than a simple lowering of interfacial tension must also be operating. Their nature will depend on whether the dispersion is in an aqueous or in a nonaqueous medium.

The alkali metal soaps—carboxylates, sulfates, sulfonates, abietates, etc.—are employed for dispersing particles in both aqueous and in nonaqueous media. But the corresponding soaps of the alkali earth and heavy metals are only useful for dispersions in nonaqueous media.

B. DISPERSIONS IN AQUEOUS SYSTEMS

There are three mechanisms which contribute to the stability of dispersions in aqueous media. The first involves the formation of electrical double layers around particles; the second involves the formation of hydrated sheaths; the third may be difficult in practice to distinguish from the second, but covers the more general case of steric barriers around particles.

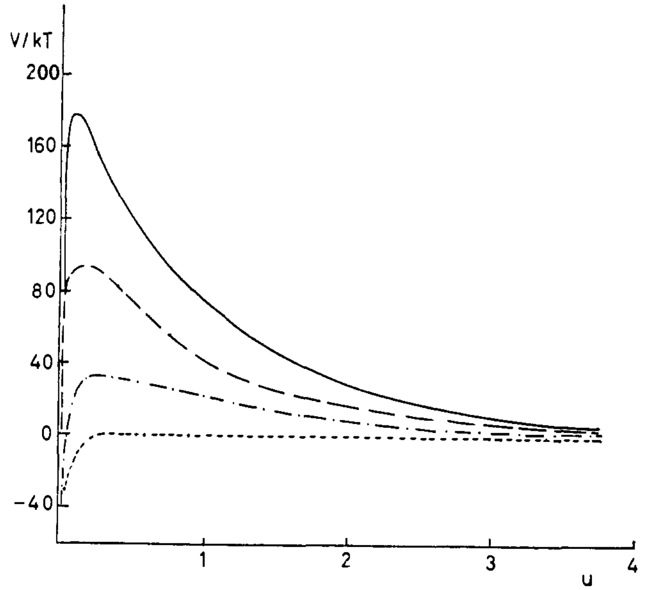

Figure 5.—V/kT *vs.* U for particles of 200-Å. radius at τ = 0.66 with potentials, ψ, of (ref. 93) ———, 100 mv; - - - -, 75 mv; – · – · –, 50 mv; . . . ., 25 mv.

In many instances all three mechanisms will be operating simultaneously; this will be expected to give rise to dispersions of maximum stability.

1. *Effect of Soaps on Electrical Double Layer*

The idea of an electrical double layer acting as a barrier to aggregation of particles dates from the work of Derjaguin and Landau (36, 37) whose theories were developed subsequently by Verwey and Overbeek (139) and more recently by Ottewill, Rastogi, and Watanabe (93).

Particles dispersed in an aqueous medium are pictured as surrounded by a diffuse double layer of charge; the energy of interaction between them is given by the expression

$$V = \frac{\epsilon a \psi^2 \exp(-\tau u)}{u + 2} - \frac{A}{12u} \qquad \text{(Eq. 19)}$$

where A is van der Waals constant (10^{-12} to 10^{-13} erg), ϵ is the dielectric constant of the medium, a is the particle radius, ψ is the surface potential, $\tau = \kappa a$, where $1/\kappa$ is the thickness of the double layer, *i.e.*, about 300 Å., and $u = H_0/a$, H_0 being the distance apart of the surfaces of the particles. Figure 5 shows the effect of surface potential on VkT for different values of u.

The stability of the dispersion depends primarily on the height of the potential energy barrier. This is denoted V_m, the corresponding value of u being denoted u_m. u_m hardly alters with ψ, and its value can be obtained from the expression

$$u_m = 2/(C - 1) \qquad \text{(Eq. 20)}$$

where

$$C^2 = \frac{12(2\tau + 1)\epsilon a\psi^2}{A} \qquad \text{(Eq. 21)}$$

The relationship between the potential energy maximum, V_m, and the stability of the dispersion, W, is

$$W = \frac{2\Pi^{1/2}}{(u_m + 2)^2} \exp\left(\frac{V_m}{kT}\right) \qquad \text{(Eq. 22)}$$

V_m being obtained from the equation

$$V_m = \frac{A}{24}\left[\frac{C^2}{1 + 2\tau} - 2C + 1\right] \qquad \text{(Eq. 23)}$$

Provided V_m is greater than $25kT$, the dispersion is stable. If it falls below this value, flocculation occurs.

Besides ψ, the variables that chiefly affect the stability of a dispersion are the radius of the particles, the ionic strength, the dielectric constant of the medium, and the value assumed for the van der Waals constant, $\psi_\delta°$. The potential at the Stern layer is considerably altered by the addition of a soap or other surface-active agent to the system. It has been shown that

$$\ln W = P\left[\psi_\delta° - \frac{Hc}{1 + k_2c}\right]^2 - Q\left[\psi_\delta° - \frac{Hc}{1 + k_2c}\right] - \frac{3}{2}\ln\left[\psi_\delta° - \frac{Hc}{1 + k_2c}\right] + R \qquad \text{(Eq. 24)}$$

where

$$P = \frac{AD^2}{24kT(1 + 2\tau)} \qquad \text{(Eq. 25)}$$

$$Q = \frac{AD}{24kT} \qquad \text{(Eq. 26)}$$

$$R = B - \frac{3}{2}\ln D \qquad \text{(Eq. 27)}$$

$$B = \ln 2\sqrt{\Pi} - \frac{1}{2}\ln (A/6kT) + A/24kT \qquad \text{(Eq. 28)}$$

$$D = c/\psi \qquad \text{(Eq. 29)}$$

c is the concentration of the surface-active agent in gram-ions/liter, and k_2 is the constant of the Langmuir isotherm equation (78).

Equation 24 can be used to relate the stability of the dispersion to the concentration of surface-active agent employed.

With anionic reagents, *e.g.*, carboxylate soaps, alkyl sulfates and sulfonates, etc., the stabilizing potential on the particles is rendered more negative. Cationics, on the other hand, tend to make the stabilizing potential more positive under the same conditions. As a result, anionics are more effective than cationics for dispersing solids in aqueous media, particularly in the presence of OH^- and multivalent ions (89).

The importance of electrical effects is illustrated as follows. Rouge, titanium white, and yellow ochre are not dispersible in pure water, but can be readily dispersed in approximately 10 m*M* solutions of ferric or aluminium chloride, both of which are highly ionized. The resulting dispersions are stable for about 3 days (85). If sodium dodecyl sulfate is added in about 10 m*M* concentration, flocculation occurs. The floccules are oleophilic and can be removed from the water by shaking with benzene. This occurs because the surface-active agent is adsorbed on to the particles with a reverse orientation, *i.e.*, with the paraffin chains turned outwards toward the water. At higher concentrations of the surface-active agent, the adsorbed molecules revert to their original configuration. This restores the negative potential between the particles, enabling the floccules to be redispersed in the water.

The control of flocculation and deflocculation in applications as diverse as the preparation of pharmaceutical suspensions (83, 92), in brewing (22), in clay technology (68, 81, 141) and paint technology (20, 28), and in dyeing and detergency (89) is generally achieved by the addition of reagents which act on the electrical double layer, increasing or decreasing the electrical potential between neighboring particles in the dispersion.

2. *Steric Effects*

An adsorbed soap film with normal orientation would provide a steric barrier to the close approach of neighboring particles even in the absence of electrical effects. In media of low ionizing power, where electrical effects are largely absent, steric effects predominate. But in aqueous systems they are usually of secondary importance.

Evidence for their existence has been provided by the work of Heller and Pugh (65, 66), who studied the effect of polyethylene glycols of different molecular weight on the stability of gold sols and found that protection against coagulation by potassium chloride increased with increasing polymer concentration to a maximum value. When the molecular weight of the polymer was varied, at constant concentration, a considerable increase in stability occurred at a molecular weight of 6000. With this size of polymer molecule adsorbed on the surface, neighboring colloidal particles were being held apart by steric interference between their peripheries.

A combination of steric interference and electrostatic stabilization occurs when polysulfonated polystyrene, with a molecular weight of 110,000, is used to stabilize a ferric hydroxide sol. This is initially positively charged and sensitization occurs at a low concentration

(10^{-6} mole/l.), but at higher concentrations the resistance to flocculation by electrolytes is much increased.

As already mentioned, under certain circumstances it is possible for ionogenic surface-active agents to be adsorbed at a solid–water interface with a reverse orientation, that is, with the paraffin chains turned toward the water. This usually causes flocculation. Reagents with more than one hydrophilic group in the molecule are less prone to this reverse orientation and are thus widely employed in industry for dispersing solids in water (86). Other practical applications in which steric barriers play a part are in the preparation of so-called dispersible powders which can be readily dispersed in water to give stable sols (89) and in the employment of builders, such as carboxymethyl cellulose (100) for increasing the soil-suspending powers of synthetic detergents.

3. Hydrated Sheaths

The normal steric barrier provided by an adsorbed soap film is usually reinforced by the existence of a sheath of water molecules which becomes attached to the surface of a particle when it is immersed in water. The concept of such sheaths dates back to the early work of Stern (125) and Derjaguin (33).

Several workers have shown that in the neighborhood of surfaces, water molecules become orientated by dipole forces and by hydrogen bonding to form layers of so-called "soft ice" (34, 41, 138). These are usually about ten molecules thick. "Soft ice" is characterized by a viscosity similar to that of butter (30), by a density significantly higher than that of normal water (8), and by a low value of the dielectric permeability (39).

The boundary between the sheath water and the continuous aqueous phase is well defined; when the dispersion is subjected to electrophoresis the sheaths move with the particles, and the value of the ζ-potential that is obtained is at the surface of shear, *i.e.*, at the extremity of the sheath.

Evidence for the existence of hydrated sheaths is provided by the observation that numerous dispersions, whose measured ζ-potentials are rather low, are, nevertheless, quite stable. For example, ferric oxide, dispersed in water with sodium dodecyl (propylene tetramer) benzenesulfonate, is more resistant to flocculation and to redeposition on cotton surfaces than would be expected from the measured ζ-potential (41).

A hydrated sheath acts in much the same way as any other steric barrier by reducing the free energy of the system, but it also gives rise to other effects. Huber Panu and Pandelescu (69) have shown that there are increases in the apparent viscosities of baryte and pyrite at particular concentrations of alkyl sulfate suspending agents. They ascribe them to the formation of hydrated sheaths around the dispersed particles. The sheaths not only physically increase the volumes of the individual particles, but also increase their volume fraction by causing water molecules to be withdrawn from the continuous phase. The effects are quite marked; for example, the viscosity of a 20% v./v. suspension of baryte can be increased by 20% and that of a 30% v./v. suspension by nearly 50% by adding about 2 g./l. of the surface-active agent. At higher concentrations of the agent, it becomes adsorbed with a reverse orientation, the structure of the hydrated sheath alters and the viscosity of the suspension falls to a value which may be as low as 50% of the initial value when no suspending agent was present.

C. DISPERSIONS IN NONAQUEOUS SYSTEMS

In considering the dispersing action of soaps and other surface-active agents in nonaqueous media, it is necessary to distinguish between solvents like benzene and xylene, which have a low dielectric constant about 2.5, and those like acetone and alcohol which have dielectric constants in the neighborhood of 20.

Stable dispersions are readily prepared in the latter solvents by grinding; as with dispersions in water, they exhibit electrokinesis and are flocculated by the addition of electrolytes (32).

It is more difficult to prepare stable dispersions of substances like Fe_2O_3, Al_2O_3, TiO_2, carbon black, etc., in carbon tetrachloride, benzene, and related solvents. The particles invariably remain flocculated unless soaps or other dispersing agents are employed.

Two different views are held regarding the parts played by the electrical and by the steric mechanisms.

1. Electrical Mechanisms

Van der Minne and Hermanie (135) (see also ref. 13) believe that electrical effects alone can account for the stability of dispersions in nonaqueous media. They used calcium diisopropyl salicylate to disperse carbon black in benzene. The rates of flocculation of 0.1% dispersions were measured microscopically, and the adsorption isotherm of the soap on carbon was derived by a colorimetric method. ζ-Potentials were obtained by electrophoresis of 0.003% dispersions.

The carbon particles become positively charged when the concentration of soap exceeds 9 μmoles/l., and stable dispersions are found to be associated with ζ-potentials between 21 and 24 mv. This corresponds to a maximum in the adsorption isotherm.

2. Steric Mechanisms

The alternative view that electrical effects can be ignored and that steric mechanisms play the major role in stabilizing the dispersions has been advanced

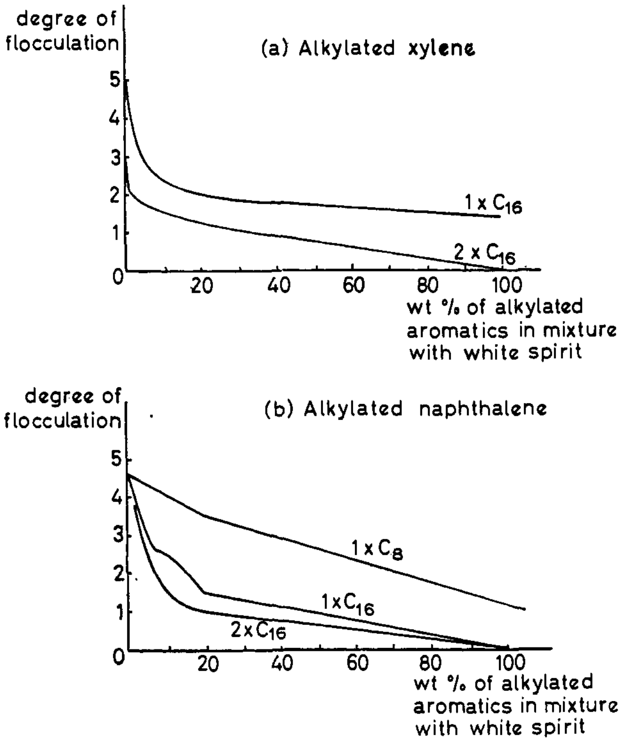

Figure 6.—Influence of alkylated aromatics on degree of flocculation of 0.1% carbon black dispersions in white spirit (ref. 136).

by several workers. Van der Waarden, for example (136, 137), dispersed carbon black (10–300 mμ in diameter) in white spirit and showed that the addition of various alkyl aryl hydrocarbons increased their resistance to flocculation, as measured by their reduced rate of sedimentation.

The stabilizing action increases with the chain length of the alkyl groups and with the number of these that are attached to each aryl group in the molecule; some typical data are plotted in Figure 6.

Adsorption of alkyl aryl compounds onto the surface of the carbon produces a steric barrier. The shape of the adsorption isotherms shows that the aromatic groups are lying flat on the surface with the alkyl chains extending into the continuous oil phase (Table II).

TABLE II

SURFACE AREAS BLOCKED BY ALKYL CHAINS AND PER CARBON ATOM OF THE CHAINS OF ADSORBED ALKYL ARYL COMPOUNDS

Adsorbed molecule	No. of carbon atoms in alkyl chain	Total area blocked per adsorbed molecule, Å.^{2}	Total area blocked by alkyl chains, Å.^{2}	Area blocked per alkyl carbon atom, Å.^{2}
Benzene	0	41	0	. .
Xylene	2	63	22	11
Naphthalene	0	67	0	. .
1 × C_8 naphthalene	8	120	53	6.6
(1 × C_{16} + 1 × C_2) naphthalene	18	180	113	6.3
(2.7 × C_{16}) naphthalene	38	360	293	7.7

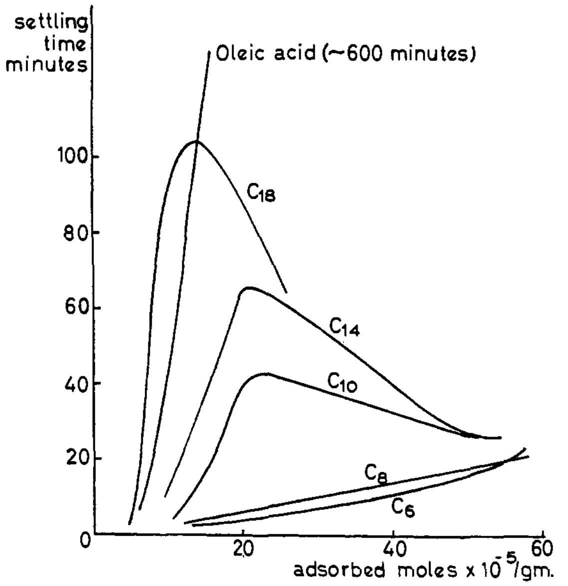

Figure 7.—Settling time of Fe_2O_3 in xylene stabilized with fatty acids, as a function of adsorption. C_{18} represents stearic acid, etc. (ref. 75).

These chains mutually repel each other and prevent neighboring particles from approaching to within the critical distance for the operation of van der Waals attractive forces.

It has been possible to calculate the magnitude of the steric barrier provided by an adsorbed layer of rod-shaped soap molecules on particles in a dispersion (82).

The molecules are pictured as lying either parallel or perpendicular to the surface with the head groups innermost. The former orientation is denoted B_2, the latter B_1. Using a statistical treatment, the configurational free energy of the system is expressed in terms of the numbers of molecules attached in each orientation to the available lattice sites on the surfaces of the dispersed particles. This enables the soap's adsorption isotherm to be calculated as a function of its activity in the continuous phase and as a function of the free energy per unit area of surface.

The free energy of repulsion between particles is given by

$$2\gamma(d)/N^s kT \qquad \text{(Eq. 30)}$$

where N^s is the number of lattice sites per unit area; γ is the free energy above some arbitrary level, per unit area of surface, and is a function of d, the distance between the particles; k is Boltzmann's constant; and T is the absolute temperature. Provided this expression is positive, the dispersion remains stable.

From measurements of the settling time, conductivity, and electrophoretic mobility of dispersions of Fe_2O_3, Al_2O_3, HgS, $BaSO_4$, $CaCO_3$, SiO_2, TiO_2, carbon, and selenium in xylene, Koelmans and Overbeek (75) have been able to evaluate the relative

TABLE III

CORRELATION BETWEEN STABILITY AND ELECTROPHORETIC MOBILITY

Powder	Stabilizer	Concn., mmoles/l.	Vol. % polar liquid added	ϵ	Charge	Sedimentation time, hr.	Velocity, μ/sec./v./cm.	ζ, mv.
Fe_2O_3	Cu oleate	5	None	2.3	+	24	0.110	53
	Oleic acid	10	2.25% CH_3OH	2.6	+	24	0.145	62
	Stearic acid	15	2.25% CH_3OH	2.6	+	24	0.165	70
	Capric acid	15	2.25% CH_3OH	2.6	+	24	0.150	65
	Oleic acid	15	2.75% CH_3OH	2.65	+	15	0.08	31
	Stearic acid	15	2.75% CH_3OH	2.65	+	2	0.05	20
	Aerosol OT	10	None	2.3	+	24	0.143	68
Al_2O_3	Oleic acid	10	2.25% CH_3OH	2.6	+	24	0.103	43
	Stearic acid	10	2.25% CH_3OH	2.6	+	24	0.110	48
	Aerosol OT	10	None	2.3	+	24	0.147	71

contributions to stability of the electrical and the steric mechanisms. Nonionic long-chain fatty acids in general have little effect on the settling time of the dispersions, increasing it at most from a few minutes to about 1 hr. This is shown in Figure 7. However, complete stabilization can be achieved if between 2 and 4% of methanol is added to the xylene, owing to the increase produced in the dielectric constant of the medium.

Ionic detergents, on the other hand, like copper oleate, calcium isopropyl salicylate, Spans 40 and 80 (sorbitan monopalmitate and oleate, respectively), and Aerosol OT (sodium dioctyl sulfosuccinate), reduce the rate of settling to several days, and the stability is similar to that in water or in organic solvents of high dielectric constant. The correlation between the stability of the dispersions and their electrophoretic mobility in xylene is given in Table III.

Figure 8 shows the adsorption isotherm of oleic acid on Fe_2O_3. A similar curve is obtained when Aerosol OT is adsorbed from xylene onto Fe_2O_3.

The interpretation of the results is as follows. On the assumption that the diffuse double layer around particles in xylene has a Debye thickness, $1/\kappa \simeq 16$, and that van der Waals constant is 10^{-12} erg, the electrical energy barrier can exceed the critical value of $15kT$ for particles of 1 μ or above.

As regards steric effects, repulsion between particles will only become effective when the adsorbed molecules are comparable in length to the sizes of the particles involved. Thus four cases can be distinguished and are summarized in Table IV.

It is seen that large particles can never be stabilized by steric mechanisms alone, while small ones can never be entirely stabilized by electrical effects. Maximum stability occurs when the two mechanisms operate simultaneously.

TABLE IV

Particle size	Stabilizing mechanism	Stability
Large	Ionic double layer	Stable
Large	Steric hindrance	Flocculated
Small	Steric hindrance	Stable
Small	Ionic double layer	Flocculated

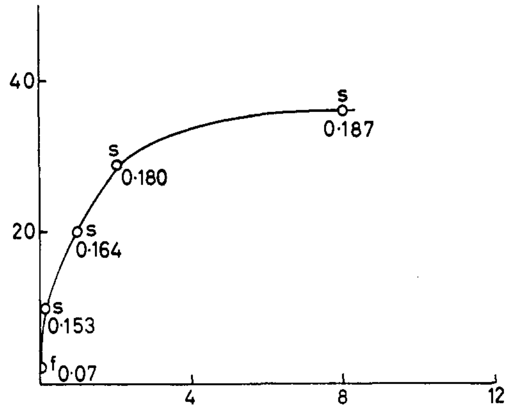

Figure 8.—Adsorption isotherm of oleic acid on Fe_2O_3 in xylene + 3.75% methanol. Numbers denote electrophoretic mobility; S = stable; F = flocculated (ref. 75).

IV. SOAP FILMS IN LUBRICATION

A. GENERAL

The rheological and mechanical properties of soap films are of great importance when considering the employment of these materials as lubricants. In the form of greases, the soap films are usually thicker than 10^{-4} cm. and are thus providing essentially hydrodynamic lubrication. When oils are being employed, it is only at high loads that mixed lubrication (27) and boundary lubrication (12) begin to operate. In the latter case, though the film may consist of 20 or more soap molecules superimposed on each other, not all the molecules will necessarily be orientated perpendicular to the solid surface, and the boundary film will, therefore, not usually exceed about 10^{-5} cm. in thickness.

The employment of soaps as lubricants and as glidants in various branches of powder technology has been practiced for many years. For example, magnesium stearate is used in the tableting of pharma-

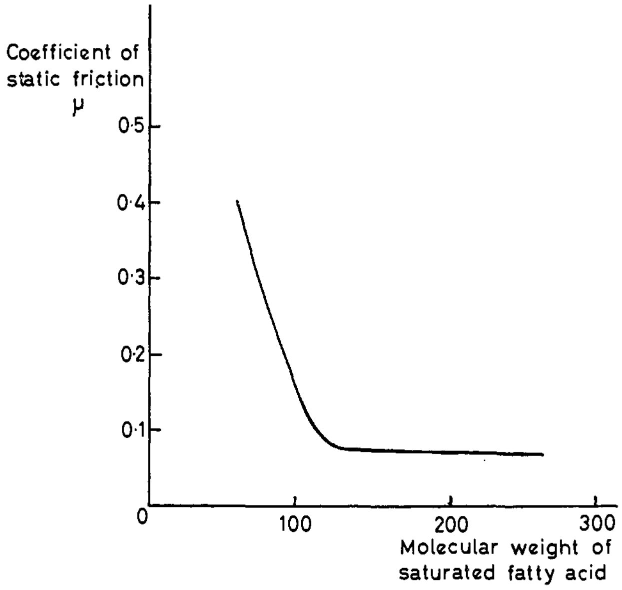

Figure 9.—Lubrication of steel surfaces by fatty acids (ref. 12).

ceutical products, calcium stearate in the extrusion of plastics. It is only quite recently, however, that fundamental studies have been made of the effects that adsorbed soap films have on the frictional and cohesive properties of powders.

B. LUBRICATION OF METALS

Soap films are formed in the presence of small amounts of moisture and metallic oxides (120, 133) by the chemisorption of fatty acids onto the surfaces of reactive metals like iron, copper, and cadmium, and traces of free acids in oils account for their ability to provide boundary lubrication (9, 11, 108).

Traces of preformed metallic carboxylates, naphthenates, and abietates in the oil also provide boundary lubrication, though in these cases the films are physically adsorbed. Whereas the preformed soaps act as boundary lubricants on both reactive and unreactive metals like silver and platinum, the pure acids are, on the whole, poor boundary lubricants for metals with which they do not form soaps. At the melting point of the acid, which is substantially lower than that of the corresponding soap, the film becomes disorientated and there is a substantial increase in the friction between the moving surfaces (62).

Figure 9 shows how the coefficient of friction between steel surfaces varies with the molecular weight of the chemisorbed soap film. It is seen that the friction approaches an asymptotic value of 0.07 as the molecular weight of the acid is increased above about 110 (caproic). This is accompanied by a marked fall in the amount of damage done to the moving surface by scaring and abrasion.

The transition between a solid or condensed boundary film and an expanded one in which the adsorbed molecules have become partly or wholly disorientated is marked by a sharp increase in the coefficient of friction from a value in the neighborhood of 0.07 to about 0.3–0.4. This is paralleled by an increase in the surface damage (110). Measurements of friction and wear thus provide a means of obtaining the "melting point" of the film and hence its chemical composition. On unreactive metals, lubricated with fatty acids, the increase in the coefficient of friction and wear occurs somewhere near the melting point of the acid. On reactive metals it occurs in the neighborhood of the softening point of the metal soap that has been formed. This is shown in Table V (10, 97, 130).

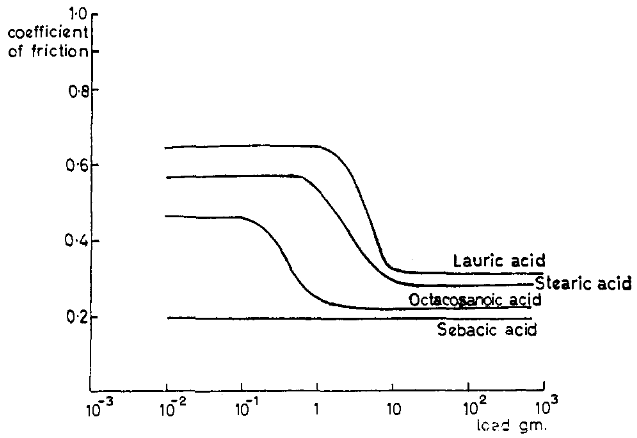

Figure 10.—Effect of load and acid chain length on friction (ref. 12).

Table V

Frictional Properties of Soap Films

Surface	Lubricant	Coeff. of friction at 20°	Transition temp., °C., smooth, stick–slip
	A. Reactive		
Cadmium	1% stearic acid in paraffin	0.07	130
Cadmium	Smear of cadmium stearate	0.05	140
Copper	1% lauric acid paraffin	0.08	100
Copper	1% stearic acid in paraffin	0.08	90
Copper	Smear of copper stearate	0.08	94
Steel	Smear of lauric acid	0.10	120
Steel	Smear of stearic acid	0.08	140
Zinc	1% lauric acid in paraffin	0.05	130
Zinc	Smear of zinc laurate	0.05	120
	B. Unreactive		
Glass	1% lauric acid in paraffin	0.3	20
Platinum	1% lauric acid in paraffin	0.25	20
Platinum	Smear of copper laurate	0.10	100
Platinum	Smear of copper stearate	0.10	110
Platinum	Smear of zinc laurate	0.10	130

It must be emphasized that the actual values that are obtained also depend on the load between the surfaces and on the speed at which they are sliding past each other.

Provided the motion between the surfaces is smooth and stick–slip does not occur, the general effect of increasing the load is to increase the frictional force, without significantly increasing the coefficient of friction. For example, the coefficient of friction of copper surfaces lubricated with lauric acid remains approximately 0.1 for loads between 10 g. and 4 kg. However, at loads below 10 g., there is a marked deviation from Amonton's law, and at 0.01 g. the coefficient of friction is 0.5 (143), *i.e.*, close to that of unlubricated surfaces. This exceptional behavior has been ascribed to the fact that at very small loads there is so little deformation of the metal surfaces that all that is being measured is the work of adhesion between CH$_2$ groups in the hydrocarbon portions of neighboring soap molecules.

It has been shown (144) that the coefficient of friction of platinum surfaces, lubricated with a monolayer of stearic acid deposited from a cetane solution, is about 0.5 at loads below 1 g., falling to 0.25 at higher loads. The electrical contact resistance is then about the same as that observed with unlubricated surfaces, and the results are independent of the metal employed. Similar frictional behavior is observed with surfaces cut from blocks of the solid fatty acids (12), and, at loads greater than 1 g., μ is less than at smaller loads. This is shown in Figures 10 and 11. In general, the longer the chain of the fatty acid, the lower the coefficient of friction. These results are most simply explained by postulating that at low loads the fatty acid molecules are orientated normal to the surface so that sliding is occurring across the ends of the molecules. The sliding surfaces are then about 40 Å. apart, and the electrical resistance between them is high. As the load is increased, however, the absorbed molecules become tilted from the vertical, and the surfaces approach to within about 5 Å. Sliding is now occurring along the molecules themselves, and the electrical resistance falls, owing to conduction occurring by the tunnel effect.

This hypothesis satisfactorily accounts for the difference on lubricated surfaces between the static and kinetic coefficients of friction (19). These are of the magnitudes that would be predicted from the forces that are acting between neighboring CH$_2$ groups in the adsorbed layer of soap.

Turning next to the effect of sliding speed on the coefficient of friction, it is found that as a first approximation, if the motion is smooth, μ hardly changes with sliding speed, in the range 0.001 to 2 cm./sec. But when there is stick–slip motion, the friction at the "stick" decreases quite rapidly with increasing speed, while that at the "slip" hardly alters. This is consistent with the fact that during "slip" the kinetic coefficient of friction is operating, while at the "stick" the static coefficient is involved. The latter is proportional to the time for which the asperities in the moving surfaces are in contact (109) and will therefore be expected to decrease as the sliding speed is increased. But at speeds above 2 cm./sec., it is practically impossible to make generalizations relating to the coefficient of friction of soap films and the speed (51). This is exemplified in the work of Lagarde and Roberts (77) who used a cone and disk apparatus of manganese steel operating at a load of 1 kg. with sliding speeds between 0.2 and 20 cm./sec. Employing paraffinic hydrocarbons, the coefficient of friction falls as the sliding speed is increased. With alcohols, esters, and palmitic acid there is an increase, but with oleic acid there is virtually no change. While both acids presumably react with the surfaces to form iron and manganese soaps, their frictional behavior differs. This indicates that factors such as film mobility, propensity to self-healing, etc., are also relevant.

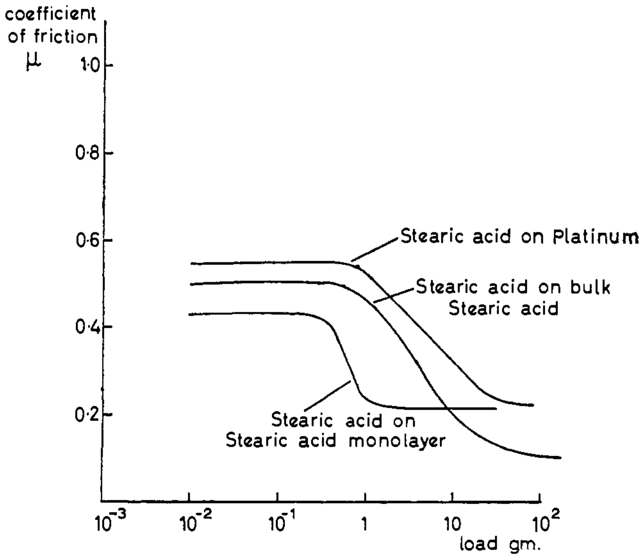

Figure 11.—Effect of load on friction (ref. 12).

Information on the structure and morphology of adsorbed soap films is obtained by electron diffraction studies. Electron reflection (15, 86) provides a general picture of how the adsorbed soap molecules are orientated on the surface. Electron transmission (84, 112) reveals how they are arranged laterally. For the latter it is necessary to vacuum deposit the metal on to a smooth glass surface, chemisorb a soap film on to the metal, and then float it off on to a fine grid for viewing in the electron beam (21). This technique has clearly revealed that the adsorption of fatty acids onto reactive metals like copper and iron is quite different to that on unreactive metals like platinum and silver.

A melt retracted monolayer of octacosanoic acid (C$_{27}$H$_{55}$COOH) on silver gives three diffraction rings corresponding to Bragg spacings of 4.13, 4.5, and 3.8 Å. (12). The first varies in intensity from experiment to experiment, is sometimes spotted, disappears on heating to about 75°, and does not reappear on cooling. Since a spacing of 4.13 Å. corresponds to the 110 planes of the acid in bulk, it seems very probable that this inner ring arises from minute crystals of acid which are deposited on the surface of the monolayer.

The 4.5- and 3.8-Å. rings are probably from the 110 and 200 planes of a face-centered rectangular array corresponding to the lateral arrangement of the acid chains on the surface of the metal. The molecules appear to be in the form of surface micelles (103) having a cross-sectional diameter of about 200 Å., and the chains are tilted from the vertical to give a corn shock structure (46).

On copper and iron substrates, by contrast, there is only a single broad halo extending from 3.9 to 4.3 Å. This shift to lower Bragg spacings is due to the formation of a soap film in which the hydrocarbon chains can pack closely together as in the bulk phase. But on raising the temperature, the Bragg spacing of the octacosanoate soap halo increases to an upper value of 4.5 Å. and disappears at about 130°. This corresponds to the softening point of the metal soap that has been formed.

The ability of adsorbed soap films to resist abrasion and wear has been extensively investigated since it is a subject of considerable practical importance in engineering. As generalizations the rate of wear is: (a) independent of the sliding speed in the range of 0.001 to 1 cm./sec.; (b) inversely proportional to the thickness of the lubricant film (61, 63, 146); and (c) independent of the coefficient of friction between the surfaces. There are a number of factors which may complicate the issue. For example, it has been found (50) that at moderate speeds, the higher the speed, the higher the temperature at which a boundary film remains effective, presumably because quasi-hydrodynamic lubrication occurs. Again, during sliding, metal surfaces are deformed and the severity of the deformation determines the minimum thickness of the boundary film required for effective lubrication (67). This is because of the rheological and mechanical properties of the films. The fact that under certain circumstances soap films are abraded more rapidly than nonpolar films (77) has been ascribed to their lack of mobility on a surface.

Measured on water, the viscosities of calcium, silver, and nickel and other soap films exceed those of the corresponding acids by a factor of 10^4 or more (134). Although the films have high shear strengths (5, 110, 142), they are ruptured by asperities in the moving surfaces and are unable to flow out sufficiently rapidly to produce self-healing.

Films consisting of perfluorinated soaps are resistant to abrasion and continue to provide effective lubrication up to temperatures as high as 250° (31), though on unreactive surfaces, the perfluoro acids tend to be less effective than the corresponding fatty acids in reducing the coefficient of friction. This is believed to be associated with their larger cross-sectional area at close packing—25 Å.^{2}/molecule in contrast to 21 Å.^{2}/molecule.

Chains of CF_2 containing n carbon atoms are roughly equivalent in their crystallinity and other properties to CH_2 chains containing $2n$ carbon atoms (30, 99). Since the abrasion resistance is directly proportional to the crystallinity of the film (146), a perfluorinated acid containing n carbon atoms would be expected to have approximately the same abrasion resistance as a fatty acid with $2n$ carbon atoms and this appears to be the case.

C. LUBRICATION OF POWDERS

The presence of an adsorbed soap film on the particles in a powder affects its dustiness, its sliding and flow properties, and the ease with which it can be compacted into tablets or pellets.

1. *Dustiness*

Considering dustiness first, at low relative humidities, the tendency of a material such as calcium carbonate to form a dust cloud is hardly affected by the adsorption of branched-chain fatty acids or perfluoro acids onto the particles (47). However, at relative humidities in the region of 50%, quite large effects are produced. The dustiness increases with the concentration of the chemisorbed calcium soap up to the completion of a monolayer. Perfluoro and branched-chain soaps produce more dustiness than the corresponding straight-chain soaps, and there is maximum dustiness with the hexanoate. These effects are ascribed partly to dipole repulsions and partly to the reduction in the cohesional energy between particles brought about by the presence of the adsorbed soap molecules.

2. *Flow Properties*

Aluminium, lithium, magnesium, and zinc stearates tend to be adsorbed onto the surfaces of other powders forming films which affect the flow and adhesive properties. While nothing has apparently been reported on the effects produced on the angles of friction (52) or angles of repose (102) of the powders, their flowability (14) may either increase or decrease depending on the nature and quantity of the soap employed. For example, zinc and magnesium stearates increase the adhesion of face and talcum powders to the skin (115), but aluminium stearate apparently forms a lubricating coating over the balls used for milling cement clinker and increases the efficiency of the milling process by preventing the balls from becoming cushioned with fines (114).

3. *Compaction*

Regarding the effect that metal soaps have on the compaction properties of powders, stearates are used as lubricants in powder metallurgy, in the extrusion

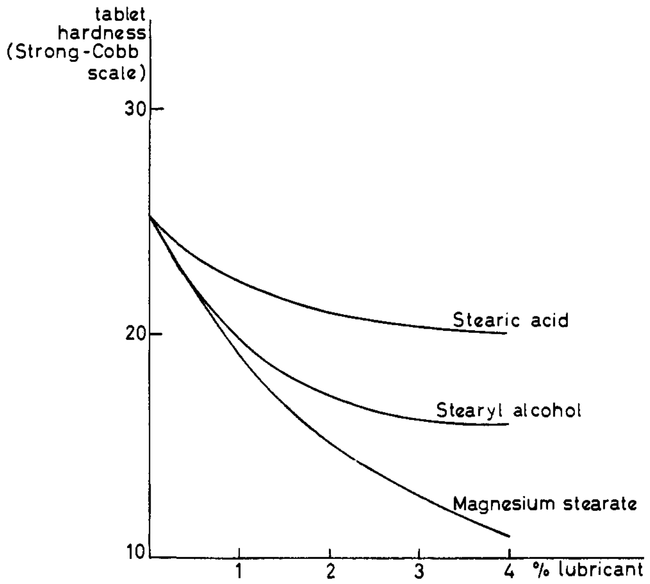

Figure 12.—Tablet hardness *vs.* percentage lubricant for sulfathiazole (ref. 126).

of plastics, and in the tableting of pharmaceutical products. Although in the latter case their function is to reduce the force needed to form the compact, they may also cause changes in its hardness, crushing strength, and disintegration time, all of which are important in practice.

In order to estimate the magnitude of the forces developed during a tablet-making process, measurements of thrust are made at the upper and lower punches of the machine, and the force required to eject the tablet is also measured. The forces are reduced in the presence of a lubricant; some typical results obtained during the tableting of sulfathiazole are given in Table VI (90).

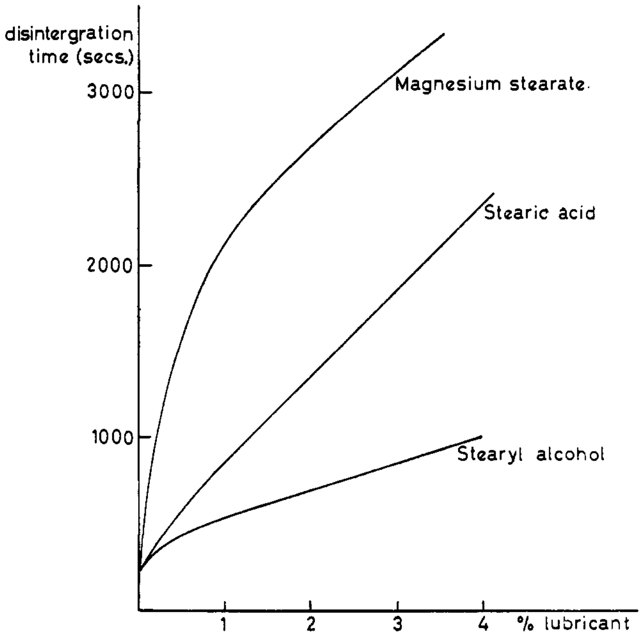

Figure 13.—Disintegration time *vs.* % lubricant for sodium bicarbonate (ref. 126).

TABLE VI

EFFECT OF LUBRICANTS ON COMPACTION OF SULFATHIAZOLE

Lubricant Type	Lubricant Amount, %	Max. force on upper punch, kg.	Ejection force, kg.	Max. force on lower punch/ max. force on upper punch, kg.
None (control)	0	1300	220	0.63
Ca stearate	0.5	1010	10	0.96
Ca stearate	2.0	995	10	0.99
Na stearate	0.5	1080	40	0.86
Na stearate	2.0	1010	20	0.96
Spermaceti	0.5	1350	160	0.56
Spermaceti	2.0	1200	120	0.68
Carbowax 4000	0.5	1140	90	0.76
Carbowax 4000	2.0	1170	100	0.74
Boric acid	0.5	1215	80	0.81
Boric acid	2.0	1200	100	0.78
Mg stearate	0.5	1125	40	0.82
Mg stearate	2.0	1080	10	0.87
Zn stearate	0.5	1080	20	0.87
Zn stearate	2.0	1080	20	0.88
Talc	0.5	1330	220	0.60
Talc	2.0	1235	150	0.67

From Table VI it is seen that the metal soaps are more effective as lubricants than most of the other materials investigated. Measurements of this sort permit an estimate to be made of the minimum useful concentration of lubricants for a particular powder: considering the mixture of sulfathiazole, starch, and sodium bicarbonate, between 0.5 and 1% of sodium, calcium, zinc, and magnesium stearates are sufficient to produce maximum lubrication. The soaps appear to concentrate on the surfaces and in the intergranular regions of the tablets. They tend to decrease their hardness and increase their disintegration times. This is shown in Figures 12 and 13 (126).

Similar effects are produced with a wide variety of other materials (121), *e.g.*, sucrose, hexamine, aspirin, and sodium chloride. In almost all cases the lubricant causes a decrease in the crushing strength of the tablet, the reduction being greatest for the crystalline materials (Figure 14 and Table VII), but provided the lubricant particles are less than 400 μ in diameter,

TABLE VII

EFFECT OF LUBRICANT ON CRUSHING STRENGTH

Material, 30–40 mesh	Crushing strength, kg. Un-lubricated	Crushing strength, kg. Lubricated	Reduction in strength, %
Sucroes	2.8	1.4	50.0
Sucrose, granulated	4.9	4.0	18.4
Hexamine	5.4	1.3	76.0
Hexamine, granulated	14.6	10.5	28.1
Aspirin	3.6	2.7	25.0
NaCl (40–60 mesh)	9.1	2.6	71.4

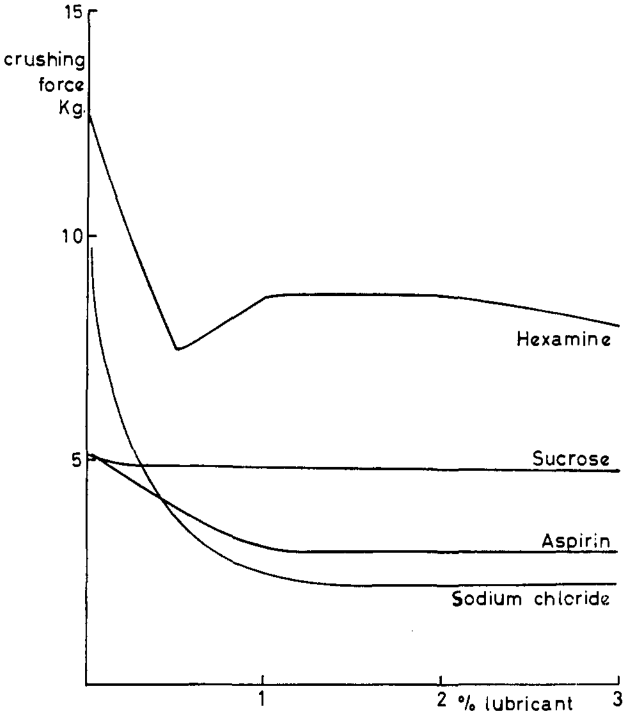

Figure 14.—Crushing force *vs.* % lubricant (ref. 121).

their size appears to have little effect on the tablets' crushing strengths.

On the basis of a limited amount of work it seems that both hydrodynamic and boundary lubrication are involved when metal soaps are being employed in the tableting of powders. But more work is needed to establish how much of their effect is due to interparticle lubrication and how much to lubrication between the powder as a whole and the punches and dies of the machines.

V. REFERENCES

(1) Abramson, M. B., and Ottewill, R. H., *J. Colloid Sci.*, **17**, 883 (1962).

(2) Agar, G. E., Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1961.

(3) Anderson, P. J., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 67 (1957).

(4) Anderson, P. J., *Trans. Faraday Soc.*, **54**, 130 (1958).

(5) Bailey, A. I., and Courtney Pratt, J. S., *Proc. Roy. Soc.* (London), **A227**, 500 (1955).

(6) Bailey, R., and Gray, V. R., *J. Appl. Chem.*, **8**, 197 (1958).

(7) Barr, J., and Dickinson, H. O., *J. Phot. Sci.*, **9**, 222 (1961); *Chem. Abstr.*, **55**, 21923*b* (1961).

(8) Bernal, J. D., *Trans. Inst. Chem. Engrs.* (London), **38**, 319 (1960).

(9) Bondi, A., "Physical Chemistry of Lubricating Oils," Reinhold Publishing Corp., New York, N. Y., 1951.

(10) Bowden, F. P., Gregory, J. N., and Tabor, D., *Nature*, **156**, 96 (1945).

(11) Bowden, F. P., and Moore, A. C., *Trans. Faraday Soc.*, **47**, 900 (1951).

(12) Bowden, F. P., and Tabor, D., "Friction and Lubrication of Solids," Vol. 1 and 2, Clarendon Press, Oxford, 1958, 1964.

(13) Bowman, A., and Hughes, W., *J. Oil Colour Chemists' Assoc.*, **34**, 412 (1951).

(14) Brown, R. L., and Richards, J. C., *Trans. Inst. Chem. Engrs.* (London), **38**, 243 (1960).

(15) Brummage, K. G., *Proc. Roy. Soc.* (London), **A188**, 414 (1947); **A191**, 243 (1947).

(16) Buckenham, M. H., and Mackenzie, J. M. W., *Trans. AIME*, **220**, 450 (1961).

(17) Burkin, A. R., and Halsey, G., *Nature*, **191**, 348 (1961).

(18) Bushell, C. H. G., and Krauss, C. J., *Can. Mining Met. Bull.*, **55**, 314 (1962).

(19) Cameron, A., *ASLE* (Am. Soc. Lubrication Engrs.) *Trans.*, **2**, 195 (1960); *Chem. Abstr.*, **55**, 6090*c* (1961).

(20) Carr, W., *J. Oil Colour Chemists' Assoc.*, **45**, 28 (1962).

(21) Chapman, J. A., and Tabor, D., *Proc. Roy. Soc.* (London), **A242**, 96 (1957).

(22) Chester, V. E., "Aspects of Yeast Flocculation," presented at the Symposium on Surface Activity, Society of Chemical Industry, London, Sept. 24–25, 1964.

(23) Cook, M. A., and Wadsworth, M. E., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 228 (1957).

(24) Cooke, S. R. B., Iwasaki, I., and Choi, H. S., *Trans. AIME*, **214**, 1 (1959).

(25) Cooke, S. R. B., Iwasaki, I., and Choi, H. S., *Trans. AIME*, **217**, 76, 237 (1960).

(26) Cooke, S. R. B., and Nummela, W., *U. S. Bur. Mines, Rept. Invest.*, 5498 (1959).

(27) Crook, A. W., *Phil. Trans. Roy. Soc.* (London), **A250**, 387 (1958).

(28) Crowl, V. T., *J. Oil. Colour Chemists' Assoc.*, **46**, 169 (1963).

(29) Cuming, B. D., and Schulman, J. H., *Australian J. Chem.*, **12**, 413 (1958).

(30) Davies, J. T., and Rideal, E. K., "Interfacial Phenomena," Academic Press, London, 1961, Chapters 4 and 8.

(31) Deacon, R. F., and Tabor, D., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 559 (1957).

(32) De Boer, J. H., Hamaker, H. C., and Verwey, E. J. W., *Rec. trav. chim.*, **58**, 662 (1939).

(33) Derjaguin, B. V., *Nature*, **138**, 330 (1936).

(34) Derjaguin, B. V., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **1**, 477 (1957).

(35) Derjaguin, B. V., and Dukhin, S. S., *Bull. Inst. Mining Met.*, **70**, 221 (1961).

(36) Derjaguin, B. V., and Landau, L. D., *Acta Physicochim. URSS*, 14, 633 (1941).

(37) Derjaguin, B. V., and Landau, L. D., *Zh. Eksperim. i Teor. Fiz.*, **11**, 802 (1941); **15**, 662 (1945).

(38) Derjaguin, B. V., and Shukakidse, N. D., *Bull. Inst. Mining Met.*, **70**, 569 (1961); *Chem. Abstr.*, **55**, 22008*c* (1961).

(39) Derjaguin, B. V., and Tityevskaya, A. S., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **1**, 211 (1957).

(40) Durham, K., *J. Appl. Chem.*, **5**, 686 (1955).

(41) Durham, K., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **4**, 60 (1957).

(42) Du Rietz, C., "Progress in Mineral Dressing," Almqvist and Wiksell, Stockholm, 1957, p. 417.

(43) Eberhardt, E., and Mehliss, G., *Z. Chem.*, 248 (1961).

(44) Eigeles, M. A., "Progress in Mineral Dressing," Almqvist and Wiksell, Stockholm, 1957, p. 591.

(45) Elton, G. A. H., and Smith, H. M., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 379 (1957).

(46) Epstein, H. T., *J. Phys. Chem.*, **54**, 1053 (1950).

(47) Evans, H. C., Shelton, A., and Winsor, P. A., Paper B/111 14, presented at the 4th International Congress on Surface Activity, Brussels, 1964.

(48) Falconer, S. A., *Trans. AIME*, **217**, 207 (1960).
(49) Fava, A., and Eyring, H., *J. Phys. Chem.*, **60**, 890 (1956).
(50) Fein, R. S., Rowe, C. N., and Kreuz, K. L., *ASLE* (Am Soc. Lubrication Engrs.) *Trans.*, **2**, 50 (1959).
(51) Forrester, P. G., *Proc. Roy. Soc.* (London), **A187**, 439 (1946).
(52) Fowler, R. T., and Chodziesner, W. B., *Chem. Eng. Sci.*, **10**, 157 (1959).
(53) Freyberger, W. L., and de Bruyn, P. L., *J. Phys. Chem.*, **61**, 586 (1957).
(54) Fuerstenau, D. W., *Trans. AIME*, **208**, 1365 (1957).
(55) Fuerstenau, D. W., and Modi, H. J., *J. Electrochem. Soc.*, **106**, 336 (1959).
(56) Gaudin, A. M., "Flotation," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1957.
(57) Gaudin, A. M., and Fuerstenau, D. W., *Trans. AIME*, **202**, 66, 958 (1955).
(58) Gaudin, A. M., Fuerstenau, D. W., and Mao, G. W., *Trans. AIME*, **214**, 430 (1959).
(59) Gaudin, A. M., Miaw, H. L., and Spedden, H. R., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 202 (1957).
(60) Goldacre, R. J., *Australian J. Appl. Sci.*, **2**, 89 (1951).
(61) Greenhill, E. B., *Trans. Faraday Soc.*, **45**, 631 (1949).
(62) Gregory, J. N., *C.S.I.R.* (Australia), Tribophysics Division Report A, 74 (1943).
(63) Gregory, J. N., and Spink, J. A., *Nature*, **159**, 403 (1947).
(64) Guggenheim, E. A., "Thermodynamics," North Holland, Amsterdam, 1950.
(65) Heller, W., and Pugh, T. L., *J. Chem. Phys.*, **22**, 1778 (1954).
(66) Heller, W., and Pugh, T. L., *J. Chem. Phys.*, **24**, 1107 (1956).
(67) Hirst, W., Kerridge, M., and Lancaster, J. K., *Proc. Roy. Soc.* (London), **A212**, 517 (1952).
(68) Hsi, H., and Clifton, D. F., "Clays and Clay Minerals," Monograph No. 11, Swineford, A., Ed., Pergamon Press, New York, N. Y., 1962, p. 269.
(69) Huber Panu, I., and Pandelescu, C., Paper No. C/VI 6, presented at the 4th International Congress on Surface Activity, Brussels, 1964.
(70) Iwasaki, I., Cooke, S. R. B., and Colombo, A. F., *U. S. Bur. Mines, Rept. Invest.*, 5593 (1960).
(71) Joy, A. S., and Robinson, A. J., "Recent Progress in Surface Science," Vol. 2, Danielli, J. F., Pankhurst, K. G. A., and Riddiford, A. C., Ed., Academic Press, New York, N. Y., 1964, p. 169.
(72) Khainman, V. Y., and Bogdanov, V. I., *Obogasch. Rud*, **6**, No. 6, 27 (1960).
(73) Klassen, V. I., and Starchik, L. P., *Dokl. Akad. Nauk SSSR*, **115**, No. 6, 1129 (1957).
(74) Klassen, V. I., and Tikhonov, S. A., *Soviet J. Non-Ferrous Metals* (English Transl.), No. 10, 4 (1960).
(75) Koelmans, H., and Overbeek, J. Th. G., *Discussions Faraday Soc.*, **18**, 52 (1954).
(76) Kraus, K. A., and Holmberg, R. W., *J. Phys. Chem.*, **58**, 325 (1954).
(77) Lagarde, F., and Roberts, M., *Rev. Inst. Franc. Petrole Ann. Combust. Liquides*, **18**, 782 (1963).
(78) Langmuir, I., *J. Am. Chem. Soc.*, 40, 1361 (1918).
(79) Last, G. A., and Cook, M. A., *J. Phys. Chem.*, **56**, 637 (1952).
(80) Leja, J., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 273 (1957).
(81) Leja, J., and Schulman, J. H., *Mining Eng.*, **6**, 221 (1954).
(82) Mackor, E. L., and van der Waals, J. H., *J. Colloid Sci.*, **7**, 535 (1952).
(83) Martin, A. N., *J. Pharm. Sci.*, **50**, 513 (1961).
(84) Mathieson, R. T., *Nature*, **183**, 1803 (1959).
(85) Meguro, K., *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **58**, 905 (1955).
(86) Menter, J. W., Ph.D. Thesis, Cambridge University, 1949.
(87) Modi, H. J., and Fuerstenau, D. W., *Trans. AIME*, **217**, 381 (1960).
(88) Moeller, A., *Z. Elektrochem.*, **59**, 296, 305 (1955).
(89) Moilliet, J. L., Collie, B., and Black, W., "Surface Activity," E. & F. N. Spon, London, 1961.
(90) Nelson, E., Naqvi, S. M., Busse, L. W., and Higuchi, T., *J. Am. Pharm. Assoc.*, **43**, 596 (1954).
(91) O'Connor, D. J., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, **3**, 319 (1957).
(92) O'Neill, D. K., and Alexander, A. E., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, 4, 218 (1957).
(93) Ottewill, R. H., Rastogi, M. C., and Watanabe, A., *Trans. Faraday Soc.*, **56**, 854 (1960).
(94) Ottewill, R. H., and Watanabe, A., *Kolloid-Z.*, **170**, 38, 132 (1960).
(95) Ottewill, R. H., and Watanabe, A., *Kolloid-Z.*, **171**, 33 (1960).
(96) Ottewill, R. H., and Watanabe, A., *Kolloid-Z.*, **173**, 7, 123 (1960).
(97) Peart, J., and Tabor, D., *C.S.I.R.* (Australia), Tribophysics Division Report A, 99 (1944).
(98) Peck, A. S., *U. S. Bur. Mines Rept.*, 6202 (1963); *Chem. Abstr.*, **58**, 13171*d* (1963).
(99) Pilpel, N., *J. Colloid Sci.*, **9**, 285 (1954).
(100) Pilpel, N., *Research* (London), 14, 319 (1961).
(101) Pilpel, N., *Chem. Rev.*, **63**, 221 (1963).
(102) Pilpel, N., *J. Pharm. Pharmacol.*, **16**, 705 (1964).
(103) Pilpel, N., *Nature*, **204**, 378 (1964).
(104) Plaksin, I. N., *Tsvetn. Metal*, **31**, No. 2, 7 (1958).
(105) Polkin, S. I., *Metallurg. Metallov. Izv. Akad. Nauk SSSR*, 156 (1958).
(106) Polkin, S. I., *Tsvetn. Metal.*, **31**, No. 2, 11 (1958).
(107) Polkin, S. I. "Proceedings of the Institute of Mineral Process Congress, London, 1960, p. 361.
(108) Proceedings of the Conference on Lubrication and Wear, Institute of Mechanical Engineers, London, 1957.
(109) Rabinowicz, E., Wear Symposium, General Motors, Elsevier, New York, N. Y., 1959.
(110) Rabinowicz, E., and Tabor, D., *Proc. Roy. Soc.* (London), **A208**, 455 (1951).
(111) Riddiford, A. C., and Elliott, G. E. P., "Recent Progress in Surface Science," Vol. 2, Danielli, J. F., and Riddiford, A. C., Ed., Academic Press, New York, N. Y., 1964, p. 111.
(112) Ries, H. E., and Kimball, W. A., *Nature*, **181**, 901 (1958).
(113) Robinson, A. J., *Bull. Inst. Mining Met.*, **69**, 45 (1959).
(114) Rose, H. E., and Sullivan, R. M. E., "Ball, Tube and Rod Mills," Constable, London, 1958, Chapter 9.
(115) Sagran, E., Ed., "Cosmetics Science and Technology," Interscience, New York, N. Y., 1957.
(116) Schulman, J. H., and Dogan, M. Z., *Discussions Faraday Soc.*, **16**, 158 (1954).
(117) Schulman, J. H., and Leja, J., *Trans. Faraday Soc.*, **50**, 598 (1954).
(118) Schulman, J. H., and Smith, T. D., "Recent Developments in Mineral Dressing," Institute of Mining and Metallurgy, 1953, p. 393.
(119) Schwartz, A. M., and Perry, J. W., "Surface Active Agents," Vol. 1 and 2, Interscience, New York, N. Y., 1949, 1958.
(120) Shooter, K. V., Ph.D. Thesis, University of Cambridge. 1951.

(121) Shotton, E., and Lewis, C. J., *J. Pharm. Pharmacol.*, **16**, 111T (1964).

(122) Sollenberger, C. L., and Greenwalt, R. B., *Trans. AIME*, **211**, 691 (1958).

(123) Spink, J. A., and Sanders, J. V., *Trans. Faraday Soc.*, **51**, 1154 (1955).

(124) Spurny, J., and Dobias, R., *Proc. Intern. Congr. Surface Activity, 3rd, Cologne, 1960*, 4, 421 (1960).

(125) Stern, O., *Z. Elektrochem.*, **30**, 508 (1924).

(126) Strickland, W. A., Nelson, E., Busse, L. W., and Higuchi, T., *J. Am. Pharm. Assoc.*, **45**, 51 (1956).

(127) Strickland, W. A., Higuchi, T., and Busse, L. W., *J. Am. Pharm. Assoc.*, **49**, 35 (1960).

(128) Sun, S. C., Snow, P. E., and Purcell, W. I., *Trans. AIME*, **208**, 71 (1957).

(129) Sutherland, L. K., and Wark, I., "Principles of Flotation," Australian Institute of Mining and Metallurgy, Melbourne, 1955.

(130) Tabor, D., *Nature*, **147**, 609 (1941).

(131) Taggart, A. F., "Handbook of Mineral Dressing," John Wiley and Sons, Inc., New York, N. Y., 1947.

(132) Tamamushi, B., and Tamaki, K., *Trans. Faraday Soc.*, **55**, 1007 (1959).

(133) Tingle, E. D., *Nature*, **160**, 710 (1947).

(134) Trapeznikov, A. A., *Proc. Intern. Congr. Surface Activity, 2nd, London, 1957*, 1, 109 (1957).

(135) Van der Minne, J. L., and Hermanie, P. H. J., *J. Colloid Sci.*, **8**, 38 (1953).

(136) Van der Waarden, M., *J. Colloid Sci.*, **5**, 317 (1950)

(137) Van der Waarden, M., *J. Colloid Sci.*, **6**, 443 (1951).

(138) Vand, V., *J. Phys. Colloid Chem.*, **52**, 314 (1948).

(139) Verwey, E. J. W., and Overbeek, J. Th. G., "Theory of Stability of Lyophobic Colloids," Elsevier, New York, N. Y., 1948.

(140) Vold, R. D., and Phansalkar, A. K., *Rec. trav. chim.*, **74**, 41 (1955).

(141) Weyl, W. A., and Ormsby, W. C., "Rheology, Theory and Application," Vol. 3, Eirich, F. R., Ed., Academic Press, New York, N. Y., 1960, p. 249.

(142) White, J. R., *Lubrication Engr.*, **10**, 340 (1954).

(143) Whitehead, J. R., *Proc. Roy. Soc.* (London), **A201**, 109 (1950).

(144) Wilson, R. W., *Proc. Phys. Soc.* (London), **B68**, 625 (1955).

(145) Wolstenholm, G. A., and Schulman, J. H., *Trans. Faraday Soc.*, **46**, 475, 488 (1950).

(146) Zisman, W. A., "Friction and Wear," Davies, R., Ed., Elsevier, New York, N. Y., 1959, p. 110.