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MECHANISMS OF DETERGENCY

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A lecture delivered before the Society on 16th January 1961.

A number of individual mechanisms contribute to the overall detergency process, e.g. preferential wetting, solubilisation, complex formation or penetration and mechanical action. The extent to which each contributes depends on the nature of the substrate, soiling matter and aqueous phase. In addition, certain specific secondary effects, such as spontaneous emulsification and osmotic swelling may complicate the process. The stability of the final dispersion is a function of the interfacial tension of the final oil phase, the phase condition of the soiling matter, and the magnitude of the double layer zeta potential.

OVER THE past 25 years the understanding of the detergency process has progressed slowly compared with the technological advances in detergent products; nevertheless a fairly clear qualitative picture has even evolved. In this review, the system is considered primarily from the textile point of view. The situation on skin surface will be similar, although possibly somewhat simpler. The particular class of compound to which all the usual detergents belong is that of the paraffin chain salt or condensation product. By virtue of the distinct and separate oleophilic and hydrophilic portions of the molecule such compounds adsorb strongly at all interfaces, lowering the interfacial tension and modifying the double layer zeta potential.

The other property of particular importance in this context is the

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ability of such molecules to aggregate into "micelles" above certain characteristic critical concentrations.

The chemical and physical nature of dirt or soiling matter varies widely and it is not possible to define in any simple fashion. Brown¹ has provided data on the extractable matter in a range of domestic textiles (*Table I*). These may be taken to illustrate a broad principle rather than anything precise and constant.

Table 1

Composition of Soiling Matter

Free fatty acids	31.4%
Triglycerides of fatty acids	29.2%
Saturated and unsaturated fatty alcohols and cholesterol		15.3%
Saturated and unsaturated hydrocarbons	21.0%

Total extractable = 0.75% of dry weight of fabrics

The high percentage of polar material (75.9%) should be borne in mind since this has a marked bearing on the mechanism of detergency to be discussed later. In addition to the oily matter, dirt includes insoluble pigment matter, e.g. carbon, silicates, etc., which is difficult to estimate and little precise work appears to have been done. Finally, traces of water soluble material are present, which, while not constituting a problem in themselves, modify the detergent process to a significant extent.

WETTING OUT

As a preliminary to the true detergency reaction, the detergent solution must come into intimate contact with the surfaces to be cleaned, thereby displacing all air from the surface, and in the case of textiles from the

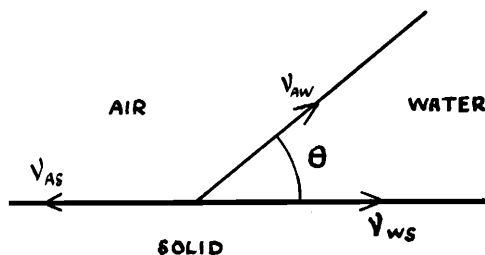


Figure 1

interstices of the fabric and yarns. When a liquid is in contact with a solid surface (*Fig. 1*) the angle of contact θ is defined by the magnitude of the relevant surface or interfacial tensions, and by resolving parallel with the surface one finds

$$\gamma_{AS} = \gamma_{WS} + \gamma_{AW} \cos \theta, \text{ or } \cos \theta = \frac{\gamma_{AS} - \gamma_{WS}}{\gamma_{AW}}$$

Detergent molecules being surface active adsorb at the solution interfaces and the corresponding interfacial tensions are reduced (viz. γ_{ws} and γ_{aw}) so that the third force (γ_{as}) is no longer balanced and the line of contact is pulled forward until a new contact angle is established. In practice, with most detergent solutions on common surfaces $\gamma_{as} > \gamma_{ws} + \gamma_{aw}$ thus $\theta = 0$ and wetting is complete.

REMOVAL OF SOILING MATTER

One of the early theories of detergency, attributed to Berzelius, stated that fatty material was removed by saponification caused by the free (hydrolytic) alkali in a soap solution. This is readily disproved by the efficiency of synthetic non-hydrolysing detergents which can act under neutral conditions.

In 1937, Adam² published his work on the "rolling up" process which formed the first major milestone in the understanding of detergent action. The action is basically similar to wetting out except that the phases are exchanged (*Fig. 2*). Here again at the line of intersection between the solid surface and the oil/water interface, the angle of contact θ is defined by resolving the forces parallel to the solid surface such that

$$\begin{aligned} \gamma_{os} &= \gamma_{ws} - \gamma \text{ and } \text{Cos } \theta \\ \text{thus } \text{Cos } \theta &= \frac{\gamma_{ws} - \gamma_{os}}{\gamma_{ow}} \end{aligned}$$

The adsorption of detergent on to the solution interfaces again lowers the relevant interface tensions so that the unbalanced γ_{os} is able to constrict the base of the oil drop progressively as shown in *Fig. 2*.

The equilibrium contact angle is a function of all the phases present. In general, the more polar the solid and oil the greater the contact angle. This is illustrated by taking a series⁸ of filaments ranging from P.T.F.E., through polythene, terylene, nylon, wool and on to cotton. Likewise a pure hydrocarbon mineral oil is extremely difficult to remove from the less polar fibres, although blends with polar oils overcome this difficulty. In the non-polar systems the oil/solid interfacial free energy is so low that it remains below the figure attainable by most detergents at the aqueous/solid interface. One prime requisite for the rolling up process is that the fatty material shall be fluid. This is obvious from the nature of the process, and is illustrated by washing studies with waxy soiling matter, where one finds a threshold temperature for detergency at the melting point of the wax. In many practical examples it is found that the oily soiling matter rolls up to a complete sphere with a contact angle of 180° whereupon the oil becomes detached and floats away under its own buoyancy. If the detergent solution, however, is in motion, viscous drag will distort the

drops and remove them before the contact angle reaches its ultimate value. With very small oil drops (approaching 1μ) Brownian movement cannot be entirely ruled out as an assisting force.

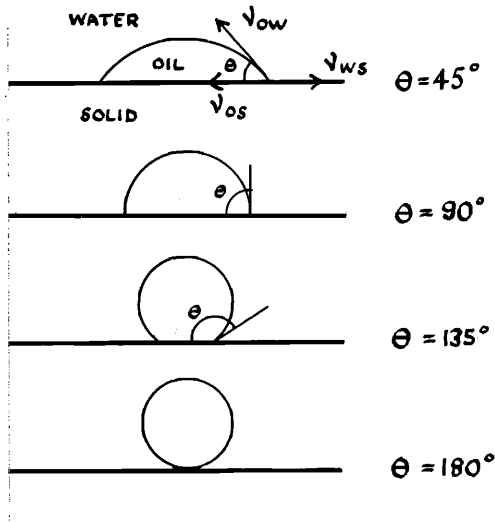


Figure 2

SOLUBILIZATION

Under certain conditions, oils and oil soluble material are rendered soluble in aqueous media by the action of surface active agents. In the form first discovered it was shown that hydrocarbons such as heptane were incorporated into the interior of the detergent micelle and in effect appeared to "dissolve" in the hydrocarbon tail core of such micelles. McBain⁵ considered this to be a promising explanation for the efficiency of detergents in removing oils. At the time, however, there were many arguments against such an explanation.

More recently a second type of solubilization has been defined whereby polar long chain, oil soluble matter (e.g. fatty acids and alcohols) are adsorbed into the "palisade" region of the micelle, to be aligned with the molecules of detergent.

Finally, of course, both types can operate simultaneously, and the presence of one type of solute in such cases increases the solubility of the other. The amount of material which will dissolve in a detergent is of an order which would correspond to an appreciable proportion of the soiling matter usually present, providing the detergent is reasonably well above the critical micellar concentration.

Solubilization is a property of detergent micelles and commences only at the critical micellar concentration. Detergent efficiency, however, rises steadily from far lower levels, and tends to level off at the critical micellar concentration. Commercial wash liquors often run very close to this value. As Preston⁶ has concluded, this would appear to relegate solubilization to a rather minor role in detergency processes.

This aspect has, however, been affected by the discovery of the penetration processes described below. It is possible that, particularly with polar fatty matter, solubilization may be a final state after intermediate processes.

COMPLEX FORMATION

Mixed Adsorbed Films

It has been known for some time⁷ that where an oil soluble surface active material is present in a system in addition to the water soluble detergent, far lower interfacial tensions are attained than would be possible with either component alone. Oil soluble surface active materials include long chain polar compounds such as fatty alcohols, fatty acids, and indeed amines, mercaptans, etc. Such material may be present within the oil phase or "solubilised" in the aqueous phase. The benefit derived from blending a polar material into a non-polar mineral oil was recognised several years ago⁸. By adding oleyl alcohol for example, the oil which formerly proved extremely resistant was easily removed. It may be shown by microscopical observation that a solution of sodium oleate (0.2%) will displace mineral oil from a wool fibre. If alkali, however, is added to the solution, the action is inhibited and the soap is then no more effective than an alkyl sulphate detergent. The efficiency of the plain sodium oleate solution is due to the hydrolytic fatty acid which serves as the oil soluble polar compound and facilitates the additional lowering of interfacial tension (to less than 1 dyne/cm) to enable the mineral oil to be displaced. In the same manner as with polar solubilisation, the oil soluble polar component merges with the "palisade" of detergent molecules adsorbed at the solution interfaces and enhance the surface active effect.

PENETRATION

As early as 1941 Kling and Schwerdtner⁹ described an interaction between oleic acid drops and a detergent, and concluded incorrectly that spontaneous emulsification was occurring. In the author's studies¹⁰ it was apparent that the type of action which Kling and Schwerdtner had observed was typical of a wide range of detergent—long chain polar compound (amphiphile) systems, and was in fact an interaction between the two species leading to a liquid crystalline phase. When a crystal of

cholesterol, *Fig. 3*, or of lauric acid, *Fig. 4*, is immersed in sodium laurate, for example, a halo forms round the material which comprises a mass of myelinic figures. This material is gelatinous, as shown in *Fig. 4* in which the original solid drop of lauric acid has become eroded and separated from the fibre, but remains anchored by the complex mass.

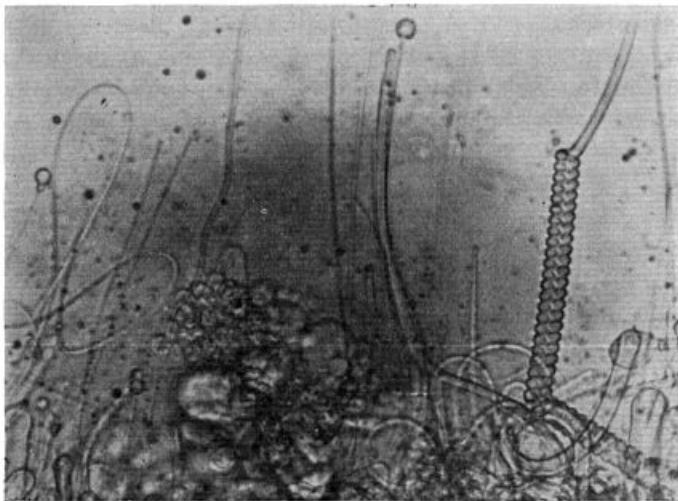


Figure 3

Myelinic figures (cholesterol-1% sodium laurate ; 20 min ; $\times 100$).

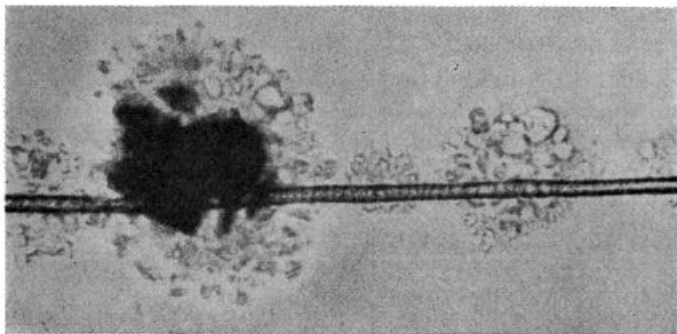


Figure 4

Lauric acid undergoing penetration by 0.5% sodium laurate ($\times 100$, 5 mins, 25°C.).

More recently, Lawrence¹¹ has obtained phase diagrams and much other data which explain in more precise terms most of the earlier observations. *Fig. 5* shows a typical phase diagram for a water-detergent-amphiphile system : L_1 is the normal soap solution containing solubilised amphiphile

(fatty acid or alcohol). L_2 is the converse, where the amphiphile is the solvent phase and water the solute. In the lower region L_1 and L_2 , the two liquids exist together and would readily emulsify into a conventional emulsion. The region LC is that of the viscous liquid crystalline material. When amphiphilic material is immersed in a detergent solution the composition of the material moves along a tie line, e.g. A—Z and as the material swells, a membrane of liquid crystalline material is formed at the surface of the amphiphile. This membrane slowly dissolves into the detergent (L_1). Lawrence postulates that as the adsorbed soap at the surface is in a condensed state the effective concentration Z is much higher than in the bulk solution. The tie line A—Z will thus be well removed from the AW axis.

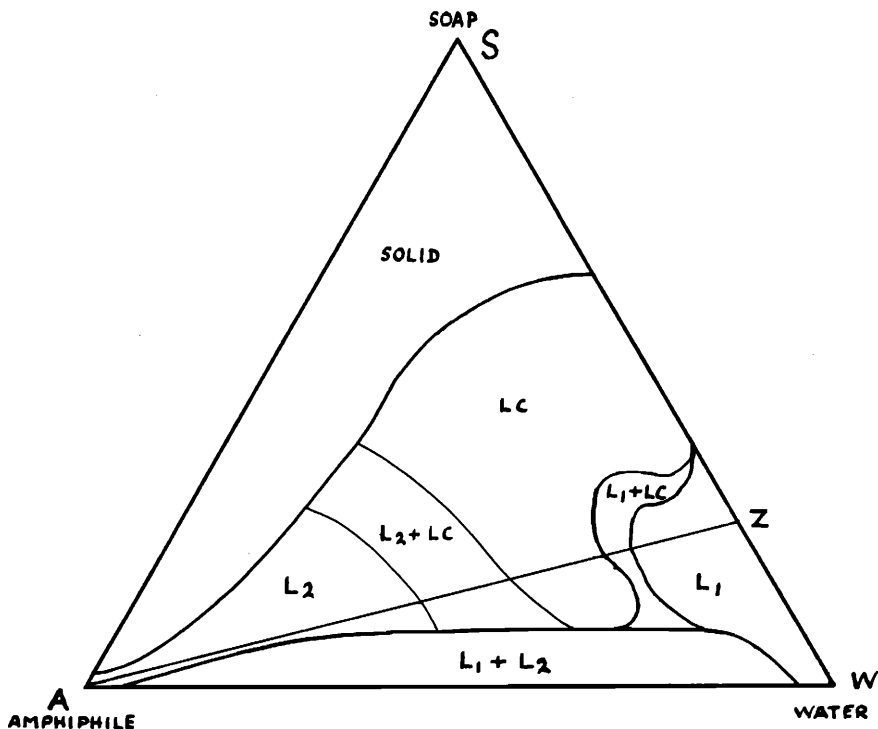


Figure 5

The penetration of polar materials such as alcohols and acids proceeds down to a well-defined threshold temperature, well below the melting point of the compound (10—40°C lower, depending on the detergent). Furthermore, the formation of eutectic mixtures of amphiphiles is reflected by a corresponding lowering of the penetration threshold temperature. Whereas the simple “rolling up” mechanism of detergency relies on the fatty matter

being fluid, penetration by detergent will remove such matter well below the melting point. At higher temperatures, the liquid crystalline phase becomes increasingly soluble and an upper consolute temperature is observed. In some cases, however, this is above 100°C. Microscopical studies of detergency process lend strong support to the view that in the large majority of practical cases penetration plays a major role in detergency. The presence of amphiphilic material is certainly well illustrated by Brown's data given above. However, such microscopical studies do not support Lawrence's assertion that cryoscopic forces are the *only* mechanism in detergency.

SPONTANEOUS EMULSIFICATION

Where the soiling matter is not entirely amphiphilic but contains hydrocarbons, esters, and less surface active material of an oleophilic nature in admixture, spontaneous emulsification occurs on contact with a detergent solution. Drops of oily material greater than 15–20 μ diameter tend to develop gelatinous "atmospheres" which contain a dispersion of droplets in the 1–5 μ range. This process is distinct from the spontaneous emulsification of oil blends containing free fatty acid when added to alkaline solutions. Observed under the microscope, the latter appears as a vigorous reaction when the surface of the oil phase violently convulses as neutralisation proceeds. The former is a quiescent process where the droplets merely "grow" in the gelatinous atmosphere. The quiescent emulsification may be explained readily by reference to Lawrence's phase diagram (*Fig. 5*). Mineral oil, etc., will be readily soluble in the amphiphile and in the amphiphile-rich liquid L_2 . It is probable that the solubility in the liquid crystalline phase will be somewhat less, and very much less in the detergent solution L_1 . Thus as the amphiphile mixture is penetrated and the phase change occurs, the non-polar oil is precipitated. This action is clearly illustrated in *Fig. 6*, in which the precipitated oil drops are held within the smaller complex atmosphere.

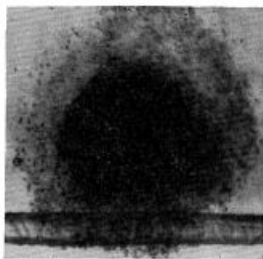


Figure 6

Removal and emulsification of a large drop of natural soil from wool, in 0.2% sodium oleate (2 min; $\times 150$).

NON-IONIC DETERGENT ACTION

The behaviour of non-ionic detergents differs in that the penetration and solubilising power appears to be even greater than their ionic counterparts. This may be expected from their non-ionic nature which renders them appreciably soluble in hydrocarbons as well as in water. Spontaneous emulsification of oil blends is replaced by direct penetration and solubilization, the detergent acting as a co-solvent. Small 5μ drops of, for example, a 25% oleic acid in mineral oil will be observed one moment and then suddenly disappears in a "puff". Larger droplets (20μ) leave the surface under the action of their own buoyancy (*Fig. 7*) before disappearing in a similar manner. (The surface tension of the drop shown is estimated to

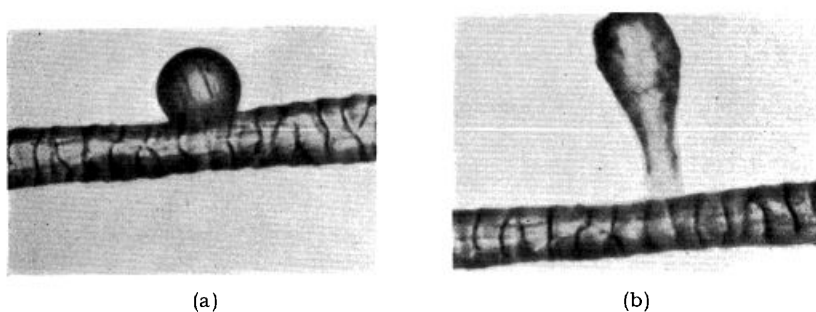


Figure 7

Removal of a 3 : 1 mixture of *Nujol* and oleic acid from wool by a 0.2% non-ionic detergent solution ($\times 300$).

(a) 30 sec.

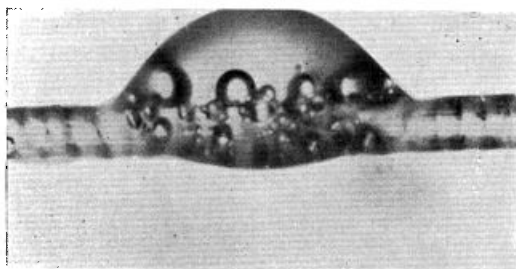
(b) $3\frac{1}{2}$ min.

be as low as 10^{-3} dyne/cm.) It appears that in this system the detergent being oil soluble penetrates the oil phase, and finally renders the oil mixture water soluble. The finite time of consolution is due to diffusion across the interface, thus the time required for disappearance is proportional to the volume/surface area ratio (which is in turn proportional to the radius).

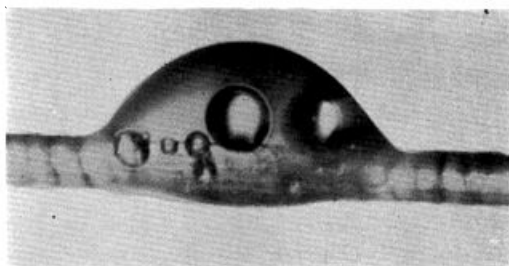
OSMOTIC EFFECTS

In most practical examples, soiled surfaces are contaminated with a finite amount of water soluble matter in addition to fatty and pigment soiling. On immersion, conditions exist for osmotic flow of water through the surface and through the oil. *Fig. 8* illustrates the simplest form of the action. In this example the wool was well impregnated with the sweat (suint) salts of the sheep although all the fatty matter had been extracted. On immersion, the uncovered areas of the fibre admit water which swells the fibre in the usual manner. The water then penetrates along the fibre

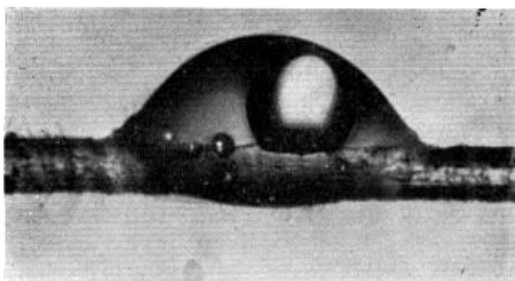
under the oil drops and saline matter present causes a positive osmotic pressure forcing droplets of water out into the oil¹². Immersion in a strong salt solution causes the aqueous droplets to disappear by reversing the osmotic gradients. The process is infinitely reversible. Very thorough aqueous extraction of the wool eliminates the effect.



(a) 1 hour.



(b) 48 hours.



(c) 7 days.

Figure 8

Aqueous droplets within a mineral oil drop on a saline wool fibre in distilled water ($\times 300$).

Under conditions where penetration of the soiling matter can occur, the gelatinous liquid crystalline phase swells to a remarkable degree under the influence of this osmotic action, reaching a diameter many times that of the fibre itself. *Figs. 9 and 10* illustrate this type of process. The action

in *Fig. 10* is further complicated by the deposition of acid soap complex due to the low pH of the sweat salts contained in the wool. In this sequence, no rolling up can be observed but rather a slow penetration, emulsification

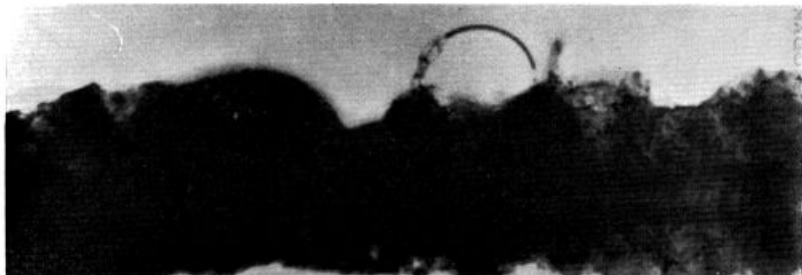


Figure 9

Osmotically inflated oil (liq. paraffin-oleic acid mixture) on wool fibre in 0.02% sodium oleate ($\times 300$). (This is in effect a coating of a water-in-oil emulsion.)

and dispersion of the soiling matter. The addition of alkali will neutralise the free fatty acid component to these complex envelopes and reduce their extent, but the fatty alcohol and sterol complexes will not be affected.

MECHANICAL ACTION

To most people the word "washing" conjures up a picture involving some form of motion. It is not difficult to visualise the need for agitation, in order to assist diffusion processes, e.g. the migration of detergent to the soiled surface and reverse migration of dirt away from the surface into the bulk solution. In particular, the viscous drag of a flow of liquid past an oil drop can cause detachment before the contact angle reaches 180° and likewise can assist the breakdown and dissolution of liquid crystalline complex gel.

In most cases, particulate or pigment dirt appears to be bound to the substrate by wetting forces, e.g. by grease films. The removal of such dirt is then governed by the removal of the fatty binder. In some cases, however, the pigment is attached direct to the surface by mechanical imprisonment (micro-occlusion) or by the normal Van der Waals London forces. In these cases, a direct mechanical force is necessary to move the soiling matter. High velocity water jets minimise the thickness of the "stagnant" layer at the surface, but due to viscous forces the velocity of the detergent at the actual surface always approaches zero. Thus it is found very difficult to achieve the same degree of cleaning by violent agitation of a fluid bath, as can be achieved by a direct wipe over with a cloth. In the latter case the two surfaces are in direct contact, and soiling particles are physically pushed from the surface.

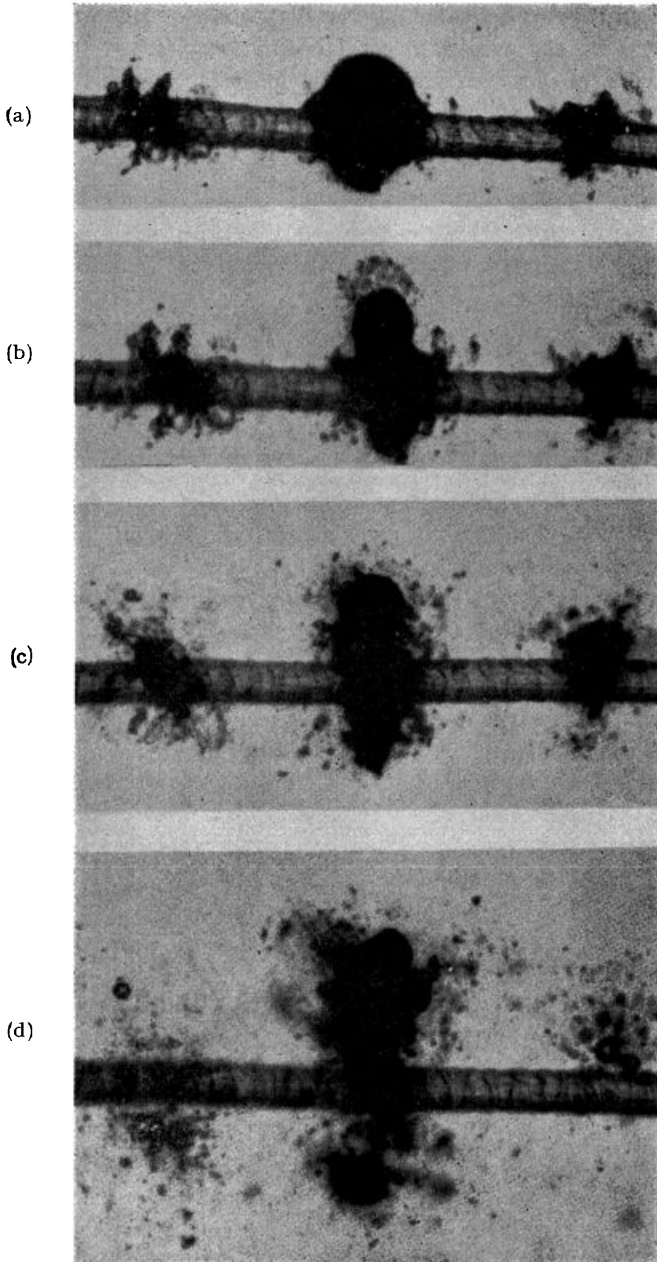


Figure 10

Removal and emulsification of a 3 : 1 mixture of Oildag and oleic acid from a naturally saline wool fibre, in 0.2% sodium oleate ($\times 300$).

(a) 1 min (b) 2 min (c) 10 min (d) 30 min

SUSPENDING ACTION

This factor is of vital importance in laundering, and in textile processing in general, where detergent liquors are operated close to the economic limit. It is frequently found that a detergent will remove the dirt but will subsequently allow a portion to be re-adsorbed on to the surface. In serious cases this may be due to loss of detergent by adsorption and absorption by the surface being cleaned, within the material being cleaned (*cf.* the high ion exchange capacity of wool and human hair), and by the dirt (both surface adsorption and complex formation). If sufficient detergent is present to overcome such losses, polar soiling matter, such as fatty acids and alcohols, will finally be effectively solubilised or held within a complex phase. Much non-polar material (e.g. mineral oil) will be removed by the rolling-up process, spontaneously emulsified, etc., when in admixture with polar oils and fats. Later on, such polar material may separate from the oil phase into the aqueous phase by preferential solubilization, or in the case of fatty acids in contact with alkaline detergent solutions, by neutralisation. This will leave the oil drop in a condition to rewet any suitable surface with which it may collide. Pigment or particulate soiling matter, as already mentioned, is often held by wetting forces arising from greasy and oily matter and the detergency processes are essentially those of the oily phase. However, just as this phase is removed from the substrate, so it is also removed from the pigment and the final detergent liquor will comprise an emulsion of oil droplets, a solution of solubilized polar oil plus some non-polar oil, a dispersion of some complex material, and finally, a dispersion of pigment matter. The latter will be free to re-adsorb on to any surface with which it collides with sufficient vigour.

DEFLOCCULATION

The ability of a detergent to maintain dirt in suspension is usually gauged in terms of its performance with respect to pigment matter. The over-riding factor controlling this is the zeta potential of the surfaces of the substrate and dirt. (An additional factor is considered by some to be deposition of a "protective colloid" film of finite thickness, acting as a barrier between the dirt particle and the substrate). As detergent molecules adsorb onto a surface, the zeta potential of the double layer changes according to the nature of the adsorbing species. Organic surfaces are inherently negative in charge, possibly due to stray carboxyl groups, over a wide range of pH values. Anionic detergents increase this charge to a marked extent¹³, whereas cationic surface active agents reduce and then reverse the charge. Non-ionic detergents are similar to, although not as effective as, anionic detergents (due to dipole orientation). The formation of a strong zeta potential at the surfaces in contact with the detergent solution

acts as a repulsive barrier and restrains the redeposition of the pigment matter. However, if the two surfaces approach to within a certain distance by direct force or by virtue of an activation in the Arrhenius sense during normal Brownian motion, the double layer barrier will be passed and the particle will adsorb on to the surface by London attraction. (Kruyt¹⁴ describes this type of system in considerable detail.) Mechanical agitation as well as assisting removal of dirt also tends to assist this type of redeposition by increasing the collision rate (*cf.* butter-churning).

The presence of non-surface active ions tends to reduce the zeta potential and lower the suspending power of a detergent. Likewise, increased temperature increases the water affinity of the surface active species, lowers the adsorption, and consequently the surface potential, quite apart from increasing the vigour of Brownian motion.

FOAM

Lastly, some reference must be made in the context in which this paper is published, to the effect of foam or lather in detergency. McBain¹⁵ once wrote that "soap and beer are popularly appraised by the amount and stability of the foam they produce". Unfortunately, it is now fairly well agreed that foam plays a very minor role indeed. One can add tributyl phosphate to soap to kill the foam (or indeed many immiscible liquids or emulsions¹⁶) without impairing its efficiency as a detergent. Conversely saponin, which foams well, has little detergency. Niven¹⁷ has attempted to draw an analogy between the froth flotation process for separating minerals and the action of foam. (In this process mineral particles adhere, due to imperfect wetting, to air bubbles and are carried to the surface.)

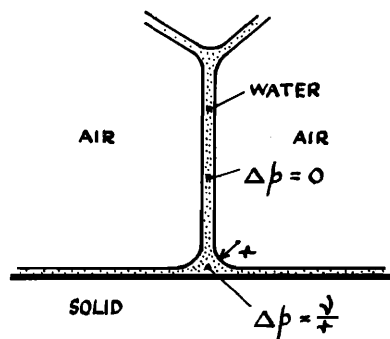
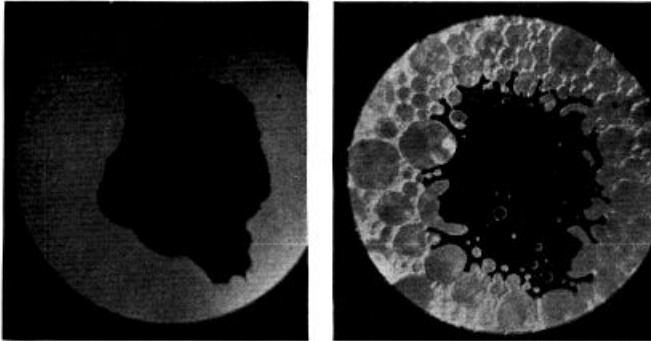


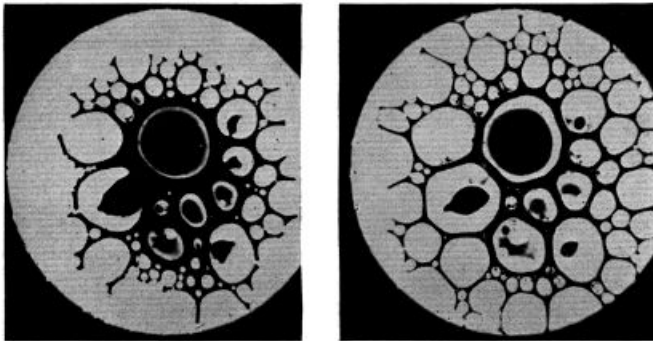
Figure 11

However, this process relies on the use of additives to make the mineral surface *hydrophobic*, whereas detergents have the opposite effect and above the critical micellar concentration¹⁸ the contact angle usually becomes zero,

i.e. wetting is perfect. Only one effect has so far been recorded¹⁹ whereby foam exerts a specific action. Physically, foam consists of a large number of lamellae or sheets of liquid phase which bind the individual bubbles. The regions where such lamellae intersect are known as plateau borders (*Fig. 11*). In the centre of the lamellae the surfaces are effectively parallel and the internal pressure is essentially the same as in the adjacent air cell. At the intersection the surface is cylindrically curved and consequently a reduction in pressure occurs, equal to γ/r where γ is the surface tension



(a) Oil patch before contact with foam. (b) After 15 sec. contact.



(c) After 45 sec. (d) After 3 min.

Figure 12

Action of fine foam (alkyl sulphate) on oil patch ($\times 8$).

and r the radius. (At the tetrahedral points where the plateau borders intersect a spherically curved surface arises with double the effect.) This pressure differential between the lamellae and the borders assists drainage of the foam. When a mass of foam comes into contact with an oily smear (*Fig. 12*), the oil is drawn into the plateau borders, and if sufficient oil is

present, a lacy 3-dimensional network of oil spreads out far beyond the original bounds of the smear. The efficiency of the process varies with the pressure differential, which varies inversely with the moisture content of

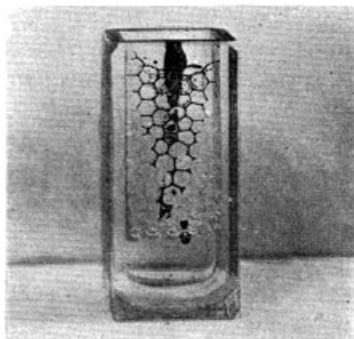


Figure 13

Action of alkyl sulphate foam on vertical oil smear.

the foam. This is clearly demonstrated in *Fig. 13*, in which the higher, and therefore drier, regions of a foam extend the oil smear more effectively. Where foam moves over an oily surface a succession of pressure waves is

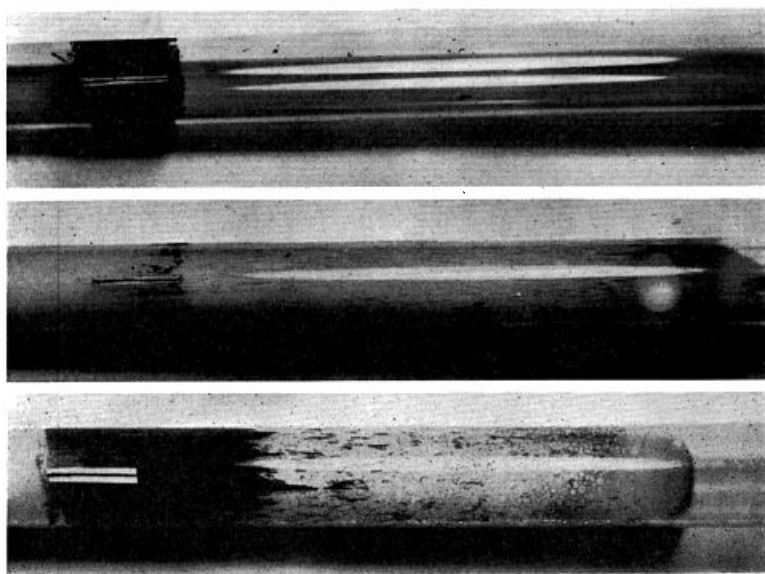


Figure 14

- (a) Before exposure. (b) Alkyl sulphate foam after 2 min.
(c) Cetyl trimethyl ammonium bromide foam after 2 min.

imposed on the surface. This assists the removal and coarse emulsification of the oil. The specific action of foam is most clearly demonstrated in *Fig. 14* where in the presence of a *cationic* surface active agent, the oil is actually spread further over a glass surface by the foam.

CONCLUSION

From the foregoing it will be appreciated that there are a number of physical and chemical processes which contribute to the removal of dirt from surfaces. The extent to which each operates depends upon the composition of all three major components of the detergent-surface-dirt system. Other factors not discussed here also operate under certain conditions.

The subject has been treated from a fundamental viewpoint. In practical detergency there are other factors which must be borne in mind, e.g. buffering action and stability towards calcium and magnesium ions. Attention to such details will ensure that the detergent composition will act in the most efficient manner, but will not affect the mechanism of the process.

While the broad principles by which detergents act are now becoming clearer there are innumerable details to be filled in. There is unfortunately a lack of incentive to elucidate the system from a fundamental viewpoint since the major developments in practice have usually been achieved by empirical experimentation; the full understanding of the process has followed at a slower pace.

ACKNOWLEDGMENTS

Figs. 3, 4, 6-10 have appeared previously in *J. Textile Inst.* **44** T12 (1953).

Figs. 12-14 have appeared previously in *J. Soc. Dyers Colourists* **68** 57 (1952).

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GAS-LIQUID CHROMATOGRAPHY AND THE PERFUMER

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Gas-liquid chromatography is an efficient separation technique which can simplify the perfumer's studies of complex raw materials. Its already numerous applications are listed, and the need for careful choice of working conditions is stressed. Examples are given of quantitative analyses and of identifications of essential oils of similar types.

THE TERM "chromatography" covers a group of closely related separation techniques, all based on partition between two phases, one fixed and one moving. Chromatographic methods are outstanding in efficiency, and have the additional merit of working under conditions which permit the safe handling of many relatively unstable compounds. Gas-liquid chromatography, distinguished by having a gas as mobile phase and a liquid as stationary phase, is applicable to substances with appreciable vapour pressures at moderate temperatures.

Perfumers frequently work with mixtures of uncertain composition (notably the essential oils) and their raw materials have odours, a property which implies some degree of volatility. Consequently chromatography has obvious applications in this field, with gas-liquid chromatography as the method of choice. The value of gas-liquid chromatography to the perfumer lies mainly in its ability to simplify his studies of mixtures. It is by no means the answer to all his problems, nor is it a sort of "artificial

*Proprietary Perfumes, Ltd., London, S.E.1.