

129. Adhesion in Detergence.

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The adhesion of particles of carborundum and calcium carbonate to quartz surfaces is examined in the presence of dilute solutions of various detergents. The results are expressed in terms of von Buzágh's adhesion number. Both cell wall and particle surface could be rendered hydrophilic or hydrophobic at will. It is shown that adhesion is decreased for low concentrations of detergent, but when micelle formation commences the adhesion number rises again.

In recent studies of the mechanism of detergence attention has been directed to the sequence of events which result in the eventual emulsification of the original film of grease and dirt adhering to the fabric, but little attention has been paid to the problem of the adhesion and detergence of small particles of solid materials. That such processes are operative in ordinary washing is clear from the fact that a number of technical tests for evaluating detergents employ solid particles such as carbon black (McBain, Brit. Assoc. 3rd Report on Colloid Chemistry, 1920, p. 26), manganese dioxide (Fall, *J. Physical Chem.*, 1927, **31**, 801), or graphite (Chapin, *J. Ind. Eng. Chem.*, 1925, **17**, 461).

The adhesion of surfaces has been studied in a quantitative manner by von Buzágh (*Kolloid-Z.*, 1929, **47**, 370; 1930, **51**, 105, 230), who investigated the relationship between the adhesion of quartz particles and a quartz surface to the electrokinetic potential existing at those surfaces. In this work an account is given of attempts to evaluate in a quantitative manner the effects of known concentrations of detergents in terms of an adhesion number, a very convenient term introduced by von Buzágh, at surfaces of known composition.

The method, an adaptation of von Buzágh's, consists in drawing a suspension of particles in a detergent solution into a small quartz cell. The particles are allowed to settle on the lower plate and then counted ($n/\text{mm.}^2$). After a certain time interval the cell is inverted and the number of particles which remain adhering to the original and now upper surface ($n_2/\text{mm.}^2$) provides a statistical measure of the adhesion, which can be defined in terms of the "adhesion number" = $100n_2/n$. Both the inner walls of the cell and particle surfaces can be rendered hydrophobic or hydrophilic at will by suitable coatings.

EXPERIMENTAL.

Two varieties of particle were employed, carborundum and calcium carbonate. Uniform carborundum particles were prepared by fractionally centrifuging high-grade grinding carborundum powder, and had a mean diameter of 20 μ . The most satisfactory method of cleaning consisted in heating them to redness for 60—90 seconds in a small platinum spoon. Particles with hydrophobic surfaces were prepared by heating as above, prior to immersion in 1 ml. of a 0.1% solution of dotriacontane ($\text{C}_{32}\text{H}_{66}$, m. p. 69.5°) in A.R. light petroleum. The petrol was allowed to evaporate slowly.

Attempts were made to prepare calcium carbonate particles by adding a 0.2% ammoniacal ammonium carbonate solution very slowly to a warm agitated 0.2% solution of calcium chloride just cleared with a drop of hydrochloric acid. The particles so prepared were very uniform but rather small, only $10\ \mu$ in diameter. Slower precipitation in more dilute solutions or ripening did not produce appreciably larger particles, and elevation of the temperature above 30° gave a needle-clustered precipitate instead of rhombs. The most satisfactory particles were obtained by grinding marble and employing the fraction which settled through 12 cm. of water during 2.5–5 minutes at 20° . The mean diameter of these particles was $20\ \mu$, but although the extreme theoretical variation in size should have been a factor of $\sqrt{2}$, the actual variation was found to be a factor of 2, owing probably to convection currents and turbulence during sedimentation. Elutriation methods similar to that described by McCrea and Wandless (*J. Soc. Chem. Ind.*, 1936, 55, 15r) were not found to be satisfactory for obtaining these particles. The calcium

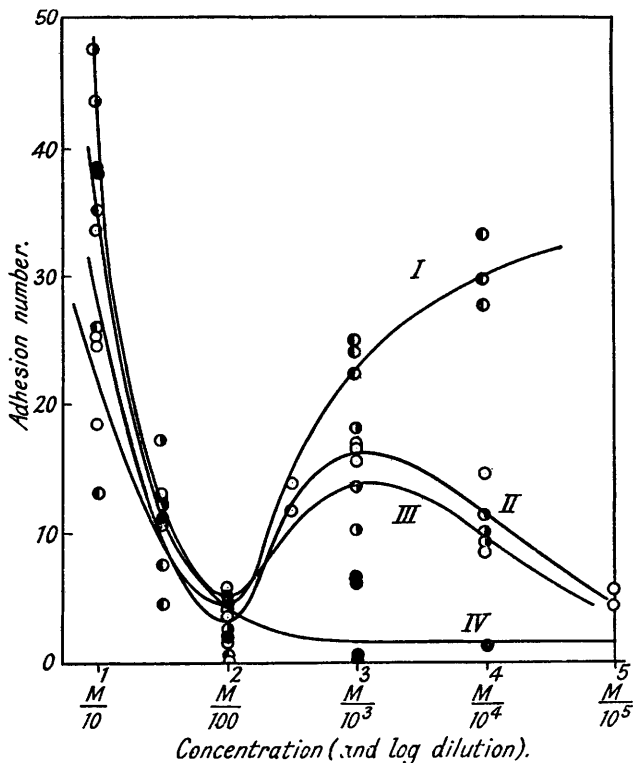


FIG. 1.
Dodecyl sodium sulphate, 45° .
I. Coated carborundum particles, coated cell.
II. Coated carborundum particles, clean cell.
III. Clean carborundum particles, coated cell.
IV. Clean carborundum particles, clean cell.

carbonate particles were well washed with water, dried, and suspended in light petroleum. A small amount (1 mg./g. of particles) of stearic or palmitic acid dissolved in a few ml. of petrol were then added. The suspension was shaken for about 15 minutes, the liquid run off, and the particles washed four times with petrol and dried. The surfaces of the particles treated in this manner were hydrophobic. If the coating is performed from ethereal solution instead of petrol, the particles are hydrophilic, being easily wetted by water. Heating for an hour under vacuum, however, renders them hydrophobic. If the hydrophilic particles are suspended in water they are readily flocculated by the addition of a small amount of sodium palmitate or stearate.

Attempts were made to prepare particles of pure paraffin wax by adding a solution of wax in light petroleum to absolute alcohol, but it was found that the size of the particles could not be controlled.

The calcium carbonate particles with the hydrophobic surface were superior to those of paraffin-coated carborundum, not only in reproducibility of results, but also because it was found that the latter gradually became more hydrophilic on exposure to air, as shown by their adhesion, whereas the former maintained their surface properties unchanged for months.

One plate of the quartz cell was coated by drawing dry air through the cell over a small

drop of light petroleum solution of dotriacontane resting on the lower plate. A little experience was necessary to produce coatings which did not peel off when the cell was filled. (If the air stream is too rapid, the hydrocarbon collects round the edges of the bottom of the cell, and if it is too slow, the hydrocarbon collects in the middle and peels off.) The cell was stoppered and placed in a thermostat at 45°. After sufficient time had elapsed for the cell to come to equilibrium, it was removed and filled with a suspension of the particles in the solution also at 45°. The cell was then fixed horizontally under a low-power microscope with the coated plate below, in a small thermostat at the same temperature. When all the particles had settled, the microscope was focused through the top of the cell on to the particles. With the aid of an eye-piece grating, the number of particles occupying a given area was counted. The support for the cell was mounted on a moving stage which enabled counts to be made at different parts of the plate; n_1 per square mm., say. After a certain time—10 minutes—from filling the cell, it is slowly turned through 180° so that the coated plate is now uppermost. Some of the particles will fall off the plate; those that remain “hanging” from those areas of the surface previously counted are brought into focus and counted and the “adhesion number” thus determined. The adhe-

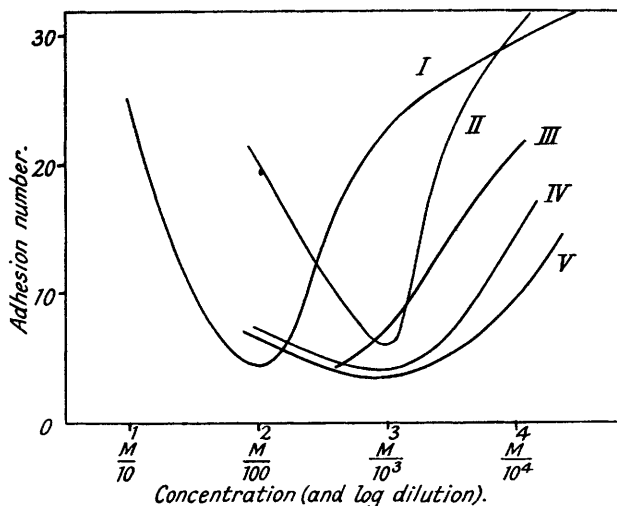


FIG. 2.

Coated carborundum particles,
coated cell.

- I. Dodecyl sodium sulphate, 45°.
- II. Cetylpyridinium bromide, 45°.
- III. Cetyl sodium sulphate, 35°.
- IV. Cetyl sodium sulphate, 45°.
- V. Oleyl-N-methyltaurine, 45°.

sion number is independent of the rate of turning of the cell provided this operation is carried out smoothly; a few seconds suffice for the purpose.

Results.—A few experiments with dilute soap solutions showed that the systems were difficult to control unless buffered. It was therefore considered advisable to deal only with paraffin-chain salts which do not hydrolyse and are not affected by carbon dioxide. The following substances, kindly supplied by Imperial Chemical Industries Ltd., Dyestuffs Group, have been used: cetyl sodium sulphate, dodecyl sodium sulphate, oleyl-N-methyltaurine, and cetylpyridinium bromide. Fig. 1 shows the results obtained with dodecyl sodium sulphate and the four possible combinations of coated or clean cell, coated or clean carborundum particles respectively. Fig. 2 shows the smoothed curves obtained with other substances, a coated cell and coated carborundum particles being used in each case. Each point on the curves in Fig. 1 was determined by measurement of about 300 particles.

DISCUSSION.

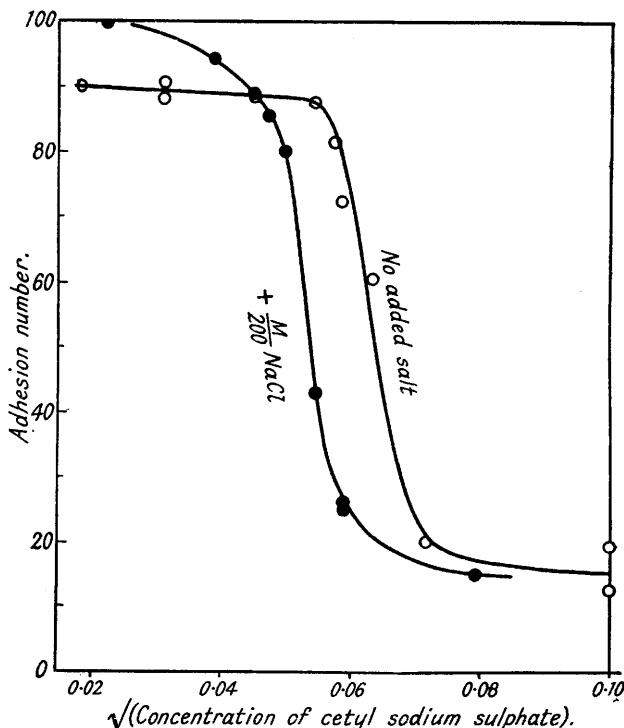
The course of curve I in Fig. 1 (particles and cell coated) indicates that, as the bulk concentration of detergent is increased, there is a simultaneous increase in the adsorption of dodecyl sulphate ions on to the wax-coated surfaces, and that the hydrocarbon “tail” of the molecules is directed towards the wax. If both surfaces are assumed to react in this way, the adhesion between the particles and the cell wall decreases, owing both to electrostatic repulsion between the heads and to the fact that water molecules can now penetrate in between the two hydrophilic surfaces, separating them to distances where the forces of adhesion become inoperative. On this view the minimum adhesion number will occur at

a concentration of detergent where the two hydrocarbon surfaces are each covered with a unimolecular film. We may conclude that in the case of dodecyl sodium sulphate with increase in concentration the surface adsorption likewise increases until at about $M/100$ the surface attains saturation.

We note that at concentrations higher than $M/100$ adhesion again sets in, owing perhaps to the particles being cemented to the surface by a micelle-like structure, for it is at this concentration that micelle formation is observed in the bulk phase. This view is also supported by the fact that in concentrations greater than $M/100$ the adhesion number is independent of the original nature of the surfaces.

From Fig. 2 it will be seen that as the chain length is increased the surface becomes saturated at a lower concentration, in accordance with expectation. Fig. 3 gives the

FIG. 3.



variation of adhesion with concentration of cetyl sodium sulphate between a wax-coated surface and particles of calcium carbonate, coated as described above. The results obtained with these particles were much more reproducible than those obtained with the carborundum particles. It is probable that the method of coating the calcium carbonate particles gives a much more uniform coating. The difference in the order of the adhesion number obtained with the two types of particle is due to a number of factors such as a small difference in mean diameter between the calcium carbonate and the carborundum particles, and to the presence of small "flats" on the crystals of calcium carbonate giving a relatively larger area of contact. With these particles the fall of adhesion with increase in concentration is much sharper than with the carborundum particles. Since the variation in size of the calcium carbonate particles was smaller than that of the carborundum particles and as any given particle must either stick or fall off, the greater uniformity of the particles causes a sharper break in the curve. There is the possibility, however, that there is some change in the nature of the adsorbed film (which can perhaps be likened to a change of phase) which occurs at a definite concentration of detergent in the solution and therefore at a certain concentration of adsorbed molecules on the surface.

The effect of M/200-sodium chloride on the adhesion of calcium carbonate particles is shown in Fig. 3, and we note a greater adsorption of detergent with increase of salt concentration. This is in accordance with expectations from consideration of the phenomenon of salting out as well as from the results of recent studies in the effect of salts on the surface tensions of paraffin-chain salts (see, *e.g.*, Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243).

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