in mixtures of that substance with air and ethylene, and in coal gas.

The authors would recommend that in the analysis of illuminating gas (coal gas), the order of procedure be: (*a*) The absorption of carbon dioxide by potassium hydroxide; (*b*) the absorption of benzene by the ammoniacal solution of nickel nitrate above described; (*c*) the absorption of the "heavy hydrocarbons" by fuming sulphuric acid; (*d*) the absorption of oxygen by alkaline pyrogallol or by phosphorus; (*e*) the absorption of carbon monoxide by cuprous chloride; and (*f*) the determination of the methane and hydrogen.

The authors have been unable to try this new method on any commercial gas mixture other than the local supply of illuminating gas. They would therefore earnestly request chemists using the method on other gas mixtures to communicate to them the results of such analyses and call their attention to any difficulties that may arise.

CORNELL UNIVERSITY, ITHACA, N. Y.,
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ON THE CLEANSING POWER OF SOAP.

BY H. W. HILLYER.

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CHEVREUL, the first to study the fats and soaps, discovered that when soaps are acted on by water they are hydrolyzed to free alkali and to an acid salt. The tendency of the reaction may be expressed by the equation

$$NaAc + H_2O = NaOH + HAc,$$

where Ac stands for the palmitic or stearic acid radical. The acid thus set free unites with more or less of the undecomposed soap to form difficultly soluble acid salts which contain more and more acid in proportion to the alkali as the dilution of the solutions from which the salts separate increases.

Rotondi, basing his conclusions on a mixed soap, decided that when water acts on the soaps, there is formed an acid salt which is soluble with difficulty in cold water and a basic salt which is easily soluble. Recent work by Krafft and his co-workers[1] have shown that Chevreul was correct and that Rotondi fell into error, prob-

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[1] *Ber. d. chem. Ges.*, **27**, 1747; *Ibid.*, **27**, 1755.

ably because he did not take into account the fact that sodium oleate is readily soluble in cold water. It was probably a mixture of this with the alkali set free by the hydrolysis of the palmitate and stearate present which was called an alkaline soap or basic salt. The more current theories of the detergent action of soap are largely based on the undoubted hydrolysis of soaps by much cold water.

The most ordinary theory is that the alkali set free by the hydrolysis of the soap acts on the fat to remove it by a process of saponification. To show that this is illogical it is only necessary to call attention to the fact that the alkali present has the opportunity of making a soap in either one of two ways: First, by acting on the glyceride to decompose it or, secondly, by acting on the fatty acid or acid salt from which it has just been separated. That it will more readily react with the latter than with the former is clear, and since, while the dilution is great, this reaction with the acid salt does not take place but rather the reverse reaction, it seems entirely improbable that the hydrolytic alkali acts chemically, if at all, on the glycerides of the fats and oils. In the use of soap for cleansing, we prefer to use hot and strong solutions but the hydrolysis is almost certainly more complete when the solutions are dilute and have cooled enough to yield a precipitate of acid salt. In the hot solution, especially if concentrated, there can be but little free alkali. Finally, paraffin oils are washed away by soaps as well as the glycerides are, and in this case it is clear that there can be no chemical reaction of the alkali upon the oil.

C. R. Alder Wright[1] assumes that the value of a soap is largely due to the alkali of hydrolysis acting in such a way as to allow contact of the water with the substance to be cleansed. Ladenburg's "Handwörterbuch," Vol. X, p. 574, favors the theory of Knapp, which lays the cleansing power of soap to the property of the soap itself of easily wetting oily substances. Knapp's original papers are not available to the writer and his evidence is not known, but it may be easily shown by a simple experiment that it is the soap itself and not the alkali which gives aqueous solutions the power of wetting oily substances.

A piece of red litmus paper is thoroughly oiled with either purified cottonseed-oil or a paraffin oil, and upon it is placed a

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[1] Muir's "Dictionary of Applied Chemistry," Vol III, p 411.

drop of dilute alkali. The alkali produces a blue spot with well-defined edges, and spreads very slowly over the oiled paper. If a drop of soap solution is placed on the paper it spreads rapidly and soon produces a large spot with ill-defined ragged outlines.

Another suggestion as to the cleansing is that the soap itself or the alkali of hydrolysis acts as a lubricant, making the tissue and impurities less adhesive to one another, and in that way promoting the removal of the latter. It is not unreasonable to consider this as a factor in the cleansing, and it will be referred to again later.

It is often suggested, either as a distinct theory or as a more or less important adjunct to the saponification theory, that the alkali set free by hydrolysis acts on the fat by emulsifying it, and carrying it away in suspension with the other impurities. This suggestion has come apparently because those who have emulsified oils with alkali have used oils not free from fatty acids. It is also suggested that the emulsification is due to the undecomposed soap, but experiments are not recorded as far as can be ascertained to sustain this view or to determine whether the action is due to the soap or to the alkali.

When good cottonseed-oil, "salad oil," is shaken with weak alkali it is largely emulsified, but by washing the emulsion with water and dilute alkali alternately for many times, the soap formed by the action of the alkali on the free acid of the oil is removed, the oil separates from the emulsion, and a product is obtained which is not emulsified by decinormal sodium hydroxide. Neither is kerosene emulsified by decinormal alkali. Both kerosene and purified cottonseed-oil easily make permanent emulsions with a decinormal solution of sodium oleate. From this experiment, it seems certain that the emulsifying power of the soap solution, is due to the soap itself rather than to the hydrolytic alkali.

The explanation of the action of soap as due to its emulsifying power is a plausible one, but no clear account has been given, or made current, at least, in chemical literature, of the physical properties which a liquid must have to be a good emulsifying agent. The great similarity between foams and emulsions in method of making and in properties, suggests the question whether any explanation given for the formation and permanence of foams will not also apply to the formation and permanence of emulsions. Plateau and Quincke have made extensive studies of substances which foam and of those which are emulsifying agents.

There will be here no attempt to detail their results or to follow exactly their reasoning but the general trend of their work will be indicated. They have shown that soap solution has a surface-tension which is lower than that of any other aqueous solution. Its surface-tension is, in fact, only about 40 per cent. that of pure water. This may be shown in several ways. When two capillary tubes of the same diameter are placed respectively in water and in soap solution, the water will be seen to rise about 2.6 times as high as the soap solution. If a given volume of water is allowed to drop from a broad-ended pipette or stalagmometer and then a soap solution is allowed to drop from the same pipette, it will be found that the soap solution will make 2.6 times as many drops as the water. The cohesion of the soap solution is so small that the surface-tension will sustain drops of a volume only about 40 per cent. of the volume of those formed by water. Plateau[1] lays the power of forming bubbles, films, and foam to two factors: first, the liquid must possess notable viscosity, that the film may not readily yield to the forces which tend to thin it to the point of rupture; secondly, it must have a low surface-tension since the surface-tension is the most active force in thinning the film. Soap solutions are ordinarily quite viscous, and this viscosity is increased in Plateau's bubble mixture by adding glycerin, which aids in making bubbles and films permanent. Soap solutions have a low surface-tension and, on account of these two factors, soap solutions easily yield and enduringly maintain films and foam.

Quincke[2] has similar fundamental views, but ascribes the permanence of a foam to the mixed character of the liquid which foams, and claims that no pure liquid will foam. According to Quincke the permanence of the foam is due to the action of surface-tension which spreads out over the surface of the film some secondary ingredient of the solution, and this tends to close up any potential ruptures in the film. Plateau calls attention to the important part played by viscosity in these phenomena and speaks of the existence of a viscosity which pertains to the liquid itself, its internal viscosity, caused by the friction of the molecules of the liquid on each other and also of a second kind of viscosity, which he calls superficial viscosity, which sometimes makes the motion of a foreign body upon the surface

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[1] Pogg. *Ann.*, **141**, 44.

[2] Wiedemann's *Ann.*, **35**, 592.

of a liquid more or, on the other hand, less ready than within the liquid. Stables and Wilson[1] have confirmed Plateau's work, and find that the motion of a body in the surface of a solution of saponin is resisted 600 times as much as it is within the same solution. By this great superficial viscosity they account for the great foaming power of saponin solution, although it has a comparatively high surface-tension.

To make these ideas clear a simple case may be used as an illustration. Suppose two bubbles of air to be lying side by side within a mass of water. The molecules of water at the point of nearest approach of the bubbles are acted on by the stress of the surface-tension of both bubbles, and this causes a thinning of the film between them. The surface-tension is great and the water is mobile so that the thinning will be rapid and soon the bubbles will coalesce by the breaking-down of the membrane. If, instead of water, soap solution is present, the stress which causes thinning will be less on account of the much smaller surface-tension and the resistance to thinning, due to the viscosity of the soap solution, will be somewhat greater and as a result the bubbles will remain separate for a much longer time. In the same way a mass of bubbles will remain permanent longer in soap solution than in water.

A table is here presented showing some observations made by the writer in confirmation of the work of Quincke and Plateau. While they claim no considerable accuracy, they show in general the tendency which solutions of high viscosity and low surface-tension have to make foams. The figures in the second column show the number of minutes required for the volume of liquid contained in the stalagmometer to flow out and consequently give a rough measure of the internal viscosity of the solutions. The third

	Time.	Drops.	Foam.
Water	3	47	—
Stale beer	..	79	+
Sweet skimmed milk	4	75	+
Saponin, 0.5 per cent	3	55	+
Albumen, 3 per cent	3	58	+
N/10 NaOH + equal volume alcohol	8	110	—
Glycerin, 50 per cent	14	60	—
Gum acacia, 6 per cent	8	49	—
N/10 rosin soap	3	104	+
N/10 sodium oleate	4	104	+
N/640 sodium oleate	3	108	little

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[1] *Phil. Mag.* (5), **15**, 406.

column gives the number of drops formed from the given volume, when the drops were formed in air. In the fourth column the plus signs indicate that the solution makes a permanent foam and the minus signs that it does not. Water gives the smallest number of drops and has the highest surface-tension. The solution of sodium resinate and the solutions of sodium oleate give the greatest number of drops, and have the least surface-tension. That viscosity alone will not account for permanent foam formation is shown by the cases of glycerin and gum acacia where there is high viscosity but also high surface-tension and no foam. Beer and milk have a higher viscosity and a lower surface-tension than water and yield foams. The decided apparent exceptions are albumen and saponin, and alcoholic alkali. Saponin and albumen have, however, in a very marked degree, the property of superficial viscosity, and this accounts for the persistent foam in spite of their low internal viscosity and comparatively high surface-tension. On the other hand, while the solution of alkali in dilute alcohol has a high internal viscosity and a markedly low surface-tension, the temporary character of its foam may be accounted for by the fact discovered by Plateau—that alcohol has a negative superficial viscosity. That the alcohol has the effect of diminishing foaming power may be seen by adding a small quantity to a soap solution, which then loses its foaming power to a marked degree.

EMULSIONS.

Can emulsification be explained by the viscosity of the emulsifying agent? In the case of very thick liquids like the gum solutions used by the pharmacists, it is probable that the extreme viscosity is a very large factor in giving permanence to the separation of the oil droplets which have been formed mechanically. That even very large internal viscosity will not make an emulsion permanent is shown by the fact that 50 per cent. glycerin and 6 per cent. gum solutions which have viscosity of a high degree will not emulsify kerosene or even a viscous oil like cotton oil. Saponin or albumen solution with their high superficial viscosity will give permanent emulsions. Dilute soap solutions which have not great viscosity have very great emulsifying power, and the same is true to a less degree of some other solutions. From these facts it must be decided that internal viscosity of the liquid will not account for its emulsifying power.

It has been seen that foaming can be explained largely by the small surface-tension of soap solution towards air. Surface-tension phenomena show themselves between two liquids as well as between a liquid and air. The question arises whether there is any peculiarity in the degree of surface-tension between soap solutions and oils, not shown by other solutions.

Quincke[1] observes that when a solution of sodium carbonate is brought in contact with an ordinary oil, phenomena are exhibited which he ascribes to the change of surface-tension between the oil and aqueous solution on account of the formation of soap. Among the phenomena accounted for in this way is that of emulsification. Quincke does not use pure oils or single soaps nor, except casually, does he refer to the low surface-tension between oils and soap solutions.

To more definitely answer the question as to the relation of surface-tension and emulsifying power, experiments were made by the writer to measure roughly, by the dropping method, the relative surface-tension of water and of soap solution toward typical oils. According to Quincke a solution of Venice soap containing 1 part in 40 of water has toward air a surface-tension of 2.563, a solution of 1 part in 400 has a surface-tension of 2.672, and one of 1 part in 4000 has a surface-tension of 2.681. In other words, according to these careful determinations, concentration has very little influence on the surface-tension of soap solution in contact with air. With this constant and comparatively small reduction of surface-tension which soap solution shows as contrasted with water, it is interesting to compare the enormous and variable reduction of surface-tension shown when soap solutions of increasingly concentration are allowed to flow through oils.

When cottonseed-oil is allowed to flow slowly up through water, it makes much larger drops than are made when it flows up through soap solution. The same is true when kerosene is used. The surface-tension between the oils and soap is much less than between the oils and water. A much more convenient method of studying the surface-tension is to let the water or solutions flow down through the oils. In this work the greater number of observations were made with a stalagmometer intended as an alcoholimeter and holding 5.35 cc.

When water flows from a stalagmometer with its tip immersed

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[1] Wiedemann's *Ann.*, **35**, 580.

in oil, large drops are formed. When a weak soap solution replaces the water, the drops are smaller. When stronger and stronger soap solutions are used, the drops grow smaller and more rapid, if the rate of flow of the liquid is not checked, until with a strong solution the rate of flow is too rapid to give time for the formation of separate drops and a very thin cylindrical stream flows from the stalagmometer. The surface-tension has become so small that it does not support the liquid long enough to form drops. In this case, gravity is strong enough to almost completely overcome the action of surface-tension and draws the solution out into a fine thread. It seems reasonable to suppose that any other outside force could easily break up this strong soap solution within the oil into small droplets, or spread it into films on account of the small surface-tension. According to the theory of surface-tension between two liquids, surface-tension will be great between them, when each liquid has strong internal attractive forces, that is, strong cohesion: and it will be small when they have slight attraction for one another, that is, slight adhesion or mutual affinity. Small surface-tension will be caused by a weak cohesion of at least one of the liquids and a strong adhesion or affinity of the liquids to one another. Water forms large drops in oil on account of its great cohesion and its small adhesion to the oil. Soap solution makes small drops or runs down in a stream; because, first it has a low cohesion and, secondly, because it has a strong adhesion to the oil or a strong affinity or attraction for it.

It would seem that this low surface-tension of soap solutions must be a prime factor in their emulsifying power. Viscosity can have very little to do with it, for solutions containing about 1 per cent. of sodium oleate are excellent emulsifying agents but have a viscosity so low that careful measurements would be necessary to show that they are more viscous than water. Using the same reasoning as in the case of bubbles and foam, we may say that when two oil drops approach each other in water, they tend to coalesce and finally do so because the great surface-tension of the drops easily withdraws the mobile water from between them till they touch and coalesce. But when the drops are in soap solution, the surface-tension is so very much less that it is not able to withdraw the solution rapidly from between the drops, and they are kept separate. If the soap solution is notably viscous, the slight surface-tension will have still greater difficulty in thinning the films to the point of rupture. A mass of droplets separated by films of a low surface-tension and notable viscosity will be a permanent emulsion.

Quantitative relations between the surface-tensions of certain solutions are given in the following table. The measurements are only approximate, but, for the purpose, adequate. The first column (K) indicates the number of drops formed when 5.35 cc. of the solutions named flow into a certain kerosene. The second column (Emul. K) indicates by a plus sign, that the solution, when shaken with the kerosene, will yield an emulsion. The third and fourth columns, C.S. oil and Emul. oil, give similar data for cottonseed-oil carefully purified from free acid by washing with dilute alkali.

	K.	Emul. K.	C. S. oil.	Emul. O
Water	17	—	9	—
Stale beer	39	little	..	—
Sweet skimmed milk	..	..	52	+
Saponin	..	..	13	+
Acacia	..	..	14	+
Alcohol and sodium hydroxide	51	little	..	..
N/640 sodium oleate	26	little	..	..
N/10 sodium oleate	296	+	167	+
N/10 rosin soap	310	+	180	+
N/10 sodium chloride	17	—	..	..
N/10 sodium hydroxide	17	—	10	—
Sodium silicate	..	..	15	—

From these data, it will be seen that the solutions which emulsify have a larger number of drops, that is, "a smaller surface-tension than those that do not."

Saponin solution containing 1 part of the glucoside to 200 of water is an excellent emulsifying agent, and yet its surface-tension toward oil is not enormously reduced from that of water, but its emulsifying power is easily understood when one observes the form of the drops produced when it flows through cottonseed-oil. Quincke has observed similar drops when albumen solution flows through oil. We may make a *soap* solution, one containing 1 part of sodium oleate in about 500 parts of water, which, when it flows through oil, will give the same number of drops as the saponin solution used. The drops of soap solution form normally, and, as they fall, assume quickly a spheroidal shape, while the hanging drop quickly takes the form of a catenoid. A drop of saponin solution (Fig. 1) as it is detached takes the form of a Rupert drop (*a*) and, falling to the bottom, takes the form of a pear (*b*) with the stem plainly visible. This stem, the remains of the filament drawn out as the drop was detached, may remain

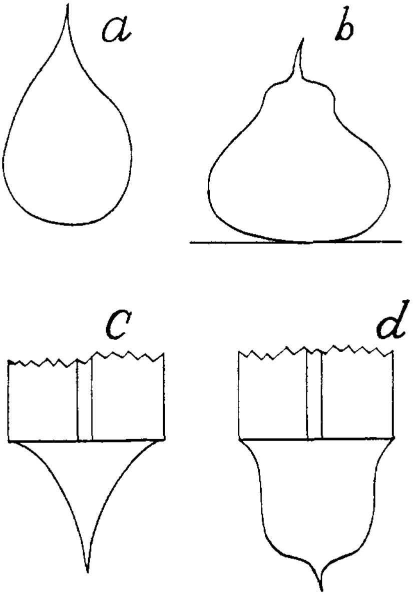

Fig. 1.

visible for many minutes. The hanging drop, if the flow of solution is stopped just after the fall of the drop, has the shape of an inverted cone, with incurved sides and a slender peak (*c*). This shape is retained a long time. When new liquid flows in, the hanging drop changes its shape only as its surface is swelled out by the inflowing liquid (*d*). That the liquid is not in itself viscous may be known by observing the ready rotations and other movements of chance particles within the drop as the liquid flows down.

Here we plainly have a new instance of superficial viscosity, a viscosity which makes motion difficult in the surface between the two liquids. This it would seem, being of so considerable a degree, may account for the resistance offered to the withdrawal of the films of saponin from between the oil droplets of a saponin oil emulsion, and consequently for the permanence of the emulsion.

The conclusion arrived at is that emulsification is due largely to the small surface-tension between oil and the emulsifying agent which allows the emulsifying agent to be spread out into thin films, separating the oil droplets. The surface-tension is not strong enough to withdraw the film from between the droplets except slowly and, if the emulsifying agent has great internal viscosity, or if great superficial viscosity is shown between the liquids, the thinning of the film becomes so slow that the emulsion is permanent.

EFFECT OF FREE ALKALI AND OF FREE ACID.

As indicated in the tables last given, decinormal sodium hydroxide solution does not show any greater number of drops than water when it flows through kerosene, and only a slight, and in this connection insignificant, increase in the case of cottonseed-oil. Since alkali does not emulsify either of these oils, we may conclude that diminution of surface-tension and emulsifying power go together, and that neither of them is caused by alkali alone. Solutions of alkali less concentrated than decinormal also show the same surface-tension and fail to give emulsions. A decinormal solution of sodium oleate will give some twenty times as many drops as a decinormal alkali. The number of drops formed by the oleate is not increased by adding excess of alkali to either concentrated or dilute solutions of oleate. On the other hand, when free oleic acid in excess is added in increasing amounts to a decinormal solution of sodium oleate, the number of drops and consequent emulsifying power are decreased as shown by the data and curve below. Mixtures were made containing 100 cc. oleate and amounts of free oleic acid varying from an amount sufficient to form the acid salt $C_{18}H_{34}O_2Na:C_{18}H_{34}O_2$ down to 1/128 of that amount, and the number of drops which each made was determined.

Decinormal Sodium Oleate and Oleic Acid.

Equivalents of oleic acid in excess.	0.	1/128.	1/64.	1/32.	1/16.	1/8.	1/4.	1/2.	1.
No. drops	274	273	270	240	216	164	117	84	58

From these facts we may conclude that the low surface-tension and the emulsifying power are due not to the alkali or to the acid salt set free by the hydrolysis but to the *undecomposed soap itself.*

We have seen before that another possible factor in cleansing, namely, the power which soap solutions have of wetting oily substances is due to the soap itself. But this wetting power may be explained also by the strong adhesion of the soap to the oil and the low cohesion of the soap solution itself. The latter will more easily be spread out over the surface, if its cohesion is small and a stronger force will be acting to spread it out, if it is strongly attracted to the oily surface.

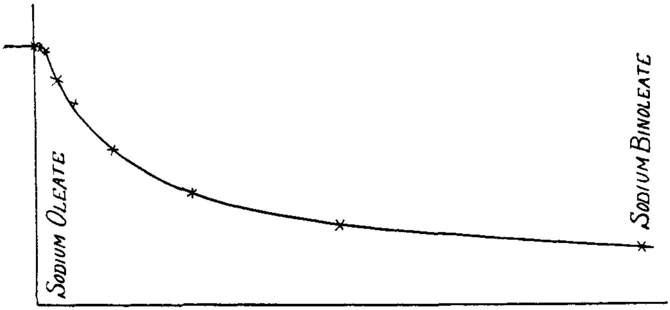

Fig. 2.

A very similar factor in cleansing is that which may be called ease of penetration, by which the aqueous solution pushes into and permeates the interstices of the fabric. If a glass tube of 3 or 4 mm. internal diameter and closed at one end is filled with cottonseed-oil and immersed in a vessel of water (Fig. 3, *a*), the oil will not leave the tube, being held there by the strong surface-tension film between the oil and water. But if a strong solution of soap is poured in, the surface-tension film is diminished in strength, the oil flows from the tube, and the soap solution penetrates into it (Fig. 3, *b*). Here the soap, on account of its weak cohesion and its strong adhesion to the oil, withdraws the oil and penetrates into the oily tube. In the same way, it may be, the soap penetrates into the capillary interstices of the fabric to be cleansed.

Even the lubricating power of soap solutions may be explained by considering the factors a low cohesion and a strong adhesion. In treatises on mechanical engineering, the chief physical property mentioned as desirable in a lubricant is that it shall have sufficient "body" or viscosity to prevent its being pressed out from between the surfaces to be lubricated. While viscosity is for this particular object no doubt a necessary thing, it would seem to be a necessary evil. As the term is used in physics, viscosity is a property of fluids which prevents the freedon of motion which their particles would have if the fluid had no viscosity, or a less viscosity. But in speaking of lubricants mechanical engineers demand, in a substance intended to promote motion, a property which physically hinders motion. If we consider as lubricants graphite or steatite or soap, or the clay on which our shoes slip in the street, we may get a clearer notion of lubrication. In these cases, at least, the lubrication is due to the fact that the lubricant adheres in a film to the surfaces

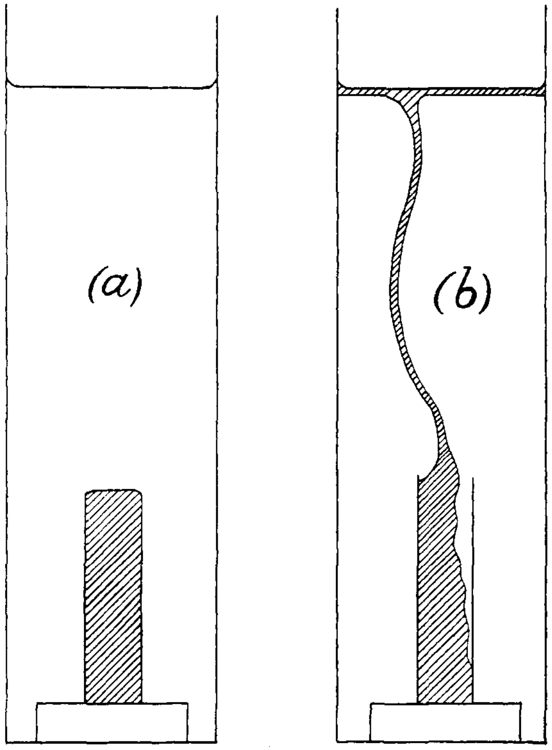

Fig. 3.

to be lubricated but does not cohere to itself. In the use of oil as a lubricant, it is also true that the oil adheres to the lubricated surfaces and soon forms two layers of oil which glide over one another. We have then strong adhesion on the part of lubricant and a weak cohesion. The same is true of soap solutions and will explain their slipperiness and lubricating power. The slipperiness we feel when alkali is used on the hands is probably due to its action on the skin or on the material which keeps in place the epithelial cells. The actual removal of these cells with the impurities attached to them and covered by them would account for the cleansing action of alkali and alkali carbonate on the skin.

The position here taken is then: that the cleansing power of soap is largely or entirely to be explained by the power which it has of emulsifying oily substances; of wetting and penetrating into oily textures; and of lubricating texture and impurities so that they may be removed easily. It is thought that all of these properties may be explained by taking into account the low cohesion of the soap solutions and their strong attraction, adhesion or affinity to oily matter, which together cause the low surface-tension between soap solution and oil.

A STUDY OF SOAP SOLUTIONS.

By H. W. Hillyer.

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It was noted in the preceding article that while toward air the surface-tensions of soap solutions vary but little as the concentration is changed, the surface-tension between soap solutions and oils is rapidly diminished as the concentration is increased. To ascertain the law connecting concentration and surface-tension, the following experiments were made. They not only show this relation but serve to confirm the idea that the diminution of surface-tension is dependent solely on the amount of undecomposed soap present in the solution. Unfortunately in this pioneer work it was not realized how desirable it was to have the same kerosene for all experiments, and consequently the results are not strictly