THEORY OF DETERGENCY AND THE DEVELOPMENT OF MAXIMUM CLEANSING POWER IN WASHING SOAP.

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Bulletin No. 62

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Bengal Government Press, Alipore, Bengal.
1934

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I. Survey of Previous Work.

(a) General.—Berzelius was the first chemist to make an effort to understand the cleansing action of soap. Since his time many theories have been put forward from time to time to explain the detergent action of soap. These theories are records of diverse opinions of different investigators. Berzelius (Lehrbuch der Chemie, II aufl, 1828, III 438) attributed the detergent action to alkali liberated by hydrolysis. Persoz (Traiter theorique et partique de l' impressions des tissrees, 354, 1846) in 1846 again expressed the same view. Jevons in 1878 observed strong "pedesis" now known as Brownian movement of particles suspended in a soap solution. He thought of the soap as loosening and washing away the dirt particles (Jevons, Chem. Ztg. 2, 457, 1878). Kolbe (Org. Chem. II Auff, 1880) in 1880 thought that the saponification of fats by the hydrolysis alkali and the entrapment of dirt particles by foam were responsible for cleansing action. Wright (quoted in Muir's Dictionary of Applied Chemistry, 3, 411) advanced the view that soap solution can "wet" the oily surface through the influence of hydrolysis alkali, hence the inability of water alone to do it. Hillyer (J. Am. Chem. Soc. 25, 511, 1903) demonstrated that the wetting property belongs to soap itself and not to alkali of hydrolysis.

Ladenburg (Hand Wörterbuch 10, 575, 1892) thought the cleansing action of soap to be due to the following properties of soap itself:—

(1) Wetting ability of oily substances.

(2) Penetrating into the capillaries of the goods and acting as a lubricant.

(3) Making the tissues and impurities less adhesive to one another and in that way promoting the removal of dirt.

Chevreul (Recherches Chimiques sur les corps gras d' orgene animate, 1823, republished 1819), Berzelius, Persoz, Knapp and others put much stress on the emulsifying power and foams toward fats. The mechanism of, or the agents responsible for, these processes could not be established by any of these authors experimentally. Some were of opinion that the undecomposed soap was all important in the matter, others were in favour of giving all credit to hydrolysis alkali.

Plateau [Ann. Physik, (2) 141, 44. 1870] after a practical study of substances which are responsible for producing foam and causing emulsification, concluded that the ability of forming bubbles, films, and foams depends on two factors: high surface viscosity and low surface tension. Qincke [Ann. Physik (3) 35, 592, 1888] thought that the mixed character of the liquid in soap solution was responsible for the permanence of foam and that no pure liquid would foam. Donnan (Z—Physical Chem. 1899, 31, 42) from his experiments

showed that lowering of surface tension and emulsification went hand in hand in the case of different soap solutions.

Hefemeister in 1880 for the first time suggested that the soap solutions are colloidal in nature (Arch. exp. Path. Pharm. 25, 6, 1888). This important suggestion did not attract any attention for some time. Kroff and Wiglow, however, in 1895 (Kroff & Wiglow, Ber., 28, 2573, 1895) from the study of physico-chemical properties of soap solutions came to the conclusion that soap solutions are colloidal. After this a host of workers like Goldschmidt (Kolloid—Z, 2, 193, 227, 1908), Mayer, Schæffer, Tarroine (Compt. rend. 146, 484, 1908) and others approached the problem from different angles and put the colloid theory of soap solutions on a firmer basis. In this connection S. A. Shorter (J. Soc. Dyers Colourists, 32, 99, 1916) observes that the view that the detergent action of soap is due to its colloidal nature suggests the idea that other colloids may possess detergent power.

From the experiments of Hillyer (J. Am. Soc., 25, 511, 1903) we got the experimental proof to the effect that, emulsifying power and wetting power, the two supposed important factors in detergent action, cannot be attributed to hydrolysis alkali but must be ascribed to undecomposed soap. This is the point in the history of the theories of detergency which marks the unanimous departure from the "alkali theory" of detergent action.

McBain in his pioneering work demonstrated by potentiometric and other measurements that soap hydrolyses generally to a very small extent, so much so, that the hydroxyl ion concentration is about N/1000 for most soap concentrations. Maximum result (percentage hydrolysis) observed so far is seven per cent.

According to McBain (Third Report, Colloid Chem. British Association for Advancement of Science, 1920), "The chemical formulæ of soaps are well ascertained, tautomerism does not occur, true reversible reproducible equilibrium is established in all solutions, and finally the definite transition from typical simple electrolyte through colloidal electrolyte to neutral colloid may be observed in all stages. This transition from crystalloid to colloid is exhibited not only in passing from salts of the lower to those of the higher fatty acids, but may be demonstrated in any one of the higher members merely upon change of temperature and concentration. In alcohol, soaps exhibit a wholly different and much simpler behaviour. The soap here exists in the form of a simple unpolymerised electrolyte as it does in true solution, whereas in most aqueous solutions it is of course a colloidal electrolyte."

Hillyer suggested another factor responsible for detergent action. He stated that soap made the tissue and impurities less adhesive to one another. He did not put forward any experimental evidence in this direction. Spring gave experimental support to the above view of Hillyer.

Goldschmidt postulated protective action of the colloidal soap upon dirt particles. Since Zsigmondy had shown that the gold number of sodium stearate (the minimum quantity to protect 10 c.c. of red gold sol. from colour change upon addition of 1 c.c. of 10 per cent. sodium chloride solution) was 10 mg. at 60° and 0·01 mg. at 100°C. The value for sodium oleate was 0·6 to 1 mg.

Donnan and Potts in 1910 (Donnan and Potts, Kolloid—Z, 7, 208, 1910) opined that the adsorbed soap at the interface, which lowers the

surface tension, along with viscous nature of the film itself, stabilize the emulsion. They further pointed out that the alkali increases the negative charge of the particles of dirt and oil. This increase prevents coagulation and redeposition of the particles.

Spring (Kolloid, Zeitsch, 1909, 4, 161, 1909, 6, 11, 109, 164; Arch. Sci. Phys. Nat., *28*, 569, *29*, 41, *36*, 80; Rec. Tran. Chem., 29, 1; Bull. Acad. Roy. Belg., 1909, 187, 949, 1911, 24, 17) made most notable contribution towards understanding the detergent action of soap. He pointed out that theories put forward by Jevons and others could not be accepted as they sought only to explain the removal of fatty impurities. Lamp-black carefully made free from fatty materials deposited as quickly from 2 per cent. soap solution as from pure water whereas in the case of ·5 per cent. solution the time of sedimentation became 10 days. This points out that soap can remove perfectly non-fatty material as well. No investigator before Spring noticed the existence of optimum concentration of soap at which maximum detergency is exhibited. Working with ferric oxide Spring found the optimum concentration to be ·5 per cent. and with potter's clay 1/32 per cent.

Alumina, however, showed remarkable periodic optima in $\frac{1}{4}$, $\frac{1}{8}$ and 1/16 per cent. soap solutions with a similar numerical periodicity of coagulation. These suspensions can pass through a filter paper—the unstabilized particles only being retained. According to him cleansing by soap is simply the formation of a sorption compound of dirt and soap in place of the sorption compound of dirt and fabric by direct substitution.

McBain considers the following scheme more logical than the above:—

(*Fabric, dirt*) + Soap ⩾ (Fabric, Soap) + (Dirt, Soap).

Sorption Compound Sorption Compound Sorption Compound.

As a matter of fact, according to McBain, it is often extremely difficult to remove soap from fabric after the operation of washing. Spring pointed out that alcoholic solutions possess poor detergency because hydrolysis is not so great. This is not true if the alcoholic soap is used in water. However, he found that whilst lamp-black took up acid soap, ferric oxide, silicic acid, and cellulose take up soap containing an excess of alkali so that his results in some cases might be more logically attributed, according to McBain, to soap itself. The basic soap of which Spring speaks does not exist. McBain refers the poor detergent action of alcoholic soap to the fact that in alcohol the soap contains only traces of colloids.

Jackson [J. Soc. Arts, 55, 1101 and 1122 (1908), Cantor Lectures] pointed out the effect of soap upon the state of subdivision of the dirt. He examined a soiled surface while attacked by the detergent solution under microscope, and observed the dirt particles and fibres of linen being brought first into oscillation and then loosened completely by soap. For this purpose alkaline oleate solution served best. He also pointed out that glycerine in soap had practically no detergent activity and that lather was not necessary but was a sign of detergency. Stericker (J. Ind. Eng. Chem. 15, 144, 1923) claimed that suds seem to lift the dirt out of the wash liquor thereby preventing redeposition.

Linder and Zickermann (Textilber, 5, 385, 1924, C.A., 18, 3285, 1924) are of opinion that lathering tendency has got important bearing upon wetting power. Addition of saponin up to 3 per cent. to all kinds of detergents tried in Berlin-Dahlem (Textilber, 5, 385, 1924) failed to increase their value. Hence too great an emphasis has been laid upon the lathering power of soap.

What has been written above can be summarised, as has been done by McBain, as follows (this includes all logical and scientific points which have stood the "test" more or less):—

(1) The necessity of having the soap in solution.

(2) It is essential in all cases that the soap should be in colloidal form.

(3) Power of emulsification, which parallels low surface tension and formation of surface films, depends, not upon the alkali of hydrolysis, but upon undecomposed soap.

(4) Wetting power, which also depends upon undecomposed soap.

(5) Lubrication of textures and impurities, which enables the latter to be removed easily. This might be considered as the action of the soap in forming non-adhesive colloidal sorption compounds with tissue and impurities due sometimes to acid soap, but more often to soap itself, and capable of remaining in stable suspension.

(6) Deflocculation or peptization of dirt particles.

(7) Foaming power to some extent.

McBain stated in 1920, "Comprehensive and quantitative work is necessary to complete and co-ordinate the existing fragmentary work in any one case. Each of these factors is capable of simultaneous determination and quantitative evaluation."

S. A. Shorter [J. Soc. Dyers Colourists, 34, 136-8 (1918)] holds the view that adsorption phenomenon plays most important part in cleansing action. The dirt particles that get released from the surface of the fabric are electrically charged due to preferential adsorption of colloidal ions. The charge is negative in sign. It is known that the little addition of alkali enhances detergent action. Shorter states that the OH' ion of the alkali increases the stability of the dirt particles released by soap, i.e., peptized, and consequently redeposition of dirt is prevented. The stability is due to the fact that by further adsorption of the negative OH ion the net charge is increased on the surface of the dirt particles.

E. O. Rasser (Seifensieder—Ztg. 48, 269-9, 290-1, 309-10, 355-7, 192A) lends support to the view that adsorption of acid soap is the main cause of cleansing. Acid soap is produced by the combination of neutral soap and the fatty acid set free by hydrolysis. This acid soap is negatively charged and consequently the sorption compound that is formed by the combination of the acid soap and dirt particles show negative charge. These facts are established by suitable electrical measurements. The conception of acid soap is due to McBain. He showed that even the external addition of fatty acid to a soap solution keeps the later alkaline. This is explained by assuming that fatty acid is adsorbed by soap molecules producing what is called acid soap.

Some authors assumed the existence of basic soap, but McBain rejects such assumption as experimental evidence goes contrary to it.

McBain represents a soap unit in solution graphically as

$$\left[\begin{matrix}(NaP)_x \\ (H_2O)_y\end{matrix}\right] P_z$$

where P represents a fatty acid ion. Each unit is called an ionic micelle. Under ordinary conditions these remain in colloidal form. Unlike other colloids, soap solutions exhibit remarkable electrical conductivity like ordinary electrolytes. Hence soap solutions are classed as colloidal electrolytes. In the above formula, x, y and z represent numerical numbers. From the formula it is also evident that each ionic micelle is heavily charged. This explains the conductivity of soap solutions. The lowering of surface tension is a consequence of adsorption process but a quantitative relation has not been established experimentally. Of course Gibb deduced thermo-dynamically a relation between the above two quantities.

R. T. A. Mus, (Z dent. Ol—Fett—Ind. 42, 235-7, 250-2; Chem. Weekblad, 19, 82-5, 1922) for the first time introduces the picture of surface orientation developed by Langmuir, Harkins and Adams to explain the detergent action of soap. Surface orientation is an established scientific truth to-day. The fundamental idea lies in the fact that like dissolves like. When a fatty acid, known to be insoluble in water, is added to the latter the active and polar carboxyl group stands on the water surface while the inert and non-polar hydrocarbon chain turns towards the vapour phase. Here the polar group of water molecule combines with the polar group of the fatty acid molecule, but the non-polar chain turns away from the water surface.

Harkins' work demonstrates that the introduction of sodium oleate in the benzene-water interface reduces surface tension to zero because of surface orientation: benzene molecule against the hydrocarbon chain of Na-oleate and the water molecule against reactive pole of Na-oleate, i.e., COONa.

The gel theory requires little solubility of the cleansing medium in the adjoining phases, the orientation theory demands a polar character in the cleansing medium, the greater the polar difference the less soluble the substance. This polar difference increases with the length of the carbon chain. But polar difference does not diminish solubility in the interface, since here only the poles dissolve in the related solvents and since both poles are occupied, the product is more stable than the hydrated soap gel itself, so that the latter will push off its molecules towards the oil-water interface and increase their concentration there, a condition which is essential for a permanent emulsion.

The impurities in dirty wash belong to three classes, (1) water soluble or polar substances, (2) insoluble or inactive substances, mainly hydrocarbon oils, and (3) earthy inactive substances. The active and inactive characteristics find their counterpart in the soap molecule and this is the essential point on the cleansing effect of soaps. Some

earthy substances like kaoline also concentrate at the oil-water interface and are capable of being wetted by oil and water. For these reasons such substances likewise have cleansing power.

R. F. A. Mus i nanother paper [Chem, Weekblad, 20, 302-4, (1923)] asserts that products of dissociation are not essential for the lowering of the interfacial tension of water and oil. It is more likely that the soap molecule as such is essential in this regard. F. H. Guernsey (Am. Dyestuff, 12, 766-8, 1923) also holds the view that in cleansing the detergent must be adsorbed more strongly by the dirt than the fibre and displace the latter.

According to Vincent (J. Phys. Chem. 31, 1281-315, 1927) maximum stabilization of dirt particles in the wash liquid occurs at the soap concentration in which the negative ions are adsorbed most strongly in comparison with the positive. Shorter adduces experiments from which he concludes that acid soaps exhibit no surface activity and that detergent action is due mainly to undecomposed soap. Excess of alkali enhances detergent action.

Hitherto in our survey we have seen that all the modern authors have sought the detergent activity of soap solutions in the colloidal form of the latter. R. M. Chapin (J. Ind. Chem. Eng. 17, 1187, 1925) wants to make a departure from the above outlook and claims from theoretical consideration and experimental data that the colloidal fraction of a soap is inert as a detergent at equilibrium. His method of testing detergence lies in the fact that when dilute soap solutions are shaken with flake graphite in presence of air the appearance of a white band at the lower boundary of the froth indicates an excess of soap. This test has been utilized to obtain an understanding of the phenomena of deflocculation and detergency and of the various factors upon which such phenomena depend.

Chapin starts from the relation $A_{pp} < A_{p,w} = A_{w,w}$ deduced by Fuchs (Exner's Report. Physik, 25, 735, 1889) which represents the ideal condition of deflocculation in water. (A_{pp} stands for attraction between particles; $A_{p,w}$, attraction between particles and water; and $A_{w,w}$, attraction of water for itself.) An effective deflocculant must accordingly possess a high attraction for water in order to impart a sufficiently high attraction therefor to the particles upon which it is adsorbed. On the other hand, it must possess a decidedly low attraction for water, else the water will not be able to extrude it to form a sufficiently dense adsorbed layer upon the surfaces of the particles (Harkins and King, J. Am. Chem. Soc. 41, 970, 1919). These two contradictory requirements can be met only by highly unsymmetrical molecules of pronounced polar-nonpolar structure which build an oriented mono-molecular layer at the interface between particles and water (Harkins, Davis and Clark, J. Am. Chem. Soc., 39, 541, 1917). From the above considerations it appears to Chapin that colloidal soap must be entirely inert as a detergent at equilibrium. Of course colloidal soap may constitute a reservoir from which molecular soap may be drawn. The molecularly dissolved higher fatty acid soaps are best deflocculants, because they are very "soluble" in water at their alkali ends and very "insoluble" in water at their hydrocarbon chain. The fatty acids themselves are ineffective because their hydroxyl ends possess too little attraction for water. "Soaps" of the lowest fatty acids are ineffective because their hydrocarbon ends are too small to be sufficiently extended by water against the inward pull of their alkali

ends. Chapin further tries to establish the fact that at optimum concentration of any particular soap, the concentration of molecularly dissolved soap in equilibrium with colloidal soap is maximum and hence the detergent action is also maximum. Above the optimum concentration of total soap the concentration of molecularly dissolved soap in equilibrium with colloidal soap falls accompanied by a fall of detergent action. Chapin also claims that the hydrolyzed portion of the soap becomes ineffective as a deflocculant; and not only that, it inactivates an additional portion of unhydrolyzed soap which is necessary to defloculate the free fatty acid produced. To Chapin it appears doubtful if any acid below caprylic will produce a soap of significant detergent power.

J. Mikumo (J. Soc. Chem. Ind. 52, 68T, 1933) from his adsorption experiments of soap solution by activated animal charcoal showed that the highest soaps in molecular or colloidal form are selectively adsorbed at the interface. He points out that capillary activity and adsorbability of soap are not always strictly parallel. High capillary activities (surface tension and interfacial tension) are observed in the region of C_{12}—C_{18} soaps and that the activity decreases greatly with the soap above C_{18} (Walker, J. C. S. 1921, 119, 1521). (Walker did not measure surface tension against oil; the surface tension of air soap-solution interface after a sharp rise becomes almost independent of concentration. This is not the case with the interfacial tension of soap solution and oil in which tension decreases with concentration up to a considerable range and then falls.)

Mikumo has further shown (J. Soc. Chem. Ind., Japan, 1931, 34, 315) that the capillary activities of binary mixed soaps, especially of behenate (C_{22}) or erucate (C_{22}) and other lower soaps are seriously influenced by the presence of the highest soaps, and that the lathering and detergent activities of these systems are also strikingly depressed. These results may obviously be connected with the fact of selective adsorption mentioned above.

From the above considerations Mikumo infers that soap has a great detergent power when adsorption produces prominent capillary activity. Under such conditions the molecules at the surface layer will primarily be oriented in a unimolecular film, as pictured by McBain and Davis. Mikumo supposes that detergent agents in a solution of pure soap are principally highly dispersed components, especially simple soap molecules, fatty ions, or very fine colloidal constituents such as acid soap sol. (Mikumo, J. Soc. Chem. Ind., Japan, 1927, 30, 75.) So we see Mikumo also puts stress on the roll of molecularly dissolved soap in detergent action. It also appears that for making good soap fatty acids of proper range alone should be used.

Snell (Ind. Eng. Chem. 25, 162, 1933) has shown that in blends of soap and alkaline salts the deflocculating and emulsifying value is the sum of the values of the ingredients when used singly.

(*b*) *Effect of Temperature.*—Some authors have studied the effect of temperature on detergent action. Vincent (J. Phy. Chem. 31, 1281, 1927) recommends 40°C. as the optimum temperature. It is supposed that at high temperature, near about boiling, colloidal nature of the soap solution is destroyed and hence the fall in efficiency. Effect of time and temperature has not been fully studied by any investigator.

(c) *Effect of Hydrogen Ion Concentration or* p_H.—It is well known that a little addition of alkali in soap solution enhances the detergent activity of the latter. Rhodes (Ind. Eng. Chem. 23, 778, 1931) in his detergent tests under conditions approximately those of laundry practice established the fact that for the same soap solution, and the same alkali added, detergent action is maximum when the p_H of the solution is made to attain the value 10·7.

In each case maximum detergency occurred at p_H=10·7 irrespective of the nature and concentration of the builder, i.e., the alkali added. At greater p_H detergent action falls. These results agree qualitatively at least with those of Vincent (J. Phys. Chem. 31, 1281, 1927) who found that the emulsifying action of soap passed through a maximum as increasing amounts of NaOH or Na_3PO_4 were added to the solution.

It appears that the magnitude of the increase in detergent action effected by the builder at the optimum p_H depends very greatly upon some specific property of the anion of the added substance, possibly upon its valence. For example, NaOH does not improve the efficiency of washing to the same extent as Na_2CO_3 or Na_3PO_4. It has been recorded in literature that NaOH lowers the surface tension more than Na_2CO_3 or Na_3PO_4. Hence it cannot be said that lowering of surface tension always goes hand in hand with detergent power of a solution.

(d) *Methods to Evaluate the Detergent Power of Soap.*—Early workers like Hillyer (J. Am. Soc. 25, 1903, 1256) used the degree of lowering of interfacial tension at the soap solution and oil interface as a measure of detergent action. These data of Stalagnometer measurements gave valuable information.

Shorter and Ellingworth (Proc. Roy. Soc., 92, 231, 1916) also made a study of interfacial tension and sought to get a measure of detergent action.

A number of investigators studied the peptization power of soap and connected the same with the cleansing action of the latter. McBain (J. Soc. Chem. Ind. 42, 372T—378T, 1923) utilized Spring's discovery—that soap solution can peptize carbon black which can pass through a filter paper without staining the latter—to express detergent power by numerical number. McBain in developing the quantitative method of determining the detergent action introduces what he calls "carbon number" which represents the detergent power of soap in question. The "carbon number" of a soap solution is the number of grammes of carbon carried through by one killogramme of soap under standard condition. The serious drawback of this method lies in the fact that the use of filter paper the pores of which retain unstabilized carbon makes the result uncertain. McBain developed two methods to measure the quantity of carbon stabilized, one gravimetric and the other colorimetric.

Fall (J. Phys. Chem. 31, 801-49, 1927) in his method did away with the use of filter paper and used a fine grade of manganese dioxide,

instead of carbon, as dirt. Like "carbon number" he introduced the term "MnO_2 value." This is defined as centigrammes of MnO_2 suspended in one litre of the solution under the condition employed. MnO_2 was estimated by the usual permanganate method. Method of procedure and factors affecting the accuracy are given in detail in the paper.

Chapin (Ind. Eng. Chem. 17, 461. 1928) developed a test for the relative deflocculating or detergent efficiency of soaps based upon the observation that when dilute soap solutions are shaken with powdered flake graphite in presence of air the appearance of a white band at the lower boundary of the froth indicates the presence of an excess of soap. The sharp boundary appears at a critical concentration of soap solution. The method of standardization of the graphite used is given.

Goldschmidt (Kolloid—Z, 2, 1933, 227, 1908) found the protective action of different soap solutions by the gold number method. He connected this property. (protective action) with detergent action. The gold numbers of different soap solutions towards a red gold sol. were determined. The higher this value, the greater the detergent power. Protective action varies greatly with temperature as shown by Zsigmondy.

Snell (Ind. Eng. Chem., 25, 162, 1933) allowed soap solutions to deflocculate oil-coated umber powder. A definite quantity of the stable suspension was withdrawn and the iron content of the umber peptized was determined volumetrically and from this the detergent power was evaluated.

Rhodes (Ind. Eng. Chem. 21, 60, 1929) does not approve the methods described above on the ground that the authors of those methods utilised one or other physico-chemical properties of soap to express actual detergent power. In his opinion it is quite likely that none of these properties is sufficient to represent the actual detergent power which results from many physico-chemical reactions all taken together. Further, it will be too risky to assume that the ability of a substance to retain carbon or MnO_2 in suspension is identical with its ability to remove dirt from cloth. From these considerations the author carried out actual washing experiments under conditions very similar to those of laundry practice. The soil prescribed by the Detergent Committee of America was used. This soil consists of a mixture of 2 grms. lamp-black, 5 grms. lubricating oil, 3 grms. tallow and 2 litres carbon tetrachloride and this soil has been used by various workers with satisfactory results.

All the experiments were carried under identical conditions. A washing machine was constructed for the purpose. The measurement of the brightness or whiteness of the washed cloth was effected by means of light reflection experiments done with the help of a specially constructed physical apparatus—may be called a sort of photometer. The experiment involves the rotation of a part of the apparatus called Macbeth Illuminometer. The degree of rotation can be expressed as a measure of whiteness. This eliminates all personal factors involved in the comparison of the washed clothes with standard papers of

different shades. In this way the degree of whiteness has been expressed in numerical numbers.

The following table gives the optimum concentration of soap solution found by different authors:—

Name of Investigator.	Dirt used.	Optimum concentration.
McBain ..	Carbon-black	4·45 per cent.*
Zhuknov and Shestakav	Laundry practice ..	0·2—0·4 per cent.
Spring ..	Ferric oxide, clay, alumina (qualitative work).	1·0 per cent., 0·5 per cent., 0·03 per cent., respectively, stand for the three dirts used.
Donnan and Pott ..	Emulsification study ..	0·6 per cent. gave best results.
Fall ..	MnO_2	0·2 to 0·4 per cent.
Rhodes ..	Laundry practice ..	0·25 per cent.

II. Proposed Theory and Experimental Results.

The foregoing survey of the literature on soap detergency shows that there has been no dearth of theories or experiments explaining the detergent action of soap and it appears that most of the investigators are correct from their respective standpoints. This volume of more or less academic research has however failed so far to throw any light on the problem of finding the relation between the composition and detergent power of soap. The chief defect which eluded the notice of some of the investigators and prevented them from getting at the right conditions governing the detergency from the standpoint of the practical soap maker was that they worked either with salts of individual fatty acids which by themselves would never be faced in practical soap making or with soaps whose internal composition was not known.

As regards composition Webb discovered the I. N. S. Factor of the stock as controlling the composition and the ultimate hardness of soap. Even then, as has been shown by one of the authors and Basu (Soap Trade Review, 1933, 252, 288) that the I. N. S. alone is inadequate to control the hardness and the ultimate composition of soap and that the Titre, i.e., the solidifying point of the fatty acids, has as much say in the matter. The I. N. S. and Titre have been taken note of in controlling the ultimate hardness of soap which can be expressed numerically as "Hardness Number" subject to an allowance being made for the presence of low molecular fatty acids.

As a result of assessment of washing power of a large number of blends by varying the different conditions necessary to develop the washing power, it appears that a number of factors simultaneously act in giving the detergent action of soap as follows:—

(1) *The wetting or dispersive power.*—The soap solution must wet the surface to be cleansed. This factor is responsible for the intimate

*This unusually high value as found by McBain has been shown to be wrong by Vincent. He has shown by increasing the time of settling of unstabilized carbon that the optimum as found by "carbon number" approaches the optimum value as found by Fall by MnO_2 method.

contact of the dirt molecules and soap units in solution and is favoured by the presence of soaps of low molecular fatty acids.

(2) *The emulsifying and peptizing power.*—The former parallels low surface tension. The soap solution must emulsify the liquid dirt which thereby get released from the fabric and dispersed throughout the solution. The solid dirt particles adsorb the soap units and become electrically charged and stabilized thereby. This is favoured by the presence of soaps of fatty acids of long carbon chains. Particles completely covered with fatty liquids behave like liquid particles.

(3) *Hydrolysis alkali, i.e., the extent of hydrolysis, which favours the cleansing action.*—The formation of hydrolysis alkali is greater in the case of higher fatty acid soaps.

All the above factors are responsible jointly for the detergent power of soap and it has been found that attempts to increase one of the factors beyond a certain optimum has invariably been found to depress or modify the others. In fact, this brings out indirectly the existence and simultaneous action of all the factors in the detergent action of soap. As pure soap is the best detergent, a balance has to be established in the soap as follows:—

(*i*) The soap should not possess much heaviness so that it can wet and penetrate which is accomplished by the presence of regulated quantities of low molecular fatty acids. If the low molecular fatty acids exceed beyond a certain optimum point, there will be quick foaming, making the lather thin with a tendency to break up, indicating a lowering of detergent power.

(*ii*) The soap should possess fatty acids of the right range of molecular weight together with unsaturated fatty acids so that the emulsifying and peptizing power is maximum consistent with the balance. If it exceed beyond the optimum, the soap will be too heavy with loss in wetting power and hence in detergency.

(*iii*) The regulating of the above factors at their optima will automatically control the hydrolysis alkali giving the proper p_H value favourable for emulsification and peptization.

The practical attainment of the maximum detergency according to the above factors will be dependant primarily on (*a*) proper compounding of stocks to get the balance between the factors involved, (*b*) and also on the control of the ultimate composition which can be secured by the non-elimination of any constituent in the niger and making the soap by the grained process by which the entire stock is converted into a homogenous soap.

The wetting power as exerted by the soap solution is represented by its action as a true solution. Sodium salts of low molecular fatty acids act as true solutions and limited quantities of such fatty acids must be present in a washing soap to give the necessary wetting power. This power, though contributing to the detergency of soap, cannot exceed a certain maximum as otherwise there will be a weakening in the action of other factors. To regulate the wetting power and keep it at its optimum, the use of low molecular fatty acids and hence of oil containing such fatty acids must be regulated to exactitude. An increase of low molecular fatty acids beyond the optimum is indicated in a practical way by the properties of the lather of the soap. The correct nature of a highly detergent lather in the cold is sloppy and yet not too heavy and lasting longest in the air. If the lather become very thin with a

tendency to break up and also become unstable, the optimum limit of wetting power has been passed accompanied by loss in emulsifying and peptizing power. To develop the maximum washing power of a soap this point should not be exceeded and it is so sharp that the transgression can be clearly noticed. Practical soap blending in accordance with the correct Hardness Number indicates that in an ordinary blend this point is reached with 15 to 15½ parts of cocoanut oil in 100 parts of stock mixture*. Irrespective of the oils and fats used, soaps of the correct Hardness Number with the above proportions of cocoanut oil show the maximum detergency.

The undernoted blends have been used for the purpose of test and it is claimed that the maximum detergency has been developed in the soaps, all made by the grained process. The first formula is with mowha oil as the major hard stock and the second one is with tallow as the major hard stock—

No. 1.

	Percentage.	Aggregate I.N.S.	Aggregate Titre.
Mowha oil	65¼	8,352	2,610
Tallow	7	1,050	336
Cocoanut oil	15½	3,875	348·7
Rosin	4	200	288
Linseed oil	3	45	45
Groundnut oil	5¼	535·5	133·8
Total ..	100	14,057·5	3,761·5

I.N.S. for unit stock = 14057 ÷ 100 = 140·57
Titre for unit stock = 3761 ÷ 100 = 37·61
Hardness Number = 140·57 + (3·7 × 37·61)
= 140·57 + 139·16
= 279·73

No. 2.

	Percentage.	Aggregate I. N. S.	Aggregate Titre.
Tallow	46·5	6,975	2,232
Cocoanut oil	15·5	3,875	348·7
Rosin	4	200	288
Linseed oil	3	45	45
Goundnut oil	31	3,162	790·5
Total ..	100	14,257	3,704·2

I. N. S. for unit stock = 14257 ÷ 100 = 142·57
Titre for unit stock = 37·042
Hardness Number = 142·57 + (37·04 × 3·7)
= 142·57 + 137·05
= 279·62

Though the major oils are essentially different in the blends, the fatty acid contents of both the soaps bear a definite proportion between the

*Datta and Basu, *loc. cit.*

low molecular fatty acids, saturated fatty acids and unsaturated fatty acids as calculated below from the constituent fatty acids of the individual oils going into the charge.

From a calculation of the amounts of each fatty acid in the respective oils making up the charge, the total percentages of the fatty acids present in the final soap are given in the following table:—

		No. 1 Formula.	Total.	No. 2 Formula.	Total.
		Per cent.	Per cent.	Per cent.	Per cent.
I	Caprylic Acid ..	1·47		1·47	
	Capric Acid	·69		·69	
	Lauric Acid	7·90	13·07	7·90	13·94
	Myristic Acid ..	3·01		3·88	
II	Palmitic Acid ..	14·83	14·83	16·61	16·61
III	Stearic Acid	13·14		10·84	
	Arachidic Acid ..	·21	13·50	1·24	13·01
	Lignoceric Acid ..	·15		·93	
IV	Oleic Acid	50·50		41·96	
	Linoleic Acid ..	3·28	54·50	9·69	52·37
	Linolenic Acid ..	·72		·72	
V	Resinic Acid	4·00	4·00	4·00	4·00

I. Low molecular fatty acids favouring wetting power.

II. Normal saturated fatty acid favouring emulsion and also formation of hydrolysis alkali to a certain extent.

III. Higher saturated surface active fatty acids favouring hydrolysis alkali and detergency in the hot as well as strong peptization.

IV. Unsaturated acids mainly favouring emulsification.

V. Resinic acid favouring lather and stability of the soap.

It should, however, be noted that the properties figured are the principal properties of the respective fatty acids though fatty acids of the different groups cannot be held to be absolutely devoid of other properties. For example, the low molecular fatty acids favouring wetting power also possess, to a lower degree, power of emulsification as the surface tension of such fatty acid soap solutions are lower than water or ordinary salt solutions.

From an examination of the fatty acid contents of both the blends mentioned above which are derived from different raw materials, it is evident that the Hardness Number not only controls the actual hardness and detergency of the soaps but also controls the constituent fatty acids coming into the soaps to give the same properties. The slight variations seen are only apparent. For example, in No. 1 blend the aggregate of the unsaturated fatty acids is 54·50 per cent. whereas in No. 2 blend the aggregate of the same acids is 52·37 per cent. In No. 2; the slightly lower amount is due to the presence of more linolenic acid which is more unsaturated than oleic acid. Here, the presence of the lather interfering arachidic and lignoceric acids is counterbalanced

by the presence of more palmitic acid and more aggregate unsaturation than in No. 1. It will be seen, therefore, that the Hardness Number accurately controls the ultimate properties of the soap irrespective of the fatty raw materials going to make up the charge. The above blends of soaps were tested for detergency with the soil recommended by the American Society of Detergent Chemists and have been found to cleanse best near about ·15 per cent. strength which is the lowest strength of optimum detergency hitherto found. The method consists in preparing standard soils with a mixture of 2 grms. lampblack 5 grms. lubricating oil, 3 grms. tallow and 2 litres carbon tetrachloride.

The emulsifying action is exerted by the sodium salts of the unsaturated fatty acids such as oleic, linoleic and linolenic. It should also be noted that acids with higher unsaturation possess greater emulsifying power than the less unsaturated ones. The presence of these acids should not be pushed to the extreme at the expense of wetting power because the increase of emulsifying and peptizing power beyond a certain optimum has been found to depress the wetting power, that is to say, making the soap too heavy and less penetrating. This can only be attained by the introduction of limited quantities of cocoanut or palm kernel oil. In fact, there should be an accurate balance of these factors and the point is attained when the lather has a tendency to get thin and break up. It is at this point that the correct balance between the wetting and emulsifying powers is obtained.

The third factor is the hydrolysis alkali. This, in fact, favours both the above factors. At the optimum condition as set forth above, the hydrolysis alkali that is produced during washing is quite normal and dependant on the correct balance between the wetting and emulsifying powers.

The hydrolysis alkali acts in facilitating both the wetting and emulsifying power and its formation is quite regulated and invariable under such conditions. If the wetting power is increased at the expense of emulsifying power by the increase of low molecular fatty acids, the degree of hydrolysis will also decrease because the soaps of low molecular fatty acids have a tendency to act like ordinary solutions. Hence it will be seen that soaps in which the emulsifying power is depressed will be less hydrolysed, and be less efficient.

In course of experiments it was found that there exists for each soap a narrow concentration region in which it exercises its best cleansing power in the boiling condition. For example, the soap having formula No. 1 showed much better cleansing power at ·15 per cent. concentration than any of the higher concentrations like ·3 per cent., ·5 per cent., ·75 per cent., 1 per cent., etc. The condition of soiling the linen and modes of cleansing and washing and time of contact with the detergent solution, etc., were identical in the above series of washing experiments, and in all cases, the anhydrous soaps were used after careful drying in the steam oven. "Sunlight" soap, on the other hand, shows its maximum detergency in the neighbourhood of ·25 per cent. At concentrations much below and much higher than ·25 per cent. the cleansing power of the soap remarkably falls. Even then the grained soap at ·15 per cent. strength cleanses somewhat better than "Sunlight" at ·25 per cent. "Ivory" soap cleanses best at the concentration of ·2 per cent. With further increase in concentration, a fall in the detergent action is noticed. "Ivory" soap at this strength exerts the same cleansing action

as ·15 per cent. grained soap. Under similar conditions, the optimum concentration of yellow Marseilles soap is ·4 per cent.

In these comparative experiments, the following order of detergent power was obtained:—

·15 per cent. Grained No. 1 = ·2 per cent. Ivory > ·25 per cent. Sunlight > ·4 per cent. Marseilles.

To carry out these experiments no utopian conditions were adopted. The household condition of washing was adopted and was clothed with scientific accuracy as far as possible. Each experiment was repeated a number of times and then the conclusion drawn. The soap was weighed accurately and then requisite amount of distilled water was added. The volume of the solution was made the same in each case. The solution was heated to boiling, the burner removed, and then the soiled cloth was introduced. After an hour the linen was squeezed inside the detergent solution for two minutes and then taken out and washed by distilled water. Finally it was dried in steam oven. In each set of experiments the linens used were taken from the same stock and soiled under same conditions. After a little practice identical and even soiling can be attained. Repetition experiments did not leave any room for doubt as regards the comparative cleansing power of the different detergent solutions used.

The grained soap from a stock having the following composition:—

No. 3.

Tallow	40½
Cocoanut oil	36
Linseed oil	3
Rosin	4
Groundnut oil	16½

should possess poorer detergency due to the presence of much low molecular fatty acids derived from cocoanut oil. As a matter of fact washing experiments fully materialised the expectation. At ·15 per cent. concentration it cleansed appreciably less than the grained soap No. 1.

It was thought desirable to find the relative lowering of surface tension of all the soaps at the kerosine-soap-solution interface. A Donnan pipette was used for the purpose. A particular brand of kerosine was taken in the pipette. It was introduced in a big test tube filled with soap solution. Drops were allowed to form in a manner that they could be easily counted during their upward journey through the solution. As the temperature has got little influence on the number of drops formed, no particular attention was paid for keeping the temperature constant. The experiments were carried out at the room temperature.

The following table gives the mean value of a number of determinations:—

Soap.	Concentration. Per cent.	Drop number.
Grained No. 1	·15	620
Ivory	·15	604
Sunlight	·15	510
Marseilles	·15	460
Water	—	142

It will be seen that at the concentration, ·15 per cent., grained soap No. 1 is most surface active or has the greatest emulsifying power. This is well reflected in the practical detergent tests with soiled linen under standard conditions.

The alkalinity due to hydrolysis of the soap prepared from the stock richer in cocoanut, i.e., No. 3 blend, was less than the grained soap No. 1 as determined by p_H measurements as was to be expected. Sunlight soap also showed less alkalinity than the grained No. 1. p_H values were determined at room temperature colorimetrically by means of a Follien Colorimeter. The p_H value of the solution at the boiling condition, however, increases greatly due to greater degree of hydrolysis. As there is no suitable method to determine the p_H value at about 100°C., the exact value cannot be determined but it can be reasonably expected that the solution having a higher p_H at room temperature than another will maintain this difference at an elevated temperature, though the p_H value of each solution increases considerably at high temperature. Another method of finding comparative degree of hydrolysis of different soap solutions is to add water to their solutions in absolute alcohol in which phenolphthalein is added. On the continued addition of water a point is reached when faint pink colour appears due to hydrolysis. Though the point in itself is not very sharp like one that we meet in acid-alkali titration, still, for comparative study, it is quite satisfactory and useful. The information obtained from these experiments has been found to be supported by p_H data. The greater the volume of water necessary to produce the first tinge of pink colour for a particular soap solution, the less is it hydrolysable in water alone. The following procedure was adopted in these experiments. Soap was weighed by difference into a jena glass conical flask. A quantity of alcohol, much less than what would be required to produce the desired strength, was added and the flask heated on a water bath and refluxed. When the soap dissolved completely, the flask was removed and cooled. The solution was then transferred to a 250 c.c. measuring flask in the usual way and 30 c.c. of ·5 per cent. solution of phenolphthalein in absolute alcohol were added into it. The volume was made up to the mark with absolute alcohol. 50 c.c. of the soap solution were pipetted out in a flask and water was added from a burette. The flask was cooled at intervals under the tap as heat was produced in the process. The addition of water was continued till the point mentioned above was judged to have been obtained.

The following table gives the results obtained:—

Soap.	Strength of alcoholic solution.	C. C. of distilled water required per 50 c.c. of the solution to produce the first tinge.	p_H of water solution of corresponding strength at room temperature.
	Per cent.		
Grained No. 1 ..	·3	105	9·0
	·15	158	7·4
Ivory	·3	113	8·6
	·15	165	7·1
Sunlight	·3	130	8·6
	·15	170	7·2
Marseilles	·3	170	8·2
	·15	290	6·4

It will be seen from the above table that grained soap No. 1 which possesses the best detergent power at the concentration of ·15 per cent. is more hydrolysable than the other soaps as required by the theory.

Summary.

A general summary of theories proposed and practical work done by different workers from Berzelius down to the present day investigators in relation to detergent action of soap has been given. This connected account gives the history of progressive growth of knowledge on the subject.

It has been pointed out that co-relation of composition and detergency of soap which is vitally important to the practical soap maker escaped attention of all the workers. This problem has been the subject of this investigation and a theory of composition and detergency has been proposed corroborated by convincing practical results. The fact has been established that preparation of pure soap of maximum detergent power demands control of its composition by regulating the stock mixture in such a manner that the physico-chemical factors responsible for detergency can lie within an optimum zone. This point can be arrived at, irrespective of difference in stocks, provided the "Hardness Number", which is the most reliable and dependable index of actual hardness and composition of soap, is fixed up at a certain figure in each case. Actual comparative detergent tests proved that grained soap, prepared with due regard to the optimum balance in stock blending and hence the correct hardness number, was found superior to any soap of repute available in the market. This soap cleansed best at ·15 per cent. concentration, this being the lowest concentration hitherto recorded at which maximum detergency is exhibited. The same for Ivory, Sunlight and Marseilles soaps are ·2 per cent., ·25 per cent. and ·4 per cent., respectively. Then again, the order of cleansing efficiency is as follows:—

·15 per cent. Grained No. 1 = ·2 per cent. Ivory > ·25 per cent. Sunlight > ·4 per cent. Marseilles.

B. G. Press—1934-35—8428B—500.