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in Washing Soap**

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On the part played by Individual Fatty Acid Soaps in the Development of Optimum Detergency in washing soap.

It has been shown¹ that the development of maximum cleansing power in soap demands control of its composition by regulating the stock mixture and, consequently, the individual fatty acids that enter into the composition of soap. This end is attained by fixing the Hardness Number² at a certain figure irrespective of the difference in stocks which ensures the physico-chemical factors responsible for detergency to lie within the optimum zone. The actual detergency of a soap produced under such conditions was found superior to any other soap while the optimum strength of such a soap was 15 per cent.

In the present Bulletin, the actual detergency under practical washing conditions, and constants responsible for the detergency of sodium soaps of typical fatty acid members, have been examined with a view to ascertain the part played by each in developing the detergency of the ideally-blended soap and also with a view to determine whether any single member possesses detergency ahead of the ideally-blended soap and whether, by the ordinary rule of average, the value of the aggregate detergency equals the actual detergency exhibited by the blended soap.

Strangely enough, practical tests prove that none of the members constituting soap can come up to the blended soap in point of detergency; while some exhibit a far lower degree of detergency, others exhibit practically no detergency at all. This points to the fact that the final detergency is not at all dependent on the aggregate value of detergency of the individual fatty acid soaps; but these fatty acid soaps mutually strengthen each other in such a manner as to produce a soap whose detergency is ahead even of the member possessing the highest detergency in spite of some members (e.g., oleic acid soap) constituting about 50 per cent. of the blended soap and possessing as low as about 40 per cent. of its detergency.

It may be thought possible that each of the factors in detergency, viz., wetting power, emulsifying power and formation of hydrolysis alkali, is advanced to an extraordinary degree by the favourable action of the other factors; but actually this is not the case as the grained soap is hydrolysed to a lesser extent than sodium stearate, yet the former has better detergent power than the latter. In a similar manner, the p_H value of grained soap has a slightly lower value than that of sodium stearate. It is, therefore, the mutual favourable action that accounts for the high efficiency of the blended soap, as the high degree of hydrolysis and high p_H value, the emulsifying power (possessed by sodium oleate) and also the wetting power present in low molecular fatty acid soaps, assist each other. This leads one to the conclusion that the aggregate efficiency of the blended soap is due to the factors responsible for detergency assisting each other to produce the maximum

¹Bulletin No. 62 (1934), Department of Industries, Bengal.
²Dato 61 (1933), ditto.

effect though the effect of any one factor is not as high as that of the individual member possessing the highest value of such factors. This lends support to the theory of detergency put forward that each of the factors is responsible for cleansing and that the optimum of the combined effect of the three factors will constitute the maximum detergency possible to be developed in washing soap.

It appears, therefore, that the correct blending of a washing soap means the introduction of the correct percentages of fatty acids so as to develop the maximum effect by mutual strengthening, that is to say, each assisting the others to produce the maximum detergency. It is claimed that such an optimum effect has been practically obtained. [*Vide* Bulletin No. 62 *loc. cit.*]

Other workers, particularly Marsden¹, noted the high detergency of stearate in the hot and stated that considerable advantage would be gained from the employment in laundries of soaps of as high a stearate content as possible. They also recommended the use of two separate types of soap, one with a high oleate content for cold washing and the other with a high stearate content for hot washing. It will be seen that properly blended soap containing only 13 per cent. stearic acid and 15-16 per cent. palmitic acid possesses better detergency than the stearate soap without possessing any of the disadvantages of a hard soap. It is evident, therefore, that there will no longer be any necessity of having any special soaps containing an unbalanced excess of any of the constituents. It is expected that the ideally-blended soap which cleanses best in the hot will also do so in the cold and experiments to prove this point will be undertaken in due course.

Experimental:

Sodium soaps of the fatty acids were prepared in the following way. A known weight of the pure fatty acid was taken in a basin and placed over a water-bath. An excess of pure sodium carbonate was added to the molten acid when the soap was formed. The mass was well stirred. The soap with the excess of sodium carbonate was transferred in a flask and a large quantity of alcohol was poured in. The flask was fitted with a straight condenser and the soap refluxed for a pretty long period. The loss of alcohol was made good by further addition of the solvent from time to time. The soap dissolved in alcohol and the excess carbonate remained undissolved. The solution was filtered hot by using a suitable hot filter. With the fall of temperature the filtrate gelatinised to a solid white mass. This was then heated over a water-bath till it was almost free from alcohol and finally dried in a steam oven to free it from the last traces of alcohol.

The washing experiments to evaluate comparative detergent power in the hot were carried out exactly in the same manner as was adopted in our earlier work on the subject². Cleansing experiments were done with sodium stearate, sodium palmitate, sodium oleate and also with sodium capriate as compared with the blended soap, using the same

¹Marsden—Detergent Action and Surface Activity, 141.

²*loc. cit.*

method in every case, and the following order of detergency was found at the respective optimum concentration:—

- 15 per cent. Grained No. 1 = ·2 per cent. Ivory.
- > ·25 per cent. Sunlight.
- > { ·4 per cent. Sodium oleate, or,
- { ·15 per cent. Sodium stearate.
- > ·4 per cent. Marseilles.
- > ·2 per cent. Sodium palmitate.

It may be noted that a lower optimum effect was developed by each succeeding member on the right. Sodium capriate failed to effect appreciable cleansing at a concentration as high as ·55 per cent.

The drop numbers of different soap solutions were found by means of a Donnan pipette containing kerosene oil and immersed in soap solution contained in a cylinder. The temperature was maintained at 47°C. as at a lower temperature sodium stearate and sodium palmitate became opaque and the drops could not be counted during their upward journey. This was not the case with the blended soaps, none of which gelatinised at such low concentration as ·15 per cent. at ordinary temperature. The formation of drops was regulated by manipulating the pressure working over the kerosene inside the Donnan pipette. The following results, showing the relative lowering of surface tension at the kerosene-soap-solution interface, were obtained:—

Soap.	Concentration.		Drop Number.
	..	Per cent.	
Sodium stearate	..	·15	900
Sodium palmitate	..	·15	892
Sodium oleate	..	·15	552

The p_H values were measured colorimetrically by a Follien Colorimeter. These values gave an idea of the concentration of hydrolysis alkali. To determine the relative degrees of hydrolysis, alongside the p_H values, volumes of distilled water required to be added to the alcoholic solutions of soaps containing a definite quantity of phenolphthalein to produce the first pinkish tinge were determined in the same way as described in Bulletin No. 62. It would be found that the greater the volume of the water to produce the first tinge, the less will be the soap hydrolysable. The following table gives these values:—

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.
		..		
Sodium stearate	..	·3	100	9·4
		·15	150	8·4
Sodium palmitate	..	·3	110	9·0
		·15	157	8·3
Sodium oleate	..	·3	170	8·6
		·15	242	7·0

The following observations can be made with regard to the detergency of the individual members.

It will be seen that, as regards cleansing in hot among the fatty acid soaps examined, sodium stearate is most efficient. It is the most surface-active soap, as is to be expected on account of its chain length, and produces the maximum hydrolysis alkali. Sodium palmitate is appreciably inferior to sodium stearate as a detergent. The introduction of double bond increases the solubility to a great extent and also raises the optimum concentration, since sodium stearate has an optimum concentration of 15 per cent. whereas the same for sodium oleate is 4 per cent. The unsaturation makes the soap a good emulsifying agent, no doubt, but, as regards cleansing in hot, the soap falls far below the mark. The advantage of a soap of unsaturated fatty acids lies in cold washing, though a higher concentration is necessary. The difficulty with higher saturated fatty acid soaps is that they all gelatinise even at 15 per cent. concentration at ordinary temperature. A soap of lower saturated fatty acid, like sodium capriate, though possessing good solubility and wetting power, is in itself not at all a good detergent. It will be seen that the drop-numbers and some of the p_H values were determined at 15 per cent. concentration. Stoichiometrically speaking, 15 per cent. of palmitic acid is a stronger solution than 15 per cent. stearic acid. Even then, as regards hydrolysis and surface activity, sodium palmitate solution falls below sodium stearate.

The most significant fact is that none of the common higher fatty acid soaps is capable of exhibiting the same degree of cleansing efficiency as a good blended soap. The reason is that, according to the theory proposed, the different physico-chemical factors responsible for detergency cannot lie in an optimum region in the case of any pure fatty acid soap. On the other hand, in the case of a blended soap obtained from a stock mixture of proper Hardness Number, these factors lie in an optimum zone because the different fatty acid soaps with the principal detergent properties, all strengthening each other and contributing towards the total detergency, enter into the composition of the blended soap in requisite proportions.

Summary:

(1) Among soaps of higher fatty acids sodium stearate is most efficient as a detergent in the hot.

(2) With the introduction of double bond the optimum concentration increases with an accompanied increase in solubility.

(3) Properly blended soap cleanses better than any single fatty acid soap and gives a better combined efficiency, very much more than the mere additive values, by a mutual strengthening of the different properties responsible for detergency. This lends support to the theory of detergency put forward by the authors inasmuch as all the three factors, viz., the wetting or dispersive power, the emulsifying power and the power of forming hydrolysis alkali, are responsible for the detergency and not one or another as previous workers suggested.