# The Determination of Some Physical and Chemical Constants of Certain Detergents 

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While much work has been done in an effort to clarify the chemistry of detergents to the end that a beiter understanding may be reached of how these substances function as cleansing agents, the precise answers are still lacking.

Certain advantages are claimed for individual detergents based on alleged differences in makeup. These claims have commercial significance and should therefore be supportable by factual evidence. The chemistry of soaps is sufficiently well advanced to indicate probable difficulty in justifying divergent advertising claims, particularly for products in the same price class.

Because of the facts stated in the preceding paragraphs, the study to be described in these and succeeding papers was initiated. It is hoped that some contribution can be made which will aid in building up a more comprehensive knowledge of the chemical and physical factors in the act of removing soil and to develop'a clear-cut and practical comparison between the detergents now available commercially.

## EXPERIMENTAL

This investigation was begun with the purchase of ten varieties of toilet soaps sold widely in drug stores. Samples of these were subjected to a series of experiments designed to compare them on the basis of their physical and chemical properties.

First, their content of volatile material was determined. The total volatile matter contained was ascertained by means of the A. O. A. C. heat method (1). The common xylene method of the A. O. A. C.

Table I.-Volatile Material Contained by the Soaps Tested

| Soap | Per Cent <br> of Total <br> Volatile <br> Matter | Per Cent of <br> Moisture | Per Cent <br> of Volatile <br> Material Not <br> Moisture |
| :---: | :---: | :---: | :---: |
| $G$ | 8.10 | 7.87 | 0.23 |
| $D$ | 7.14 | 6.50 | 0.64 |
| $B$ | 6.38 | 6.24 | 0.14 |
| $H$ | 6.16 | 5.79 | 0.37 |
| $A$ | 5.98 | 5.73 | 0.25 |
| $I$ | 4.97 | 4.54 | 0.43 |
| $F$ | 4.61 | 4.31 | 0.30 |
| $J$ | 3.90 | 3.74 | 0.16 |
| $C$ | 3.14 | 3.10 | 0.04 |
| $E$ | 2.96 | 2.88 | 0.08 |

(2) gave the amount of moisture present. The non-moisture volatile matter was calculated in the usual way by difference. Table I shows the results of these determinations. In it the soaps are listed beginning with the one having the highest content of total volatile matter.
Plotting the total volatile matter contained by each soap against its percentage of moisture developed the curve shown in Fig. 1. From the graph it would appear that some correlation existed between the two properties used in its formation.


Fig. 1.--Total Volatile Matter and Moisture.

Samples of the soaps were next extracted with alcohol, then with water in order to determine their content of alcohol-soluble and water-soluble material. The residue from the extractions was called the insoluble matter. The data pertaining to these values are expressed in Table II. The soap containing the greatest amount of alcohol-soluble matter is listed first.

Table II.-Alcohol-Soluble, Water-Soluble and Insoluble Matter in the Soaps Studied

|  | Per Cent <br> of Alcohol- <br> Soluble | Per Cent <br> of Water- <br> Soluble <br> Matter | Per Cent of <br> Insoluble <br> Matter |
| :---: | :---: | :---: | :---: |
| Soap | Matter | 1.79 | 0.08 |
| $I$ | 98.13 | 3.04 | 1.52 |
| $D$ | 95.44 | 5.60 | 0.46 |
| $G$ | 93.94 | 4.36 | 1.88 |
| $A$ | 93.76 | 7.07 | 0.07 |
| $J$ | 92.86 | 4.82 | 2.39 |
| $C$ | 92.79 | 6.03 | 1.28 |
| $B$ | 92.69 | 7.12 | 3.23 |
| $H$ | 89.65 | 8.13 | 2.54 |
| $E$ | 89.33 | 5.18 | 30.88 |
| $F$ | 63.94 | 5.18 |  |

Figure 2 is the result of plotting the percentage of alcohol-soluble matter for each soap against its concentration of water-soluble material. It is


Fig. 2.-Alcohol-Soluble and Water-Soluble Matter.
obvious no feasible mathematical correlation can be made between the values used in developing the curve.
Significance is frequently attached to the hydro-gen-ion concentration of soaps in standard dilutions.


Fig. 3.-Comparison of Soil-Removing Ability with the Property of Seeds Formation.

Therefore, the $p_{\mathrm{H}}$ value of 0.25 per cent solutions of each of the ten soap samples was determined with a Leeds and Northrup potentiometer using a glass electrode. The values obtained are given in Table III. The highest value is listed first.

Table III.-pH Values of $0.25 \%$ Aqueous Solutions of the Soaps

| Soap | $p_{\mathrm{H}}\left(25^{\circ} \mathrm{C}\right.$. $)$ | Soap | $p_{\mathrm{H}}\left(\mathbf{2 5 5 ^ { \circ }} \mathrm{C}\right.$. $)$ |
| :---: | :---: | :---: | :---: |
| $H$ | 10.5 | $E$ | 10.3 |
| $I$ | 10.5 | $A$ | 10.2 |
| $J$ | 10.4 | $G$ | 10.1 |
| $D$ | 10.4 | $B$ | 9.4 |
| $C$ | 10.3 | $F$ | 8.8 |

Inasmuch as surface tension is an important factor in the efficiency of detergents, its value for the soap samples used in the $p_{H}$ work was determined. The data were obtained by means of a du Noüy Precision Tensiometer. The results are shown in Table IV where the largest surface tension expressed in dynes is given first.

Table IV.-Surface Tensions of 0.25 Per Cent Aqueous Solutions of the Soaps

|  | Surface <br> Tension <br> ( $25^{\circ} \mathrm{C}$.) |  | $\begin{aligned} & \text { Surfaace } \\ & \text { Tension } \\ & \left(25^{\circ} \mathrm{C} .\right) \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| Soap | in Dynes | Soap | in Dynes |
| A | 30.5 | I | 28.5 |
| $J$ | 29.5 | C | 28.4 |
| G | 29.2 | E | 28.1 |
| D | 29.1 | F | 27.4 |
| H | 29.0 | $B$ | 26.4 |

The ability to form copious and lasting suds is often taken as a criterion of an efficient soap. To test this property 25 cc . of a 0.25 per cent aqueous solution of each soap at $20^{\circ} \mathrm{C}$. were placed in a $100-$ cc. glass-stoppered graduated cylinder and inverted completely ten times. Readings of the volume in cc. of the suds were recorded immediately after the tenth inversion and at the end of one-, two- and twenty-four-hour periods. Table V shows the results. In it the soap producing immediately the greatest amount of suds is listed first.

Table V.-Height of Suds above the Supporting Columns of 25 Cc . of $0.25 \%$ (Dry Weight) Soap Solutions at $20^{\circ} \mathrm{C}$.

| Soap | 0 Hour, <br> Cc. | 1 Hour, <br> Cc. | 2 Hours, <br> Cc. | 24Hours, <br> Cc. <br> $G$ |
| :---: | :---: | :---: | :---: | :---: |
| 52 | 42 | 29.5 | 4.5 |  |
| $E$ | 42.5 | 33.5 | 24.5 | 0 |
| $A$ | 40 | 31.5 | 29 | 5 |
| $D$ | 34.5 | 30 | 13.8 | 0 |
| $J$ | 29.5 | 26.5 | 24.5 | 4.75 |
| $I$ | 29.5 | 20.5 | 5 | 4.5 |
| $C$ | 28 | 25 | 23 | 0 |
| $F$ | 27.5 | 23.5 | 20.5 | 3.5 |
| $B$ | 23.5 | 21 | 20 | 7 |

An attempt was made to rate efficiencies of the soaps as soil removers. A practical determination of this ability would furnish an effective basis for beginning a correlation, if any is possible, between the efficiency and the previously determined physi-
cal and chemical properties. To this end the various samples were submitted to soil tests in a specially constructed machine.

The apparatus consisted of a $500-\mathrm{cc}$. glass jar provided with a screw cap. Through the cap and into the jar was fitted a twisted wire agitator which went to and fro as the handle was raised and lowered. The agitator carried a removable tin container for the soil, the size of which was $4 \times 4 \times 1 \mathrm{~cm}$. The soil used was a 5 per cent ointment of lampblack in tallow.

The test was performed as follows: 240 cc . of 0.25 per cent soap solution were placed in the jar. The previously weighed tin of soil was attached to the agitator, placed in the solution and set in motion at the rate of 240 revolutions per minute at $20^{\circ} \mathrm{C}$. The agitation was continued for exactly five minutes. The tin was then removed, partially dried in a current of air and dried in a sulfuric acid desiccator to constant weight. A blank determination using pure water was run. The difference between the loss of weight in the soap solution and that in pure water represented the weight of soil removed by the soap. The resulting data are shown in Table VI.

Table VI.-Detergent Test; Soil Washed for Five Minutes, 240 R. P. M., $20^{\circ} \mathrm{C}$. in 240 Cc . of $0.25 \%$ Soap Solution

|  | Average Loss, <br> Gm. | Loss over <br> That of Water, <br> Gm. |
| :--- | :---: | :---: |
| Water | 0.0508 | $\ldots .0$ |
| Soap $J$ | 0.0891 | 0.0383 |
| Soap $H$ | 0.0784 | 0.0276 |
| Soap $E$ | 0.0781 | 0.0273 |
| Soap $G$ | 0.0660 | 0.0152 |
| Soap $I$ | 0.0608 | 0.0100 |
| Soap $B$ | 0.0585 | 0.0077 |
| Soap $A$ | 0.0579 | 0.0071 |
| Soap $C$ | 0.0579 | 0.0071 |
| Soap $D$ | 0.0555 | 0.0047 |
| Soap $F$ | 0.0538 | 0.0030 |

Ability to form copious suds seems to have little relationship with ability to remove soil. Figure 3 where the two properties are plotted against each other shows plainly this lack of relationship.

Alkalinity of the soaps was determined by titrating solutions of one Gm . of each with normal sulfuric acid. The results are shown in Table VII.

For the sake of comparison the total alkalinity and $p_{\mathrm{H}}$ values of the soaps were plotted against each other. Figure 4 is the result.

Table VII.-Number of Cc. of Normal Sulfuric Acid Required to Neutralize the Alkalinity of 1 Gm. of Soap

| Soap | No. of Cc. of <br> Normal Acid <br> Required | Soap | No. of Cc. of <br> Normal Acid <br> Required |
| :---: | :---: | :---: | :---: |
| $A$ | 1.3671 | $C$ | 1.0473 |
| $I$ | 1.3671 | $E$ | 0.6236 |
| $D$ | 1.3111 | $G$ | 0.6076 |
| $J$ | 1.2791 | $B$ | 0.5356 |
| $H$ | 1.1752 | $F$ | 0.1679 |

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Fig. 4.-Total Alkalinity and $p_{\mathrm{G}}$ Values.

## SUMMARY

Ten soaps were examined and the following properties determined for each: percentage of volatile matter, moisture, non-volatile matter, alcohol-soluble matter, watersoluble matter, and insoluble matter, the $p_{\mathrm{H}}$ value, surface tension, ability to form suds, ability to remove soil and total alkalinity.

## REFERENCES

(1) "Association of Official Agricultural Chemists," Second Edition, page 56.
(2) "Association of Official Agricultural Chemists," Fourth Edition, page 58.

Robert Bárány (1876-1936) was awarded the Nobel Prize for physiology and medicine in 1914 for his work on the physiology and pathology of the human vestibular apparatus. To this day, his graduation thesis is regarded as the source of all scientific knowledge on the vestibular apparatus.

