X.—*The Detergent Action of Soap.*

By SPENCER UMFREVILLE PICKERING.

ALTHOUGH the detergent action of soap is much increased by the presence of excess of alkali, it exists independently of such excess, and cannot be attributed to the alkali liberated by hydrolysis, since that would imply a reversal of the action liberating it. Hillyer (*J. Amer. Chem. Soc.*, 1903, **25**, 511) considers that the cleansing action 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 textures and impurities so that they may be removed easily: and it is thought that all these properties may be explained by taking into account the low cohesion of soap solutions, and their strong attraction, adhesion or affinity to oily matter, which together cause the low surface tension between soap solutions and oil." Although low surface tension cannot now be accepted as an explanation of emulsification, emulsification is certainly an important factor in the detergent action of soap, for emulsified globules are surrounded by a pellicle which prevents them from wetting and rendering oily any solid matter present.

Spring (*Bull. Acad. Roy. Belg.*, 1909, 187, 1128) considered Hillyer's explanation insufficient, and showed that dirt, as exemplified by lamp black, silicic acid, clay and cellulose, combines with the acid soap resulting from hydrolysis to form colloidal absorption compounds, and in some cases increases the amount of acid soap formed. It is doubtful, however, how far this action is of practical importance, for it could not occur if excess of alkali sufficient to prevent hydrolysis were present, yet the detergent action is actually increased by such excess.

A factor which neither of these investigators appears to have recognised is probably the most important of all, namely, that oils are actually soluble in soap, and to a very large extent; even paraffin oil will dissolve in quantities up to 100 per cent. of the soap present. This solubility is probably not altogether unknown to soap manufacturers, for it was certain observations communicated by a manufacturer which led the author to examine the matter; yet H. H. Cousins, who investigated the subject ("The Chemistry of the Garden," 1916, p. 132), appears to have concluded, erroneously, that paraffin was insoluble in soap, but that it would dissolve to a certain extent in the presence of naphthalene, the latter being known to be soluble in it.

EXPERIMENTAL.

Substances Used.

Potassium Stearate.—This contained, after drying, $K=12.65$; calc., $K=11.99$ per cent. It dissolved to form a 20 per cent. solution at 100° , from which, on cooling, nearly the whole of the stearate separated in a very fine state of division, the mixture forming a thick paste. This paste was used in the following experiments. Another, and apparently less pure, sample, containing $K=12.96$ per cent., was used in a few cases; the results obtained with it differed somewhat in magnitude from those with the first sample.

Potassium palmitate behaves with water in the same way as the stearate. The sample used contained $K=12.65$; calc., $K=13.06$ per cent.

Potassium oleate was examined only sufficiently to show that the action with it was substantially the same as with the stearate and palmitate.

A soft potash soap, known as "Chiswick Imperial," made by the Yalding Manufacturing Co., formerly the Chiswick Co. It is manufactured chiefly from soya-bean oil, and contains 8.4 per cent. of potassium oxide as soap and 1.15 per cent. as carbonate. Most of the glycerol has been extracted from it,* and the water lost at 100° amounted to 47.6 per cent. This soap therefore contains about 50 per cent. of dry soap. It is stiff, fairly transparent, and undergoes very little hydrolysis with water.

A soft soda soap, which has been used as a substitute for the above since the war began. It contains 7.15 per cent. of sodium oxide as soap, and 0.53 per cent. as carbonate and hydroxide. Water, 42 per cent. It is somewhat less transparent than the potash soap, melts and dissolves less readily, being scarcely fluid at 100° , and gives a considerably larger proportion of acid soap when dissolved.

One or two other soft soaps have been examined, and were found to behave in the same way as the above; this was also the case with hard soap.

The oils used were:

A. Paraffin oil freed from olefines, sp. gr. at 15° 0.713, b. p. $90-96^{\circ}$, consisting therefore mainly of heptane.

B. A similar oil, sp. gr. 0.784, b. p. $196-200^{\circ}$, consisting mainly of dodecane.

* From observations on the subject, it appears that glycerol would be without action on paraffin oil in the present experiments.

C. A similar oil, sp. gr. 0·815, b. p. 255—260°, consisting mainly of pentadecane.

D. Pratt's motor spirit, sp. gr. 0·697, initial b. p. 75°, 58 per cent. of it boiling below 100° and 28 per cent. between 100° and 125°.

E. "Royal Daylight" lighting oil, sp. gr. 0·803, initial b. p. 165°, 39 per cent. of it boiling below 250°.

F. Carless's solar distillate, sp. gr. 0·858, initial b. p. 240°, 94 per cent. of it boiling above 250°.

G. Pure benzene, sp. gr. 0·85, b. p. 80·5°.

Emulsions.

As shown in previous communications (T., 1907, **91**, 2001; Reports of the Woburn Experimental Fruit Farm, 1906, **6**, 196; 1908, **8**, 18), paraffin oil, when churned with a soap solution, forms a milky liquid, from which the true emulsion gradually rises to form a creamy layer containing from 65 to 85 per cent. by volume of oil, generally about 74 per cent., which is the volume occupied by close-packed spheres of uniform size. By the further churning of this cream with more oil, the percentage can be raised even to 99 per cent., the emulsion becoming a stiff, nearly transparent jelly, in which the oil globules must approximate in form to dodecahedra, there being no longer sufficient medium left to allow of their remaining spherical. Viscidity characterises all emulsions, and on emulsification it appears suddenly, the resistance to motion of the oil particles increasing very rapidly when these become reduced below a certain diameter.

The low surface tension between oil and soap solutions must favour emulsification by facilitating the breaking up of the liquids into minute globules, but it cannot explain why one of the liquids, and not the other, should remain broken up; moreover, Hillyer has shown (*loc. cit.*, p. 524) that the surface tension is reduced continuously with an increase in the concentration of the soap solution, whereas the emulsifying power of such solutions increases with concentration only up to a certain point (about 2 per cent.), and subsequently decreases (T., *loc. cit.*, 2018; Woburn Report, **6**, 197). This behaviour is in accordance with the author's explanation that the emulsification is due to the encasement of the oil particles by minute particles of solid, for example, of acid soap in the case of soap solutions, which view was established by showing that the mere presence of solid particles in a fine state of division, such as the freshly precipitated basic sulphates of metals, is sufficient to emulsify oils in water itself. It has also become emphasised by the author's recent work showing that in many

scores of cases metallic salts of organic acids are precipitated as emulsions, the media in such cases being saline solutions, which would not exhibit any exceptionally low surface tension.

The present and recent work necessitates a qualification of one statement originally made, namely, that the emulsified substance must be insoluble in the menstruum. This should be modified to read, that in a *permanent* emulsion, the emulsified globules must be in a condition such as to preclude them from dissolving the menstruum. The substance composing them may itself be soluble in the menstruum, but the globules may be precluded from dissolving, either by the menstruum being already saturated with the substance in question, or by the globules being enclosed in a pellicle which prevents their contact with the menstruum. We may even have an emulsion in which the emulsified substance and the menstruum are identical (see p. 96). Numerous instances have been obtained of substances being precipitated as emulsions which redissolve immediately, hence the necessity of introducing the word "permanent" in the above statement.

Behaviour of Soaps with Oils.

In the following experiments, the quantity of soap taken was generally 30 or 60 grams, heated to 55°, so as to render it less viscid, although this heating is not absolutely necessary, and was dispensed with when a diluted soap was used. With potassium stearate and palmitate, 50 grams of the cold paste, containing 10 grams of the salt, were employed. The oil was added to these substances, and the mixture worked with a spatula. With soap and paraffin oil, the incorporation often requires some time, the soap slipping about in the oil at first, but when the last of the oil is absorbed, the mixture suddenly becomes opaque and almost solid, and adheres to, or "wets," the containing vessel. With the soda soap, the final mixture is almost transparent instead of opaque. These mixtures are quite permanent, provided concentrated soap has been used. When treated with excess of water, they dissolve completely, forming solutions which are either clear—except for the presence of some acid soap—or, if the proportion of oil is larger, milky, owing to the presence of an emulsion, which rises to the surface as a cream in the course of some hours or days.

The sudden solidification at the final absorption of the oil is not indicative of chemical combination, and seems to be merely the result of the oil globules attaining a diameter sufficiently small for them to show the resistance characteristic of emulsions. A similar sudden change to a stiff, opaque mass occurs when water, or even air, is worked up with the soap, the only difference in such

cases being that the products are not permanent; in the case of water, the soap gradually dissolves, leaving a clear jelly; in that of air, the bubbles gradually coalesce, leaving a coarse, honey-combed mass. The volume of the air particles enclosed in such a mixture is about 50 per cent. of that of the soap. The possibility of incorporating water with fats or melted waxes was first recognised by Galen, since which time products thus obtained have been in use as cosmetics, cold cream being one familiar instance. They exhibit some of the properties of emulsions, due to the enclosed globules being comparable in size with those in emulsions, but, as the globules are not encased in a pellicle, their permanence depends on the semi-solid condition of the menstruum. Mercurial ointment is another instance. Air may similarly be enclosed in soft caramel, as is done in the manufacture of sweetmeats exhibiting a silky texture.

In the incorporation of oil with soaps, three stages may be recognised; they are most marked in the case of potassium stearate paste and benzene. The first consists of a thickening of the paste, due to the incorporation of the oil to form a coarse sort of emulsion, with a consequent increase in the extent of the oil-water surface; then the mixture becomes limpid, due, as will be shown, to the gradual combination of the oil with the solid stearate to form a soluble compound; lastly, this liquid, whether the stirring be continued or not, rapidly solidifies to an opaque, stiff mass, this stiffening being the result of the globules of oil present becoming reduced, by combination with the stearate, to a magnitude sufficient to permit of their forming a true emulsion. The extent to which these stages are marked depends on the proportion of emulsion formed, the viscosity of the reagents, and other factors. With potassium palmitate and benzene, no final thickening occurs; with potassium stearate and paraffin oil, a slight thickening only is observable; with concentrated soap and any of the oils, the only change is a considerable thickening, but with less concentrated soap the mixture afterwards becomes quite limpid, although this change is not followed by a subsequent thickening.

With undiluted soap there is a definite limit to the volume of paraffin which may be incorporated with it, but in the case of soap previously diluted with one to two volumes of water, or in that of stearate paste, no definite limit is evident, especially with benzene, any excess of oil mixing with the solution, and, on being left, rising to the surface, mixed with the emulsion.

Method of Analysis.

In order to examine the nature of the product obtained, this was dissolved in a volume of water equal to nineteen times that of the anhydrous soap (9·5 times that of the actual soap) or stearate present. The solution was left in a separating funnel for one to three days for the emulsion to rise to the surface, and the volume of the latter, retaining unavoidably some of the solution, determined. Acid was then added to this, and the liberated oil—with some fatty acid dissolved in it—measured, after which 10 c.c. of the original solution were added, and the volume of oil redetermined. The measurements give the data for calculating the oil in the emulsion itself, and hence that remaining dissolved in the liquid.

The extent to which uniformity is obtainable may be judged by the following results:

30 c.c. of solar distillate with 100 grams of soap.*		30 c.c. of solar distillate with 100 grams of soap diluted.		150 c.c. of benzene in 100 grams of stearate as paste.	
Dissolved.	Emulsified.	Dissolved.	Emulsified.	Dissolved.	Emulsified.
21·8	8·2	1·0	29·0	85	65
23·6	6·4	0·8	29·2	85	65
22·6	7·4	2·2	27·8	84	66
Mean 22·7	7·3	1·3	28·7	85	65

* Wherever soap is mentioned in the following tables without the qualification of "anhydrous" it refers to the soap in its ordinary condition, that is, containing 50 per cent. of water.

Thus, errors of 1 to 2 c.c. may be expected in the value when referred, as above, to 100 grams of soap.

Effect of Manipulation, Temperature, and Dilution.

Differences in the manipulation do not much affect the results; for instance, taking a stearate mixture diluted sufficiently (to 5 per cent.) to admit of its being churned with a syringe, the following results were obtained:

Benzene to 100 Grams of Dry Stearate.

Taken.	Dissolved.	
	When churned.	When not churned
100 c.c.	69	70
200 c.c.	86	104

Thus churning increases the proportion of oil emulsified, but only appreciably so in extreme cases. No recognisable difference

was made in the results whether the oil were added gradually or all at once.

A rise of temperature increases the proportion of oil dissolved, although not to such an extent that accidental temperature variations would produce an appreciable effect.

Solar Distillate and Soap.

Temp.	Taken.	Dissolved.
47°	30 c.c.	21.9 c.c. to 100 grams of soap.
66	30 "	24.9 " " "
90	30 "	25.4 " " "

Benzene and Stearate. (Second sample, p. 87.)

17°	150 c.c.	74 c.c. to 100 grams of stearate.
55	150 "	89 " " "

The validity of the method adopted for analysing the product must depend on the product not being decomposed by water, and this was proved to be nearly strictly the case by the following experiments. Lighting oil was incorporated with potash soap in the proportion of 40 c.c. to 100 grams, and when dissolved in water equivalent to x times the volume of soap present gave:

Oil dissolved	$x =$	3	6	9	18.5
	$=$	34.2	34.4	35.0	36.0 c.c.

Again, a product containing 69 c.c. of benzene in 100 grams of soap, after being dissolved in 950 c.c. of water, was further diluted twenty- and one hundred-fold, but gave no trace of decomposition. Similar results were obtained in other cases.

That water should not separate any of the oil from the product appears, at first sight (although the explanation will be found below, p. 94), to be inconsistent with the fact that dilution of the soap before treatment with oil generally results in a reduction of the proportion of oil dissolved. Thus, if the soap is previously diluted to the full extent adopted in these experiments—9.5 volumes of water—only about half as much oil, or in some cases less, passes into solution as when undiluted soap is taken, and the product subsequently diluted, the temperature of the reagents being the same in all cases (55°).

Oil dissolved when the soap was diluted.

Oil added.	Before adding oil.	After adding oil.
33 c.c. lighting oil	7.2 c.c.	18.5 c.c.
67 " " "	17.7 "	29.9 "
33 " solar distillate.....	4.4 "	20.6 "
67 " " "	11.4 "	23.8 "

The effect of previous dilution of the soap taken is more fully shown in the following series. Taking the determinations with

soap and lighting oil or benzene, it will be seen that the amount of oil dissolved decreases with an increase in the proportion of water present, but only up to a certain point, after which it remains constant. This point depends on the proportion of oil; with 33 c.c. of oil to 100 grams of anhydrous soap (1) it occurs at about 900 c.c. of water, with 80 c.c. of oil (2) at about 500 c.c. of water, and with 300 c.c. of benzene (7) at about 100 c.c. of water, or less. The values enclosed in brackets cannot be considered in this connexion, for in those cases the benzene was insufficient to saturate the soap, and the product dissolved completely without forming any emulsion. The results with potassium stearate do not offer any instance where constancy was attained, but with potassium palmitate it occurs with 150 c.c. of benzene (16) when the water reaches 900 c.c. With the palmitate the values are, however, not very trustworthy, owing to the difficulty of analysing the product, the layer of oil and palmitic acid obtained not presenting a well-defined meniscus.

TABLE I.

Volume of Oil Dissolved per 100 Grams of Anhydrous Soaps at Various Dilutions.

Oil taken c.c.		Oil dissolved (c.c.) by 100 grams of soap diluted with							
		100 c.c.	200 c.c.	300 c.c.	400 c.c.	500 c.c.	900 c.c.	1400 c.c.	1900 c.c.
Potash soap and lighting oil.									
1	33	29.4	21.8	18.6	—	13.0	3.2	—	3.6
2	80	53.2	23.2	19.4	—	5.6	2.8	—	5.4
Potash soap and Benzene.									
3	67	(67)	—	(67)	—	(67)	—	—	—
4	100	(100)	—	—	—	—	—	—	—
5	133	122	—	104	—	90	—	—	—
6	200	128	—	—	—	—	—	—	—
7	300	138	—	134	—	136	—	—	—
Potassium stearate and benzene.									
8	50	—	—	—	(50)*	—	—	—	—
9	75	—	—	—	69*	—	59	49	—
10	100	—	—	—	96	—	—	—	—
11	150	—	—	—	116	—	57	40	—
12	200	—	—	—	121	—	—	—	—
Potassium palmitate and benzene.									
13	50	—	—	—	47*	—	—	—	—
14	75	—	—	—	60*	—	50*	41*	—
15	100	—	—	—	60*	—	—	—	—
16	150	—	—	—	79*	—	46*	47*	48*
17	200	—	—	—	76*	—	—	—	—

* In these cases, uncombined stearate or palmitate is present, and gradually settles in the liquid.

These facts have an important bearing on the use of soap as a detergent. To obtain the most economic results, the soap must evidently be used at the maximum concentration possible; this in practice is done when washing our bodies, but not always in other cases. The importance of doing so may be illustrated by smearing the hands all over with paraffin oil, when it will be found that the use of 3 grams of soap (which at first slips about in the hands, and then suddenly becomes stiff and adherent), and a subsequent rinsing in a litre of water, will suffice to remove the oil; whereas washing them in a litre of water with 3 grams of soap previously dissolved in it is quite ineffectual.

The fact that the compounds of oils with soap are not decomposed by water is also essential to the detergent action of soap, for otherwise, rinsing with water after the application of the soap would regenerate the oil.

Looking down the columns in table I, it would appear at first sight that the action between oils and soaps presents features inconsistent with the characteristics of chemical combination or dissolution, for the solubility of the oils seems to be dependent on the proportions present: thus, although stearate of a given concentration will dissolve 121 c.c. of benzene per 100 grams, yet when 75 or 100 c.c. only are added, even the whole of these smaller volumes are not dissolved, and in some of the cases, marked by asterisks, a portion of the oil remains uncombined, although there is evidently uncombined soap present also. The explanation of this is that a part of the oil added—so long as it is present in considerable proportions—always becomes emulsified in the manner already indicated, and that once emulsified it is no longer soluble, the particles being protected from contact with the liquid by the pellicle surrounding them.

There is, however, no constant proportion between the oil dissolved and emulsified; thus, with potash soap and benzene, the proportion dissolved decreases with an increase in the amount present, varying from 100 to 46 per cent. of the total. The encasing of the oil globules by particles of acid soap must be a process requiring some time, and if the actual quantity of oil present is small, the dissolution of it will be rapid, and there will be less opportunity for the globules to become thus encased. Dilution with water, by increasing the quantity of acid soap, would increase the proportion of oil emulsified, in spite of the fact that the compound of soap and oil is not itself decomposed by water, an apparent anomaly alluded to above (p. 92).

Composition of the Products.

Taking the results with stearate and benzene, where both reagents are of definite composition; the benzene dissolved by stearate of any given degree of concentration appears to attain a value beyond which a further increase in the proportion of benzene taken would produce little or no increase in the amount dissolved. Taking 121 c.c. as the maximum in the case of the most concentrated stearate, this represents $4.5\text{C}_6\text{H}_6$ to each $\text{C}_{18}\text{H}_{35}\text{O}_2\text{K}$, and with the two more dilute liquids examined, 2.2 and $1.7\text{C}_6\text{H}_6$, respectively; these quantities are in direct proportion to the concentration, the values obtained by dividing them by the percentages of stearate being 0.23, 0.22, and 0.25, respectively. If such a proportion holds good for all concentrations, the anhydrous stearate should combine with $23\text{C}_6\text{H}_6$, or 100 grams with 620 c.c. It has not been possible to realise this, probably owing to anhydrous stearate being in a much less finely divided condition than that in the paste; some digested with benzene at the ordinary temperature for forty-eight hours combined with (that is, rendered soluble) only 108 c.c. per 100 grams. The solubility of benzene in soft soap, it will be seen, is about 70 c.c. per 100 grams, or 140 c.c. per 100 grams of anhydrous soap, somewhat more than that of benzene in the most concentrated stearate examined; its solubility in potassium palmitate is considerably less, about 80 c.c. The compound formed in all these cases is quite insoluble in the excess of benzene.

Sodium stearate, it may be remarked, unites with very large proportions of alcohol. A solid fuel, known as spiritine, consists of 95 parts of alcohol and 5 parts of the stearate; but it appears to be a mechanical mixture only, the alcohol being imprisoned in a network of crystals of the stearate, from which it can easily be withdrawn by blotting-paper. No such withdrawal is possible in the case of the compounds of oil with soft soap, and these, moreover, are scarcely inflammable. Even when they contain such a readily inflammable oil as benzoline, they cannot be ignited unless the proportion of oil is about 67 to 100 of soap, and, even then, the flame generally dies out as soon as the match is withdrawn.

The combination of oils with stearate or ordinary soap was also examined by leaving the reagents in contact with each other. In the course of a few days, a layer of clear, limpid liquid began to form between the viscid stearate, or soap, and the supernatant oil; this slowly increased in bulk until all the soap disappeared. At the same time, an opaque layer gradually formed between the clear layer and the oil; this consisted of an emulsion. The

emulsion formed in a case where benzene was used was separated and analysed, the excess of benzene being removed by filter-paper. It was found to contain 84 per cent. of benzene, and as it evidently contained excess of soap solution which could not be removed, the true percentage of benzene in the emulsion must have been higher. It is therefore an emulsion of benzene, not an emulsion of soap solution, and it presents the curious phenomenon of an emulsion in which the emulsified substance and the menstruum are the same, each emulsified sphere being surrounded by a pellicle, probably consisting of solid particles, and also by some of the aqueous solution, which keeps it from coming into contact and coalescing with the menstruum. The spontaneous formation of an emulsion between two liquids in contact with each other and at rest is also somewhat remarkable; the locus of its formation appears to be chiefly the sides of the containing vessel, and it is probable that the breaking up of the liquid into globules is dependent on changes of temperature or unavoidable vibrations. Where ordinary soap is used in such experiments, it should be diluted with about double its weight of water, since with concentrated soap the clear layer which begins to form between the liquids seems to be soon absorbed by the soap, and renders it opaque.

The results obtained with various oils and potash soap are given below, and it will be seen, especially when comparing those with the three purified paraffin oils, that the proportions passing into solution are not dependent solely on the physical properties of the oil, for those with oil boiling at 257° are intermediate between those of the two oils boiling at 98° and 198° . A similar dependence on the chemical nature of the oil is evident on a comparison together of the results with petrol, lighting oil and solar distillate, or of those with benzene and the paraffin oils.

Volume of Oil Dissolved by 100 Grams of Soap.

Oil taken.	Paraffin, b.p.			Petrol. Lighting. Solar.			Benzene.
	93° .	198° .	257° .	—	14	13	
17	(17)	13	13	—	19	21	(33)
33	26	20	23	24	22	23	(50)
50	32	22	28	35	30	24	61
67	44	25	40	—	37	—	64
100	62	42	—	—	—	—	—

Where the values are enclosed in brackets, the oil was not in sufficient proportion to saturate the soap.

The combination oil and soap, when the two are worked together, generally occupies about fifteen minutes. The course of the reaction may be followed by checking it at different stages, this being done by the addition of a large volume of water. Potassium

stearate paste and benzene when examined in this way, using 200 c.c. of benzene to every 100 grams of stearate present, gave:

66 c.c.	dissolved at the first thickening.
86 c.c.	„ „ „ subsequent thinning.
104 c.c.	„ „ „ final thickening.

In another case, using 150 c.c. of benzene and 100 grams of potash soap, there were:

70 c.c.	dissolved when the mixture had thinned.
84 c.c.	„ „ after the final thickening.

Thermal Changes.

The thermal phenomena attending the interaction between oils and soap are equally emphatic as to the dependence of the results on the chemical character of the oils taken. The temperature changes occur slowly and continuously throughout the three stages of the reaction (p. 90), and apparently for some little time after the final thickening has occurred. This slowness of the action, and the semi-solid condition of the products, rendered any accurate thermal determinations impossible. In the following cases, either 50 grams of a 20 per cent. stearate paste, or 30 grams of potash soap diluted with 60 grams of water, were used. The actual temperature alteration (initial temperature, 15°) is entered, and that per gram of oil dissolved. The determination of the oil dissolved in the case of the paraffin oils and stearate was, however, impossible, as the emulsion could not be separated from the undissolved stearate.

		Temperature alteration.		Evolution per gram dissolved.	
Stearate with	20 c.c. benzene ...	—	—2°.65	—0°.035	—25 cal.
„	„ 10 c.c. paraffin b.p. 93°	93°	—0°.35	—	—
„	„ 10 c.c. „ „ 257°	257°	+0°.30	—	—
Soap	„ 20 c.c. benzene ...	—	—1°.58	—0°.102	—11.2 cal.
„	„ 10 c.c. paraffin b.p. 93°	93°	—0°.20	—0°.041	—4.5 „
„	„ 10 c.c. „ „ 198°	198°	+0°.25	+0°.080	+8.8 „
„	„ 10 c.c. „ „ 257°	257°	+0°.18	+0°.340	+37.4 „

It will be seen that the magnitude and sign of the thermal disturbance depends on the nature of the oil used; doubtless the combination of it with the soap is exothermic in all cases, but the heat evolved is generally more than counterbalanced by that absorbed in the attendant fusion of the solid stearate or of the semi-solid soap.

Naphthalene and Soap.

Cousins, in the little book already mentioned, claims that as the results of "exhaustive experiments" he had established that

the presence of naphthalene greatly assists in producing "a paraffin emulsion of a kind and perfection superior to that obtainable with paraffin and soap alone," and he secured a patent (1895, No. 13201) for such a substance for use as an insecticide under the name of paranaph, the directions for the preparation of which were: melt 100 grams of soft soap with 38 parts of water; then dissolve 10 parts of naphthalene in it, after which 16·7 volumes of paraffin oil are incorporated in it. The results of these exhaustive experiments have, however, never been published, and no evidence seems to exist that the insecticidal properties of such a substance are greater than those of ordinary paraffin emulsion (see *J. S.-E. Agric. Coll.*, 1896, **5**, 51, where some trials on hop aphids are given, but without comparison with those obtained with other insecticides). It is not clear in what condition Cousins considers the paraffin to be present in this substance, for he states that "it dissolves readily in cold water so as to give a milky emulsion—from which no visible separation of oil takes place even after standing for several weeks in open air." But if the paraffin is dissolved, it is not present as an emulsion, and if it is emulsified, it is not dissolved, and in the latter case would certainly (in part at any rate) rise to the surface, for its specific gravity would be about 0·9. The facts of the case appear to negative all Cousins's contentions; paraffin oil, as has been seen, dissolves in soap without the addition of naphthalene; naphthalene, on the whole, diminishes its solubility; the greater part of the naphthalene separates from the liquid on dilution, and if the paraffin is present in such proportions as not to be entirely dissolved, the excess rises to the surface as an emulsion.

The behaviour of naphthalene with soap exhibits none of the peculiarities shown by paraffin; it dissolves to a small extent in heated soap, rendering it more liquid, but, on cooling, some of the naphthalene separates in the crystalline form. The solubility seems to be increased by the addition of a little water, but diminishes on further dilution. Thus, with potash soap:

		Grams of naphthalene dissolved		
Soap ...	+	Water.	at 100°	at 5°
100	+	0	(5)	(2·0)
100	+	100	(7)	(3·5)
100	+	200	—	(4·0)
100	+	300	—	5·9
100	+	600	—	5·4
100	+	1000	—	5·0
100	+	2000	—	4·0

but the values with the more concentrated soap solutions (enclosed in brackets) are very uncertain, as the liquids cannot be filtered,

and cannot be diluted without altering their composition; whether the naphthalene has dissolved or not has to be determined by the clearness of the solution, and this is interfered with by frothing.

In another instance, 10 grams of naphthalene were digested at 100° with 100 grams of soda soap previously diluted with 38 c.c. of water, and the product, after cooling, dissolved in x c.c. of water; the results were:

$x = 300$,	naphthalene remaining dissolved	=	1.8	grams.
$x = 600$,	"	"	1.5	"
$x = 1000$,	"	"	1.3	"
$x = 2000$,	"	"	0.9	"

A considerable tendency for the naphthalene to remain in a state of supersaturation for many hours was observed in these experiments.

When to a solution of naphthalene in soap paraffin oil is added, and the product dissolved in water, then, according to the proportions of the reagents taken, there occurs either complete dissolution, or partial dissolution with the separation of some emulsion and crystallised naphthalene, which latter either sinks to the bottom, or becomes entangled in the emulsion at the top. Much of the naphthalene must also be dissolved in the oil globules, since its solubility in lighting oils is 12 grams in 100 c.c. at 15° .

In the following experiments, 10 grams of naphthalene (volume 8.7 c.c.) were dissolved in 100 grams of soap, then worked with oil, and the product dissolved in 950 c.c. of water. The emulsion was determined in the usual way, and any deposit of naphthalene in the liquid separated and dried. The data obtained gave the volume of oil + naphthalene which remained in solution (entered in column II); the volumes taken are entered in column I, and the volumes of each which would remain in solution if either the oil or the naphthalene had each been present alone, as determined by separate experiments, are given in column III, whilst the difference between the sums of these latter volumes and of that dissolved when the two substances are present together are given in column IV.

In Nos. 8—10, 38 c.c. of water were previously added to 100 grams of soap, so that in No. 8 we have the same proportions of all the substances as in Cousins's paranaph, the soap, however, being soda, instead of potash soap, and in soda soap the whole of the oil becomes dissolved without the formation of any emulsion.

It will be seen from Nos. 6, 7 and 10, where the volume of oil taken is large, that the presence of naphthalene results in a considerable reduction in the volume of oil dissolved, the volume of oil + naphthalene dissolved being even less than that of the oil

TABLE II.

Naphthalene (N) and Oils Dissolved in 100 Grams of Soap.

Volumes taken. I.		Volumes dissolved.				Difference. IV.
		Taken together. II.		Taken separately. III.		
Potassium soap and lighting oil. (L).						
1	L. 16.7 } N. 8.7 }	25.4	13.7 } 16.2	L. 14.2 } N. 2.1 }	16.3	- 0.1
2	„ „ }	„ 19.7 }				
3	„ „ }	„ 15.2 }				
4	L. 33.3 } N. 8.7 }	42.0	21.6 } 20.3	L. 18.5 } N. 2.1 }	20.6	- 0.3
5	„ „ }	„ 19.0 }				
6	L. 66.7 } N. 8.7 }	75.4	25.5 } 24.8	L. 29.9 } N. 2.1 }	32.0	- 7.2
7	„ „ }	„ 24.2 }				
Soda soap (diluted) and lighting oil.						
8	L. 16.7 } N. 8.7 }	25.4	25.4	16.7 } 1.3 }	18.0	+ 7.4
9	L. 33.3 } N. 8.7 }	42.0	22.8	22.7 } 1.3 }	24.0	- 1.2
Soda soap (diluted) and Benzene. (B).						
10	B. 66.7 } N. 8.7 }	75.4	35.1	47.5 } 1.3 }	49.0	- 13.9

dissolved when oil alone is taken. Where, however, the proportion of oil taken is smaller (Nos. 1—4 and 9), there is a similar reduction, although quite insignificant in amount. In No. 8, however, we have an exception, the presence of the two substances together resulting in much more of them being dissolved than when they are taken separately; but this increase is due, not to more paraffin, but to more naphthalene having been dissolved, for the whole 8.7 c.c. of this substance, instead of only 1.3 c.c., have remained in solution. Doubtless this is an accidental case, the naphthalene having remained dissolved in a state of supersaturation; and in one or two other cases, besides those already mentioned (p. 99), it was noticed that a similar supersaturation was maintained until the liquid was drawn off from the emulsion. Such an instance, however, lends no support to the view that naphthalene increases the solubility of paraffin.

Summary.

The detergent action of soap is due, in part to its power of emulsifying oil, the oil globules of which become enclosed in a pellicle which prevents them rendering contiguous substances oily; in part to the lowness of surface tension between oil and soap solution; and perhaps in part to the union of dirt with the acid soap produced by hydrolysis. A more important factor is that oils, even paraffin oils, dissolve in soap to form soluble compounds, which contain in some cases nearly equal weights of oil and soap. Except when the oil added is small in amount, a certain proportion of it becomes emulsified, and incapable of combining with the soap, owing to the protecting pellicle, hence considerable excess of oil must be taken for the soap to combine with the maximum amount of oil possible. The compound formed is not decomposed by excess of water, but dilution of the soap previous to its treatment with oil results in much less oil combining with it, because a larger proportion of the latter becomes emulsified.

The combination of soap with oil is accompanied by a series of physical changes explicable by the nature of the products formed—a soluble, limpid compound, on the one hand, and an emulsion, which is almost solid, on the other. The proportions of oil and soap which will unite with each other depend on the chemical, and not merely physical, nature of the reagents, and an appreciable heat-disturbance, either negative or positive, accompanies the reaction. Naphthalene does not behave towards soap as paraffin does, but dissolves in it to a limited extent, some of the crystalline substance separating on cooling or dilution. The presence of naphthalene decreases the amount of paraffin dissolved by soap.

HARPENDEN.

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