CXCVI.—*Emulsions.*

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IN the Sixth Report of the Woburn Experimental Fruit Farm (Eyre and Spottiswoode, 1906), were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until that here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, should have arrived at an explanation of emulsification which is essentially the same as that given here.

Emulsions with Soluble Emulsifiers.

When any liquid insoluble in water is mixed with the latter and broken up into minute globules, as when it is forced through a syringe, the globules remain more or less permanently emulsified whenever the water contains soap or some other emulsifying agent in solution. The whole of the liquid, however, is not an emulsion, properly so called, but a mixture of the emulsion with excess of soap solution; on standing, the true emulsion separates, and, if

the substance emulsified is lighter than water, rises to the surface. This is precisely analogous to the separation of cream from milk.

The time required for an emulsion to rise, and for the volume occupied by it to become constant, depends, naturally, on various circumstances, and varies between several days and many weeks. The line of demarcation between the emulsion and the excess of liquid is generally well marked, for the liquid becomes almost clear, and, if it contains much soap, quite clear, whilst the emulsion is opaque. In many cases, the emulsion itself separates into two layers, evidently of different composition, the line of demarcation between these being fairly distinct.

A rise of temperature facilitates emulsification with soap solutions, but there appears to be no difference between emulsions of the same composition when made at different temperatures. For each temperature, and for each proportion of paraffin oil, the quantity of emulsifier which must be present ranges between certain definite limits; thus, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain from about 0·7 to 1·8 per cent. of potash soap; but for 40 volumes of oil to 60 of water, emulsification is possible with from 0·3 to over 25 per cent. of soap. The explanation of the existence of such limits (especially of the superior limit) will be discussed below, but it may be remarked that the above figures apply to only one particular soap, and that soaps, even when of the same brand, vary greatly in their emulsifying power, it being difficult to obtain emulsification at all in some cases, even with the aid of heat.

Emulsification appears to occur suddenly : when soap is used, and the solution is not very strong, it is possible to judge immediately by the working of the syringe whether it has occurred or not; but when it has not occurred, no continuance of the pumping, without altering other conditions, will produce emulsification.

The increase of viscosity on emulsification is easily explained by the great increase in the extent of the oil-water surface on the oil being reduced to minute globules. An ordinary emulsion, although containing 70 to 80 per cent. of mobile paraffin oil, is as viscid as thick cream, and its viscidity increases with the proportion of oil present, even when that oil is a very light one, such as a benzine. With very high percentages of oil, the emulsion becomes practically solid, resembling a blancmange. Emulsions containing as much as 99 per cent. of ordinary lighting oil have been made, the remaining 1 per cent. being a 1 per cent. solution of soap. Such strong emulsions, however, cannot be obtained directly ; they must be made by taking a weaker emulsion, and gradually increasing the paraffin in it, churning it after each addition. Even these strongest emulsions are true emulsions of the oil; that is, it is the oil which is in

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globules, and the water, although so small in amount, which is the menstruum. There are no signs of the existence of an emulsion of water in oil. As a consequence of this, an emulsion (even a 99 per cent. one) will mix perfectly with water to form a weaker emulsion, but it will not mix with more paraffin, unless, of course, that paraffin is emulsified with it by further churning. Indeed, the addition of any paraffin in bulk to an emulsion eventually causes the de-emulsification of the whole, the globules of the emulsion being attracted by, and coalescing with, the mass of unemulsified paraffin. It is for this reason that an imperfectly made emulsion will eventually de-emulsify on standing, and so will a very strong emulsion, for it is generally an imperfect emulsion also, as it is so viscid that the whole of the paraffin in it cannot be churned up with it properly. Spontaneous de-emulsification is usually a question of weeks or months, sometimes of years; possibly a very perfect emulsion would never de-emulsify spontaneously at all, but once de-emulsification has started, it progresses at an increasing rate.

Strong emulsions, especially the semi-solid ones, are very bad conductors of heat. When one of them is heated in a wide test tube, it partially melts, de-emulsifies, and boils; but, although the boiling point may be 160° to 170°, ebullition can be continued for five or ten minutes, while a nucleus of the emulsion remains at a temperature far below 100° in the centre of the boiling paraffin. The water becomes gradually concentrated in this nucleus, and finally volatilises explosively.

Although one of these semi-solid emulsions, when kept in a closed vessel, will only gradually de-emulsify in the course of months, yet, when exposed to dry air, it will do so in a very short time; the edges of the lumps assume the appearance of a transparent, slightly blue jelly, and the whole liquefies in the course of some hours. No such change occurs in moist air. It is evident, therefore, that the change to the transparent condition must be due to the loss of moisture, but it is difficult to see in what the change consists. The opaque emulsion appears to contain a few globules of about 0·0003 mm. in diameter, but the bulk of it seems to be devoid of structure, and, if composed of globules, as presumably it is, these must be less than 0·0001 mm. in diameter. The transparent jelly presents nothing at all visible under the microscope. Thus the difference between them seems to consist in the presence or absence of a few larger globules, but why these should disappear throughout the mass on exposure to air is not at all clear. The transparent jelly is as stable as the opaque emulsion, when kept in a closed vessel. On placing a portion of it in water it instantly becomes opaque, and gradually disseminates in the water, forming a weak, milky emulsion.

In a collection of close-packed spheres of uniform size, whatever that size may be, the volume of the spheres is 74·048 per cent. of the total volume of the mass; with an emulsion of uniform spheres, the volume of the oil would be less than this, as the spheres are not in actual contact, the separating film of medium being of appreciable thickness. But in emulsions, the spheres are not uniform, and there does not therefore appear to be any reason why the ratio of the volume of the oil to the total volume of emulsion should be of any particular magnitude. The ratios actually found, however, do not differ very widely from that for close-packed uniform spheres, being generally from 65 to 82 for every 100 volumes of emulsion. This is independent of the proportions in which the oil and solution are taken to start with, so long as the former does not exceed 80 per cent.

In a number of experiments which were quoted in the Woburn

FIG. 1.
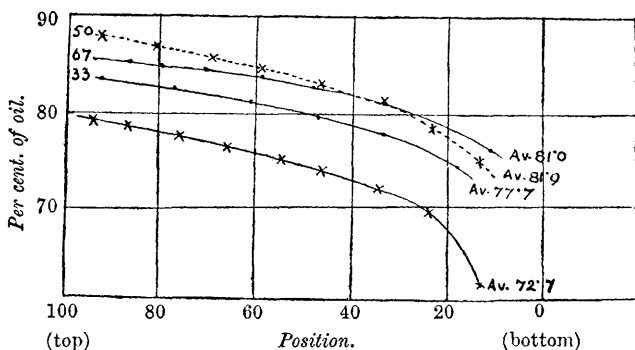
Composition of emulsions. "Solar Distillate" in soap solutions.

Report, the proportions for the oil to water composing emulsions were found to be in the simple ratios of 2 : 1, 3 : 1, or 4 : 1. It was not possible to suggest any explanation of this, and the results (although similar ones have been obtained subsequently) were probably fortuitous. This seems to be established by the fact that these emulsions vary more or less in composition throughout their mass. The nature of this variation will be seen best by an inspection of Fig. 1. Three emulsions were made by churning a 1 per cent. soap solution with "Solar Distillate," a paraffin oil distilling almost entirely between 240° and 350°, sufficient to make mixtures containing, respectively, 67, 50 and 33 per cent. by volume of the oil. These were left undisturbed for twelve weeks, after which the emulsions, which had risen to the top, contained, on the average, 81·0, 81·9 and 77·7 per cent. of oil, in the three cases, respectively. The emulsions were

analysed from top to bottom, removing for the purpose successive layers, and analysing each by adding to it a trace of acid, which de-emulsified it. The percentage (by volume) of oil diminishes throughout from the top of the column downwards, but very slowly at first, and more rapidly towards the bottom. The examination cannot well be extended to the very bottom of the column, as it is difficult to remove the emulsion without drawing with it some of the watery liquid from below. The three emulsions, as will be seen, do not differ much in composition, in spite of the different proportions of the oil and solution taken in their manufacture, and such differences as exist do not vary regularly with these proportions. In none of these cases were there visible any different zones, such as are often noticed, but the analysis gives some evidence of the existence of one in the case of the curve marked 67, for the first three portions removed, embracing a quarter of the whole emulsion, gave the same values, namely, 84·7, 84·5 and 84·6 per cent. A more conspicuous instance of the arrangement in zones of equal strength will be mentioned below.

The emulsification of 50 per cent. of paraffin was repeated with a 5 per cent., and with a 0·2 per cent. solution of soap as well. The results with the former, when plotted, were almost coincident with those with the 1 per cent. solution shown in the figure (marked 50); those with the 0·2 per cent. solution gave lower values throughout, and are represented by the lowest curve in the diagram.

Differences, such as those exhibited between the emulsions portrayed in Fig. 1, are, no doubt, merely due to differences in the size of the globules, and must be largely accidental. An examination under the microscope was sufficient to indicate that the average size of the globules in the emulsion giving the lowest curve was somewhat greater than that in the others, although no differentiation of these others amongst themselves was possible.

All emulsions contain globules of different sizes, and it is possible to form only a very rough estimate as to what is the average, or, rather, most frequent, size of the globules present. With most paraffin oils emulsified in soap solutions containing from 5 to 0·5 per cent. of soap, the most frequent size seems to be about 0·0075 mm. in diameter, but there are present some globules of three or four times this size, as well as smaller ones down to one-tenth of it, or less. In the semi-solid emulsions, as already stated, the globules are much smaller. Imperfect churning of the mixture results in larger globules, but a dozen vigorous strokes of a syringe fitted with a rose jet seems to be sufficient to break up the oil as far as is possible. A deficiency in the proportion of soap to the paraffin results in larger globules, and, if reduced too far, no permanent emulsification can be obtained.

The character of the oil, also, has an effect on the size of the globules; emulsions with the lighter paraffins, such as the various benzines and motor spirits (sp. gr. 0·7 to 0·75), are more coarse-grained than those with lighting oils (sp. gr. 0·8) or " Solar Distillates " (sp. gr. 0·86) ; but with mineral naphtha and benzene, the reverse is the case, emulsions with these being exceptionally fine-grained. With crude petroleum, sp. gr. 0·955 (which contains much vaseline), a very thick, unmanageable emulsion is obtained. Turpentine and olive oil do not emulsify with soap solution in the same way as do the paraffin oils, a large portion of the material remains unemulsified, and the line of demarcation between the layers of different composition is not clearly marked. With turpentine, that portion of the mixture which most resembles an emulsion contains only 5 to 6 per cent. of the oil, but with olive oil there is a small layer, intermediate between the free oil on the top and the solution at the bottom, which appears to be a true emulsion, as it contains about 70 per cent. of oil.

Compared with the oil globules in cream, paraffin .emulsions are more coarse-grained, and much less uniform. In cream, the globules are 0·003 to 0·005 mm. in diameter. They are, however, collected together in groups, and are not distributed uniformly throughout the medium as in the case of paraffin emulsions.

So long as thorough emulsification has been produced, there does not appear to be marked variations in the size of the globules of an emulsion throughout the mass; the only difference observable between the upper and lower layers is, that in the former the globules are more closely packed than in the latter.

Other soluble substances, besides soap, will act as emulsifiers for paraffin, and some of them are used practically in America. Sour milk and scorched flour are amongst the latter, and the author has also examined the results obtained with solutions of glue, starch, egg-albumen, saponin and extract of quillaia bark. All these substances give emulsions more or less closely resembling those with soap, but they all appear to be inferior to the latter as regards the fineness of texture of the product, and, consequently, the emulsions separate from the excess of liquid more rapidly. With saponin and quillaia, this is notably so, and with proportions of these materials which have been recommended for use (0·025 per cent. of quillaia), emulsification is so unsatisfactory that de-emulsification sets in after twenty-four hours, whilst, if the proportion of paraffin taken for the mixture is large (67 per cent.), only partial emulsification is obtainable. With some of the other substances mentioned above, for example, milk, it is not possible to obtain a strong emulsion unless the paraffin is added gradually, churning after each addition.

De-emulsification.

The de-emulsification of an emulsion may be brought about, (1) by the presence of unemulsified paraffin, as already mentioned; (2) by adding a liquid, such as alcohol, in which the paraffin and water are both soluble; or (3) by destroying the emulsifier. The most convenient de-emulsifier to use when determining the percentage of oil in an emulsion made with soap is a small quantity of mineral acid. With a very strong semi-solid emulsion, a mere trace of hydrochloric acid is sufficient to convert it almost instantly into a mass of liquid oil, with a few drops of water below it. Any sodium salt produces de-emulsification, owing to the conversion of the potassium soap into the comparatively insoluble sodium soap. De-emulsifying action does not appear to be in any way dependent on the de-emulsifying agent being an electrolyte, for potassium salts are without effect on emulsions in potassium soap, and even hydrochloric acid will not produce de-emulsification (as will be shown immediately) in cases where the emulsifying agent is not destroyed by it.

In the Woburn Report, it was shown that a paraffin emulsion containing 2 per cent. of caustic soda possessed valuable insecticidal and detergent properties, but the practical de-emulsification produced by the soda detracted from the merits of the mixture, making constant agitation of it necessary during use, and rendering a uniform distribution difficult. The amount of paraffin recommended for this wash was six volumes per cent., and the soap was reduced to 0.5 per cent., so as to minimise the bulk of solid thrown out when the soda was added. From such a mixture, the soda soap generally separates as a flocculent mass, which rises to the surface, mixed with the paraffin, and forms with it a bulky scum which occupies about one-third of the total volume. This scum, as will be shown below, is what may be termed a quasi-emulsion. It varies considerable in its nature according to the character of the soap used, and with one example of soap in our possession (although of the same brand as other samples) it is scarcely distinguishable from a true emulsion. (Caustic potash, it may be mentioned, cannot well be used as a substitute for caustic soda, on account of its price, and, if much soap is present, the soap is gelatinised, forming a magma which cannot be used for spraying.)

To avoid the disadvantages attaching to the separation of soap in these caustic emulsions, some more suitable emulsifier was sought. When quillaia or glue was used, the addition of caustic soda produced de-emulsification, and the same occurred to a slight extent

with egg-albumen or starch; milk, also, is not very satisfactory, as it clots, even when caustic soda is not present. Attention therefore was turned to the possibility of obtaining an insoluble substance to act as emulsifier. This did not seem impracticable, from the fact that lime had recently been stated to produce emulsification.

Emulsions with Insoluble Emulsifiers.

Lime united with petroleum was first used for spraying purposes under the name of "limoid." A certain magnesian lime of a very fine-grained character was found to absorb double its weight of petroleum, and the mixture thus obtained, disseminated in three to nine times its volume of water, was used as a spray-fluid. Subsequently it was found that any ordinary lime would make an emulsion with petroleum, and the proportions recommended in America are 2·2 grams of quicklime to 11 c.c. of kerosene and 88 c.c. of water. There does not appear, however, to be any reason for adhering to these particular proportions, for they may be varied largely without materially affecting the results.

Much work was done on these lime emulsions before a clue was obtained as to their real nature, but only a brief reference to this work will be necessary here. Limes from various sources were examined, and all gave substantially the same results as calcium oxide prepared from marble, to which the following remarks apply.

On churning up lime with paraffin and water, a sort of emulsion is obtained, which either rises or sinks in the excess of liquid, according to the proportions used. The separation of the emulsion from the excess of water is much more rapid than in the case of emulsions in soap solutions. By suitably adjusting the proportions, an emulsion of a specific gravity of unity can be obtained; there is then no sinking or rising, so long as the proportion of water present is not more than 50 to 70 per cent., but, on dilution, part of the emulsion rises and part sinks; both these parts contain some oil, but the upper part most.

The volume occupied by emulsions with lime, and the percentage of oil contained in them, present no features analogous to emulsions in soap solutions, for here the lime itself occupies much of the total volume, and by its weight it drags down the oil and prevents any close-packing of the oil globules.

The general behaviour of these lime emulsions suggests that they are merely gross mechanical mixtures of lime and paraffin, and not true emulsions. An examination under the microscope confirms

this view; the oil globules present in them are very large, and show great variations in size, being, under the most favourable conditions, ten times the diameter of the globules in a soap emulsion : they appear to be merely caught by, and entangled in, the particles of lime. Moreover, their size, instead of being practically constant, independent of the proportions of emulsifier and of oil, as in the case of soap emulsions, seems to be entirely dependent on them, and, if the lime is not present in considerable quantity, the globules are so large that they become visible to the naked eye, the liquid then being an evidently non-homogeneous mixture, which can claim no title to be called an emulsion. With a further reduction in the amount of lime, or an increase in that of oil, a separate layer of the latter appears.

In one series with " Water White " oil in proportions ranging from 1·5 to 67 per cent. by volume, and with lime equal to 2·2 grams CaO per 100 c.c. of the mixture, the product became visibly non-homogeneous when about 35 per cent. of paraffin was reached. A rather lower limit (about 30 per cent.) was obtained in a similar series with " Solar Distillate." In another series with the latter oil, where the paraffin was kept constant at 50 per cent., and the amount of lime varied, an apparently homogeneous emulsion was not obtained until the lime reached 10 grams per 100 c.c. of the mixture. With a very light oil, such as motor spirit, no homogeneous emulsions could be obtained at all, even when the percentage of lime exceeded that of the oil.

Other finely-divided substances have been examined, and found to give results similar to those with lime, although minor peculiarities are noticeable in the case of each substance ; plaster of Paris, precipitated chalk, precipitated silica and alumina were amongst those which more closely resembled lime in their behaviour.

Mechanical mixtures of such substances with paraffin may conveniently be termed quasi-emulsions, for, with certain proportions between the solid and the paraffin, they approximate to emulsions in character, and may serve the same practical purposes as true emulsions do. Yet, as will be shown immediately, they are essentially different in constitution from true emulsions.

A quasi-emulsion with lime may be mixed with caustic soda without any change being produced, beyond rendering it somewhat more viscid, and it can be mixed with other insecticides and fungicides, notably with copper sulphate, thus giving it an advantage over emulsions with soap. On the other hand, it presents decided disadvantages, in the coarseness of the emulsion produced, the large porportion of lime required, and the difficulty of spraying it without clogging or destroying the nozzles of the machines

When copper sulphate was added to the lime before emulsifica-
tion, it was noticed that the emulsion produced was altogether
different from that with lime alone, and, following up this indica-
tion, it was ascertained that the basic sulphate of copper, precipi-
tated by the action of the lime on the copper sulphate, is, by itself,
capable of emulsifying paraffin and water, almost as finely as, and
much more easily than, soap. If excess of lime is to be avoided,
and all the copper is to be precipitated, the basic sulphate should
be obtained by adding about 134 c.c. of lime-water to every gram
of $CuSO_4,5H_2O$; if otherwise, solid lime may be added to the copper
sulphate solution, and, although the quantity of pure lime required
is only one-seventh of the weight of $CuSO_4,5H_2O$, it is advisable in
practice to increase this to one-third if commercial lime is used, and
to make this into a milk, running it through sacking into the copper
sulphate, so as to eliminate any gross particles. On adding paraffin
oil to this, and churning, one stroke of the syringe is sufficient to
produce a perfect emulsion, and even shaking the mixture will
form an emulsion good enough for practical purposes.

Such an emulsion possesses nearly all the characteristics of one
made with soap, except that, there being a heavy and bulky solid
present, the volume occupied by the emulsion proper does not
depend solely on the oil globules, and the emulsion may rise or
sink in the excess of solution according to the proportions of oil
and basic sulphate used. It generally forms a very smooth
cream, with a perfectly clear-cut line of division between it and
the excess of liquid. In texture, it appears under the microscope
to be identical with emulsions in soap, although the average size
of the component globules is about twice as great. Nothing but a
mass of oil globules can be seen, as the particles of basic sulphate
are generally too small to be visible. If enough of the basic sul-
phate is present, the proportion of paraffin can be increased up
to a very high point, the emulsions becoming thicker, until they are
almost solid. With an insufficient proportion of basic sulphate,
emulsification is imperfect; the minimum with strong emulsions of
"Solar Distillate" is, approximately, 1 gram of $CuSO_4,5H_2O$, con-
verted into basic sulphate, for every 120 c.c. of oil; if the emulsion
is weak, the proportion of basic sulphate required is less. In the
case of the sulphate of iron, which, as will be mentioned imme-
diately, may be used in the same way, the proportions are of the
same order of magnitude, 1 gram of $FeSO_4,7H_2O$ being required
to emulsify about 200 c.c. of oil to make a 6 per cent. emulsion,
100 c.c. to make a 20 per cent. emulsion, and 30 c.c. to make a
60 per cent. emulsion.

To obtain satisfactory emulsions with the basic sulphates, it

seems necessary to use a paraffin oil of high boiling point, such as a
" Solar Distillate " ; with ordinary lighting oil, emulsification is not
perfect, unless the proportion of basic sulphate is very large, and
with motor spirit the paraffin is never more than partially emulsi-
fied.

For practical purposes, an emulsion with basic copper sulphate
presents many advantages over one made with soap. In the first
place, it is a fungicide as well as an insecticide, for it contains all
the elements of Bordeaux mixture; secondly, it is very bulky, and
the tendency to separate from the liquid is much less. If the
copper sulphate taken is 1·6 grams to 100 c.c. (the quantity used
in " normal " Bordeaux mixture made with milk of lime), 3·5 c.c.
of " Solar Distillate " (sp. gr. 0·858) makes with it an emulsion
which neither sinks nor rises, and if the " Solar Distillate " is
increased to 6 c.c., as it might be for winter use, or reduced to
1—2 c.c. for summer use, the tendency to rise or to sink, respectively,
would be but small, the slightest agitation being sufficient to keep
such emulsions disseminated throughout the liquid. With
Bordeaux mixture made with lime-water, as recommended in the
preceding communication (p. 1997), only 0·7 gram of copper sulphate
to every 100 c.c. is used, and 1·4 c.c. of " Solar Distillate " will
make this into an emulsion which will neither sink nor rise, and
which is of a most convenient strength for general summer use.

Besides the facility and certainty with which these emulsions
can be made, they possess the advantage of being much more per-
manent than emulsions made with soap. No single instance has yet
occurred in which any one of them has de-emulsified spontaneously.
Also, they can be mixed with caustic soda (2 per cent. being
generally used) to make a detergent winter wash, without becoming
de-emulsified, as in the case of soap emulsions.

In connexion with the use of soda with these emulsions, one or
two points must be mentioned. Copper hydroxide will not emulsify
paraffin as the basic sulphate does, and, although caustic soda
precipitates the basic sulphate $4CuO,SO_3$ when added in the proper
proportions, excess of alkali converts it into the hydroxide, so that
soda cannot be used for the preparation of a caustic copper emul-
sion. But if the $4CuO,SO_3$ is precipitated by lime, and then
emulsified, the excess of soda may be added without producing any
appreciable change; it is only after the lapse of a month or more
that an emulsion made in this way will show any signs of the
presence of copper hydroxide, and begin to blacken. This differ-
ence in behaviour, according to which alkali is used for the pre-
cipitation, naturally caused much perplexity, until the investigation
of the basic sulphates, detailed in a previous communication, had

shown that the precipitate with lime is not merely $4CuO,SO_3$, but a compound of that sulphate with calcium sulphate.

If fungicidal properties are not required in the caustic wash, ferrous sulphate may be substituted for the more expensive copper sulphate. The emulsions with the iron salt have certain advantages over those with the copper salt. The oil globules in them are smaller (about one-third to one-fifth of the diameter) and the emulsions are more bulky, and separate from the excess of liquid more slowly. Moreover, ferrous hydroxide, unlike copper hydroxide, is itself capable of emulsifying, and hence the precipitation with lime may be dispensed with and the caustic soda alone be used. A much finer emulsion, however, is obtained if lime is used as the precipitant, as in the case of copper. Where soda is used, that required for the precipitation, as well as the extra 2 per cent., may all be added to the iron sulphate at once before emulsifying with paraffin. The basic ferrous sulphate, or ferrous hydroxide, as the case may be, is, of course, partially oxidised, and the emulsion becomes nearly black. On keeping it in a closed vessel, it sometimes (especially if excess of lime is present) becomes almost colourless, organic substances in the paraffin apparently reducing the ferric compounds; on exposure to air, it becomes orange-red, ferroso-ferric oxide being formed. These changes do not appear to affect the emulsification.

One drawback to the copper emulsion is that it cannot be prepared in a concentrated form like a soap emulsion. The percentage of oil present may be increased, but not that of the copper, for lime must be used as the precipitant, and, if this is added to a strong solution of copper sulphate, the precipitated basic sulphate forms a compact mass which will not emulsify the oil properly. With ferrous sulphate, however, where soda can be used as the precipitant, this difficulty does not exist, and it is possible to make an emulsion of which 100 c.c. contain 60 c.c. of oil, this being ten times the strength generally required for spraying. The amount of iron which can be got into such a strong emulsion, however, is not large, and, consequently, the emulsion is light, and rises rapidly to the surface when diluted, necessitating agitation during use.

Some of the copper emulsions were examined by analysis in the same way as soap emulsions. It will be sufficient to quote the results with one of them only, and these are given in the accompanying table and in Fig. 2. The mixture taken for emulsification contained 20 c.c. of " Solar Distillate " and 0·18 gram of CuO, in the form of sulphate, per 100 c.c. Portions of the emulsion proper were analysed throughout their mass after twenty-four hours, ten days, and twelve weeks, the average proportions of oil in them then

being 33·3, 38·0 and 42·6 per cent., respectively. The emulsion becomes more concentrated as time elapses, and, at the same time, the curve representing its composition becomes flatter, although in all cases there is a rapid fall in concentration towards the bottom of the column. The most marked feature, however, is the ultimate arrangement of the emulsion into layers of uniform composition, which, although not visible as separate layers to the eye, are made evident by the analysis. Such an arrangement has

Fig. 2.
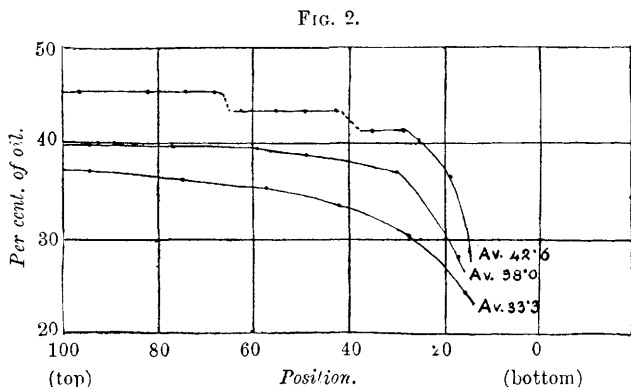
Composition of emulsions. " Solar Distillate" with basic copper sulphate.

already been noticed in the case of emulsions with soap. As will be seen from the table, the percentage of basic sulphate in the emulsion decreases from the top to the bottom with the percentage of oil, but not so rapidly as the latter, so that the proportion of it

Composition of Emulsions of " Solar Distillate " with Basic Copper Sulphate.

After 24 hours.		After 10 days.		After 12 weeks.			
Position.	% Oil.	Position.	% Oil.	Position.	% Oil.	% CuO.	CuO : Oil.
100—83	36·8	100—85	40·1	100—93	45·3		
83—66	36·0	85—69	39·9	93—86	43·5		
66—50	35·4	69—53	39·4	86—79	45·3	0·408	0·907 : 100
50—34	33·5	53—37	38·7	79—72	45·3		
34—19	30·1	37—22	36·7	72—66	45·3		
19—7	22·8	22—8	26·4	66—60	43·4		
				60—53	43·3	0·394	0·916 : 100
				53—47	43·1		
				47—39	43·3		
				39—31	41·3		
				31—25	41·3	0·378	0·928 : 100
				25—22	40·0		
				22—17	37·2	0·352	1·071 : 100
				17—11	28·5		

to the oil increases downwards.   It is noticeable, however, that this
increase is very small; in spite of the differences in specific gravities,
about 2·5 and 0·86, there is very little separation of these two
substances, and the union between them must, therefore, be of a
decidedly intimate character.

The Nature of Emulsions.

It is evident that emulsions with basic copper sulphate are
strictly similar in nature to those with soap, and are quite different
from the quasi-emulsions with lime.   Many other substances act
in a manner similar to basic copper sulphate, but few of them so
satisfactorily.   The action, however, is not distinctive of basic salts,
some of them, such as the basic sulphates of copper, iron and nickel,
form true emulsions, whereas those of zinc, aluminium and cadmium
form quasi-emulsions only; other substances when freshly precipi-
tated behave in a similarly arbitrary manner, calcium arsenate, for
instance, forms a good emulsion, whereas with barium sulphate, no
signs of emulsification are obtained.   On the other hand, no con-
nexion between emulsification and the nature of the metal present
can be traced; copper hydroxide will not emulsify, although the
basic sulphate will, whereas both ferrous hydroxide and basic
ferrous sulphate are good emulsifiers.   Nor is the mere bulki-
ness of the precipitate any guide to its emulsifying powers; pre-
cipitated aluminium silicate, although very bulky, does not
emulsify, nor does gelatinous silica.   The colloidal condition of the
substance, also, has no influence on the results, for paraffin will not
emulsify in a dialysed solution of silica.

The view which the writer was eventually led to adopt as to
emulsification, was that it depended solely on the size of the par-
ticles constituting the precipitate.   When the oil is broken up into
small globules by being forced through the syringe, and these
globules find themselves in the presence of a number of very much
more minute solid particles, the latter will be attracted by the
globules, and will form a coating or pellicle over the globules,
preventing them from coming in contact and coalescing with their
neighbours.   Whether gravitation alone is sufficient to account for
such a result, or whether other forces come into play, must be left
for others to determine, but that the solid particles do congregate
closely round the globules, there can be no doubt, for they can
often be seen under a powerful microscope.   With basic copper
sulphate this is so, although the particles are so nearly ultra-micro-
scopic that they cannot be resolved sufficiently to admit of any
estimate being made as to their actual size : with basic iron sulphate,

they are still smaller, and quite invisible, but their aggregation round the globules is evident from the brown ring encircling the latter.

Further evidence that the globules must be enveloped in some covering is found in the fact that these emulsions do not make the containing vessel oily; indeed, this forms a very good distinctive test between a true emulsion and a quasi-, or imperfect, emulsion. The same test may be varied by dropping a little of the liquid into a basin of water; if unemulsified paraffin is present, the surface of the liquid becomes oily, but not so if the paraffin is present as a true emulsion.

An emulsion on this view, however much it is diluted with water, will suffer no de-emulsification, whereas with a quasi-emulsion, where we simply have oil globules entangled with the gross particles of a solid, it should always be possible to separate the greater part of the oil by adding enough water. This, as a matter of fact, is found to be the case. It is also possible to remove the oil from a substance with which it forms only a quasi-emulsion, by adding another substance with which it forms a true emulsion. Thus a quasi-emulsion of lime and paraffin of a suitable strength will rise in a mass to the surface of water, but, if some sodium arsenate is added, calcium arsenate is formed, and, as this is a true emulsifier, it forms an emulsion with the oil, and rises to the surface, whilst the lime, deprived of the oil, sinks to the bottom.

Neither in the case of a true emulsion nor in that of a quasi-emulsion does the nature of the menstruum appear to have any influence on the emulsification, so long as it does not react chemically with the emulsifier or the oil; a variety of salts may be dissolved in water containing an emulsifier without affecting the emulsion, beyond making it in some cases (notably when caustic soda has been added) more viscid, due, no doubt, to an increase in the coefficient of friction. Even strong mineral acids have no effect in a case such as that of clay (some clays will act as emulsifiers), where the solid emulsifier is insoluble in acids.

Although emulsions and quasi-emulsions are radically different in their nature, various substances will yield results showing every possible gradation between the two, for the simple reason that substances may consist of particles of every gradation of magnitude, some small enough to emulsify the oil globules, and others too large to do more than form quasi-emulsions. In the same way, there is every gradation between a quasi-emulsion and the complete separation of the oil and water into independent layers.

The power of emulsifying, not being an inherent property of the substance, but simply depending on the size of its particles, it

follows that this power should be destroyed by aggregation; that this is so, can easily be proved. The basic sulphates, calcium arsenate, Oxford clay, &c., all of which form true emulsions, are found to be quite incapable of doing so after they have been dried, however finely they may then be powdered.

The average size of the globules in an emulsion seems to be dependent on the size of the particles of the emulsifier. Thus the particles of basic ferrous sulphate are more minute than those of basic copper sulphate, and the emulsion is decidedly finer-grained also; with nickel basic sulphate, both the particles and the oil globules are of about the same size as with the copper salt, whereas with cadmium and zinc basic sulphates the particles are gross and the emulsion is very coarse, being to a large extent only a quasi-emulsion. Whether, however, the chemical nature of the emulsifier is altogether without effect on the results or not, and whether the size of the particles is the sole determining factor, it is impossible to decide with certainty, without a more extended series of observations, aided by better eyesight and better microscopic appliances than were available in the present case. It seems, however, that the attraction between the oil globules and the solid particles may be sufficient to modify somewhat the chemical behaviour of the latter. The basic sulphate of copper precipitated by lime, when treated with excess of caustic soda, will blacken after a few weeks, owing to the formation of copper oxide, but, when emulsified with "Solar Distillate," this blackening does not commence nearly so soon; it is more rapid when a lighting oil is used, this forming a coarser emulsion, and much more so if petrol is used, when the emulsification is very imperfect indeed. Similar evidence is obtained by making emulsions with the same oil, but using different proportions of it; that which contains more oil will blacken more slowly. Analogous results are obtained with ferrous sulphate, the colour of the emulsions, due to different degrees of oxidation, differing according to the nature of the oil used. It is possible, however, that in these cases the retardation of the action of the soda on the basic sulphate, or the oxidation of the compounds present, may be due to a chemical action of impurities in the oil.

A few instances exist which seem at first sight to negative the view that the power of emulsifying is conditioned by the size of the solid particles. Thus, precipitated sulphur, purple of Cassius, and ferric ferrocyanide, all of which are in an extreme state of sub-division, will not emulsify paraffin at all. The behaviour of sulphur gives a clue to this result. When flowers of sulphur, thoroughly incorporated with water, are churned with paraffin, the latter abstracts the whole of the sulphur from the water, forming

with it a greasy mixture, which sticks obstinately to the syringe, containing vessel, &c., the paraffin evidently wetting the sulphur in a way which the water does not. A similar effect is observed in the case of purple of Cassius and ferric ferrocyanide; although the paraffin is not emulsified at all, it abstracts the whole of these substances from the water, becoming intensely coloured by them, and leaving the water colourless, just as if they dissolved in the paraffin. The view therefore that emulsification depends solely on the minuteness of the solid particles must be so far modified as to apply only to such solids as are wetted more easily by water than by oil, otherwise there is no emulsification at all.

The explanation of emulsification here advanced would hardly be acceptable unless it could be applied equally to cases where the emulsifier is a liquid, and there seems to be but little difficulty in doing so; for these liquid emulsifiers are all substances which, under the conditions obtaining, partly separate from the solution, and yield sufficient solid particles to form a pellicle over the oil globules. Liquid emulsifiers are all distinguished, so far as we know, by a feeble affinity for water; in many cases they are, or contain, protein substances, which, as Ramsden has shown, form a skin of solid matter at any boundary between the solution and another fluid, whether liquid or gaseous. In other cases, the deposition of some particles of the solid would result from this solid being insoluble in the paraffin. The water in the neighbourhood of a paraffin globule would become impregnated with paraffin, and the dissolved substance, having but a small affinity for water, would be thrown out of solution. Solutions of egg-albumen, glue and starch, when covered with a layer of paraffin, all form a slight opaque film at the junction of the two liquids. In this way, each globule of oil would obtain for itself the solid particles necessary for its emulsification; but these particles would, no doubt, often be redissolved, whilst others, in their turn, would be deposited, and, in the course of such changes, opportunities would occur for the coalescence of neighbouring globules. This explains why emulsions in soap will generally de-emulsify spontaneously, if left long enough, whereas emulsions with a really insoluble emulsifier seem to be quite permanent.

Formed in this way by solid deposited *in situ,* an emulsion in soap, or similar substances, would naturally be more fine-grained, and the globules would be more closely packed, than in cases where a separately formed precipitate is the emulsifier. A rise of temperature, or an increase in the volatility of the oil used, would result in the soap solution becoming more permeated with paraffin particles, and depositing more of the dissolved soap, thus facilitating emulsification. With soap, a rise of temperature does facilitate emulsifica-

tion, and an increase in the volatility of the oil sometimes does the
same (pp. 2002, 2006). With insoluble emulsifiers, however,
neither a rise of temperature nor an increase in volatility favours
emulsification, indeed, the latter materially hinders it (p. 2009),
owing, no doubt, to the more volatile oils being more mobile.

Whether any soluble inorganic substance exists which would
emulsify oil in the same way as does soap, appears to be very
doubtful; it is certainly probable that any substance which is
crystalline would be incapable of emulsifying. Saturated solutions
of calcium hydroxide and sulphate, as well as of sucrose, dextrose
and dextrin, have been tried, with negative results.

With soap, the particles requisite for emulsification are also
provided in another way; for when soft soap is dissolved in much
water, or when a strong solution of it is diluted, a considerable
amount of a very fine deposit is obtained, and this is often in such
a minute state of division that it remains suspended in the liquid
for weeks. The separation of this precipitate on dilution, and its
redissolution or concentration, explains a fact previously noticed
(p. 2002), which otherwise would present considerable difficulty,
namely, that for each proportion of paraffin and water the amount
of soap necessary for emulsification must not only be in excess of
a certain minimum, but also must not be in excess of a certain
maximum. The existence of the superior limit is explained if the
emulsification depends to any large extent on the presence of solid
particles precipitated by dilution, for the tendency to deposit such
particles would be less in stronger than in weaker soap solutions.

(It should be mentioned, however, that a superior limit does not
seem to exist in the case of all soaps. This is not surprising, for
soaps vary largely in composition, even when they are of the same
brand, and from the same factory, and they differ considerably in
their behaviour on dilution.)

That the formation of a pellicle of solid particles over the oil
globules affords an explanation of emulsification, is, as has been
mentioned, the conclusion to which Dr. Ramsden also was led, and
the view that such a pellicle exists in the case of the oil globules
in milk was advocated long ago. So far as can be seen, this view
seems to harmonise with all the observed facts.

Behaviour of Various Substances.

It would be tedious and unprofitable to describe at length the
behaviour of the many substances which have been examined as
regards their emulsifying powers; but they may be briefly
enumerated, classing them roughly into those which give true

emulsions, those which give imperfect emulsions or quasi-emulsions, and those which do not seem to emulsify at all. In some cases, however, it is rather difficult to decide in which class to place a particular substance, and, in others, the method of preparation affects the behaviour of the substance in question.

Good Emulsifiers.—Amongst soluble, or partially soluble, substances, soft soap seems to be the best; dissolved starch, milk and flour are good, although the latter forms a flocculent, and not a creamy, emulsion, and milk gives rise to solid clots; glue emulsifies well, and so does egg-albumen, but the emulsion with the latter is rather frothy, owing to enclosed air bubbles; saponin and quillaia bark give good emulsions when the proportion of oil present is not large.

Amongst insoluble emulsifiers, the basic sulphate of iron is the best, followed by those of copper and nickel; the basic sulphates of zinc and aluminium generally give good emulsions at first, but aggregation of the particle seems to occur, and causes partial de-emulsification. Ferrous hydroxide and the higher oxides of iron (hydrated) are good. The precipitate obtained by adding sodium carbonate to copper sulphate is a very good emulsifier, so are calcium carbonate and calcium arsenate when first precipitated, but the latter soon become crystalline, and de-emulsification follows; lead arsenate, freshly precipitated, is good, and zinc oxychloride, or basic chloride, is fair, although the emulsion with it is flocculent; some fine clays (unheated), such as Oxford clay, give good emulsions, but they, naturally, contain many gross particles which sink to the bottom unemulsified; ferrous hydrosulphide gives a good emulsion if the proportion of oil present is small.

Substances producing Quasi-Emulsions, or producing Partial Emulsions.—Lime, silica, alumina, plaster of Paris and many fine powders which have been dried; also the following precipitated substances when in the liquids from which they have been precipitated: basic cadmium sulphate, magnesium hydroxide, copper hydroxide, the basic sulphates of zinc and aluminium, stannous oxychloride, purple of Cassius, lead arsenate paste (a commercial preparation for insecticidal purposes), some clays and brick-earths, copper hydrosulphide, ferrous hydrosulphide (unless the proportion of paraffin is very low), and precipitated soda soap.

Substances showing little or no Power of Emulsifying.—Precipitated lead chloride, lead sulphate, barium sulphate, neutral silica solution, sulphur precipitated by adding acid to sodium thiosulphate, flowers of sulphur and dried Paris-green (in both of which cases the powders seem to absorb the oil, forming a sticky mass which adheres to the syringe and containing vessel in an obsti-

nate manner); an alcoholic solution of resin precipitated by water, ferrous ferricyanide, ferric ferrocyanide, and purple of Cassius (in the last two cases the precipitate is carried up by the oil in sufficient quantities to colour it strongly); and, lastly, any coarse, or even fine, powders, especially when present in small proportions.

Summary.

When paraffin oil is churned up with a solution of soft soap, an emulsion is formed which rises to the surface and generally contains 65 to 82 per cent. by volume of oil. Emulsions containing as much as 99 per cent. can, however, be obtained, and these are so stiff as to be almost solid. The character of the oil does not much affect the results, neither does the extent of the churning nor the proportion of soap, so long as this proportion is within certain limits.

The amount of oil in an emulsion which has arrived at a state of equilibrium decreases somewhat from the top downwards, but there is often a tendency to arrange itself in layers of approximately uniform composition.

Solutions of other organic substances, such as glue, flour, milk, starch, albumen, saponin, &c., act as emulsifiers for paraffin oil. All these emulsions will often spontaneously become de-emulsified, and this occurs at once if the emulsifier is destroyed; for example, if an acid or any sodium salt is added to an emulsion with soap. Electrolytes, as such, seem to have no de-emulsifying action. The addition of unemulsified paraffin to an emulsion will gradually de-emulsify the whole.

The oil globules in an emulsion are probably prevented from coalescing by being enveloped in a pellicle consisting of particles of solid much more minute than the globules themselves. The solid particles would be derived from the solution, which in all cases contains a substance with but little affinity for water, and insoluble in paraffin, it being, therefore, precipitated in the neighbourhood of the paraffin globules.

Apparently, a precipitate consisting of any insoluble substance which is wetted more easily by water than by oil, if in a sufficiently fine state of division, will equally act as an emulsifier, and in some cases it is possible under a microscope to see the coating of solid particles which envelop the oil globules. Emulsions made with an insoluble emulsifier are in every respect similar to those made with soap, &c., except that they never seem to de-emulsify spontaneously; spontaneous de-emulsification being, no doubt, due to the fact that the solid particles, as in the case of soap, are soluble

in water, and are continually being redissolved and reprecipitated, thus affording opportunities for the coalescence of the oil globules.

The basic sulphates of iron and copper are amongst those substances which give excellent emulsions. They may be formed by adding lime, or lime-water, to the normal sulphates, and then the paraffin, when the slightest churning, or even shaking of the mixture, produces emulsification. Besides the ease of manufacture, and the absence of spontaneous de-emulsification, these emulsions possess the advantage of not being decomposed by the addition of caustic soda, as are emulsions with soap, and caustic soda is required when the emulsion is used as a winter wash for trees. When the copper salt is used, the emulsion possesses all the fungicidal properties of Bordeaux mixture.

Many other precipitated substances act as emulsifiers, but this property is destroyed as soon as they have been dried, or have by any other means been deprived of their fine-grained structure.

Solids which are not sufficiently fine-grained to emulsify will, in many cases, when present in considerable proportions, form quasi-emulsions. In these, the particles of oil are merely entangled with the particles of solid, and may be separated from them by such simple means as dilution with water. Lime is an instance of a substance which forms a quasi-emulsion which can be used for spraying purposes. Other substances, including many recently-formed precipitates, and, probably, all crystalline solids, seem to be incapable of forming even quasi-emulsions.