PERCENTAGE ANALYSES OF MIXTURES

Mixture	No. 1 W-S	No. 1 Ins.	No. 2 W-S	No. 2 Ins.	No. 3 W-S	No. 3 Ins.	No. 4 W-S	No. 4 Ins.
April 21st, Immediately after mixing..	6.15	1.07	8.30	1.15	10.50	1.24	2.40	0.83
May 10th...........	3.05	1.30	5.84	1.26	8.66	1.37	0.99	0.98
June 12th...........	3.31	1.39	6.39	1.66	8.15	1.59	1.10	1.11
Sept. 13th...........	3.38	1.46	3.31(a)	1.33	8.05	1.46	0.87	1.08

(a) This is probably an error as an analysis in November, 1913, gave about five per cent water-soluble.

I was surprised that more insoluble phosphate was not formed in these mixtures, especially the half and half mixture.

In order to test the effect of larger mixtures than used by Dr. Brackett and also to try the effect of fresher acid phosphate, I made up some mixtures last summer and used acid phosphate a month old and some which had been made only a few days and was warm when mixed. I used ground oyster shells instead of ground limestone.

TABLE I—MATERIALS USED

Material	Total	Percentages Phosphoric Acid Insoluble	Water-Soluble
New acid phosphate..................	19.33	2.41	15.78
Month-old acid phosphate.............	18.13	1.04	14.80
Ground oyster shells..................	0.51	....	.....

TABLE II—MIXTURES AND RESULTS OF ANALYSES

Acid Phosphate Used: Mixture	Date Analyzed	Old Phosphoric Acid (%) Insol.	Old Phosphoric Acid (%) Water-Sol.	New Phosphoric Acid (%) Insol.	New Phosphoric Acid (%) Water-Sol.
190 lbs. Acid Phos....	8/16	2.50	15.05	0.82	13.72
10 lbs. Oyster Shells..	9/20	2.70	14.00	0.24	11.28
Theory		2.32	14.99	1.02	14.06
180 lbs. Acid Phos....	8/16	2.45	14.50	0.79	13.38
20 lbs. Oyster Shells..	9/20	3.44	7.08	1.50	3.05
Theory		2.22	14.20	0.99	13.32
160 lbs. Acid Phos....	8/16	2.40	12.15	0.84	11.10
40 lbs. Oyster Shells..	9/20	2.99	4.30	1.57	1.05
Theory		2.03	12.62	0.93	11.84
140 lbs. Acid Phos....	8/16	1.65	10.08	1.14	10.58
60 lbs. Oyster Shells..	9/20	3.26	1.50	1.95	0.65
Theory		1.84	11.05	0.89	10.36
100 lbs. Acid Phos....	8/16	1.95	5.55	1.12	7.60
100 lbs. Oyster Shells	9/20	2.32	0.30	1.11	0.35
Theory		1.46	7.89	0.77	7.40

In studying this table there are some inconsistencies, but taking the results as a whole it is seen:

1—That the new acid phosphate is acted on more readily by the oyster shells than the older.

2—That action begins at once.

3—That the action continues on standing.

4—That the greater the amount of oyster shells the greater the action.

5—That with 30 and 50 per cent shells virtually all of the water-soluble phosphoric acid disappears.

These results, on the whole, agree with Dr. Brackett's. I intend to make further analyses of these samples.

It has generally been considered that water-soluble or mono-calcium phosphate is more valuable to crops than citrate-soluble, or di-calcium phosphate. If that is true then mixing larger quantities of calcium carbonate with acid phosphate would reduce the value of the phosphate very greatly, by reducing the water-soluble phosphoric acid to the vanishing point and also by increasing the insoluble phosphoric acid.

As the fertilizer laws are at present, fertilizer manufacturers certainly could not afford to mix much calcium carbonate with their acid phosphates on account of the high insoluble phosphoric acid which would be produced.

As this question is a very important one to both farmers and fertilizer manufacturers, I have thought it well to make public my results in order to have more light thrown on the subject.

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A CONTRIBUTION TO THE THEORY OF EMULSIFICATION BASED ON PHARMACEUTICAL PRACTICE[1]

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INTRODUCTORY

The practical knowledge of emulsions, which has been handed down to the pharmacists from generation to generation, has been surveyed by physical chemists, but this pharmaceutical experience has been neglected almost entirely as an aid in developing a rational theory of emulsification. Several theories of emulsification have been proposed which differ according to the factor held responsible for the stability of the emulsion, but objection has been raised to all of them. It is probable that none of these theories is of universal application, and though each may cover special cases or classes of emulsions, their inadequacy is generally admitted.

The surface tension theory upheld by Plateau,[2] Quincke[3] and notably Donnan[4] was shown to be inadequate when Pickering[5] emulsified "solar distillate" with the aid of such materials as the basic sulfates of iron and copper, hydrous ferric oxide, etc., materials which do not influence surface tension. The viscosity theory, whose origin is obscure, was attacked by Hillyer,[6] who pointed out that although extreme viscosity was an important factor in the preparation of some pharmaceutical emulsions, nevertheless, viscous materials, such as 50 per cent glycerine or 6 per cent gum solution, are not able to emulsify kerosene or cottonseed oil, though dilute, comparatively mobile soap solutions do so easily.

While admitting the favorable influences of high viscosity and low surface tension, Pickering[7] put forth the view that the deciding factor is the formation of films of insoluble particles around the droplets. Donnan[8] attacked this hypothesis bitterly, but Bancroft[9] pointed out that the criticism was beside the point and that the theory was not intended to be a complete one. Clowes[10] has described experiments in which these films were distinctly visible and he attributes their action in part to a purely mechanical action in keeping the particles from coalescing, in part to lowering of surface tension and in part to repulsive action of the electrically charged particles.

Fischer[11] has recently proposed that emulsification is due to, or accompanied by, the formation of a hydration colloid compound. He says: "In reviewing the empirical instructions for the preparation of emulsions, and in our own attempts to formulate such as would always yield permanent results, we were struck with the fact that their production is always associated

[1] The work reported in this article constitutes the basis of a thesis submitted by Leo Roon to the Faculty of the Graduate School of New York University, in part fulfillment of the requirements for the degree of Master of Science.

[2] *Pogg. Ann.*, **14** (1870), 44.

[3] *Wied. Ann.*, **35** (1888), 589.

[4] *Z. phys. Chem.*, **31** (1899), 42.

[5] *J. Chem. Soc.*, **91** (1907), 200.

[6] *J. Am. Chem. Soc.*, **25** (1903), 513.

[7] *Z. Koll. Chem.*, **7** (1910), 11.

[8] *Ibid.*, **7** (1910), 214.

[9] *J. Phys. Chem.*, **16** (1912), 504.

[10] *Ibid.*, **20** (1916), 415.

[11] *Science*, **43** (1916), 468.

with the discovery of a method whereby the water (or other medium) which is to act as the dispersing agent is all used in the formation of a colloid hydration (solvation) compound. In other words, when it is said that the addition of soap favors the formation and stabilization of a division of oil in water, it really means that soap is a hydrophilic colloid, which, with water, forms a colloid hydrate with certain physical characteristics and that the oil is divided in this. The resulting mixture cannot, therefore, be looked upon as a subdivision of oil in water, but rather as one of oil in a hydrated colloid." Fischer gave no experimental details of his work and though he promised their future publication, neither his method nor results were available to us. The work described in this paper had been under way for several months before the appearance of Fischer's article, but our results and conclusions coincide so closely with his views, that in the absence of his own data, our findings seem to constitute at least a partial confirmation of his theory.

PHARMACEUTICAL EMULSIONS

The preparation of emulsions is a regular practice in pharmacy, but the pharmacist, in contrast to the physical chemist, recognizes only the oil-in-water type of emulsions, even though he has, as official pharmacopoeial preparations, lanolin, carron oil, etc., which are of the water-in-oil type. These latter preparations, however, he classes with the ointments and liniments, respectively. Every pharmaceutical emulsion consists of three principal parts: (1) the liquid to be emulsified; (2) the emulsifying agent; (3) water. The liquids used are limited to fixed and volatile oils and other liquids immiscible with water, such as chloroform, ether, etc. The emulsifying agents most generally employed are gum arabic (acacia), gum tragacanth, Irish moss, dextrin, gelatin, extract of malt, yolk of egg. Of these, powdered or granulated acacia is by far the best. In addition to the standard emulsifiers mentioned above, condensed milk, casein, starch and various mixtures of any of those named have been used with more or less success.

There are two methods of preparing pharmaceutical emulsions, the English and the Continental.

1—*The English method* consists in triturating the gum with water to make a mucilage, and then adding oil and water alternately in small portions, triturating after each addition until the emulsion is completed. This method is not considered very satisfactory by most pharmacists. For example, Arny[1] states that "this method of manufacturing emulsions is slow and uncertain and cannot be compared with the Continental method in simplicity." It has been our experience that not more than two per cent of the average students of pharmacy are able to make good emulsions by this method. It is of interest to note that the *hydration of the emulsifying agent occurs progressively and not all at one time and for the greater part is not accomplished in the presence of the internal phase.*

2—*The Continental method* consists in first making what is called the emulsion nucleus with certain definite quantities of oil, gum and water. This creamy, viscous nucleus may then be diluted with any quantity of water to form a good emulsion. In this case *all of the emulsifying agent is hydrated at one time and in the presence of the internal phase.* Remington[1] says concerning this method: "This has the great merit of never failing to produce a good emulsion if the proper proportions are used to form the nucleus, and if the directions are strictly followed." Text-books and practitioners are divided as to what may be considered the proper proportions of oil, gum and water for making the nucleus. The majority of pharmacists use the materials in the proportion of 4 parts oil, 2 parts acacia, 3 parts water. Remington and Arny both recommend 4 parts oil, 2 parts water and 1 part acacia; the National Formulary[2] recommends 8 parts oil, 2 parts acacia and 3 parts water. In any case, it is evident that the proportion of water to the emulsifying agent, acacia, is practically constant. The proportion of 4 parts oil, 2 parts acacia and 3 parts water is considered most reliable for making the nucleus and has been used as the standard for the purposes of this research. To make a good emulsion nucleus, *strict adherence to the mode of procedure* is just as important as taking the proper proportions of materials. The standard method consists in placing the oil (4 parts) in a dry mortar, adding the acacia (2 parts) and triturating until a smooth paste is formed. The water (3 parts) is added, not in portions, but all at once, when, upon trituration, a thick creamy nucleus is formed. This is now perfectly miscible with water in all proportions.

A survey of the literature shows that some physical chemists also have found that the use of certain definite proportions of materials leads to good emulsions. For example, Gad[3] found that when oil containing the *proper* percentage of fatty acid was placed on the surface of a sodium carbonate solution, a beautiful spontaneous emulsion resulted, and from this he held that neither shaking nor any other mechanical process was necessary for the formation of an emulsion. His method consisted in taking a series of watch glasses containing 0.25 per cent sodium carbonate solution and then placing drops of oil, containing various amounts of free fatty acid on the surface of the solutions in the glasses. He observed that the oil which contained 5.5 per cent fatty acid emulsified spontaneously at room temperature and that the oils containing very little more or less than 5.5 per cent yielded incomplete emulsions. He, therefore, concluded that the limits of good spontaneous emulsion were not only constant but quite narrow.

Robertson[4] has published some interesting results which also serve to illustrate the importance of the use of definite proportions of the materials for emulsification. He states: "If one shakes up thoroughly, equal parts of slightly alkaline water and olive oil, a very stable emulsion is formed in which olive oil

1 "Principles of Pharmacy," 1911, p. 267.

1 "Practice of Pharmacy," p. 1155 (5th edition).
2 "National Formulary," 1906, p. 46 (3rd edition).
3 Arch. Anat. Physiol., 1878, 181.
4 Z. Koll. Chem., 7 (1910), 7.

forms the internal phase and water the external phase; that is, the oil is suspended in spherical droplets in the water. If we increase the proportion of water, the resultant emulsion still continues to exist as drops of oil suspended in water until the proportion of water to oil reaches a definite critical value. When this critical ratio is reached, the character of the emulsion undergoes an abrupt change. From being a viscid, creamy white emulsion of oil in water, it becomes a fluid yellow emulsion of water in oil." Bancroft[1] does not agree with Robertson's conclusion that there is necessarily a critical ratio, with one type of emulsion existing below this value and the other type above it, although he admits the possibility of there being a given point at which an emulsion might become unstable.

A search of the literature revealed very little concerning quantitative measurements of the critical proportions of emulsions, nor could we find records of the results of varying the order in which the ingredients of emulsions were added to each other and our work was undertaken with a view of studying several typical emulsions from these standpoints. The results were rather striking and we believe throw some light on the process of emulsification. It is probably true that the critical values determined are valid only for the quantities used in our work and apply only to emulsions prepared by shaking in test tubes, but our basic conclusions are probably of universal application.

Only two emulsifying agents, acacia and soap, were employed. Acacia (gum arabic) is considered by pharmacists to be the best emulsifying agent, and soap has been mentioned by the physical chemists as the most efficient emulsifier. Only those emulsions were dealt with in which water constituted the external phase. As internal phases, substances were employed which represented different types of liquids immiscible with water: hexane, chloroform, carbon tetrachloride, benzene, white mineral oil and cottonseed oil. The work dealt with practical emulsions rather than with theoretical emulsions such as were prepared by Lewis[2] and Ellis.[3]

Those dispersions were considered as good emulsions which were uniform throughout in color and consistency, which were perfectly miscible with water, which uniformly wetted the walls of the containing vessel and which did not separate on standing into three parts—a layer of internal phase; a layer of external phase; with an interfacial ring of partially emulsified internal phase separating the two layers. On standing, most good emulsions cream, or separate into two layers, a layer of completely emulsified internal phase and a layer of external phase. In this connection, Scoville[4] says: "Good emulsions often separate into layers on standing, but without showing any separated oil. An emulsion should not be condemned for this, because the separation is due, not to faulty manipulation in making the emulsion, or to improper ingredients

1 *J. Phys. Chem.*, **16** (1912), 746.
2 *Z. Koll. Chem.*, **4** (1909), 211.
3 *Z. phys. Chem.*, **78** (1911), 352.
4 "Art of Compounding," **1895**, p. 82.

or proportions therein, but to excess of dilution, and a little shaking will quickly rediffuse it. The same thing occurs in milk—the best type of natural emulsion—in which the true emulsion portion separates as cream."

EXPERIMENTAL

The following materials were used in this research:
1. Hexane, specific gravity 0.691.
2. Chloroform, specific gravity 1.526.
3. Carbon tetrachloride, specific gravity 1.597.
4. Benzene, specific gravity 0.877.
5. Oil of turpentine rectified.
6. Mineral oil, specific gravity 0.853.
7. Cottonseed oil, winter yellow, specific gravity 0.921.
8. Squibb's soft soap. An alcoholic solution containing 50 grams of soap in 100 cc. of solution was used.
9. Powdered acacia (gum arabic) first selection.
10. Mucilage of acacia, 33 grams of acacia contained in 100 cc. of mucilage.

I—ACACIA EMULSIONS

All the acacia emulsions were made by shaking in 30 cc. test-tubes, except those containing cottonseed oil and mineral oil, which, because of their high viscosities, had to be made by trituration in a mortar. The method and order of adding the necessary constituents, was, however, the same in all cases. The acacia was added to and mixed with 10 cc. of the internal phase; 7.5 cc. of water was then added at once, and the mixture rapidly triturated (cottonseed or mineral oils), or briskly shaken in a test-tube. The quantities of internal phase, gum and water taken were in accord with the standard pharmaceutical proportions of 4 : 2 : 3, respectively, or in other words, 10 cc. of internal phase, 5 g. acacia and 7.5 cc. of water. The volumes of internal phase (10 cc.) and of water (7.5 cc.) were kept constant throughout, but the amount of acacia was varied and the effect on the condition of emulsification noted in order to determine the presence of a critical point, *i. e.*, the minimum quantity which would emulsify the given volumes of water and oil. Such points were observed and are indicated in the results given in Table I.

It was found on taking 10 cc. mineral oil, adding 5 g. acacia, triturating to a smooth paste and then adding water in 0.5 cc. portions, that the acacia immediately absorbed the water and formed large translucent lumps. On adding more water, vigorous trituration being maintained, the mixture grew whiter and whiter until suddenly a perfectly white, creamy emulsion resulted. At this point of emulsification, however, several of the rubbery lumps of acacia still remained, showing that 5 g. acacia were in excess of the amount necessary to emulsify the 10 cc. of oil. For this treatment, 11.5 cc. of water, in small portions, had been used, whereas when 7.5 cc. of water (pharmaceutical ratio 4 : 2 : 3) was added *all at once*, a beautiful white creamy viscid emulsion was produced. Evidently then, 5 g. of acacia are more than sufficient to emulsify 10 cc. of oil, and 7.5 cc. of water added at

TABLE I—ACACIA EMULSIONS

Internal Phase	Mixture	Acacia Grams	Size of Globules Microns	Trituration Sec.	Emulsion	Critical Point
Cottonseed Oil	A 1	5.0	3–8	20	Thick creamy	
	2	3.0	5–10	35	Good	2.2
	3	2.5	10–30	150	Miscible	to
	4	2.4	15–40	180	but	2.3
	5	2.3	25–50	210	thin	grams
	6	2.2	...	300	None	acacia
Mineral Oil	B 1	5.0	4–8	30	Good	
	2	3.0	8–15	60	Good	2.4
	3	2.7	15–30	150	Good	to
	4	2.6	20–30	150	Good	2.5
	5	2.5	15–30	220	Good	grams
	6	2.4	...	300	None	acacia
Oil of Turpentine	C 1	0.5	...	...	Good	
	2	0.4	...	...	Good	
	3	0.3	...	...	Good	Apparently
	4	0.1	...	...	Good	None
	5	0.05	...	...	Partial	
	6	0.02	...	...	Partial	
	7	0.01	...	...	None	
Benzene	D 1	5.0	3–10	...		0.09
	2	3.0	10–20	...	Excellent	to
	3	1.0	15–20	...	and	0.10
	4	0.5	15–20	...	Stable	grams
	5	0.1	15–40	...		acacia
	6	0.09	...	...	None	
Carbon Tetra-chloride	E 1	0.50	10–25	...	Good	0.08
	2	0.10	15–30	...	Good	to
	3	0.09	20–50	...	Good	0.09 gram
	4	0.08	...	...	None	acacia
Chloroform	F 1	2.0	8–15	...	Good	0.55
	2	1.0	10–20	...	Good	to
	3	0.56	10–30	...	Good	0.56 gram
	4	0.55	...	...	None	acacia
Hexane	G 1	0.5	25–50	...	Translucent,	Between
	2	0.1	25–100	...	resembling	0.005
	3	0.05	30–100	...	starch paste	and
	4	0.03	50 & over	...	in color and	0.01
	5	0.01	50 & over	...	consistency	gram
	6	0.005 (approx.)		...	None	acacia

SPECIAL CASES

A (a) Emulsion 6 plus five drops of Emulsion 1 gave good emulsion.
  (b) Oil 10 cc. plus acacia 3.0 g. plus 15 cc. water gave no emulsion.
  (c) Oil 15 cc. plus acacia 3.0 g. plus 3.5 cc. water gave no emulsion.
  (d) Oil 10 cc. plus acacia 2 g. (below critical point) plus 7.5 cc. water gave no emulsion; plus 0.3 of 5 per cent NaOH solution gave a good emulsion.

D (a) 10 cc. benzene plus 3 cc. mucilage of acacia gave no emulsion.
  (b) 10 cc. benzene plus 3 cc. mucilage of acacia plus 3 cc. water gave no emulsion.

E (a) 10 cc. carbon tetrachloride plus 0.09 g. acacia plus 7.0 cc. water gave no emulsion.
  (b) 10 cc. carbon tetrachloride plus 0.09 g. acacia plus 15.0 cc. water gave emulsion, but not as good as that resulting from the addition of 7.5 cc. of water to Emulsion 3.

F (a) 10 cc. chloroform plus 0.56 g. acacia plus 7.0 cc. water gave no emulsion.
  (b) 10 cc. chloroform plus 0.56 g. acacia plus 10 cc. water gave emulsion not as stable as that resulting from Nucleus 3 subsequently diluted with 3 cc. additional water.

one time will bring about better and more rapid emulsification than 11.5 cc. of water added in small portions.

Mixtures Ea and Fb show that adding an excess of water (more than 7.5 cc.) *at once* to the internal phase and acacia gives an emulsion, but these emulsions are not exactly of the same color, consistency, stability or general excellence as those made by first diluting to the required volume a previously prepared nucleus—the usual pharmaceutical method.

Mixtures Da and b where the critical point is 0.09–0.10 g. acacia illustrate well the fact that the hydration process of the acacia must be accomplished at the moment of agitation. In these cases, there were taken 3 cc. of mucilage of acacia (representing 1 g. acacia or ten times the quantity actually needed) and this was shaken thoroughly with the benzene. There was absolutely no indication of emulsification. Likewise there was no effect when benzene was shaken with mucilage diluted with an equal quantity of water (Db).

Mixture A6 represents an incomplete emulsion of cottonseed oil. However, on adding 5 drops of a good

emulsion (1) and triturating, the emulsification of 6 was easily accomplished. This seems to show that a good emulsion is an emulsifier, a fact utilized by pharmacists in redeeming cracked emulsions by the addition of a small volume of a good emulsion.

Sodium hydroxide solution was added to the cottonseed oil which ordinarily contained some free fatty acid; in order to determine the effect of reduced surface tension caused by the soap formation: 0.3 cc. of 5 per cent sodium hydroxide solution was added to the incomplete emulsion A6, with the result that the emulsification was completed.

In order to illustrate the striking phenomenon of the existence of these critical points which appeared with the regularity and sharpness of titration endpoints, a set of chloroform emulsions was prepared and photographed (see Fig. I). Many important points are illustrated by this print. The upper layers are, of course, aqueous and the lower chloroformic. As the amount of emulsifying agent is steadily increased, the interfacial ring becomes broader and broader,
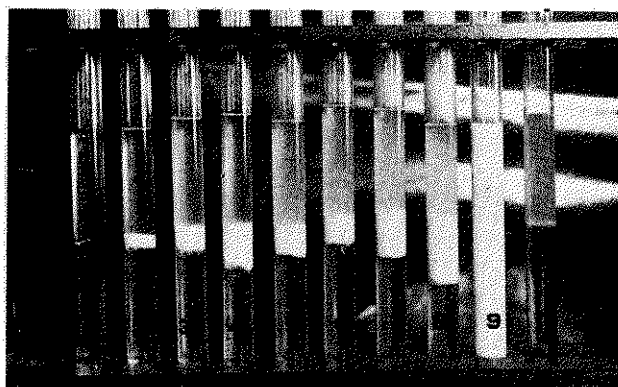

FIG. I—ACACIA-CHLOROFORM EMULSIONS

Chloroform, 10 cc.   Water, 7.5 cc.
No................ 1   2   3   4   5   6   7   8   9
Grams Acacia........ 0.00 0.49 0.50 0.51 0.52 0.53 0.54 0.55 0.56
  No. 10: 8 cc. Mucilage of Acacia and 10 cc. Chloroform (No Water)

while the upper aqueous layer becomes more and more opalescent until at 9 we have a uniform white emulsion. The clarity of the lower chloroformic layers in Nos. 1 to 8 can be readily seen and illustrates what is meant by the term "incomplete emulsion," as used in the introduction. At the point of emulsification, No. 9, no emulsified chloroform can be seen and although on standing for some time, this emulsion creams downward because of the higher specific gravity of the chloroform, there will be at all times only two layers, one of emulsified chloroform, the other consisting of the excess dispersion medium. Tube 10 contains chloroform and viscid mucilage of acacia (equivalent to about 3 g. acacia). These have been vigorously shaken but it is very evident that the interfacial ring is narrower than in 2, which contains only 0.49 g. of acacia, emphasizing again the importance of hydrating, at the moment of agitation, whatever acacia is present.

II—SOAP EMULSIONS

All the soap emulsions were prepared by shaking in 30 cc. test-tubes; 10 cc. of internal phase were taken in a tube and 1.0 cc. of soap solution run in from a

burette. A definite quantity of water was then added from another burette, the contents of the test-tube suddenly and briskly shaken, and the degree of emulsification noted. The quantity of water was varied over a considerable range to determine the possible presence of critical points, *i. e.*, the minimum quantity of water required to bring about the emulsification of the given volumes of the other ingredients. Such points were found in all cases as is indicated in the results, shown in Table II.

TABLE II—SOAP SOLUTIONS

INTERNAL PHASE	Mixture	Water Cc.	Size of Globules Microns	EMULSION	Critical Point
Cottonseed Oil	H 1	2.0	1 and less	Good	1.4 to
	2	1.5	1 and less	Good	1.5 cc.
	3	1.4	......	None	water
Oil of Turpentine	I 1	12.0	......	Good	9.9
	2	11.0	......	Good	to
	3	10.0	3–10	Good	10.0 cc.
	4	9.9	......	None	water
Mineral Oil	J 1	2.8	Av. 2	Good	2.6 to
	2	2.7	Av. 2	Good	2.7 cc.
	3	2.6	......	None	water
Benzene	K 1	4.5	1–2	Good	4.2
	2	4.4	1–2	Good	to
	3	4.3	1–2	Good	4.3 cc.
	4	4.2	......	None	water
Carbon Tetrachloride	L 1	7.2	1–2	Good	7.0 to
	2	7.1	1–2	Good	7.1 cc.
	3	7.0	......	None	water
Chloroform	M 1	6.0	2 (approx.)	Good	5.5
	2	5.7	2 (approx.)	Good	to
	3	5.6	2 (approx.)	Good	5.6 cc.
	4	5.5	......	None	water
Hexane	N 1	7.0	15 (approx.)	Good	6.8 to
	2	6.9	15 (approx.)	Good	6.9 cc.
	3	6.8	......	None	water
*Hexane-Carbon Tetrachloride	O 1	10.1	......	Good	9.9 to
	2	10.0	......	Good	10.0 cc.
	3	9.9	......	None	water
*Hexane-Mineral Oil	P 1	3.0	......	Good	2.5
	2	2.7	......	Good	to
	3	2.6	......	Good	2.6 cc.
	4	2.5	......	None	water

*Specific gravity 1.0 (*see Special Cases below*).

SPECIAL CASES

H (*a*) Oil 10 cc. plus soap solution 1 cc. plus water in portions of 0.2 cc. emulsifies when a total of 5.6 cc. of water has been added. Compare above.

(*b*) 1.0 cc. soap solution diluted with 1.5 cc. water (critical amount) plus 10 cc. oil gave partial emulsion.

(*c*) Oil 10 cc. soap solution 1.0 cc. plus 5.0 cc. water gave emulsion but not so stable as one made by making Nucleus 2 and diluting it with 3.5 cc. additional water.

J (*a*) Oil 10 cc. plus soap solution 1 cc. plus water in 0.2 cc. portions emulsifies when a total of 6.5 cc. have been added.

(*b*) Oil 10 cc. plus soap solution 1 cc. plus water 5 cc. gave emulsion not so stable as one made by diluting Nucleus 2 with 2.3 cc. additional water.

(*c*) 1 cc. soap solution plus 2.7 cc. water (critical amount) plus 10 cc. oil gave emulsion. This is an exception to the results obtained in all other cases.

K (*a*) Benzene 10 cc. plus soap solution 1 cc. plus water in 0.5 cc. portions emulsifies when the total of 10.5 cc. water have been added.

(*b*) 1 cc. soap solution diluted with 4.3 cc. water (critical amount) and 10 cc. benzene added gave no emulsion.

L   1 cc. soap solutions plus 7.1 cc. water to which 10 cc. carbon tetrachloride were added, gave no emulsion.

M   Observations of this emulsion with high magnification showed that the very small globules contained nuclei closely resembling those in protoplasmic cells. These nuclei were seen to vibrate with a motion, which especially for the smaller globules, resembled very closely the so-called Brownian Movement. The larger globules contained many of these highly refractive particles of varying sizes. The larger particles vibrated rather slowly, but the smaller ones darted about very vigorously, often colliding with one another. The phenomenon was only observed in the chloroform emulsion.

N   1.0 cc. soap solution diluted with 6.9 cc. water (critical amount) plus 10 cc. hexane gave no emulsion.

O & P   A mixture possessing a specific gravity of 1.00 and a relatively low viscosity was prepared from 59.7 cc. hexane and 30.9 cc. carbon tetrachloride. Another mixture also of a specific gravity of 1.00, but of a relatively high viscosity, was prepared from 59.7 cc mineral oil and 14.7 cc. carbon tetrachloride. These mixtures, of the same density as water, were then treated in the same way as the pure substances had been, to determine whether emulsibility was in any way dependent upon specific gravity. No relation was found.

In connection with some other work, it has been our experience that, in the preparation of large quantities of soap emulsions of certain volatile oils, in which definite volumes of soap solution and volatile oil were taken, that the addition of an excess of water to the soap and oil mixture produced much foaming and a comparatively thin emulsion resulted; that the addition of an insufficient amount of water produced an incomplete emulsion which streaked down the sides of the container; that between these limits of over-emulsification and incomplete emulsification there existed a point at which perfect emulsification occurred without foaming and streaking. This experience was found useful and was employed as a means of judging the excellence of the emulsions prepared from 10 cc. internal phase, 1 cc. soap solution and varying volumes of water. The foaming is plainly indicative of excess of water and the non-wetting of the sides of the container is a sign of incomplete emulsification due to insufficient water. The critical point between the incomplete and the perfect emulsion is strikingly sharp and may be determined within less than 0.1 cc. of water. At the critical point the emulsion seems to form almost spontaneously, and only one to two seconds shaking are necessary for complete emulsification. However, those systems which are within a few tenths of a cc. below the critical point in water content, will emulsify if allowed to "age" for about 10 minutes before being vigorously shaken. These critical points are applicable only to emulsions prepared with the quantities used in this research. For instance, if 20 cc. of benzene are to be emulsified with 2 cc. of soap solution, then 2 times 4.3 cc. water (critical volume for 10 cc. benzene and 1 cc. soap solution) will not be the correct value for emulsification. In general, as the total volume of the emulsion to be formed increases, we note a relative decrease in the critical volume of water.

If the water be added in small portions to the mixture of internal phase and soap solution, a larger volume is required to bring about emulsification. For instance, in Mixture H*a*, 5.6 cc. of water must be added in 0.2 cc. portions before emulsification occurs, while if 1.5 cc. of water (critical volume) are added *all at once* to the mixture of internal phase and soap solution, and the whole then shaken, a rich, creamy emulsion is produced. The same fact is shown in Mixture J*a*, where 6.5 cc. are used instead of 2.7 cc. (critical volume); in Mixture K*a*, where 10.5 cc. are used instead of 4.3 cc. (critical volume); in Mixtures H*c* and J*b*, we see that adding more than the critical volume of water *at one time* and then shaking yields a thin, foamy emulsion incomparable in general excellence to those emulsions prepared by first diluting a completed nucleus (made with the critical volume of water) to the required volume.

Mixtures H*b*, K*b* and L*a* show that no emulsification results if the requisite 1 cc. of soap solution be first diluted with the critical volume of water and this diluted (hydrated) solution of soap then shaken with the 10 cc. of internal phase. This is analogous to the use of mucilage of acacia in acacia emulsions. Hence

the hydration process of soap must be accomplished at the moment of agitation and in contact with the material to be emulsified. The mechanism of the formation of the emulsions may then be viewed as follows: the agitation disperses the internal phase and the resulting droplets are immediately coated with hydrated colloid formed at the same instant, this coating, according to Fischer's theory, being the *sine qua non* of emulsification. Mixture J*c* apparently is an exception to this rule.

An examination of Table II will also show that the globules in soap emulsion are considerably smaller than those of the corresponding acacia emulsions. The special note under Mixture M is of interest since it describes certain vibrations of particles in the films surrounding the globules or perhaps in the globules

FIG. II - SOAP EMULSIONS

Benzene, 10 cc. Soap Solution, 1 cc.	Cottonseed Oil, 10 cc. Soap Solution, 1 cc.	Mineral Oil, 10 cc. Soap Solution, 1 cc
No 1 2 3	5 6 7	9 10 11
Cc. Water.. 4.3 4.2 4.1	1.5 1.4 1.3	2.7 2.6 2.5

No. 4—Benzene and Water (No Soap)
No. 8—Cottonseed Oil and Water (No Soap)
No. 12—Mineral Oil and Water (No Soap)

themselves. These vibrations resembled the well-known Brownian Movement. It is strange that this should appear only in chloroform emulsions. However, an examination of all the other emulsions revealed nothing but clear, transparent coated droplets of internal phase, with no evidence of vibrating particles.

The sharpness of the critical point and the other characteristics of the complete and incomplete emulsions are illustrated in the accompanying photographs of soap emulsions of benzene, cottonseed oil and mineral oil (Fig. II).

CONCLUSIONS

In the main, our results have confirmed Fischer's theory, though in certain particulars we are not in entire agreement with his statements. We have found (1) that the presence of a hydration compound

is necessary for emulsification; (2) that this hydration compound is most efficiently used if formed at the moment of dispersion of the internal phase—in other words, the three constituents, internal phase, emulsifier and water, in critical proportions, must all be mixed at one time in order to form a properly hydrated nucleus; (3) slight variations from the proper procedure or from the critical proportions yield either less stable emulsions or none at all; (4) no emulsion results if the emulsifier is diluted (hydrated) before dispersion of the internal phase; (5) emulsions of better color, consistency and stability result from the dilution of a properly hydrated nucleus prepared from critical proportions, than are formed by agitation of the same quantities of internal phase, emulsifier and a volume of water equal to the total volume present in the above diluted emulsion.

We agree with Fischer in his statement that a hydrated colloid is an essential part of an emulsion, especially as applied to emulsion nuclei, but we do not agree with his contention: "An emulsion breaks whenever the hydrophilic (lyophilic) colloid which holds the aqueous dispersion means, is either diluted beyond the point at which it can take up all the offered water or is so influenced by external conditions that its original capacity for holding water is sufficiently reduced." If all the water be used to form the colloid hydration compound, we do not see how this nucleus may be so greatly diluted and still yield good emulsions.

SUMMARY

I—Definite critical points of emulsification have been shown to exist.

II—These critical points depend on (*a*) the quantities of internal phase and of emulsifier; (*b*) the nature of the internal phase and of emulsifier; (*c*) the procedure followed in the preparation of the emulsion.

III—Fischer's hydration theory of emulsification has been sustained, in part.

IV—Preparation of nuclei to be subsequently diluted lead to the best emulsification. This is in conformity with the usual pharmaceutical practice.

V—Nuclei of one composition act as stabilizers for incomplete emulsions of other compositions.

VI—Nuclei of one composition act as emulsifiers for other internal phases.

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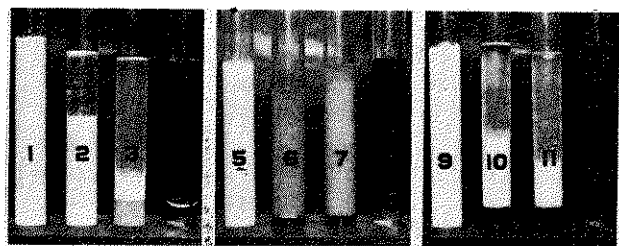NEW YORK UNIVERSITY, NEW YORK CITY

LABORATORY AND PLANT

RECENT DEVELOPMENTS IN CHEMICAL ENGINEERING EQUIPMENT[1]

By H. D. MILES

As it is impossible in the time at my disposal to describe adequately the development of chemical engineering equipment, I shall merely review briefly some of its more important phases as they have come under my observation in the manufacture of chemical equipment, by the company of which I am president.

This Company was organized sixteen years ago on what at that time was considered a radical departure, namely, the operation of a modern foundry on a scientific laboratory-controlled basis. At that period, the large majority of foundries were operated by rule of thumb methods, and no attention was paid to the chemical compositions of the metals used. Metal mixtures were made on a grade basis, known as Nos. 1, 2, 3, and 4, gray forge, scrap iron, etc., the grade being determined by the appearance of its texture rather than by its chemical composition. Very little attention