The major portion of the ammonia passes over in the first few minutes but the prolonged distillation is necessary in order to remove the last traces of ammonia from the condenser. Benedict¹ found that the last traces of ammonia could be rapidly removed from the condenser by steaming for a short time, thereby lessening the time necessary for a distillation. He recommends draining the condenser after 15 min. of boiling and continuing the boiling until the receiving solution is slightly warmed.

Benedict's recommendation has been followed for two reasons, both to remove quickly the last traces of ammonia from the apparatus, and to keep the volume of solution in the receiver as small as possible, *i. e.*, about 100 cc., in order to reduce the hydrolysis of the indicator salt. The length of time of a distillation recommended by Benedict was found to be insufficient to remove the last traces of ammonia from the boiling solution. We have, therefore, adopted a different procedure. The solution is distilled slowly for the first 20 min. with cooled condenser, during which time about 80 cc. of distillate are collected. The condenser is then drained and the distillation continued for 15 min. longer with somewhat more rapid ebullition. The receivers are then removed, covered to prevent the absorption of carbon dioxide, cooled and titrated.

¹ *J. Am. Chem. Soc.*, **22** (1900), 259.

During the slow distillation with the cooled condenser the ratio of ammonia to steam passing over is much greater than with rapid boiling, yet the rate of distillation of ammonia is about the same. The steam passing over after the condenser is drained condenses in the receiving solution until the acid solution becomes hot, after which it passes out of the solution thoroughly scrubbed of any ammonia which it carried. That the ammonia is completely recovered by this method of distillation is shown by the data in Table I. The figures were obtained by digesting pure solu-

TABLE I—THE RATE OF DISTILLATION OF AMMONIA
(Nitrogen Taken—5.045 Mg.)

CONDENSERS COOLED		CONDENSERS DRAINED		TOTAL 35 Min. Mg.
First 10 Min. Mg.	Next 10 Min. Mg.	Next 15 Min. Mg.		
3.872	0.990	0.177		5.039
4.513	0.546	0.033		5.092
4.618	0.456	0.106		5.030

tions of ammonium sulfate with 15 cc. of concentrated sulfuric acid, 0.5 g. copper sulfate, and 5 g. of potassium sulfate and distilling with 50 cc. of strong alkali (ammonia-free) into *N*/50 acid. The volume of solution in the receiving flask is kept small by this method of distillation and at the same time the solution in the distilling flask is not reduced in volume. The above procedure has been found entirely satisfactory for the amounts of nitrogen which are encountered in total nitrogen determinations.

ADDRESSES AND CONTRIBUTED ARTICLES

A REVIEW OF THE LITERATURE OF EMULSIONS¹

By Arthur W. Thomas

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Emulsions have been the subject of lively comment in chemical literature for the past twenty years. No general theory for emulsification has been elucidated, although many have been proposed from time to time, only to be shown subsequently to apply to special cases. There has accumulated, however, a mass of arbitrary data which can be profitably applied.

An emulsion is a heterogeneous system consisting of one liquid dispersed as tiny droplets in another liquid. It has been definitely established that three phases are essential for the formation of a stable emulsion: (1) Liquid A, (2) Liquid B, and (3) an emulsifying agent. The two liquids must be immiscible, or nearly so, in one another. The common types of emulsion are those wherein water constitutes one of the liquid phases, and we recognize two main types: (1) A liquid (oil, for instance) dispersed in water, and (2) water dispersed in oil. The factor which controls the type of emulsion, *i. e.*, whether water or oil is the external phase, is the nature of the emulsifying agent.

In general, if the emulsifying agent is more easily wetted by water than by oil, then water will be the external phase and oil the dispersed phase, while if the emulsifier is more easily wetted by oil than by water, the reverse will be true. Or, as Bancroft² puts it: If the surface tension between Liquid A and the emulsifying agent is lower than the surface tension between Liquid B and the emulsifying agent, Liquid A will be the dispersing and Liquid B the dispersed phase. Since the emulsifying agent is almost always recognized as a colloidal substance, it is fairly safe to say that a hydrophile colloid as emulsifying agent will

emulsify oil in water and a hydrophobe colloid will emulsify water in oil. This latter statement is subject to modification, however, which will be considered later.

There is a very simple and reliable method of determining the type of emulsion. Upon addition of an emulsion of oil-in-water (*i. e.*, oil dispersed phase and water external phase) to water, it will disperse. Similarly, a water-in-oil emulsion will mix with oil. In short, an emulsion will freely mix or dilute with more of its external phase, but not with more of its internal phase.

Robertson¹ suggested a method of staining with Soudan III (a fat-soluble dye). He stated that if Soudan III is sprinkled upon the surface of an oil-in-water emulsion the red color will be confined to the oil droplets and a mass of discontinuous red specks will result, whereas when sprinkled on the surface, a water-in-oil system will become uniformly red. This test has lately been severely criticized, and it has been shown that Robertson was led into misinterpretation of his olive oil-water-NaOH emulsions. He claimed to show critical concentrations leading to emulsions of water-in-oil. This has since been shown to be highly improbable.

OIL-IN-WATER EMULSIONS

There are three main classes of this type of emulsion:

(1) The emulsifying agent is an electrical charge on the oil particles, probably due to selective adsorption of the OH⁻ ion of water by the oil particles.

(2) The emulsifying agent is a water-soluble colloid.

(3) The emulsifying agent is an insoluble, or very slightly soluble colloid.

There are many cases also where a combination of two or even three of the above may function as emulsification agents.

(1) ELECTRICAL CHARGE AS EMULSIFYING AGENT—These emulsions are the simplest. They are identical with those observed

¹ Read at the December 5, 1919, Meeting of the New York Section of the American Chemical Society, Chemists' Club, New York, N. Y.

² *J. Phys. Chem.*, **17**, (1913), 501.

¹ *Kolloid-Z.*, **7** (1910), 7.

in the condensate from steam engines. They may be prepared in any of three ways.¹

(a) By shaking a small amount of mineral oil (2 cc.) with a larger volume of water (100 cc.) for 48 hrs.

(b) By boiling a drop of mineral oil with excess water under a reflux condenser for 30 hrs.

(c) When a small amount of mineral oil dissolved in alcohol is poured into water an emulsion results immediately.

Lewis found the size of the particles in these emulsions to be alike no matter how made, and of the order of 0.4 micron. They are negatively charged, the potential difference of the double layer (Helmholtz effect) being -0.05 volt. His measurement of the size of the charge on the droplets, by electrophoresis method, indicated 4.4×10^{-7} electrostatic units. These emulsions owe their stability to the electrical charge and Brownian movement.

The origin of this electrical charge is obscure. Ellis² ascribed it to difference in dielectric constants, according to the rule of Coehn that a substance of high dielectric constant is positive to one of a lower dielectric constant when one is dispersed in the other. This, to be sure, does not explain. He prepared mineral oil emulsions by the shaking method and obtained a concentration of one part oil in 10,000 parts of water, the size of the particles being 1 to 2 microns in diameter, and the specific conductivity of the emulsion was 18×10^{-8} mhos. He found the potential of the double layer to be -0.05 volt, as Lewis did; but his measurement of electrical charge showed 2.12×10^{-6} electrostatic units for the 1-micron particles. He also noted that they were most stable in the presence of $N/1000$ sodium hydroxide. He ascribed the stability of this type entirely to the electrical charge and stated that surface tension had nothing whatever to do with it.

Hatschek³ suggested that the stability of such mineral oil emulsions might be due to the fact that the specific gravities of the phases were close to each other, but Groschuff⁴ contested this view.

Powis⁵ prepared this type of emulsion by the shaking method and determined the double layer potential to be -0.046 volt, which checks fairly well with Lewis and Ellis. He studied the effect of addition of electrolytes to the emulsion and noted that anions have the power to increase this negative potential, while cations decrease it. Very small amounts of KCl and $K_4Fe(CN)_6$ (up to 0.001 molar) increased it, while larger amounts decreased it. Salts with polyvalent cations always decreased it, due to the predominating positive charge of the cations over the anions. He noted later⁶ that while an immediate sharp change in the contact potential occurred upon addition of salt, there always ensued a secondary slower change; in the case of a salt like $BaCl_2$ the change is continuous in the same sense, whereas in cases like $AlCl_3$, it reverts back a little, due to loss of Al^{+++} on account of hydrolysis. Powis' studies on coagulation of these emulsions by means of electrolytes will be discussed later.

(2) WATER-SOLUBLE COLLOID AS EMULSIFYING AGENT—Good emulsifiers of this class are sodium and potassium soaps, egg albumin, gelatin, glue and other water-soluble proteins, gum arabic (acacia), gum tragacanth, Irish moss, milk, starch saponin and quillaia bark extract.

Previous to 1899, NaOH was classified as an excellent emulsifying agent for fatty oils in water, but Donnan's⁷ investigation showed that its emulsifying powers were really due to the soap formed by interaction with the small amount of free fatty acid that is always present in fatty oils. He proved this by means of the drop number method, and stated that those fatty acid

salts which greatly lower the surface tension are good emulsifiers, and that since they lower the surface tension they must concentrate in the surface layers about the droplets of oil, and since the soap layer is still more concentrated at the points of contact, where bubbles might happen to come together, capillary forces tend to separate them.

In a later work, Donnan and Potts¹ measured the drop numbers of aqueous solutions of the sodium salts of the fatty acids. They noted that all lowered surface tension, the lowering increasing with the higher molecular weights, but that it is strongly evident first with sodium caprylate. Emulsifying powers are not evident with this salt, but commence with sodium laurate. The emulsifying power increases with increase in concentration to $N/300$ soap solution, above which it decreases, due to the coagulating effect of Na^+ ions.

They objected to Pickering's theory (see later) and stated that stability of emulsions is due partly to the electrical charge and partly to presence of surface tension lowering substances which, according to the theories of Willard Gibbs, must concentrate in the surface layer.

A classic study of emulsions was published by Pickering² in 1907. He pursued his investigations in order to make a suitable germicidal spray for agricultural purposes. In all his experiments he emulsified a paraffin oil in water, by pumping it back and forth through a rose-nozzle garden syringe. He found potash soaps to be better than sodium soaps as emulsifiers and noted that a certain critical concentration of soap was required for each proportion of oil and water, *e. g.*, to emulsify 75 volumes of oil with 25 volumes of water, the latter must contain 0.7 to 1.8 per cent potash soap. For 40 volumes oil to 60 of water, 0.3 to 25 per cent soap can be used.

He noted that soaps vary greatly in emulsifying power, some brands being useless and, in fact, two batches of the same brand may vary greatly in emulsifying power. He noted also that while rise in temperature facilitated emulsification, it had no influence on the composition.

Pickering's 70 to 80 per cent oil emulsions were viscid like thick cream, even when benzine was used. Size of particles was about 0.1 micron. He succeeded in emulsifying 99 cc. of paraffin oil in 1 cc. of 1 per cent potash soap solution by successive additions of small portions. This famous emulsion was pure white and as stiff as a blanc-mange. It could be diluted with water but not with oil, hence was of the oil-dispersed-in-water type.

He noted that his strong emulsions were poor conductors of heat. It is possible to boil a beaker of such an emulsion at 160° to 170° C. for several minutes, while the center remains at less than 100° C. When kept in closed vessels they were permanent for months, but cracked soon after exposure to dry air. Strange to say, his emulsions generally separated, no matter what the starting composition, to form a permanent 65 to 82 volume per cent emulsion of oil in water.

Five emulsions of "Solar distillate" (a paraffin oil distilling between 240° and 350° C.) were prepared by Pickering, as follows:

SAMPLE	Oil Vol.-Per cent	Soap Solution Per cent
1	67	1
2	50	1
3	33	1
4	50	5
5	50	0.2

After standing 12 wks. they had all separated into emulsions containing from 72 to 82 per cent oil (as emulsion) in the upper layer and water below. Analysis showed a steadily decreasing oil content in the emulsions from the top downwards. In each case one-quarter of the column of emulsion from the top deviated but slightly from 84.5 per cent oil. The effect of de-

¹ Lewis, *Kolloid-Z.*, 4 (1909), 211.

² *Z. physik. Chem.*, 78 (1912), 321.

³ *Kolloid-Z.*, 9 (1911), 159.

⁴ *Ibid.*, 9 (1911), 257.

⁵ *Z. physik. Chem.*, 89 (1914), 91.

⁶ *Ibid.*, 89 (1914), 179.

⁷ *Ibid.*, 31 (1899), 42.

¹ *Kolloid-Z.*, 7 (1910), 208.

² *J. Chem. Soc.*, 91 (1907), 2001.

creasing the soap percentage is to increase the size of the globules finally to a point where permanence is no longer possible. Pickering reported some novel effects with solid emulsifying agents which will be discussed under that heading later. Of the water-soluble emulsifiers he stated that soap is the best and that dissolved starch, milk and flour are good, although the last named gives a flocculent rather than a creamy emulsion and milk forms solid clots. Glue is good. Egg albumin is good but gives rather frothy effects owing to inclosing air bubbles. Saponin and quillaia bark are good if proportion of oil is small.

In 1912 Newman¹ reported results of attempts to emulsify water and benzene, using oleates. He found that when benzene and water are emulsified by sodium oleate, water is always the external phase and that it is possible to make homogeneous emulsions up to 0.5 per cent benzene, and from 80 to 90 per cent benzene. Failure to make the intermediate emulsions, he ascribed to his method of shaking. He made a stiff jelly with 99 cc. benzene and 1 cc. water, using 0.05 g. sodium oleate. This emulsion was stable for more than 6 wks. With his shaking machine it was possible to get concentrated emulsions only by gradual addition of the liquid which is to be the internal phase.

Briggs² measured the amount of sodium oleate adsorbed by benzene emulsions in water and found that the amount of soap adsorbed increases with the degree of dispersion of the benzene particles. He constructed an ingenious laboratory type of homogenizer for the preparation of his emulsions.

In a subsequent paper³ Briggs and Schmidt found that the drop number test cannot be used to judge the power of an emulsification agent for benzene in water. While 1 per cent solutions of both gum arabic and gelatin gave lower drop numbers than water when benzene was run into these solutions from a drop pipette, still the gum and gelatin will emulsify benzene in water, due, no doubt, to the elastic semi-solid films which they form around the benzene droplets. They are not as good as soaps, however. The optimum amount of soap to form a good emulsion was found to be 0.01 per cent of the total volume.

Fischer's⁴ theory of emulsions is that a hydration compound is essential, *i. e.*, the oil globules must be covered with films of a hydrated colloid. He evidently is not familiar with the lubricating oil emulsions of Lewis, Ellis, Powis and Hatschek, nor with the solid emulsifying agents of Pickering.

Roon and Oesper⁵ and later Crockett and Oesper⁶ studied emulsions used in pharmaceutical practice. By the trituration-in-a-mortar method they learned that it is best to add the proper amount of water to the internal phase and the emulsifier and then triturate, and that it is best to form an emulsification nucleus in this manner, which can be modified afterwards. The proportions giving the best results are 4 parts of oil, 2 of gum arabic, and 3 of water. This nucleus is miscible in all proportions with water. Nuclei of one composition act as stabilizers for incomplete emulsions of other compositions and nuclei of one composition act as emulsifiers for other internal phases. They found Irish moss and gum tragacanth to be good emulsifiers, with the exception that tragacanth cannot be used with turpentine and forms unmanageable masses with fatty oils. They say "traces" of soap crack Irish moss emulsions, while they aid gum arabic emulsions. They are inclined to accept Fischer's hydration theory.

Davey,⁷ in searching for a substitute for organic solvents in Japan varnish, found that he could emulsify linseed oil with water by addition of ammonium hydroxide and slowly stirring

in a closed heated receptacle. He made the interesting discovery that such emulsions scum when exposed to air containing carbon dioxide at 17° C. or higher, but not when exposed at 16° C. or lower, or to air free from carbon dioxide at any temperature. The particles of dispersed phase were negatively charged. This emulsion proved to be a good paint.

(3) INSOLUBLE OR ONLY SLIGHTLY SOLUBLE COLLOID AS EMULSIFYING AGENT—Tfol¹ reported that Arabs in Northern Africa used an argillaceous earth as a substitute for soap in washing linen. He found that this earth readily emulsified oils in water.

Pickering² was probably the first to study the efficacy of certain solids as emulsification agents. He found that basic copper sulfate (made by adding 1 part of CaO to 7 parts CuSO₄·5H₂O) in solution in water is an excellent emulsifier. At least one part of CuSO₄·5H₂O converted to the basic salt is needed to emulsify 120 parts of paraffin oil. Immediate and stable emulsification results by one stroke of the syringe and the product is very efficient as a germicidal spray in agriculture. These emulsions resembled his potash soap emulsions in all properties, except that the stable layer contained about 40 per cent oil. The ratio of CuO to emulsified oil was fairly constant, about 0.92 part of CuO to 100 parts of oil. His experiments with other solid substances yielded results as classified below.

Substances which emulsify—Basic ferrous sulfate, basic copper sulfate and basic nickel sulfate are the best. Ferrous and ferric hydroxides are good. Basic zinc and basic aluminum sulfates give good emulsions temporarily. The precipitate formed by adding sodium carbonate to copper sulfate is good. Calcium carbonate and arsenate are good when freshly precipitated but they soon become crystalline and de-emulsification follows. Lead arsenate and some unheated fine clays are good. Iron sulfide is good for small amounts of oil and zinc oxychloride is fair.

Substances which produce quasi-emulsions—Lime, silica, alumina and plaster of Paris, dried, and the following when freshly precipitated, act: Basic cadmium sulfate, magnesium hydroxide, copper hydroxide, basic zinc and aluminum sulfates, tin oxychloride, lead arsenate paste, copper sulfide, iron sulfide.

Little or no emulsifying power—Precipitated lead chloride, lead sulfate, barium sulfate, silica hydrosol, sulfur, flowers of sulfur, Paris green, alcoholic solution of rosin precipitated by water, ferrous ferricyanide, ferric ferrocyanide and purple of Cassius. In these cases the oil seems to wet the precipitates more than water does.

Later Pickering³ stated that while high viscosity and low surface tension of a liquid facilitates the emulsification of an oil in it, yet it is possible to make an emulsion in a liquid which does not possess these properties. The most important condition is the presence of small particles insoluble in the dispersion medium which coat over the oil particles and prevent them from coalescing. In order that such particles have the power to form emulsions they must show only a slight tendency to unite with one another, must be readily wetted by water and must not be crystalline. He also made the novel discovery that potassium cupric tartrate will emulsify a mixture of alcohol and water. If this salt be added to an aqueous solution of alcohol, it will cause the water and alcohol to separate into two layers. Agitation results in emulsification.

Hofmann⁴ used silver dichromate to emulsify chloroform in water.

In 1915, Briggs and Schmidt⁵ found that colloidal ferric hydroxide (formed by hydrolysis of ferric acetate solution), was a fairly good emulsifier for benzene in water.

WATER-IN-OIL, EMULSIONS

Calcium and aluminum soaps are used in lubricating greases. Holde⁶ published a discussion of these greases in 1908. They

¹ *J. Phys. Chem.*, **18** (1912), 34.

² *Ibid.*, **19** (1915), 210.

³ *Ibid.*, **19** (1915), 479.

⁴ *Science*, **43** (1916), 468.

⁵ *THIS JOURNAL*, **9** (1917), 156.

⁶ *Ibid.*, **9** (1917), 966.

⁷ *Physical Review*, **11** (1918), 138.

¹ *Pharm. J.*, [4] **6** (1898), 1228.

² *Loc. cit.*

³ *Kolloid-Z.*, **7** (1910), 11.

⁴ *Z. Biol.*, **63** (1914), 395.

⁵ *Loc. cit.*

⁶ *Kolloid-Z.*, **3** (1908), 270.

are solutions of lime soaps (15 to 23 per cent) in heavy mineral oil with 1 to 4 per cent water emulsified in them. Some American lubricating greases, especially for automobiles, consist of aluminum soaps dissolved in mineral oils with water emulsified in them by the aid of rosin.

Bancroft¹ states that lanolin is an emulsion of water (22 to 25 per cent) in wool wax and that it is possible to emulsify as much as 80 per cent water in wool wax. The writer believes that this may be due to the cholesterol which wool wax contains. These emulsions are stable for years.

Newman² found that while sodium oleate emulsifies benzene in water, magnesium oleate emulsifies water in benzene. He stated that it is never possible to emulsify water in an oil by means of sodium soaps, contrary to Robertson's findings. By using proper procedure he succeeded in emulsifying 96 per cent water in benzene. The stability is increased by the addition of a little sodium oleate. He stated that in mixed paints water is dispersed in the oil and that this is due to the presence of rosin as an emulsifying agent, and not to the pigments. In conclusion he presented his theory that whether one liquid is emulsified in another or not depends upon the emulsifying agent. A hydrophilic colloid will tend to make water the external phase, while a hydrophobic colloid will tend to make water the internal phase and the colloid must be able to make a suitable coherent film around the globules to be an emulsifying agent.

Briggs and Schmidt³ found that for the emulsification of water in benzene, magnesium oleate is fair (forms quasi-emulsions finer than aluminum palmitate). Magnesium resinate, copper resinate and lead oleate are unsatisfactory. Aluminum palmitate forms quasi-emulsions.

Clowes⁴ has performed some striking experiments with soap emulsions of olive oil and water. By addition of calcium chloride to an emulsion of oil in water (with sodium oleate as emulsifying agent), when the calcium concentration exceeds the chemical equivalence to sodium, the emulsion passes through a critical point and changes to water dispersed in oil. He found that sodium, potassium and lithium soaps emulsify oil in water while magnesium, strontium, barium, iron and aluminum soaps emulsify water in oil. The first series of soaps are soluble in water and not in oil, while the second series are soluble in oil but not in water. The alkali soaps are wetted more by water than by oil and since it is thought that the surface tension is lower on the water side than on the oil side of the globules, the film will bend convex to the water and concave to the oil, enveloping the oil articles, because the area of the inner surface of a sphere is less than that of the outer surface. Similar reasoning holds for the dispersion of water in oil by the other soaps mentioned.

Clowes illustrates this phenomenon by the accompanying diagram.

In 1918 Schlaepfer⁵ reported his experiments with carefully purified carbon black (gas black, soot) as emulsifying agent. This substance must be wetted more by oils than by water, because in all cases he obtained dispersions of water in the oil and never oil in water. As dispersion media he used kerosene, turpentine, benzene and toluene. With 60 cc. kerosene, 240 cc. water and 1.5 g. soot, he obtained an almost solid emulsion.

Moore⁶ checked Schlaepfer's results. He was able to emulsify water and ammonium chloride solutions in kerosene with lamp black. Highly calcined lamp black and petroleum coke would not function as emulsifying agents. As the concentration of the ammonium chloride solutions was increased, the drops grew larger, due to high surface tensions of the solutions. He found that water wets raw lamp black more readily than ex-

tracted lamp black, while normal ammonium chloride solutions wet raw lamp black more readily than purified lamp black.

BREAKING OF EMULSIONS

In general, de-emulsification can be accomplished by:

- 1—Addition of excess of dispersed phase.
- 2—Addition of a liquid in which the two liquid phases are soluble.
- 3—Destruction of the emulsifying agent.
- 4—Filtration.
- 5—Heating.
- 6—Freezing.
- 7—Electrolyzing.

The problem of breaking mineral oil emulsions in steam engine condensates has interested engineers for a long time.

Hatschek¹ offered a solution of the difficulty in a filtration method. He found that such emulsions when filtered through *amorphous* $MgCO_3$ or $CaCO_3$ (causticizing mud) came through free from oil. On a 4.5-sq. ft. filtering surface covered 0.125 in. thick with *amorphous* $CaCO_3$ he was able to filter 30 cu. ft. per hr. under 10 lbs. per sq. in. pressure. The adhering oil broke loose from the filtering surface and floated to surface. The permeability of the filter was but slightly diminished after 6 hours' filtration. He advises using the $CaCO_3$ in a filter press at not higher than 50 lbs. pressure because higher pressures squeeze the emulsified oil drops between the interstices in the filter bed.

EMULSIFYING AGENT OR FILM	EMULSION FORMED
(1) Sodium oleate alone or sodium oleate in excess of calcium oleate equivalent	Oil in water
(2) Chemically equivalent proportions of sodium oleate and calcium oleate	Critical point
(3) Calcium oleate alone or calcium oleate in excess of sodium oleate equivalent	Water in oil

This method worked also for emulsions of kerosene, petroleum oils, fatty oils, etc., where soap or saponin had been used as emulsifiers.

He also mentions that addition of alum and alkali, and also passing oily water between iron electrodes works well. Ferric hydroxide is formed at the anodes and combines with the oil particles and coagulates them. These methods do not appear to be practicable for commercial use.

For laboratory purposes, Hatschek recommends the ultra-filter, using Bechhold's 5 per cent collodion papers, as highly satisfactory.

In 1911 Hatschek² tried hydrochloric acid and sodium sulfate as coagulators. At, or near, the isoelectric point the particles did coalesce to form larger ones (about 3 microns diameter), but oil particles of even this size rise very slowly, about 2 cm. in 48 hrs.

Ellis³ showed that these emulsions are most stable in presence of $N/1000$ NaOH; and least stable in presence of $AlCl_3$ (0.00022 g. molar); $CuCl_2$ (0.004 g. molar); $NaCl$ (0.16 g. molar).

Powis⁴ showed that greatest instability of these emulsions

¹ *J. Phys. Chem.*, **17** (1913), 501.

² *Loc. cit.*

³ *J. Phys. Chem.*, **20** (1916), 407.

⁴ *J. Chem. Soc.*, **113** (1918), 522.

⁵ *J. Am. Chem. Soc.*, **41** (1919), 940.

¹ *J. Soc. Chem. Ind.*, **29** (1910), 125.

² *Kolloid-Z.*, **9** (1911), 159.

³ *Z. physik. Chem.*, **80** (1912), 597.

⁴ *Ibid.*, **89** (1914), 186.

was attained when the contact potential reached ± 0.03 volt. This potential was found in the presence of

KCl, 51 millimolar	AlCl ₃ , 0.02 millimolar
BaCl ₂ , 1.9 millimolar	ThCl ₄ , 0.007 millimolar

A slight increase over these concentrations charges the particles with positive electricity and they become stable again.

In 1914 Ellis¹ showed that colloidal ferric hydroxide from 0.0017 to 0.0039 per cent final concentration coagulates this type of emulsion. Higher concentration results in reversal in charge of the dispersed phase and stability ensues.

Philip² advised that the emulsification tendencies of a lubricant be tested before using. He found that very slight contamination of a good nonemulsifying mineral oil by Mexican, Trinidad or Persian crude oils greatly increased the tendency to emulsify. He described a test for the purpose.

Harris³ proposes to break emulsions of water and petroleum oil by passing a heavy electrical current. The electrodes must be close together.

Dijxhoorn⁴ removes emulsified lubricating oil from condenser water by passing 110-volt current through the water as it passes through the feed water pipe.

Rogers⁵ breaks emulsions of mineral oil and water by adding sodium salt of a sulfonated mineral oil (0.25 to 4 lbs. per barrel of mixture) and heating.

McKibben⁶ passes emulsion of petroleum and water (heated sufficiently to produce vaporization) through an intensified electrical field. The vapors are condensed and cooled and the water drops out.

¹ *Z. physik. Chem.*, **89** (1914), 145.

² *J. Soc. Chem. Ind.*, **34** (1915), 697

³ U. S. Patent 1,281,952 (1919).

⁴ *Le Papier*, **22** (1919), 53.

⁵ U. S. Patent 1,299,385 (1919).

⁶ U. S. Patents 1,299,589 and 1,299,590 (1919).

McNear and Bowles¹ have patented an apparatus for electrical treatment of emulsions.

Attempts have been made to precipitate emulsified water in linseed oil, etc., by high tension electrical discharge, but so far as can be learned the method has not been perfected. The sparks tend to jump over the surface rather than through the mixture.

Pilat and Piotrowski² favor heat treatment under pressure for breaking of crude petroleum emulsions consisting of oil, salt water and earthy matter. In closed kettles holding 40,000 kg., the crudes were heated by steam to 120° to 130° C. at 3 to 3.5 atmospheres pressure. A practically quantitative separation took place in 5 hrs. at 3 atmospheres pressure. The separation was accomplished more quickly at higher pressures.

Koetschau³ claims that by heating Roumanian and Galician petroleum to 120° to 130° C., the emulsions broke within a few hours. He recommends heating acidified distillates with steam at 3 to 4 atmospheres pressure.

Newman⁴ found that emulsions of oil-in-water with soap as emulsifying agent are irreversibly broken by freezing.

One could continue indefinitely discussing special means of breaking emulsions, but from a knowledge of the nature of a given emulsion and application of the principles laid down at the head of this chapter, one ought to be able to deal with each special case.

Since foams are closely related to emulsions it is of interest to note here that Fiske⁵ has found isoamyl valerate to be an excellent inhibitor of foaming. He describes methods of preparations of this ester.

¹ U. S. Patent 1,297,378 (1919).

² *Petroleum*, **13** (1918), 1045.

³ *Z. angew. Chem.*, **32** (1919), 45.

⁴ *J. physik. Chem.*, **18** (1914), 34

⁵ *J. Biol. Chem.*, **35** (1918), 411.

FOREIGN INDUSTRIAL NEWS

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FUEL DEPOSITS IN ESTLAND

According to an article in *Engineering*, Estland seems to be better off than most of her neighbors as regards fuel. Large deposits of shale extend from the coast to Wegenberg over an area 80 versts long by 10 versts wide, containing an amount estimated at 1,500,000 tons. The shale contains so large a percentage of oil that it burns if a light is applied. It is being used for the production of gas and electricity in Reval and also for factories and private houses. Preparations are also being made for its application in the driving of locomotives. In the powdered state it is used for firing boilers and is said to give satisfaction. While its calorific value is from 50 to 60 per cent that of coal, its cost is only one-fourth that of coal. The deposits are being worked by the Estnian state and are also attracting attention in England.

SULFURIC ACID MANUFACTURE

A short account of the effective "Grillo" plant erected in England by the government for the manufacture of sulfuric acid by the contact process is given in the *Journal of the Society of Chemical Industry* for October 15. The catalyst employed is platinum, deposited on granules of calcined magnesium sulfate in the proportion of 0.3 per cent. The purified gases from the sulfur burners heated to about 350° C. are passed through two converters in parallel, each containing 10,000 lbs. of the platinized

mass distributed on four trays. For absorbing the trioxide produced, towers packed with quartz are used and practically perfect absorption can be obtained. The purification of the gases, which is important in preventing deterioration of the catalyst, is effected by passing the cooled vapors through coke columns and sulfuric acid drying towers; arsenic is thus eliminated and less than 0.02 per cent of other impurities (water and inert dust) retained. Details of efficiency and production-costs are given.

GROWTH OF FRENCH CHEMICAL INDUSTRY

According to *Schweiz. Chem. Zeit.*, September 10, 1919, the French chemical industry has developed greatly during the war. The annual output of sulfuric acid was doubled, increasing from 1,000,000 to 2,000,000 tons. The output of nitric acid per month is three times greater than the total annual output of pre-war days. The yearly output of cyanamide has increased from 8,000 tons in 1913 to 100,000 tons at the present time. Prospects are favorable for the absorption of the surplus war products for agricultural purposes, and viniculture should benefit in particular. Copper sulfate is indispensable in the vine industry and of the yearly output of 50,000 tons, 40,000 tons are absorbed by viniculture. The necessary copper, which is mined in Spain, is, however, controlled by English interests.