constants, the formate is saponified 350 times as rapidly as the acetate. It is probable that the methyl formate formed was nearly all saponified before the flasks could be put on the steam bath.

It appears that normal butyl alcohol, which can now be obtained in great purity at a moderate price, offers many advantages as a medium in which to carry on saponification. We have found this alcohol particularly suited for the quantitative saponification of fats, waxes, etc., results on which will be published shortly.

CONCLUSIONS

1—The alcoholysis of esters is to be taken into account in quantitative saponification.

2—Low results are to be expected when acetates are saponified in ethyl alcohol solution unless good condensers are used.

3—Normal butyl alcohol appears to be the best medium in which to carry on saponifications.

OIL-FIELD EMULSIONS

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PROPERTIES AND TREATMENT OF OIL-FIELD EMULSIONS FROM THE GOOSE CREEK (TEXAS) FIELD

The infiltration of water into the oil sands in drilling operations has been the source of much trouble and expense to the oil producer and refiner and there have been various methods advocated for shutting off water from wells.² Not only does the inflow of water decrease the productivity of the oil-bearing sands, but there is increased cost of production due to the expense of pumping water and replacing corroded tubing, casing pumps, and other fixtures.

From still another standpoint, also, the water has a detrimental effect in oil production. This arises from the fact that the water, mixing with the oil under the conditions of production, forms emulsions with the oil. The stability of the emulsions so formed varies considerably, not only for different fields and different wells in the same field but even for the same well during different periods of productivity. From certain emulsions the water separates upon standing; others are decidedly permanent in nature and show no tendency to separate, and it is these more stable ones which give the most trouble to the producer and refiner.

The amount of water varies from traces up to 60 per cent or more, but the majority of emulsions contain about 25 per cent. It has been assumed by many workers in the oil fields that all these will separate either oil or water, leaving an emulsion that is an exactly equal mixture of oil and water and to this they have given the name of "B. S." The term originated in the fact that when oil containing water, even a trace,

is stored in large tanks, such as are in use at the pipe line pumping stations, there gradually accumulates a sediment known as "bottom settlings." These bottom settlings usually contain about 50 per cent water and considerable asphalt. It is very doubtful, however, whether all the emulsions will have this ratio as their settling end-point. By adding water to some of the more stable oil-field emulsions and agitating the mixture, it has been found possible to prepare emulsions containing as high as 90 per cent water which were quite stable and showed no appreciable separation after months of standing.

In order to be salable, or classed as "pipe line" oil and accepted by the transporting companies, a crude oil must contain no more than 2 per cent water. This is a purely arbitrary limit that has been fixed by the operating companies in accordance with their experience in refining. This necessitates, however, some treatment of the emulsions in the field.

PROCESSES FOR SEPARATION OF WATER

(1) FILTRATION PROCESS—The process of filtration has very little bearing on the treatment of oil-field emulsions, since it would not be possible to handle large quantities of oil economically, even if it were otherwise feasible. These filtering devices have been applied mainly to the separation of lubricating oils from water. The filtering medium is wetted initially with the external or dispersing phase and hence is not wetted during the filtration by the internal or dispersed phase. The tendency, however, is to cause a clogging of the filter. The filtering process has been improved somewhat by combining it with a certain electrical treatment.¹

(2) EVAPORATION PROCESS—This method consists in heating the emulsion in open tanks or pits by means of coils containing superheated steam. It is uneconomical from the standpoint of fuel consumption and oil-evaporation loss, but oil production has been notorious for its wasteful methods and, until recent years, possibly even to this day, most of the dehydration of emulsions has been accomplished in this way. The fuel consumption is roughly 25 barrels of fuel oil per 1000 barrels of oil recovered. The oil-evaporation loss is about 5 per cent, depending upon the nature of the oil treated as regards the percentage of low boiling constituents. The heating of emulsions preparatory to other treatment is advantageous, but this heating is usually limited to a temperature of from 150° to 180° F. and is carried out in closed systems.

(3a) ELECTRICAL PROCESS. ALTERNATING CURRENT—The pioneer patent in the electrical treatment of oil-field emulsions was taken out by F. G. Cottrell.² This process depends for the demulsification upon the action of high potential alternating current electricity. The water is dispersed as finely divided globules throughout the oil and these are caused to coalesce by the action of the electrostatic forces. Quoting from the patent:

These globules are thereby subject to electrostatic forces dependent upon the relative potentials and dielectric constants

¹ Read at a meeting of the Southeast Texas Section of the American Chemical Society, at Houston, Texas, May 31, 1919.

² F. B. Tough, "Methods of Shutting Off Water in Oil and Gas Wells," Bureau of Mines Bulletin 163.

¹ Cottrell, U. S. Patent 987,114 (1911).

² Cottrell and Speed, U. S. Patent 987,115 (March 21, 1911).

of the materials in contact, and caused to coalesce into masses which may be readily removed from the body of the oil by well-known processes, such as settling.

The Petroleum Rectifying Company, of California, operating under this and other patents, has installed a number of plants in California, Oklahoma and Kansas.

(3*b*) ELECTRICAL PROCESS. DIRECT CURRENT—This process consists in passing the emulsion between electrodes connected to a source of direct current electricity with a potential of from 250 to 400 volts, with a current varying from a few milli-amperes to 10 amperes. The patent¹ under which the direct-current electrical treatment is operated claims that the process depends upon cataphoresis or electrical migration. The original experiments which served as a starting point for the development of this patented process were performed by the author with the help of Mr. G. W. Jones in May 1917, and the idea was based upon the known migration of colloidal particles when subjected to electrical stress.² We will see later, in the consideration of our experimental data, that this migration of particles must be a factor. Some electrolysis doubtless takes place since the electrodes are only about $\frac{1}{8}$ in. apart and at times a considerable current passes.

(4) CENTRIFUGAL PROCESS—The application of the centrifuge to the separation of water from these emulsions is rather limited. It is mainly useful in separating the last traces of water which have been discharged by other means. Thus it is used in the final step of the electrical treatment.

(5) CHEMICAL PROCESSES—The possibilities along the line of chemical treatment will be apparent from a consideration of our results and from the discussion of the action of certain treating compounds already on the market.

(6) GENERAL PROCESSES—Very often a number of the different methods are applied so that one supplements the others. The treatment of oil-field emulsions practiced by the Gulf Production Company in the Goose Creek (Texas) field consists of a combination of closed heating, settling, direct current electrical treatment and final separation of the remaining portions of the water by means of the centrifuge. Settling may be resorted to between the various stages of the treatment and the oil may be subjected to more than one electrical treatment, if necessary. In this combined process there is very little loss of the lighter fractions through evaporation and the fuel consumption is only about 10 barrels of fuel oil per 1000 barrels of oil recovered.

THEORETICAL CONSIDERATION OF THE MECHANISM OF COLLOIDAL SOLUTION AND EMULSIONS

The stability of colloidal solutions has been explained as due to the formation of surface films on the dispersed particles, preventing them from coalescing. These films may be either electrical or nonelectrical, or both, and when they are destroyed, agglomeration and precipitation of the particles occur. That elec-

trical films may function in preventing coalescence, due to the repulsion of like charges, has been recognized for a long time. The fact that there was a movement of colloidal particles when subjected to electrical stress was recognized by Linder and Picton,¹ and this migration could only be indicative of the existence of charge of definite polarity on the particles themselves. In line with the general theory of the protecting action of surface films, it is assumed that these electrical films are formed by the preferential adsorption of an ion of an electrolyte. The fact that charged colloidal particles are discharged by solutions of electrolytes, due to the adsorption of an ion carrying a charge opposite to that already on the particles, is in accord with this surface condensation of ions. It was shown by Picton and Linder² that the precipitated material was contaminated by the electrolyte, and particularly by that ion of the electrolyte which, due to its charge being opposite to that of the colloidal particle, functioned as the effective precipitating agent. Hardy's³ assumption that the ion of the electrolyte, having the same charge as that of the particles, had no effect in the precipitation is probably unreliable and it has also been shown that the point of coagulation does not always correspond to the point of electrical neutrality. It is clearly recognized, however, that ion adsorption plays a rôle.

It is usually assumed that emulsions are a special type of colloidal solution and that they differ from ordinary liquid-solid colloidal systems to a greater extent than could be explained, by the fact that the disperse phase is a liquid instead of a solid.

That ions may function as emulsifying agents, analogous to their action of forming protective films on colloidal particles, seems entirely possible and the work of certain investigators seems to indicate that they do so. Thus, the investigations of Wilson⁴ and of von Lerch⁵ on the curvature of the interfaces between nonmiscible liquids, point, according to Bancroft,⁶ to ion adsorption. Ellis⁷ has even prepared emulsions which owe their stability to ion adsorption. In working with phenol-water mixtures it was noticed that the "cloud" formed upon the separation of the second liquid layer from a saturated solution of phenol in water persisted for hours. It is not unlikely that any slight stability which this phenol water emulsion has is due to hydrogen ion adsorption. Work is in progress on the three-component system, phenol-water-acetic acid, and the preliminary results indicate that the clouds formed in this system are more permanent than in the two-component system, phenol-water.

With a liquid as the disperse phase, however, it is not surprising that in general it should require a rather tough coherent film such as could be obtained only from solid particles. The ordinary emulsifying agents are themselves colloids and the conditions for regu-

¹ *J. Chem. Soc.*, 67 (1895), 63.

² *Loc. cit.*

³ *Z. phys. Chem.*, 33 (1900), 385.

⁴ *J. Chem. Soc.*, 1 (1848), 174.

⁵ *Drude's Ann.*, 9 (1902), 434.

⁶ *J. Phys. Chem.*, 19 (1915), 276, 280.

⁷ *Z. phys. Chem.*, 80 (1912), 597.

¹ Seibert and Brady, U. S. Patent 1,290,369 (January 7, 1919).

² *J. Chem. Soc.*, 67 (1895), 63.

lating which liquid shall function as the disperse phase have been very well defined. Thus, according to Bancroft,¹ "A hydrophile colloid will tend to make water the dispersing phase, while a hydrophobe colloid will tend to make water the disperse phase." Even in such cases, where the films protecting the disperse phase are colloids, we have charges upon the particles in so far as the colloids themselves carried charges.

EXPERIMENTAL

The emulsions studied were obtained in the Goose Creek (Texas) field and, although they may or may not be representative of oil-field emulsions in general, the results are interesting, nevertheless, from the standpoint of the general theory of emulsification. As they are representative of the more stable of the Goose Creek emulsions, the results are applicable to the general treatment of the product of this region.

These emulsions are systems of water dispersed in oil as an external phase. This is clearly shown by the ordinary tests applied in the identification of phases in such systems.² One of the most satisfactory tests in such cases is the treatment of the emulsion with some component of one of the two phases. If the emulsion spreads in or mixes with the added component or phase, that phase is evidently the external or dispersing phase. It was found that these emulsions mixed readily with dry crude oil in all proportions but did not mix with water or salt solutions. The emulsified water contains salt (sodium chloride, etc.), sometimes up to 10 per cent, and if such aqueous solution was the external phase the emulsions would conduct the current readily. As a matter of fact, with electrodes 2 in. apart and with a potential difference of 250 volts impressed, it is not possible to notice any deflection of the needle of a sensitive milliammeter placed in the circuit. Clearly, then, the oil is the external phase.

The particles of water forming the disperse or internal phase are very finely divided and are apparent as a "fuzziness" in thin layers of the oil. Practical oil-field men identify the presence of water in an oil by placing a few drops on a piece of glass and holding vertically so as to allow drainage and form a thin film of oil on the surface of the glass. A dry oil will appear as a clear, amber colored film, while an oil containing water will appear "fuzzy."

THE CHARGE ON THE PARTICLES—The attempt was made to get some information as to whether or not the particles were charged and, if so, the nature of that charge. A drop of the emulsion was placed on the slide of a microscope and two small platinum wires, connected into a 70-volt direct current circuit, were brought into contact with the drop of oil. It was impossible to get any results in this way, due to the capillary effects, since the oil flowed from the center and collected about both wires. Some of the emulsion was then placed in a cell, Fig. 1, and a potential of

70 volts was impressed after connecting the electrodes to a direct-current circuit. It was thought that it might be possible to get an indication of migration and hence of the charges on the particles by measuring the percentage of water in the two sides of the cell after the experiment had run for some time. The cell was left connected for 22 hrs. and at the end of that time considerable change in outward appearances had taken place in the two sides. The color of the original emulsion was a yellow-brown. After the 22-hr. run the oil in the positive side of the cell was much darker than the original emulsion and the oil in the negative side much lighter. The presence of more water particles would cause a lighter appearance, and the less the number of particles the nearer would the color approach the dark green-black of dry oil. This would seem to indicate that water particles had migrated from the positive to the negative side, and that there was a positive charge on the particles. In neither side was there any discharged free water in the bottom of the cell. When determinations of the water content on the two sides of the cell were made, no difference was found, all the oil in each side of the cell being tested.

FIG. 1—MIGRATION OF PARTICLES

This result was rather surprising in view of the quite evident color changes that had taken place. After running a number of these tests, however, it was noticed that upon withdrawing the electrodes from the oil a mass of water particles adhered to the positive electrode, and upon examination it was found that the water particles in the negative side had been driven to the outside against the side of the vessel. This clearly pointed to a negative charge on the particles. In that case they would be attracted to the positive electrode and collect around it, causing a darkening in the outside layer of the oil as they migrated to the center. On the negative side they would be repelled by the electrode and forced to the outside layers near the glass, causing a lighter color. It was therefore decided that the particles were negatively charged.

PRECIPITATION BY ELECTROLYTES—If the particles were negatively charged, this charge might be neutralized by some readily adsorbed cation, and pre-

¹ *J. Phys. Chem.*, 19 (1915), 275. Note—The term hydrophobe colloid is applied to a substance forming a colloidal solution in some nonaqueous solvent and not doing so in water; the term hydrophile colloid to a substance forming a colloidal solution in water but not in the nonaqueous liquids considered.

² *J. Phys. Chem.*, 18 (1914), 34.

precipitation brought about. Hydrogen ion is more strongly adsorbed than most ions, as a rule, and it was therefore decided to try the effect of various concentrations of different acids. The experiments were carried out as follows: 200 cc. of the emulsion containing 25 per cent water were placed in a 500 cc. ground-glass-stoppered graduate and 50 cc. of the acid added. The mixture was then shaken on an electrically driven shaking machine for 20 min. in order to insure intimate contact. It was then allowed to stand for 22 hrs., after which the percentage water in the oil layer was determined.

When more water was added and the mixture agitated, it was possible to incorporate this added water with the emulsion, the color becoming lighter with increasing proportions of water. In the case of the addition of hydrochloric acid solution, a change was quickly apparent as the emulsion became darker colored almost immediately. The notes in connection with Table I, where the results with hydrochloric acid are tabulated, refer to this color change.

Number	Emulsion, Cc.	ACID MIXTURE		Oil Layer, Per cent	Hydrogen Ion Concentration Normality	Color when Taken from Shaker	Remarks
		Conc. HCl, Cc.	Water Cc.				
1...	200	2.0	48.0	36.0	4.89×10^{-1}	Yellow	Total emulsification
2...	200	5.0	45.0	15.0	6.02	Dark brown	Honey comb structure
3...	200	7.5	42.5	7.0	8.87	Brown-black	Separation of good
4...	200	10.0	40.0	1.0	10.00	Green-black	Oil started at once

Temperature 25° C.

In order to show that the hydrogen ion was functioning as the precipitating agent, a series of experiments was performed, using sulfuric and acetic acids. The results of these experiments are given in Tables II and III.

Number	Emulsion Cc.	ACID MIXTURE		Water in Oil Layer Per cent	Hydrogen Ion Concentration Normality	Color when Taken from Shaker
		Conc. H ₂ SO ₄ , Cc.	Water Cc.			
1.....	200	5	45	19.0	1.88×10^{-1}	Dark brown
2.....	200	10	40	12.0	3.04	Dark brown
3.....	200	20	30	2.5	3.86	Black-green
4.....	200	30	20	1.75	10.00	Black-green

Temperature 25° C.

Number	Emulsion Cc.	ACID MIXTURE		Water in Oil Layer Per cent	Hydrogen Ion Concentration Normality	Color when Taken from Shaker
		Glacial Acetic Cc.	Water Cc.			
1.....	200	2	48	40.0	0.45×10^{-1}	Yellow-brown
2.....	200	5	45	38.0		Dark yellow-brown
3.....	200	10	40	30.0	0.86	Brown-black
4.....	200	20	30	30.0	2.51	Dark brown-black
5.....	200	35	15	5.0	8.53	Green-black

Temperature 25° C.

The hydrogen ion concentrations, expressed in Tables I to III, were determined by means of the hydrogen electrode. In our experiments we had added 50 cc. of an acid mixture to 200 cc. of the emulsion and, as the emulsion was 25 per cent water, we always had 100 cc. of acid solution in the system. For the hydrogen ion concentration measurements the quantities of acid used in the various experiments to make up the 50 cc. of added mixture were diluted

to 100 cc. The e. m. f. of the cell (normal calomel electrode-hydrogen electrode in the given acid solution) was balanced against a known e. m. f. and the hydrogen ion concentration computed according to the following equation:¹

$$E = 0.058 \log 1/c + 0.28$$

When the H ion concentrations are plotted against the water percentage in the separated oil layer the curves as given in Fig. 2 are obtained.

FIG. 2—PRECIPITATION OF WATER PARTICLES BY HYDROGEN ION

Since it is not safe to follow Hardy² and assume that the ion carrying a charge opposite to that of the colloidal particles is the only effective ion, we would expect the hydrogen ion concentration necessary for complete discharge to vary somewhat; and particularly, on account of the preferential adsorption of ions, we would not expect the curves to coincide. Since, however, the hydrogen ion concentration necessary for the complete discharge of the water from the oil ranges around the value 10.0×10^{-1} normal, we can safely ascribe the precipitation to the effect of hydrogen ion, and our previous conclusions regarding the existence of a negative charge on the particles are substantiated.

Since the hydrogen ion neutralized the charge on the particles and precipitated the emulsion, it ought to be possible to discharge them in a similar manner by means of other strongly adsorbed cations. In line with the generally strong adsorption of ferric ion by various substances, and from the general consideration of the stronger precipitating power of polyvalent ions over that of ions of less valency, it was of interest to

¹ Hildebrand, J. Am. Chem. Soc., 35 (1913), 847.

² Z. phys. Chem., 33 (1900), 385.

see what effect ferric ion would have. 200 cc. of the emulsion were treated with ferric chloride solution, as in the previous experiments with acids. Table IV gives the results of these tests.

TABLE IV

Number	ADDED MIXTURE		Sp. Gr. of Added Mixture	Water in Oil Layer Per cent
	FeCl ₃ Solution Cc.	Water Cc.		
1.....	2.0	48.0		22.0
2.....	5.0	45.0		8.0
3.....	7.5	42.5		2.0
4.....	10.0	40.0	1.0610	1.5
5.....	20.0	30.0	1.1213	1.5
6.....	35.0	15.0	1.2050	0.5
7.....	50.0	0.0	1.2878	0.5

Temperature 25° C.

¹ Ferric chloride solution used in making up added mixture contained 66.24 g. of FeCl₃ per 100 cc.

REMARKS

Sample 4, after 22 hrs., contained 150 cc. of a black jelly with a layer of good oil above it. This jelly flowed easily and upon being disturbed broke up, depositing most of its water phase.

Sample 5, after 22 hrs., contained 125 cc. of black jelly very similar in action to that of Sample 4.

Samples 6 and 7, after 22 hrs., contained 180 cc. of stiff black jelly which was very stable. Good oil on top.

As in the case of hydrogen ion, we found that ferric ion discharged the emulsions. In lower concentrations the action was perfectly regular, but in the higher concentrations as in Expts. 4 to 7, we did not get a separation of the water phase itself, but obtained jellies of varying stability. The jellies obtained in Expts. 6 and 7 were very stable indeed; the cylinders containing them could be turned over and the supernatant oil drained off without disturbing or displacing them. Upon removing some of these jellies with a spatula they were found to be of the consistency of a very stiff apple butter, and transference or manipulation did not destroy them. Jelly 6 contained 60 per cent by volume of ferric chloride solution, and Jelly 7 contained 56 per cent. Jellies 4 and 5 were very unstable.

Although hydrogen ion resulting from the hydrolysis of the ferric chloride might have had some effect, particularly in Expts. 1 to 5, nevertheless the results of Expts. 6 and 7 clearly show the influence of the ferric ion. It might seem, since the jellies contained from 56 to 60 per cent of the water phase, that they resulted from a partial precipitation or insufficient positive ion adsorption. If this were the case, hydrogen ion should cause the discharge of these jellies into their separate phases. Samples of the two stiff jellies were treated with varying concentrations of hydrogen ion but in no case were the jellies destroyed. Evidently the particles of which the jellies were composed were no longer negatively charged or they would have been discharged by the hydrogen ion of the acid.

It is a well-known fact that certain colloids are positively or negatively charged, depending upon the character of the dispersing phase. Thus albumin is positively charged in acid solution¹ and negatively charged in alkaline solution.² Since the jellies we obtained were evidently not negatively charged it seems possible that the adsorption of ferric ions had carried the particles past the neutral or isoelectric point and that

¹ Hofmeister's *Beitr. chem. Physiol.*, 5 (1904), 27.

² Pfäuger's *Archiv.*, 24 (1887), 247; cf. Bancroft, *J. Phys. Chem.*, 19 (1915), 350.

they were now positively charged. Since a stiff jelly of this character does not lend itself to measurement of migration in an electric field, the only other way seemed to lie in testing the effect of strongly adsorbed anions upon the jelly.

Just as hydrogen ion is one of the most strongly adsorbed cations, so hydroxyl ion is one of the most strongly adsorbed anions. It was not possible, however, to use hydroxyl ion to identify the charge on the jelly because of the ferric ion present. In a study of the order of adsorption of anions by precipitated barium sulfate the following order was found:¹

Ferrocyanide>nitrate>nitrite>chlorate>permanganate>ferricyanide>chloride>bromide>cyanide>sulfocyanate>iodide.

Since nitrate ion is strongly adsorbed and there is no interfering action between it and the ions already present, it was selected as being suitable for our purpose. Sodium ion is known to be very little adsorbed, hence we used sodium nitrate in these experiments. When the gel obtained from the original treatment of the emulsion with ferric chloride was treated with a saturated solution (25° C.) of sodium nitrate, it was destroyed and the oil freed. It seemed, then, that the jelly was composed of positively charged particles.

In line with the action of these gels, ferric nitrate should precipitate the original emulsion without the formation of jellies, since the adsorption of nitrate ion would counteract to some extent at least the adsorption of ferric ion. Experiments were carried out to determine the effect of the simultaneous adsorption of ferric and nitrate ions on the emulsion. Table V shows the results of these determinations.

TABLE V

Number	ADDED MIXTURE			SEPARATED		Water in Oil Layer Per cent	Color after Standing 22 hrs.
	Emulsion Solution Cc.	Fe(NO ₃) ₃ Solution Cc.	Water Cc.	Solution Cc.	Sponge Cc.		
1...	200	5	45	5	None	32.0	Light brown
2...	200	10	40	15	70	16.0	Brown
3...	200	15	35	25	80	5.0	Dark brown
4...	200	25	25	65	35	1.0	Dark brown
5...	200	50	0	65	35	0.5	Green-black

The temperature of liquids during these experiments was 25° C. The sponge obtained in these experiments was very mobile and broke up upon the slightest agitation. Ferric nitrate solution used in making up the added mixtures contained 67.32 g. Fe(NO₃)₃ per 100 cc.

These results with ferric nitrate clearly show that both ions have an effect in the precipitation and bear out our previous conclusions as to the strong adsorption of nitrate ion.

In order to see to what extent the increase in the density of the water phase influenced these precipitation results, a number of experiments were run, using saturated solutions (25° C.) of sodium sulfate, sodium chloride, sodium carbonate and sodium bicarbonate, but in no case did we obtain a discharge of the water particles.

EFFECT OF ORGANIC SOLVENTS—There are a number of methods in use for determining the percentage of water in an emulsion. Most books on petroleum analysis recommend the distillation method. This

¹ Weiser and Sherrick, *J. Phys. Chem.*, 23 (1919), 205.

consists in adding toluene to a sample of the emulsion and distilling. The added toluene keeps down the troublesome frothing that usually occurs when undiluted emulsions are distilled. The water, toluene, and certain light portions of the oil come over, and as they separate into layers without emulsifying the percentage of water can be computed. The method most in vogue in the oil fields, on account of its simplicity, is to add a high-grade gasoline to a sample and centrifuge it. The volume percentage of water can then be read off directly on the graduated centrifuge glass. Usually the results obtained by these two methods will check, but occasionally the emulsions will not respond to this gasoline treatment. It has been found that ether is even better than gasoline for this centrifuge method. The explanation usually offered for this method is that the addition augments the difference in density of the two phases, causing a greater tendency to settle. This may be true to some extent but it cannot be the only effect, as will be shown.

The existence of negative charges on the water particles has been shown, but it is doubtful whether the ions alone function as the emulsifying agent. It seems probable that the ions which are responsible for the charge are condensed on solid particles which in turn form the protecting films. In many of these emulsions there is considerable earthy material and it may be possible that this material serves as the emulsifying agent, being itself peptized by ion adsorption.

On the other hand, the asphalt in these oils may be responsible for the formation of the films. Some slight amount of asphalt is present in colloidal solution in these crude petroleums, as a hydrophobe colloid, and would cause the formation of an emulsion with water as the disperse phase. It was found to be possible to prepare an emulsion of salt solution in pure white paraffin oil by using 0.5 per cent of asphalt. The emulsion so formed was not as stable as the natural oil-field emulsions and no definite charge on the particles could be identified; nevertheless it was much more stable than the suspension made by shaking the pure oil with the salt solution.

It is entirely possible that this system is even more complicated than the previous assumptions would indicate. Thus we might have the earthy material adsorbing asphalt or other heavy hydrocarbons from the crude oil, and these in turn forming protective films about the water particles, with the consequent adsorption of ions to impart a charge to the particles.

Richardson¹ found that the earthy matter in Trinidad asphalt had a high adsorption capacity for the bitumen of the asphalt.

Now in so far as the asphalt, either alone or condensed upon earthy matter, acted as the emulsifying agent, it would seem that the action of the ether in facilitating a separation of the two liquid phases might be due to the solvent action of the ether on the asphalt rather than to any augmentation of the difference in density of the two phases. If this were so, a liquid, miscible with the oil phase and having a high

solvent action on the asphalt, should discharge the emulsion even if it had the same density as the emulsion itself. In order to test this point the specific gravity of the emulsion was determined and a mixture of ether and carbon disulfide having this same specific gravity was made. When this solvent mixture was added to a sample of the emulsion it discharged the water even more readily than ether alone. It would seem then that the action of these organic solvents was due to solvent effects rather than to differences in density.

COMMERCIAL COMPOUNDS AND CHEMICALS FOR TREATING OIL-FIELD EMULSIONS

There are on the market certain compounds for the treatment of oil-field emulsions. These compounds are usually crude soaps or sodium salts of sulfonic acids, obtained by sulfonating either a coal-tar oil or a petroleum.¹ All of such compounds examined were hydrophile colloids, which seems to be the explanation for their action in discharging these oil-field emulsions.

Just as there is selective adsorption of ions, so there is selective adsorption of colloids, and certain hydrophile colloids might have a much greater tendency than others to destroy an emulsion formed by means of a given hydrophobe colloid. Just as precipitation of colloidal particles is due to the adsorption of an ion with a charge opposite to that upon the particles, so colloids of opposite charges precipitate one another. But in the destruction of an emulsion formed by a hydrophobe colloid it is not necessary that the hydrophile colloid be of an opposite charge. Thus we have negatively charged soap particles precipitating the negatively charged water particles of these emulsions.

These properties and actions of oil-field emulsions would indicate in a general way the methods for their efficient treatment. It must be borne in mind, however, that the emulsions from different fields may differ markedly in properties and therefore might require entirely different treatment. In so far as they do differ, each field would have to be investigated in order to indicate the best method of treatment. In any case, it may be advantageous to combine a number of processes to supplement one another.

The author hopes to be able to procure samples so that representative emulsions from the other oil fields of the country may be examined.

SUMMARY

The results of this investigation are summarized as follows:

- 1—The emulsions occurring in the Goose Creek (Texas) oil fields have been studied.
- 2—These emulsions consist of salt solution as disperse phase and oil containing asphalt as the dispersing phase.
- 3—The water particles migrate to the anode under electrical stress and are therefore negatively charged.
- 4—Strongly adsorbed cations neutralize the negative charge on the particles and precipitate the water.

¹ *J. Phys. Chem.*, 19 (1915), 245-6.

¹ Francis and Rogers, U. S. Patent 1,299,385 (1919).

5—Ferric ion is adsorbed to such an extent that it will carry the particles over from a negative charge through the isoelectric point to a condition of positive charge in a manner analogous to the reversal of charge on albumin particles.

6—From the experiments with ferric chloride and ferric nitrate it is apparent that both ions of an added electrolyte are effective in precipitation of the charged particles.

7—The decrease in stability of these emulsions upon the addition of ether is probably due to the solvent action of the ether on the asphalt rather than to any increase in the difference in density of the two liquid phases. An ether-carbon disulfide mixture of the same gravity as the emulsion will discharge the water.

8—The action of certain commercial treating compounds is probably due to the fact that they are hydrophile colloids. A hydrophile colloid should discharge an emulsion formed by the use of a hydrophobe colloid, while a hydrophobe colloid should discharge an emulsion formed by the use of a hydrophile colloid.

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TESTING THE MILDEW RESISTANCE OF TEXTILES¹

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A study of the fundamental factors determining the effectiveness and durability of processes of waterproofing and mildewproofing textile fabrics, such as cotton duck and cotton canvas, was undertaken with the primary object of finding simple formulas and methods for treating cloth which are applicable for small-scale use on the farm and also suitable for use by commercial treating plants. Prerequisites for successful work on the main problem are, of course, suitable methods for determining water and mildew resistance. The method here described, which is not regarded as final but subject to improvement with experience and greater knowledge of the problems involved, has been used for the past two years and has proved to be useful in judging the probable serviceability of mildew-resistant treatments. The methods used for testing the water resistance of fabrics are described in a separate paper.²

Mildewing is due to the development of various mold growths on and in the fabrics. The number of species responsible for the deterioration is large, but chief among them are species of *Alternaria*, of *Cladosporium*, and some *Mucors*. The simultaneous occurrence of different kinds of molds seems to play an important part, and the production of pink and yellowish discolorations is probably due, at least in some cases, to the growth of both a *Mucor* and a mold pro-

ducing a substance having a pink appearance in alkaline or neutral reaction and a yellow one in an acid reaction.

Gueguen¹ is of the opinion that the spores causing the mildewing of fabrics are usually introduced into the fibers by the dead parts of the parent cotton plant, where they have been either in a dormant or germinating state, and concludes that mildew is hardly ever due to contamination of the fabric after weaving.

The presence in the air of spores of cellulose-destroying fungi has been demonstrated by McBeth and Scales,² who have isolated from plates exposed to air contamination over a dozen cellulose-destroying organisms, among which *Cladosporium herbarum* has been identified. Davis, Dreyfus and Holland³ have shown that astonishingly large numbers of mold spores rain into the mill vats containing sizing materials used on the component threads, thereby becoming introduced into the woven fabric.

We have repeatedly mildewed pieces of treated and untreated fabrics by inoculating their surfaces with pure cultures of *Cladosporium*, *Alternaria*, and other molds, and have found that, under laboratory conditions, converted canvas may be completely destroyed by several species of *Aspergillus*.

Sterilized duck inoculated with spores and mycelial fragments of species of *Alternaria* and of *Cladosporium* and incubated for two weeks, developed mold growth which, at the end of another two weeks, entered deeply into the fabric. Furthermore, heavy fabrics, subjected to certain finishing processes having a sterilizing effect on the preëxisting mold spores and mycelial fragments, readily mildew under favorable field conditions. It is clear, therefore, that even canvas apparently free from original mold impregnation will mildew if exposed to air contamination and to conditions encouraging mold growth.

METHODS USED TO DETERMINE MILDEW RESISTANCE

Tests for mildew resistance of fabrics have been in use heretofore. One, occasionally followed, is, briefly, to bury a sample of the cloth under ground at a depth of 12 to 15 in. for a period extending over one month. The ground is kept moist by occasional watering. The condition of the fabric at the end of the test period is considered to indicate the degree of mildew resistance.

This method may give valuable information regarding the resistance of fabrics to bacterial action, but its value for determining mildew resistance is questionable. Waksman⁴ found that soil samples taken from a depth of 12 to 30 in. on plating out developed only *Zygorhynchus*, and that *Aspergillus*, *Alternaria*, *Cladosporium*, *Penicillium*, and other organisms commonly present in the soil had not appeared in the plates in 24 hrs.; while in the upper soil strata there may be 1,000,000 fungi per gram of soil. This, really, is a small number of organisms,

¹ *Compt. rend.*, **159** (1914), 781.

² U. S. Dept. of Agr., Bureau of Plant Industry, *Bulletin* **266**, pp. 24-25.

³ "Sizing and Mildew in Cotton Cloth," 1880, Palmer and Howe, Manchester.

⁴ *Science*, N. S., **44** (1916), 320-23.

¹ Read at the 57th Meeting of the American Chemical Society, Buffalo, N. Y., April 7 to 11, 1919.

² *This Journal*, **12** (1920), 26.