THE APPLICATION OF COLLOIDAL PHENOMENA IN THE SEARCH FOR BETTER METHODS OF BREAKING CRUDE OIL EMULSIONS

By

Charles R. Houssiere, Jr.

B.S., Spring Hill College
1934
B.S., Oklahoma University
1938

Submitted in Partial Fulfillment of the
Requirements for the degree of

MASTER OF SCIENCE

from the

Massachusetts Institute of Technology

1939

Signature of Author .
Department of Chemical Engineering

Signature of Professor
in Charge of Research . . . . . .

Signature of Chairman of Department
Committee on Graduate Students .

TABLE OF CONTENTS

INDEX

APPENDIX

ACKNOWLEDGMENT

ACKNOWLEDGMENT

The author wishes to express his appreciation to The Humble Oil and Refining Company, The Stanolind Oil and Gas Company, The General Crude Petroleum Company of California, and Charles R. Houssiere, Sr. for aid in procuring emulsions which were representative of those found over the country and which, as a general rule, give the most trouble.

An expression of thanks is due Professor E. C. Hottel for his aid in procuring samples for this work.

The author also wishes to thank Mr. J. E. Lynn for his helpful suggestions and cordial aid.

Last, however not least, the author wishes to express his utmost thanks and deepest appreciation to Dr. E. A. Hauser, in charge of the Colloid Chemical Laboratories of the Department of Chemical Engineering of the Massachusetts Institute of Technology, for his unfailing interest and stimulus and guidance throughout this work.

PART I

SUMMARY OF INVESTIGATIONS

SUMMARY

The object of this thesis was to uncover new possibilities of attack by applying new colloidal concepts to the problem of breaking crude oil emulsions rather than to attempt to solve the difficulty completely. Basically it was an attempt to solve the problem of separating the water and oil into two bulk phases.

It was found that the use of ultrasonics rendered effective results where heating had failed. This method proved especially useful in attacking higher viscosity oils. It was fairly effective using non-treated emulsions but very effective in attacking a treated emulsion. Besides effecting a more complete dehydration of the oil, the time consumed by this process was considerably less.

The use of wetting agents, namely, Ultravet, Aerosol OT, Nekal A, and Nekal BX, was effective as treating agents in the lighter viscosity oils. In the heavier viscosity oils these agents were not quite as effective due to the viscosity of the emulsion. Aerosol OT seemed to give the best results.

It was found by rough experiment that there is an optimum rate of shaking to give best results.

In the belief that excess water might help at least the heavier viscosities to give up their water, work was done on this possible solution. A ratio of 2-1 was found

effective in the heavier oils but it was found that the use of excess water was undesirable in the case of the lighter viscosity oils. This limit was in the neighborhood of 100 centipoises at room temperature.

The use of "weighting" salts to increase the relative difference in specific gravity between the oil and the water was tried with NaCl. Good results were achieved from oils of 100 centipoises on up to the heavier viscosities.

The problems relative to any emulsion are individual as far as that emulsion is concerned, and its behavior under different types of agents cannot be predicted offhand. However, it is believed that a further study along lines typical to these might be the solution to some of the more difficult problems. Further work may uncover correlative details but the following fact must be borne in mind. When dealing with the heavier viscosity oils, even though the viscosity is not the cause of the emulsion, it is a contributing factor to its stability. Therefore, some properties of the oil must be accepted as unavoidable. The previous statement should give a hint to immediate treatment if it is planned to allow a reservoir of oil to stand. This would prevent the separation of the oils into layers in which the heavier viscosity would be separated from the light viscosity instead of working at a happy medium between the two.

PART II

THESIS

INTRODUCTION

It seems appropriate to review first the literature on the subject and then to discuss briefly the theories advanced thus far. Therefore a brief discussion follows and emphasis is placed on those theories which seem to show the most logic and promise.

The Viscosity Theory supports the idea that the viscosity of the disperse and aqueous phase relative to one another at the interface plays an important part in the "stability" of the emulsion. High viscosity tends to resist thinning of the liquid films to the rupture point, while the surface tension must be low in order to decrease the pull between the molecules, which tends to promote the thinning. In working on experiments to prove that viscosity does not promote thinning, Hillyer concludes that "emulsification is due largely to the small interfacial tension between the oil and the emulsifying agent, which allows the emulsifying agent to spread out into thin films separating the oil droplets. The surface tension is not strong enough to withdraw the agent from between the droplets except slowly. If the emulsifying agent has great internal viscosity, or if great superficial viscosity is shown between liquids, the thinning of the films is so slow that the emulsion is permanent." He explains that the viscosity is the determining factor in many cases.

Pickering and Marshall conclude that the viscosity factor is over-emphasized. In some cases it was shown that increasing the viscosity of the soap solutions destroyed the emulsions.

The majority of investigators have accepted the conclusion that viscosity aids emulsification solely by virtue of the hindrance offered to coalescence of the dispersed globules and that it is not the cause of emulsification.

The Hydration Theory was proposed by Fisher, who postulated that emulsions can only be formed when the liquid which is to become the continuous phase is all used up in the formation of a hydrated compound of the emulsifying agent employed. According to this theory one must consider the oil in the aqueous soap solution as a colloidal hydrate. The theory postulates a minimum and maximum amount of H_2O present sufficient to form the hydrated colloid, otherwise no emulsion will be formed. If this were absolutely true then one could form water-in-oil types by using oil soluble colloids. No evidence exists to prove that this is true. This theory completely ignores Pickering's concentrated emulsions. It postulates an even distribution of colloid throughout the aqueous phase. The theory appears to be a little one-sided as far as the treatment of emulsions as a whole is concerned.

In the Surface Tension Theory Quincke showed that interfacial tensions between oils and solutions of NaOH are lower than between oils and pure H_2O in oil-in-H_2O emulsions. For solutions of Na-salts which are not capable of forming colloidal solutions emulsion formation is impossible. For each salt there appeared to be a maximum concentration where the emulsifying power was at a maximum. There appears to be a salting-out effect due possibly to excess Na+ -ions which coagulate negatively charged drops. Up to Na- Laureate, ineffective emulsifying properties are exhibited because the coagulating action of the Na^+-ions exceeds the effect of the emulsifying tendencies due to interfacial tension lowering. Quincke showed a maximum surface "activity" with Na-myristate.

Donnan and Potts concluded that "changes in interfacial tension at the boundary of the oil-H_2O are connected with changes in the electric potential, in which the selective adsorption of ions probably plays a part." He also concluded that "the existence of a gelatinous film, which was consequent upon lowering of the interfacial tension at the oil-H_2O boundary."

The <u>Wedge Theory</u>, which has to do with the relative differences in diameter of the molecule on its opposing ends, postulates that the end with the small diameter was adsorbed on the disperse globule and that the larger end exercises the repulsing effect on the other globules, similarly arranged, and consequently emulsions must be formed. However, this theory has been disproved in many cases by experiments designed to attempt to prove its validity. At present it has been generally discarded.

The Adsorbed Film Theory is the one which has proved most favorable by investigation, and it has been proved repeatedly by photographs. Therefore the following discussion will deal with it more in detail than has been considered necessary in the previously mentioned theories.

In studying the coagulation of these emulsions it has been found that large quantities of electrolyte at high concentration were required to destabilize the system. Upon studying the zeta potential it was found that the electrolyte used was greatly in excess of that needed to discharge the globule. As a result, the theory of the adsorbed film was advanced which stated that the globules preferentially adsorb on their outer faces certain soluble constituents, soluble in the dispersion medium. This film was strong enough to resist the shear resulting from Brownian motion if the globules were small enough, or thermal motion if the globules were large. Consequently, even though the globules were completely discharged still there would be no coaslescence of the minute droplets. The theory further states that "Emulsions are formed by adsorption of the emulsifying agent in the interface with subsequent orientation of the agent into a tough elastic film." In the study of soaps it was found that stability of emulsions is due to adsorption of highly colloidal soap micelles. The more soap adsorbed, the more stable the emulsion. The agent is adsorbed at the interface and forms an oriented film. Both the oil and the water wet the film and set up differences in surface tension on both sides of the film. The side with the higher surface tension becomes concave and tends to envelop the liquid on that side. (Figure 1)

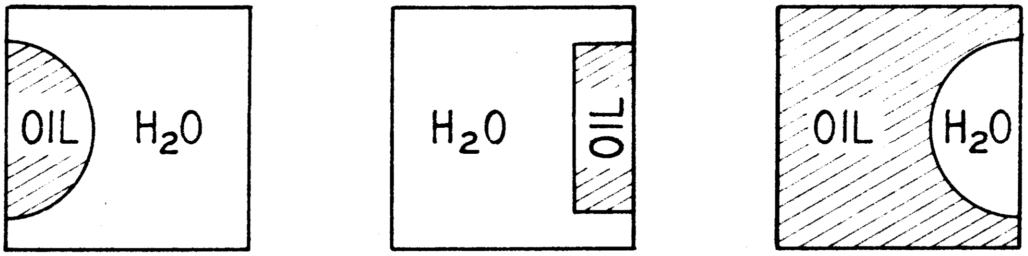


Figure 1

Agents preferentially wetted by one liquid tend to make that liquid the continuous phase. Therefore, hydrophilic colloids tend to form O/W emulsions; organophilic but hydrophobic colloids, W/O emulsions. Monovalent soaps easily wetted by water make the surface tension lower on the water side and yield O/W emulsions; polyvalent soaps more readily wetted by oil do the reverse. The mixing of mono- and poly-valent soaps in the right proportion will prevent formation of a stable emulsion. In W/O emulsions stabilized by polyvalent soaps, the configuration is as shown in Figure 2a. In O/W emulsions stabilized by monovalent soaps, as in Figure 2b.

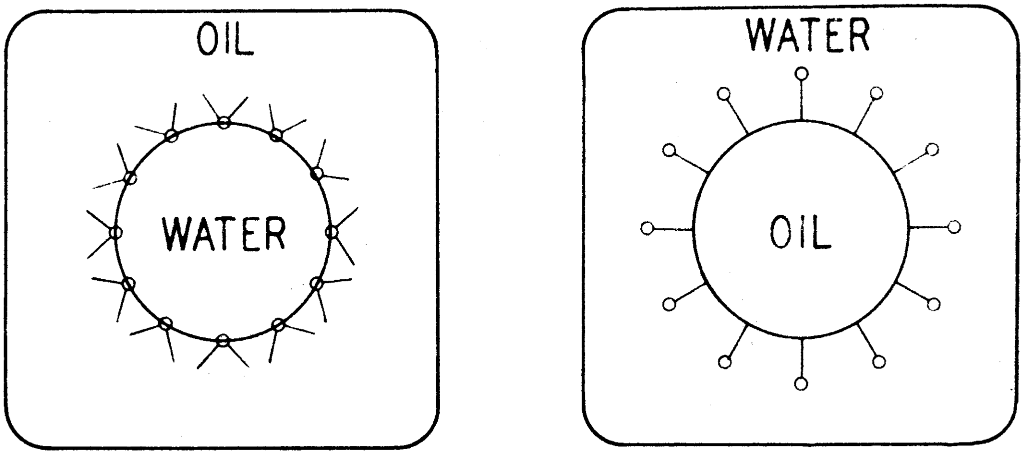


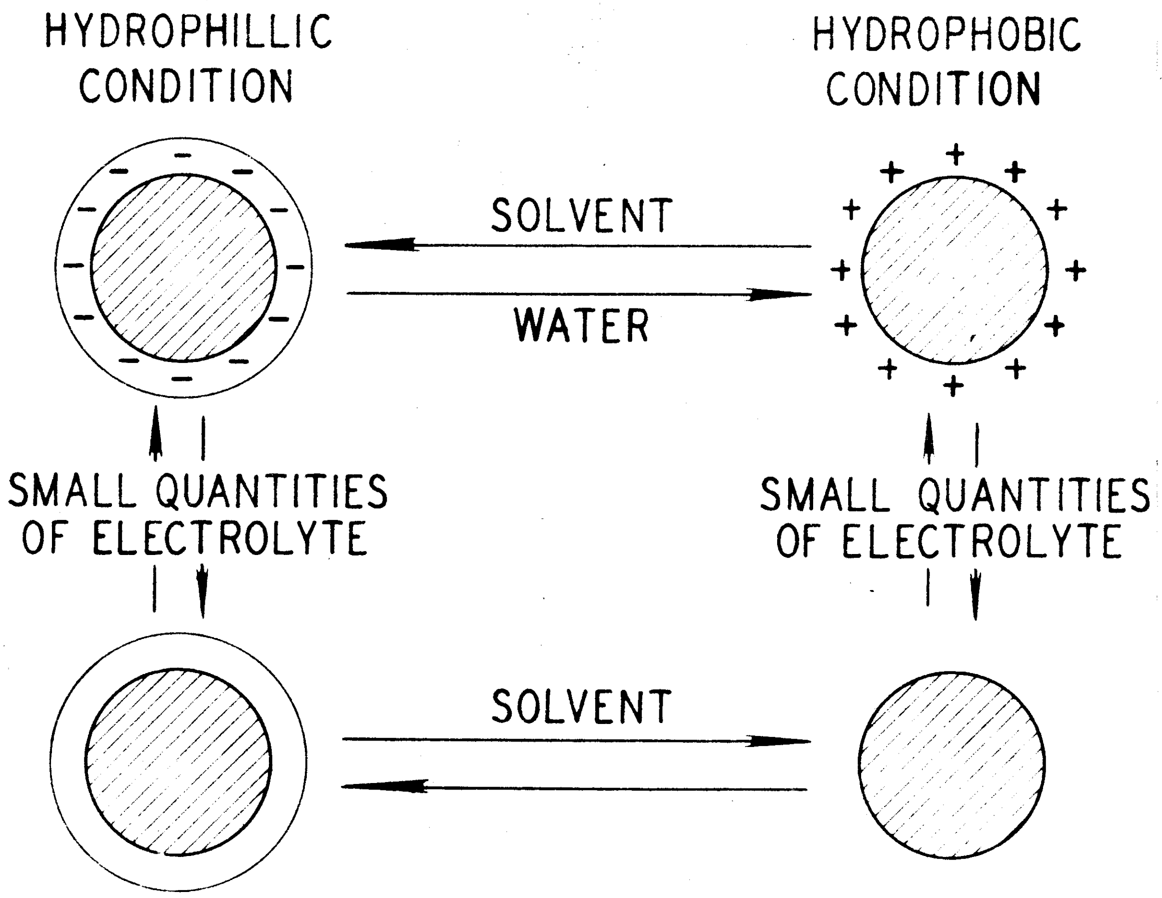
Figure 2

The configuration is such that there will be a minimum abruptness of change between the phases (Hardy-Haskins rule). The theory supports the claim that after a close-packed monomolecular layer of soap is formed there will be no more adsorption despite increased concentration of the soap in the interface. This is contrary to experiment -- McBain's work on surface tension of soap solutions indicates that adsorption forces do not occur in a monomolecular film.

In the Adsorption Theory one must not lose sight of the effect of ion adsorption. Colloids which preferentially adsorb negative ions favor O/W emulsion, and vice versa. The most stable emulsions result when the interfacial tension is zero, when the potential drop is a maximum. Anything tending to decrease the potential difference decreases the emulsion stability. At the same time adsorption is decreased due to an increase in the interfacial tension.

Once having accepted the adsorbed film theory it is seen that the proper way to de-emulsify a system is to negate the effect of the solvated hull resulting from adsorption, as well as the charge carried by the water particle. Theoretically, it is possible to visualize a system stabilized by either the solvated hull or the electric charge, but practically the stability is usually a result of a combination of both. The thick lyospheres provide sufficient protection to keep the sol stable even at the iso-electric point. A suitable "de-solvation" of the particles is necessary for the coagulation of these "isostable sols." Hence, considerably greater concentrations would be required to coagulate lyophilic than lyophobic sols.

It may be said, therefore, that a change in the electric properties and the lyophilic properties must be taken into consideration to determine the deciding part in the coagulation. The coagulating process may be controlled more by one than by the other of these factors, according to the nature of the system. The Hardy-Schulze Law applies in general for the electric properties, and Hofmeister's lyotropic ion series for the process of desolvation.


HYDROPHILLIC CONDITION
HYDROPHOBIC CONDITION
SOLVENT
WATER
SMALL QUANTITIES OF ELECTROLYTE
SMALL QUANTITIES OF ELECTROLYTE
SOLVENT

SOME PREVIOUS INVESTIGATIONS ON EMULSIONS

(1) Emulsions formed by dissolving oil in alcohol and then mixing with H_2O gave particles of 0.4 microns which were negatively charged, with a Helmholtz potential of -0.05 volt. According to Professor Thomas they owe their stability to electric charge and Brownian movement; the cause of the charge is obscure and Cohen says that a substance of high dielectric constant which is positive to one of low dielectric constant when mixed or rather dispersed one in the other is responsible. Ellis described this difference of potential as responsible for the charge. However, this explanation does not seem acceptable.

Powis found that anions had the power to increase negative potential while cations had the power to decrease it. Very small amounts of KCl or $K_4Fe(CN)_6$ up to 0.001 molar increased it, while larger amounts decreased it. Salts with polyvalent ions always decreased it, due to the predominating positive charge of the cations over the anions. Powis noted later that an immediate sharp change in the contact potential occurred upon addition of the salt, but that a secondary change always ensued. Salts like $BaCl_2$ are continuous, but in the case of $AlCl_3$ it reverts back a little due to loss of Al^{+++} on account of hydrolysis.

In the case of the water soluble colloid as emulsifying agent, the emulsifying powers of the NaOh were due to the soap formed from the free fatty acids in fatty oils. Fatty acid salts which greatly reduce the surface tension are good emulsifiers. Since they lower the surface tension, they must concentrate in the surface about the droplets of oil, and since the soap layer is still more concentrated at points of contact where the bubbles might happen to come together, capillary forces tend to separate them.

Donnan and Potts noted that Na salts of fatty acids lowered surface tension. Lowering increases with the molecular weight beginning with Na laureate. Increasing in emulsifying power increases with concentration up to N/300, after which decrease due to coagulating effect of the Na^+ ions takes place. These investigators protested Pickering's statements by saying that stability is due partly to electrical charge and partly to surface tension lowering substances in the surface layer. Decreasing the soap percentage increases the size of the globules to the point where permanence is no longer possible.

Pickering postulates the presence of small particles insoluble in the dispersion medium which coat over the particles and prevent them from coalescing. The particles must not be crystalline and must be easily wetted by the dispersed phase.

Newman testified that Na Oleate emulsifies certain oils in water and that magnesium oleate emulsifies the H_2O in the oil. A hydrophile colloid will form H_2O as the external phase, while a hydrophobe colloid will form the H_2O as the internal phase. The colloid must be able to make a suitable coherent film around the globules to be a good emulsifying agent.

Clowes made the following observations. On adding $CaCl_2$ to an emulsion of oil-in-water having Na oleate as the emulsifying agent, when the "Ca" concentration exceeds the chemical equi-valence of "Na", the emulsion phase passes through a critical point and changes to H_2O dispersed in oil. The alkali soaps are wetted more easily by H_2O than by oil, and since it is thought that the surface tension is lower on the H_2O side than on the oil side of the globules, the film will bend convex to the H_2O and conceve to the oil enveloping the oil particles because the outer area of the inner surface is less than the area of the outer surface.

The breaking of an emulsion can be accomplished by the following:

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

Hatschek, in 1911, used HCl and Na_2SO4 as coagulators. At or near the isoelectric point the particles did coalesce to form larger ones, but the oil particles of this size (3 microns) rise very slowly.

Ellis showed that these emulsions are most stable in the presence of N/1000 NaOH and least stable in the presence of $AlCl_3$ (0.00022 gm.mol.); $CuCl_2$(0.004 gm.mol.); NaCl (0.16 gm.mol.).

Powis showed that the greatest instability was present 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	"	$ThCl_4$	0.007	"

A slight increase in this concentration charges the particles positively and they become stable again.

Ellis found that colloidal $Fe(OH)_2$ (0.0017-0.0039%) final concentration coagulates this type of emulsion. Higher concentrations result in reversal of charge of the dispersed phase and stability ensues.

Newman points out that emulsions of oil-in-H_2O with soaps as the emulsifying agent are irreversibly broken by freezing.

(2) Anything which tends to prevent concentration at the interface also tends to prevent a stable emulsion. Addition of flocculating agent gives the opposite effect.

If a powerful flocculating agent is used, agglomeration into large particles may prevent the formation of emulsions. Addition of NaCl to a suspension of Ferric Oxide drives the Ferric Oxide out of suspension and, as shaking with benzene proceeds, forces oxide into the interface and acts as the emulsifying agent. $BaCl_2$ will give the same effect, but Na_2SO_4 is too strong a flocculating agent.

Shaking arsenious trisulfide with benzene gave an emulsion on addition of NaCl. When large amounts of the salt were used, emulsions became less complete and coarser. Evidently weak flocculation went too far and a fine film was no longer attainable.

The general conclusions of Briggs follow.

1) Emulsions with finely divided solids are similar to emulsions in which the so-called soluble emulsifiers are used.

2) It is absolutely necessary that the finely divided solids form a suitable film at the interface between the two liquids which are to be emulsified.

3) If a finely divided solid forms a stable suspension in one of the liquids it may be necessary to add a weak flocculating agent before a satisfactory emulsion can be produced, but a powerful flocculating agent will usually prevent emulsification.

4) Certain finely divided solids, such as carbon black and silica, are mutually antagonistic as far as the formation of emulsions is concerned and in this respect are analogous to sodium and calcium oleates.

Generally speaking, Sherrick has found that H_2O particles charged negative electrically and that both direct and alternating current could be used to discharge them. Though this phenomenon might be due to preferential adsorption of ions, it can hardly be blamed for 10% to 60% dispersion. Sodium oleate and sodium salts render these types of emulsions unstable if added in the proper proportion. The correct proportion must be added before reaching the unstable point in order to prevent reversing. The following materials present in these emulsions are:

1) Electrolytes in solution in the water phase
2) Hydrated earthy material
3) Heavy hydrocarbons such as asphalt, asphaltenes, etc., and are probably present in all oil emulsions.

It seems probable, then, that the hydrated earthy material adsorbing the heavy asphalt-like bodies of the crude oil in a manner similar to hydrous ferric oxide, becomes an oil-soluble, and as such forms a tough elastic film about the drops of H_2O.

If the particles are too small, subsidence of the particles is impossible. If the viscosity of the continuous phase is too high, subsidence may be slow. In crude emulsions, the particles are as a rule never too small for subsidence. Heating aids subsidence by decreasing the viscosity. The use of materials more easily wetted by oil than by H_2O is good for the diffusion of the oil by filtration. Using cellulosic material more easily wetted by the H_2O, the medium is more easily wetted by H_2O, and the continuous oil passes through. Dispersed water passes through but contact with the cellulosic material causes some coalescence.

The wrong way to conduct de-emulsification is to agitate with the aqueous solution. The proper way to use the soap is to put it in such a form that it will be colloidally soluble in the oil. For instance, one may prepare Na oleate with oleaic acid, or Na resinate with free resin that will go readily into apparent solution in the continuous phase. In this way contact with every water particle is assured and coalescence is always immediate. A very small percentage of the hydrophile is enough to insure complete coalescence by contact, if the emulsion is given time to come to equilibrium. Thus it appears that whatever the stabilizing hydrophobe may be it is of low power and present in all crudes in approximately the same amount.

If the hydrophobe is earthy material, colloid particles are smaller than 1 micron. Those having particles larger than 1 micron usually result in old oil accumulations. In Treto-Lite the claim is that the compound acted as a water softened and allowed the silt to sediment along with the insoluble soaps formed. Oil soluble portions of the compound decreased the surface tensions of the oil films and allowed the tiny droplets of water to collect and finally separate from the oil.

(4) The conclusions of Parsons and Wilson follow.

1) Di-valent and tri-valent salts dissolved in water could completely invert oil-in-H_2O emulsions.

2) In the limited range studied ($MgSO_4$ and $MgCl_2$) there is apparently very little effect due to the variations in the anions of the added salt.

3) In the inversion of metathesis, ratio of equivalents of inverting agent to emulsifying agent was the determining factor rather than the absolute concentration of the inverting agent.

4) When the equivalent concentration of the polyvalent salt exceeded the monovalent complete inversion took place. When it was less than the monovalent concentration a pseudo-equilibrium was established whereby some of both types of emulsion was produced.

5) The mechanism of the above inversion indicated first a chemical reaction destroying the film, then a breaking of the emulsion and the forming of a polyvalent soap; finally, resulting in the solution of the polyvalent soap in the oil and emulsification with the phases was inverted.

In general sodium oleate, a monovalent, produced more stable emulsions than the polyvalent soaps in the case of the Nujol systems. Of the polyvalent soaps studied, magnesium oleate apparently gave the greatest stability.

Nacl was used to break down a Na oleate emulsion. It should be expected that an aqueous solution of a salt would not give a well defined reaction with H_2O-in-oil emulsions on account of the inability of the salt in the aqueous phase to get at the emulsifying film, since in the case of H_2O-in-oil, the external phase is oil.

Generally speaking, to influence the properties of a particular film of emulsifying agent any substance added should be soluble in, or wetted by, the external phase of the emulsion in question.

In general it was found that the neutral monovalent salts, such as sodium chloride, iodide, and sulfate, give no noticeable inverting action of oil-in-water emulsions of Nujol, but broke the emulsions by salting them out when the salt concentrations were sufficiently high. The salting-out effect was a function of the concentration of the salt added and not of the ratio of the concentration of the salt added to the emulsifying agent. In contrast to inversion by metathesis anions here appeared to have an appreciable effect.

A check was made on the effect on the properties of oil-in-water emulsions produced by adding sodium oleate, and adding to these emulsions various substances known to be present in, or to exert an influence upon these emulsions. Substance of the class of sulfonates and alcoholic extracts from acid-treated oil were used as addition agents. These showed little emulsifying tendencies. The effect of amylene showed a much higher concentration of NaCl was required. Water and amylene together give unstable emulsions, but amylene alone tends to stabilize water-in-oil emulsions.

Several crude oils and a commercial lubricant were emulsified with Na Oleate. The crude oils were obtained from the wells. In Pennsylvania crudes it appeared that the substance present aided the Na oleate to form weak water-in-oil types or else the salting-out effect counteracted the Na Oleate. In the Mid-Continent crude, whether Na Oleate was added or not, water-in-oil emulsions were formed. The oil probably contains some emulsifying agent tending to produce fairly stable water-in-oil types and requiring fairly high concentrations of NaCl to break.

Neutral monovalent salts, such as Na_2SO_4, NaCl, and Na I, had no inverting action on the oil-in-water emulsions but when present in sufficient concentration broke the emulsion presumably by "salting-out" the soap film. The "salting-out" effect was a function of the salt concentration and not of the ratio of the concentrations of the soap to the salt. Variation in the anion appeared to have some effect in inversion by salting-out, the minimum effects being as follows:

Na_2SO_4... 0.24; NaCl... 0.22; NaI ... 0.18

(5)

There is the importance of the presence of the soap gel in the non-aqueous phase in systems which yielded only water-in-oil emulsions. Removing the gel and shaking the two phases resulted in no emulsification. Larger amounts of colloidal soap appeared in the non-aqueous phase of unshaken systems at equilibrium when sufficient NaCl was added to salt out the soap, or when sufficient bi-valent salt had been added to react with all the water-soluble soap present. Systems in which solid or colloidal material were shown to be present in the non-aqueous phase yield water-in-oil emulsions.

The addition of electrolytes produces profound change in the character of the interface of unshaken systems. The height of the interfacial meniscus was greatly reduced and the boundary itself took on an appearance of wrinkled tin-foil. Later tests showed this to be a highly benzenated gel. Qualitative tests proved that NaOH (1n) in aqueous phase induced rapid transfer of the soap from 0.002 N Na stearate solution to benzene. Qualitative indications of the amount of soap transferred from the aqueous solutions of various concentrations showed that the amount of soap remaining in the aqueous solutions is constant and perhaps roughly corresponds to the solubility of the Na soaps in water saturated with benzene. Weicherez, Harkins, Beeman, Mead and McCoy have done work which more less substantiates this.

Experiments on the distribution of soap between the two phases suggested that the transfer of the soap from one phase to the other might be governed by the solubility of the soaps or their tendency to form solvates. Conditions which might be expected to influence these factors are temperature, ratio of volumes between the two phases within certain limits, presence of electrolytes, specific nature of the organic liquid, and the state of aggregation of the soap in the aqueous phase.

Many investigators have inverted stable oil-in-water emulsions stabilized by water soluble alkali soaps to the more unstable water-in-oil systems by the addition of salts of the bi- and trivalent metals. Similar inversion takes place in the case of certain sodium soaps when NaCl is present in sufficient concentration. About all that may be said with certainty regarding the phenomenon is that it is accompanied in each instance by the appearance in emulsion systems of soap when the solubility in the water is very low.

The suggestion is that it is not a result of antagonism between the cations involved but a balance between cations on the one hand and anions on the other. These are supposedly adsorbed on or reacted with the soaps or other colloidal constituents of the surface films or membranes.

A recent patent fixes attention on the conception of "balance" regarding polar and non-polar groups in the molecules of the emulsifying agents. An outstanding characteristic of the agents is stated to be the balance of hydrophile and lipophile groups. Agents concentrate at and orient in the O/W interface. Excess of either greatly reduces efficiency.

$C_{16}H_{33}$	O-S=O	$C_{16}H_{33}$	OH
Lipophile	Hydrophile	Lipophile	Hydrophile

The excess OH group in alcohol is entirely swamped by the strong $C_{16}H_{33}$ radical. The HSO_4 group, on the contrary, confers a more pronounced hydrophilic character. It appears that in a given homologous series there is a point or range at or within which the hydrophile and lipophile characteristics are so balanced that an optimum power for the prevention of "spattering" is imparted to the molecules. On either side of this point one or the other of the opposite characteristics predominates.

The reason for marked stability of the bubbles from some colloidal solutions has been shown to lie in the fact that the surface films are gel-like plastic solids rather than viscous liquids.

Failure of other solutions with low surface tension to give stable emulsions is due to the fact that they give only fluid films.

Plastic films are colloidal rather than of molecular dimensions and require matters of hours to build up to maximum strength.

Solutions which form plastic solid films have erroneously high surface tension results by the Du Nuoy and presumably by other methods because the yield value of the plastic solid film is added to the true reversible surface tension.

There is evidence of similar behavior in the case of some liquid-liquid interfacial films in emulsifying agents, but the production of such films appears to require much higher concentrations than in the case of surface films.

Plastic solid films of similar properties were shown to play an extremely important part in lubrication as the determining factors in the oiliness of a lubricant which reduces friction at low speeds and high loads.

PRESENT DAY TREATMENT OF OIL EMULSIONS

The chemistry of oilfield emulsions has in reality a threefold claim to a place in colloidal chemistry. First, the dispersed phase consists of droplets of varying sizes, sometimes consisting of droplets so small that they actually become within the particle size range often referred to as the colloidal range. Secondly, practically all oilfield emulsions are stabilized by the presence of colloids, in the broadest sense of this term. Finally, the modern commercial demulsifying agents, or their subsequent reaction products which are used to break oilfield emulsions, have certain colloidal properties. Various phenomena accompanying the colloidal state may be looked for when investigating oilfield emulsions and their chemical demulsification. These phenomena lead in three directions - first, the particle size of the dispersed phase, secondly, the inherent characteristics of the emulsifying colloids themselves, and last, certain colloidal aspects of the chemical demulsifying agent.

Petroleum emulsions represent the water-in-oil type in which the emulsifying agent is oil-soluble, or wettable. The "solutions" of such emulsifiers may be termed as "organosols". There is much less information regarding organosols than aquasols. As a result, much information must be obtained by analogy to a corresponding situation wherein an aquasol is concerned.

Stated briefly, if a water-in-oil emulsion of the type found in oilfields is subjected to certain agencies which would bring about an inversion of the emulsion and which would convert it into the oil-in-water type, it would, at least theoretically, have to pass through an intermediate point at which there is either no emulsion at all or else there is a balanced tendency to produce both types of emulsion. It so happens that only by the most careful regulation can both types of emulsion be produced. This is equivalent to saying that if gravity, coalescence, and time be permitted to act on the emulsion at this stage, the emulsion will be resolved or separated into its component parts. One of the most interesting ways in which to bring about coalescence is to pit against each other protective colloids of opposite types - the hydrophile against the hydrophobe.

Finely divided materials which are water-wettable, such as finely pulverized sand, may produce an oil-in-water emulsion. If certain forces are made to act upon a water-in-oil emulsion which is stabilized by the presence of oil-wettable carbon black, so that the nature of the surface of the carbon black is changed, and its surface becomes water-wettable, then the emulsion should break. It may be stated that it is really immaterial as to whether the de-emulsifying colloid (hydrophile) passes into the water, because at the interface there may be produced water-wettable materials which may adsorb on the particles of oil-wettable carbon black and convert them into particles which are water-wettable. If the particles become water-wettable then the emulsion would be expected to break, if coalescence and gravity are permitted to act. It is true that some petroleum emulsions may be stabilized by finely divided sand or paraffin particles on which there is adsorbed asphaltic material, so that for the practical effect the action is the same as though there were present finely divided asphalt or finely divided carbon black. On the other hand, it is more likely that these emulsifying agents, the asphaltic materials, may be dissolved colloidally in the oil and might be referred to as oleophile colloids - that in them the equivalent in oil of the hydrophile colloid in water has been produced. The problem remains fundamentally the same. What can be done to this oleophile colloid to change it into an "oleophobe"? An oleophobe colloid is one which is unwetted by oil, or is wetted at least preferentially by water, and is thus hydrophile to that extent, at least.

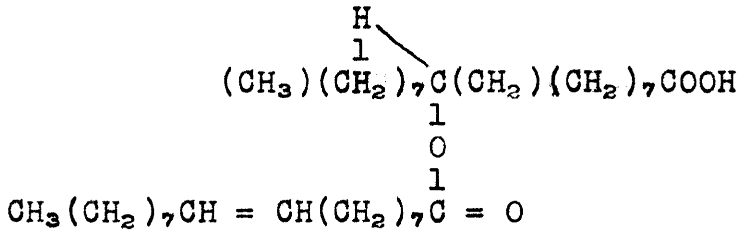
Colloids, or more properly, colloidal sols, are divided into two classes; one is known as hydrophile, or non-electrocratic, the other is known as the hydrophobe, or electrocratic type. It is indeed true that many colloidal sols partake of the properties of both of these types - or, more correctly stated, every electrocratic sol has to a certain degree the property of the non-electrocratic sols, and every non-electrocratic sol has to a certain extent the properties of the electrocratic sols. There is no absolute line of demarcation. If the colloid which is responsible for the formation of the water-in-oil smulsion, that is, the oil soluble, oil dispersable, or prefentially oil-wettable colloid, happens to be electrocratic in nature, the emulsion would be expected to break by adding to the oil certain materials which would directly affect the stabilizing electric charge and which would break the emulsion in the same manner in which an electrocratic suspension can be coagulated. Stated briefly, the colloids present in crude oil are rarely affected in this particular manner without at least certain other forces coming into play. The oleophile colloid has to a large degree the same properties as the hydrophile colloid in water.

The asphaltic materials present in crude oil are substantially chemically inert. They cannot be expected to combine with something else, a demulsifying agent, to form a new product which, instead of being olephile, is oleophobe in character. The most that could be done is to add to such crude oil emulsion a material which, like the asphaltic material, is drawn to the interface and adsorbed on the asphaltic material so as to render it oleophobe instead of oleophile. This is one reason why Barnickel considered water softening agents as effective demulsifiers (due to the physical adsorption of certain precipitated water-insoluble hydrated water-wettable alkaline earth salts, which are present in amounts exceeding their saturation points).

This being true, it can be readily seen why the emulsion chemist interested in breaking oilfield emulsions of the water-in-oil type is concerned primarily with adsorption. The problem confronting this chemist is essentially one of introducing into the emulsion in relatively minute quantities a reagent which is attracted to the interface, and which is adsorbed on certain oleophile emulsifying materials by a force akin to chemical attraction to render them oleophobe, or water-wettable. As a result of this action there is a tendency for the emulsion to invert and, under properly controlled conditions, break or resolve.

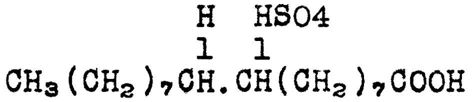
Even though a discussion of the phenomena of adsorption is beyond the scope of this paper the following remarks may be made. In water-in-oil emulsions of the type which ordinarily occurs in oilfields the emulsifying material present in the substantially non-polar oil is of the non-polar oleophile type. As far as unsaturated or off-setting outside residual valencies manifested by the interfacial tension is concerned, the effect produced by the naturally occurring non-polar emulsifying material in non-polar oil is analogous to the effect of finely divided insoluble solids in water and, therefore, notwithstanding the existence of a persistent emulsion, the residual unsaturated valencies (as manifested by the static interfacial tension) still exist at approximately optimum value at the interface. Thus there is attracted to the interface the added chemical de-emulsifying agent. This is especially true if the chemical demulsifying agent is colloidal disperse in the oil. Then, if the chemical demulsifying agent is further characterized by the presence of a hydrophile and hydrophobe radical or atom which orientates as such, or in the form of an alkaline earth salt under proper conditions, the outer surface of the hydrophobe emulsifying material, or at least that part of it in contact with the water of the emulsion, is converted into an adsorption compound which is oleophobe, or at least water-wettable. The tendency toward inversion sets in permitting the emulsion to break under the action of coalescence and gravity, assuming that sufficient time is allowed for it to act.

The modern emulsifying agents are based primarily on these principles. Briefly, the following examples may be taken as illustrative of these various types used for chemical demulsification of oilfield emulsions:



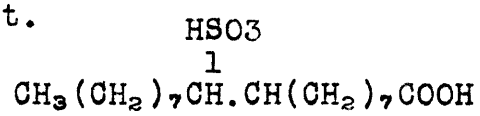
$$\begin{array}{c}\mathrm{(CH_3)(CH_2)_7\overset{H}{\overset{|}{C}}(CH_2)(CH_2)_7COOH} \\ | \\ \mathrm{O} \\ | \\ \mathrm{CH_3(CH_2)_7CH = CH(CH_2)_7C = O}\end{array}$$

Oleilhydroxystearic acid --- or its salt.



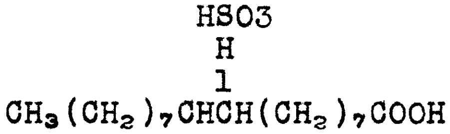
$$\mathrm{CH_3(CH_2)_7\overset{H}{\overset{|}{C}H}.\overset{HSO4}{\overset{|}{C}H}(CH_2)_7COOH}$$

Oleic acid hydrogen hydrogen-sulfate; used in form of mono- or di-salt.



$$\mathrm{CH_3(CH_2)_7CH.\overset{HSO3}{\overset{|}{C}H}(CH_2)_7COOH}$$

Hydroxy-olei-sulphonic acid: used as such or mono - or di-salt.



$$\mathrm{CH_3(CH_2)_7CH\overset{HSO3}{\overset{H}{\overset{|}{C}}}H(CH_2)_7COOH}$$

Benzene sulphostearic acid: used as such or as mono- or di-salt.

$C_{20}H_{27}SO_3H$ and $C_{24}H_{33}SO_3H$

Petroleum sulphonic acids: used as such or as mono- or di-salt. (Formulae are intended to be illustrative only.) Although these examples show variety as to chemical composition it is to be noted that they almost invariably present five features, namely:

(a) They give colloidal dispersions in oil, at least when very dilute, thus tending to adsorb at oil-water interfaces.

(b) They contain hydrophile and hydrophobe groups, radicals or residues, so that they not only adsorb at interfaces but, either as such or in the form of the corresponding alkaline earth salts, they orientate at the interface between the oil and the water.

(c) There is present a radical (or radicals) which, when combined with a calcium or magnesium atom, will produce an insoluble salt if the concentration is great enough (water softening effect); and the hydrated calcium or magnesium salts of these materials, as exemplified by the forms produced by precipitation in dilute solutions, are water-wettable even though water-insoluble.

(d) Into a hydrophobe group or radical there is introduced another group, radical or residue, which may be hydrophile or hydrophobe, but in any event it is ionogenic in the broad sense mentioned.

(e) In regard to those of the above-mentioned compounds which happen to be modified by fatty acids in the sense that the term was used by Barnickel, in comparison with sodium oleate or oleic acid the following distinction is very marked: In oleic acid, or sodium oleate, there is a polar compound in which there are several nuclei or foci of polarity, as exemplified by "secondary" valencies, and which are arranged terminally to each other, whereas in the modified fatty acids, or salts or esters thereof, there are at least three nuclei or foci of polarity and they are not arranged terminally, at least one focus or nucleus being in a non-terminal position, and characterized moreover by being located in the hydrophobe residue. Our knowledge of various factors, such as orientation of complex multipolar molecules at interfaces, the relationship of polarity and valence, is still too meagre to evaluate the exact mechanism by which this offset "secondary" valency or nucleus of polarity operates. Possibly the modern demulsifying agent acts by virtue of a peculiar orientation of multipolar molecules, so as to break oil-field emulsions so much more effectively than the older, simpler types of reagents, such as oleic acid or sodium oleate.

In the use of modified fatty acids, even though the amount of calcium or magnesium salt formed is within the limits of water solubility of such calcium or magnesium salts, it is possible that adsorption of these still soluble magnesium and calcium salts takes place from solution due to the peculiar forces above indicated. In other words, instead of possibly mere physical adsorption of certain magnesium and calcium salts, there may result a selective adsorption which renders dissolved magnesium and calcium salt (present in amounts smaller than their saturation limits) insoluble by combinations having at least some characteristics of true chemical combination.

Generally in emulsions the liquid with the greater surface tension, against the other liquid constituting the other emulsion phase, especially after allowing for mutual saturation and solution of the emulsifier (usually a soluble colloid in the other liquid), is almost invariably the dispersed phase. Sometimes the situation is confused by the presence of a polar or multipolar emulsifier which orientates in one manner against air, for example, and in another manner against water or oil. Thus to reverse or invert an emulsion these "surface" tensions must be reversed. In an oilfield emulsion, even the removal of the relatively non-polar oleophile colloid from the oil (unlike the removal of soap from an aqueous solution) would not markedly raise the surface tension of the oil. The removal of soap from water restores the original high surface tension thereof. For this reason one cannot, under conditions of commercial use, reverse or invert an oilfield emulsion by the conventional use of modern chemical demulsifiers.

However, by making the surface of contact between two adjacent or touching water droplets permeable or wettable by some agent, coalescence is permitted to take place and it continues until the droplets grow by repeating the process to the point where the droplets got to the bottom of the vessel. At this point emulsifying films are ruptures by the great increase in size of the water droplets.

Hence, the demulsifying action of the modern chemical agent lies in the direction of reversion or inversion of emulsions, but only so far as to break the emulsion and not to actually reverse or invert the emulsion under ordinary conditions of use.

The former discussion has dealt wholly with the application of chemical methods to the breaking of these emulsions. In spite of this it is only fair to state the other means used, which deserve considerable credit; they are probably not as effective but in some respects, at least, prove to be more economical.

The use of steam to heat above a certain minimum temperature has the effect of reducing the viscosity of the phases; it increases the difference in relative density of the oil and the water, and the thermal motion resulting increases the velocity of impact. If the film is not too rigid it may be ruptured and coagulation takes place.

Excess phase has been used, but not effectively. If an excess amount of free H_2O is added and slow agitation takes place the small particles of water in the oil will have a much greater possibility of being removed, not by agglomeration among themselves, but they would pass into the bulk of the water.

By far the greater number of patents relating to the breaking of crude oilfield emulsions are concerned with electrical treatment. (a) The emulsion is subjected to mechanical vibration, both while in the pre-treatment zone and while passing between high tension electrodes. (b) The emulsion is introduced within an inner perforated rotatable electrode and passed through the perforations of this electrode. A surrounding drum constitutes the other electrode. (c) Passing the emulsion in a flowing stream between a pair of electrodes between which a potential of 250-600 volts is maintained. The electrodes are spaced sufficiently far apart to prevent passage of any substantial amount of current. (d) The emulsion is subjected to the action of an electrical field of an alternating high potential character produced by the use of a non-oscillatory alternating potential of a frequency between 60 and 10,000 cycles per second.

Other patents along these lines have been developed but are too numerous to mention. The theory behind all of them is that either the particles are subjected to a constant reversal in direction, which results in coalescence from bombardment, or also by the forming of chain-like aggregates which eventually settle out.

It is to be pointed out that the foregoing methods of steam heating and agitation and the method of electric potential depend for results upon the coalescence of the water particles through rapid bombardment of each other by some means or other, and not by chemical phenomena. However, the application of chemical principles before this agitation helps materially in destabilizing these emulsions.

PROCEDURE

Recognizing the fact that a system tends to arrange itself in such a manner as to have the least free energy, an analysis of what happens to form an emulsion is in order. It is impossible to say whether or not the emulsifying agent is in solution in the oil when down in the sediments or adsorbed on the sand grains at the interface between the oil and the sand. Be that as it may, it is a fact that the emulsifying agent comes up mixed in the two fluids in some way, either in solution or in mechanical suspension. Based upon the theory of the hydrophile colloid being responsible for the formation of an oil-in-H_2O emulsion, it is fair to assume that in the case of the average crude oil emulsion (W/O) the emulsifying agent is preferentially soluble in the oil and probably exists in that state in the sediments.

However, on production of the fluids, it has been found that the less the restrictions are in the flow line, the smaller will be the degree of emulsification if the particular formation is subject to emulsification of its fluids. This correlates with the idea that the necessary factor of comminution which takes place, either by shear or high velocity, is the primary cause of emulsion formation in the oilfields. What probably happens is that the particles, so finely comminuted, become dispersed and the whole system seeks a minimum of surface energy, allowing the emulsifying agent to orient itself in the interface. If emulsification could be attacked immediately upon flowing into the tanks, the fluid would be caught at its least stable "age." Any delay in treatment allows further chance of orientation and the droplets become more tightly held in suspension.

It is unfortunate that the resulting emulsion is not directly reversible along the same path by which it was formed. If it were this would probably be the most economical path. Therefore, one must seek a different way in which to arrive at the original conditions. Theoretically, at least the same amount of energy must be used to break it as was used to form it, and, practically speaking, more than that amount would be required .

As a means of achieving this result the following procedure was adopted. Since we are dealing with particles of 0.5-1.5 microns, we are confronted with surface phenomena rather than with bulk phemonena. Therefore we will attack this from a colloidal standpoint and apply theories developed in analogous cases. In shipping these emulsions by rail over greater distances it was noted that some of them were broken completely, or at least partially. This fact gave a lead towards determining the optimum rate and type of shaking, or the use of ultrasonics.

The type of emulsion, whether oil-in-water or water-in-oil, was determined by the use of the fluorescent light microscope or by the method of dilution. In all cases the emulsions were found to be of the water-in-oil type. After this was determined the following effects were investigated:

1) Effect of electrolytes on these emulsions.
2) " " fatty acids and alcohols on emulsions.
3) " " modern wetting agents on emulsions.
4) " " ultrasonic waves on emulsions.
5) " " the rate of shaking on these emulsions.
6) " " excess volume on emulsions.
7) " " added "weighting" salts to water added in #6.
8) " " heat on these emulsions.

A series of seventeen emulsions was obtained from the Gulf coast fields of Louisiana, the field of northern Louisiana, the fields of central Texas, and the fields of the western coast of California. As before mentioned, these emulsions were tested as to their type and also as to the charge carried on the water particles. The water particles, as a rule, were found to be negatively charged - as is the usual case in petroleum emulsions. However, there were some emulsions which contained positively charged particles.

The apparatus consisted of a shaker set on a solid base 12" by 30". The bottles were fixed firmly on the shaker and oscillation was obtained by a series motor, the speed of which could be controlled. The oscillation obtained was horizontally backward and forward with a movement of about ten inches. The speed of the motor was controlled through a resistance coil, and the oscillations could be varied from 25 to 90 per minute.

The first tests made on these emulsions were performed when using electrolytes. NH_4OH and Na_3PO_4 were used on the positively charged particles. HCl, $AlCl_3$, and $Fe(NO_3)_3$ were used on the negatively charged particles.

In a further search for de-emulsifiers the effect of fatty acids and alcohols was studied. The following reagents were used:

1) Butyl Alcohol
2) Ethyl Alcohol
3) Glycerol
4) Ethylene Glycol
5) Phenol
6) Oleic Acid
7) n-Butyric Acid
8) Salycylic Acid
9) Acetic Acid

Working on the assumption that if the emulsifying agent could be rendered more wettable by the water an unstable point could be reached whereby the particles could be vibrated together. Therefore the use of wetting agents was investigated; the four obtainable were Ultrawet, Aerosol OT, Nekal A, and Nekal BX. Of these wetting agents, 0.3% by weight solutions were made up and their effect observed.

The effect of increasing the volume of the disperse phase was studied as well. The addition of "weighting" salts to this disperse phase (water) to increase the difference in density between the two phases was attempted.

Since the ultimate aim was the agglomeration of the disperse water particles, a new means of energy input was applied. We tried using ultrasonic waves generated by a piezo-electric quartz plate crystal between two electrodes, obtaining a frequency of 500,000 oscillations per second. The quartz and the electrodes were immersed in an oil bath and the energy transmitted through a test tube suspended with its tip in the oil fountain.

Still working on the idea of "slamming" these particles together, the effect of the rate of shaking was determined in a roughly quantitative manner by varying the rate of shaking.

RESULTS

It was noted that the concentration of electrolytes required for satisfactory breaking of the emulsions was excessive at times approaching saturated solutions.

In using fatty acids and alcohols it was found that they materially decreased the amount of de-emulsifying agent required as compared to the electrolytes, and that less concentration of acid than alcohol was required to obtain the same effect. The difficulty with these was the appearance of a "lace" at the interface between the clear oil and water.

Modern wetting agents seemed to give good results at exceedingly low concentrations. One needs a certain amount of wetting agent to destabilize the emulsion, and in the case of highly viscous oils an excess amount of H_2O should be added. The point at which this amount of excess H_2O comes into effect when added to these heavier oils is about 2-1 by volume. In using the lighter viscosity crudes and also the lower density crudes, the addition of excess H_2O appeared to be detrimental. This detrimental effect shows up at about 100 centipoises at room temperature. It was found that Ultrawet, Nekal A, Nekal BX, and Aerosol OT were all effective on oils below 75 centipoises at room temperature, while the best effect above that viscosity was shown by Aerosol OT.

In the use of Ultrasonics fair results were achieved without treating the emulsions. However, on treatment with the de-emulsifier agent much better results were obtained on application of ultrasonic. It might be well to point out that wetting agents alone were used to treat before application of these ultrasonics. The solution was noticed to heat up on the application of these high energy waves.

With reference to the rate of shaking, it was found in the comparatively crude set-up that a rate of 80 shakes per minute gave the maximum breaking with the least amount of reagent.

The excess volume of water was most effective when using a high viscosity high density emulsion. In the low viscosity suspensions there was no aid and at times it showed up to be detrimental.

In the heavier density emulsions we found difficulty in settling out the destabilized emulsion, due to the viscosity effect. Application of heat required too high a temperature. Therefore we added saturated NaCl, which brought the density of the water up to 1.2, that of water without the salt. This effect was transmitted to the droplets after the film was ruptured and the droplets shaken out more feasibly. It was found that in the intermediate viscosity emulsions of around 300 centipoises at room temperature that this density difference aided remarkably.

DISCUSSION OF RESULTS

It may be quite definitely concluded that any oilfield emulsion which remains stable for any period of time is not solely dependent upon its charge for stability. In fact, the effect of the surface film in these emulsions must be considered to a great extent. Since it was observed that once having broken the emulsions, particles of carbon showed up in the oil as well as small accumulations of jelly, which were not previously visible, it can be safely said that these particles have gone through a change in state. Possibly the jelly which appears is the organic matter which makes the particles of carbon more water-wettable and aids to stabilize the system.

That there is some effect of these fatty acids cannot be denied. From the effect of these comparatively simple organic compounds it can be fairly well understood that the higher ones actually used are effective in destabilizing oilfield emulsions. The crude oil itself probably acts as the solution medium for the de-emulsifying agent, allowing this agent to orient itself in the interface between the oil and water and exerting its opposing effect to the emulsifying agent. The emulsifying agent is probably a colloidal material readily peptized by oil. The carbon particles mentioned above were probably asphalt. An emulsifying agent could best be nullified therefore by a de-emulsifier which would have by its own organic properties good solvent properties as well as preferential radicals of orientation. These acids and alcohols always left a scum or lace effect at the interface. This would require further treatment.

"Wetting agents" have recently been developed and have served materially in industry. Here, too, they may find their application.

It was found that using unusually low concentrations of wetting agent it was possible to break emulsions which required a much higher concentration of other types of de-emulsifying agent. The de-emulsifying agents refer to the electrolytes and acids used in this work. These wetting agents are used to make the emulsifying agent either more wettable by water or less effectively wettable by the oil. In either case a point of maximum instability would be reached on increasing the wetting agent to a certain point. After that point breaking still occurs, but at a faster rate. There was no reversal observed, as might be expected in other types of emulsions.

If the agent is added to a light density, light viscosity oil, the emulsion will be broken. However, if an excess phase of water were added, keeping the total amount of wetting agent equal to the sample without excess water, the same results will not appear. There will be a strong tendency to form a very foamy upper layer, which remains quite stable for some time. Upon standing four or five hours, the foam disappears leaving the emulsion broken. Heating tends to decrease the foam effect. The foam will not appear when no excess water is added. The foam effect is not observed in the higher viscosity crudes.

The three wetting agents, Nekal A, Nekal BX, and Ultrawet, seemed to do their best work with the oils of less viscosity than 75 centipoises at room temperature; they do good work with those above that viscosity but the viscosity effect must be removed by heating. Aerosol OT was found to do good work with these higher viscosity emulsions, and worked very satisfactorily with the lighter viscosity emulsions. It may be well to point out that one must be resigned to the use of heat when attacking these high viscosity, high density, crudes of the West Coast and Texas. When a drop of water (which is in the vicinity of one hundred times those found in emulsions) is dropped on the surface of these high viscosity crudes it does not even depress the surface of the crudes. Therefore it is unreasonable to expect that one of these minute droplets with which we are dealing will settle against these high resistance forces of viscosity of its own accord. It must be remembered, too, that the ratio of mass to surface is many times smaller, and the viscosity naturally can be more effective to these surfaces. On the other hand, it is rather fortunate that these heavy oils have a high viscosity index as a general rule. This allows enough decrease in viscosity with rise in temperature to show considerable effect on sedimentation rate. The temperatures required for high viscosity emulsions would be between 110°F and 160°F. The reason for feeling this way on this point is that in every case when the reagent was shaken into the oil it did not have too much trouble reaching the surface of the water bubbles when the excess water was in the ratio of two-to-one. Therefore, it was necessary to heat these emulsions to a temperature of 160°F before complete breaking could be secured in four hours' time.

If there were a greater difference in specific gravity between the oil and water, possibly lower temperatures could be used to break these emulsions. Therefore, the use of "weighting" salts in an attempt to increase the specific gravity of the water was attempted. The results were satisfying in that the temperature of breaking for the same length of time was 135°F. Previous breaking of these untreated emulsions required 190°F.

The use of ultrasonic waves gave much better results than were expected. Every emulsion tried resulted in some breaking; some were completely broken. The lighter density emulsions gave little trouble. The heavier density, higher viscosity non-treated emulsions were sufficiently well broken although a much longer time was required to do the work. It was necessary to work at ten-minute intervals for sixty minutes in order to get almost complete breaking. The reason for working at intervals is due to the limits of the cooling bath for the quartz crystal. It is presumed that stopping at these intervals resulted in some agglomeration of these droplets. This agglomeration was not too much affected by the viscosity effect as the temperature of the oil was raised to the temperature of 120°F. which materially affected the viscosity.

It was found on treating these heavier emulsions with Aerosol OT by shaking in the shaker that the ten-minute intervals required in the ultrasonic apparatus were reduced to between three and four. In other words, the Aerosol OT cut the ultrasonic time in half. No work was done in adding the treating agent to the emulsion and using only the ultrasonic waves to give the required mixing. When about five cc. of water were added to a test tube over which was poured about 20 cc. of Aerosol OT treated emulsion the following took place. The initial rate of breaking increased. This can probably be explained by the fact that the destabilized particles were knocked out of the emulsion through the interface of the excess water and the emulsion. The interface probably acted as a type membrane through which the bubbles migrated to the main body of water. The addition of the excess water eliminated the necessity of building an excess out of the small bubbles in the emulsion.

An optimum rate of shaking might be found for the proper mixing between the de-emulsifier and the emulsion. Not enough work was done on this, but rough indications point to the possibility of such a rate being present.

Not too much can be said relative to the results that could be achieved by adding salts to the excess water in order that in shaking the particles of water in the emulsion would have their specific gravity increased. Using NaCl, as previously mentioned, the temperature of heating was lowered some twenty degrees. The reason for this was obvious. Tests of these emulsions with their particle specific gravity changed gave good results in the ultrasonic machine. However, the data obtained were too meagre to be included in this treatise.

Although there is much that has not been mentioned regarding the use of solids, Silica Gel, $BaSO_4$, and Fuller's earth were used. Some success was achieved in the lighter viscosity emulsions.

CONCLUSIONS

The work done on this thesis has lead us to conclude that there is need of further investigation on the following:

1) The use of present day wetting agents as a means of combating these emulsion troubles.
2) The effective use of ultrasonics as a substitute for heating and electrical methods.
3) The further study of increasing the density of the bubbles when dealing with highly viscous emulsions.
4) The use of excess volumes of water to allow the particles to have more chance to be "slammed" into a like phase.
5) Though not much was done on the rate of shaking of the system, still evidence points to possibilities.

It is believed that if the idea of ultrasonics can be worked out to a greater extent, the use of the steel bottoms of treating tanks can be approved as the transmission medium of the energy. Although high frequencies were used, it is pointed out that lower frequency set-ups may be used over a longer period of time with the same results. It might be that increasing the power of a lower frequency set-up will give the same effect as a higher frequency low power apparatus as used.

Lower concentrations of wetting agent might be used if longer periods were allowed for orientation after shaking. The combination of wetting agents and ultrasonics seems to offer a formidable means of attack.

Special theses on each of these particular problems may result in very interesting correlations.

PART III

APPENDIX

DATA

(Summarized)

Using electrolytes — Shaker: 20 minutes

1)	2.5 cc HCl	Little or no change
2)	5.0 cc HCl	Grouping somewhat better
3)	10.0 cc HCl	Large bubbles formed which settled out completely in 24 hours
4)	15 cc HCl	Emulsion broken on 60 secs. shaking with blue layer formed at interface

Note: All acid in this test was saturated (33%) HCl and was added to 5 cc medium viscosity oil, approximately 50 centipoises.

1)	5.0 cc $AlCl_3$	No effect noticeable
2)	10 cc $AlCl_3$	No effect noticeable
3)	20 cc $AlCl_3$	No effect noticeable
4)	30 cc $AlCl_3$	No effect except slight discoloration

Note: All solution used in this test was saturated $AlCl_3$, and was added to 5 cc of medium viscosity oil, approximately 50 centipoises.

In the use of these electrolytes, even on heating to 80°C. or 176°F., no real satisfactory results were obtained.

Using alcohols — Shaker: 20 minutes

20 cc oil plus Butyl Alcohol

1)	5 cc alcohol	Emulsion broken but blue compound formed with slight jelly at interface
2)	10 cc alcohol	Ditto

3)	15 cc alcohol	Emulsion broken but blue compound formed with slight jelly at interface
4)	20 cc alcohol	Ditto
5)	25 cc alcohol	Ditto

20 cc oil plus Ethyl Alcohol

1)	3 cc alcohol	No effect after shaking and heating to 170°F.
2)	9 cc alcohol	No effect after shaking. Heating to 170°F. broken.
3)	15 cc alcohol	Emulsion broke up into two layers, clear oil and very darkly unstable emulsion
4)	18 cc alcohol	Broken
5)	21 cc alcohol	Broken
6)	24 cc alcohol	Broken

Oils used were light and medium viscosity.
Other alcohols used with effective results.

1) Glycerol
2) o-Cresol
3) Diethylene Glycol
4) Prylene Glycol
5) Ethylene Glycol
6) Phenol (very effective)
7) b-Cresol

Acids used which gave about the same effect as alcohols

1) Oleic Acid
2) Acetic Acid (2N)
3) Salycylic Acid (sat.)
4) n-Butyric Acid

Solids used

1) $BaSO_4$
2) Fuller's Earth
3) Silica Gel

Using ultrawet   Shaker: 20 minutes

20 cc heavy viscosity oil plus 100 cc H_2O plus Ultrawet solution

1)	3 cc Ultrawet	Unstable and broken by heating for 2 hours 120°F.
2)	6 cc Ultrawet	Broken, with small bits of black solid seen
3)	9 cc Ultrawet	"
4)	12 cc Ultrawet	"
5)	15 cc Ultrawet	"

20 cc heavy viscosity oil with no excess H_2O plus Ultrawet solution

1)	5 cc solution	No effect except slight increase in size of few bubbles
2)	10 cc solution	"
3)	20 cc solution	"
4)	30 cc solution	"

Heating for four hours had no effect at 170°F.

40 cc heavy viscosity oil plus ultrawet   Shaker: 20 minutes

1)	5 cc Ultrawet	plus 20 cc H_2O	No effect - even on heating to 170°F. for 12 hours
2)	5 cc Ultrawet	" 40 "	Same as above
3)	5 cc Ultrawet	" 60 "	" " " but slight increase in size of bubbles
4)	5 cc Ultrawet	" 80 "	From 80 cc excess H_2O on up through 140 cc, emulsion broke on heating to 140°F. for 12 hours
5)	5 cc Ultrawet	" 100 "	
6)	5 cc Ultrawet	" 120 "	
7)	5 cc Ultrawet	" 140 "	

Using 40 cc Heavy viscosity oil plus Ultrawet. Shaker: 20 minutes

As above, but using only 2 cc ultrawet it was found that effective breaking started at 80 cc. excess H_2O when heated up to 140°F.

40 cc low viscosity oil plus ultrawet Shaker: 20 minutes

1)	1 cc Ultrawet	No effect
2)	2 cc Ultrawet	"
3)	4 cc Ultrawet	Bubbles closely adhere
4)	6 cc Ultrawet	Half broken
5)	8 cc Ultrawet	Broken

On heating to 120°F. all of the above were broken except No. 1.

Aerosol OT, Nekal A, and Nekal BX

These wetting agents were used as Ultrawet above, and found to give as satisfactory results. In some cases, if any outstanding effect were noticed it was in the case of Aerosol OT. All of the emulsions obtained were broken, with Aerosol OT being used in lesser concentration than any other.

LITERATURE CITED

1) Thomas, A. W. "Review of Literature of Emulsions" Jour.Ind.Eng.Chem., Feb.1920, pp.177-181

2) Briggs, T. R. "Emulsions with Finely Divided Solids" Jour. Ind. and Eng.Chem.,Vol. 13, Nov. 2, 1921. p.1008.

3) Parsons and Wilson "Factors Affecting the Stability and Inversion of Oil-in-H_2O Emulsions" Vol.13, Ind.Eng.Chem. Dec. 1921.

4) Ayres, E.E.,Jr. "Common Characteristics of Emulsions" Ind.Eng.Chem., Nov.13, 1921 #11.

BIBLIOGRAPHY

1) Bhatnager, S.S. "Studies in Emulsions"
Jour.Chem.Soc., Vol.117, 1920, pp.542-552

2) Clayton, W. "The Modern Conception of Emulsion"
Jour.Soc.Chem.Ind., Vol.38, May 1919
pp.113-118

3) Padgett, F.W. "The Colloid Chemistry of Petroleum"
Chem. and Met.Eng., Vol.28, Feb.27,1923
pp.249-253

4) Dodd, H.V. "The Resolution of Petroleum Emulsions"
Chem. and Met.Eng., Vol.28, Feb.27,1923
pp.249-253

5) Matthews, R.R. and Crosby, P.A. "Recovering Petroleum
from Emulsions by Chemical Treatment"
Jour.Ind.Eng.,Chem., Vol.13,Nov.1921,
pp. 1015-1016

6) Wilson, R.E. and Ries, E.D. "Surface Films as Plastic
Solids", Vol.59, #83, Bull.M.I.T.
Chem.Eng.Dept.

7) DeGroote, M. "Chemical Demulsification of Crude
Petroleum", Science of Petroleum,
Vol.III, pp.616-630

8) Wellman, V.E. "A Study of the Factors Controlling
the Type of Water-Soap-Oil Emulsions"
Reprint from the Jour. of Phys.Chem.,
Vol. XXXIV, pp.309-409, 1930.

9) "New Processes of Dehydration of Crude Oil" - Oil and
Gas Jour., Jan.2, 1930, pp.38

10) "Continuous Treating with Centrifugal Separation"
Oil and Gas Jour., May 24, 1934, p.40

11) Van Dedem, M.I., Jr. "Chemical Methods for Separating
Petroleum Emulsions"
Oil and Gas Jour., p. 65, Aug.12,1937

12) "Providing Chemical Treatment for Petroleum Emulsions"
Oil Weekly, April 27, 1929, p.66

13) Abbot, F. and Boyd, J.H.,Jr. "The Emulsifying Power
of Soap Solutions"
Chem.Eng.Prac. Thesis Case, 1926

14) Allamb, A.B. "Relative Merits of Na Oleate and Laureate in Emulsifying"
Chem.Eng.Prac.Case, 1924

15) E.C.Blarcom "Some Studies of Stabilities of Emulsions"
Chem.Eng.Prac. Thesis, 1926

16) Cobb, R.M. "Many Unaccountable Limitations Shown in Old and New Soaps"
Chem.Eng.Prac.Thesis Case. 1923

17) Connor, H.A. "Breaking H_2O-in-Oil Emulsions"
Chem.Eng.Prac. Thesis Case, 1922.

18) Gartland, A.G. "Finely Divided Solids as Emulsifying Agents" 1922 Chem.Eng.Prac. Thesis Case.

19) Lyon, L.E. "Breaking of Commercial H_2O-in-Oil Emulsions"
Chem.Eng.Prac. Thesis Case, 1923

20) McConnell, S.P. and McFarland, J.B. "Study of Commercial Petroleum Emulsions"
Prac.Case, 1923

21) Mead, E. "Further Studies on Factors Underlying the Stability of Oil-in-H_2O Emulsions"
Chem.Eng.Prac.Case, 1922

22) Freundlich "Cappilary and Colloid Chemistry"
1926 Emulsions, pp.836-838, 605-645.

23) Clayton, Wm. "Theory of Emulsions" 1935
Chap. XII De-Emulsification
Chap. VI Theories of Formation
Chap. VII Dual Emulsions and Emulsion Inversion
Appendix. Separation of Technical Emulsions Particularly Crude Oil Emulsions

24) Thomas, A. W. "Colloid Chemistry" 1934, 1st Ed.
Chap. XVI Emulsions

25) Dunnan, A. E. "Science of Petroleum" 1938 Ed.,Vol.I.
pp.616-637

26) Krantz, J.C. and Gordon, Neil K. "Emulsions and Hydrogen Ion Concentration Effect Upon their Stability" Colloid Symposium Monograph, Vol.6, 1928, pp.173-207

27) Mead and McCoy "A Study of Oil Soluble Emulsifying Agents" Colloid Symposium Monograph, Vol.4, 1926. pp.44-58

28) Harkins, Davis and Clark J.Am.Chem.Soc.,Vol.39, p.549, 1917

29) Stamm and Kraemer J.Phys.Chem.,Vol.30,992 (1926)

30) Yothers and Winston J.Agr.Res.,Vol.31,p.59 (1925)

31) Schlaepfer J. Am.Chem.Soc.,Vol.113,p.522 (1918)

33) Moore J.Am.Chem.Soc., Vol.41,p.940 (1919)

34) Holmes and Anderson Ind.Eng.Chem.,Vol.17, p.280 (1925)

35) Sellner J.Phys.Chem., Vol.42, 1071 (1938)

36) Bhatnager J.Chem.Soc., Vol.117, p.542 (1920)

37) Clowes J.Phys.Chem., Vol.20 p.407 (1916)

38) Parsons and Wilson Ind.and Eng.Chem., Vol.13, p.1116 (1921)

39) Applied Colloid Chemistry, 3rd Ed. New York, p.371 (1932)

40) Bull and Gortner J.Phys.Chem., Vol.35, p.700 (1931)

41) Moyer and Bull J.Gen.Physiol., Vol.19, p.239 (1935)

SYSTEMS	CALLED	EMULSIONS
Mechanical Emulsions		True Emulsions
Factors Involving Stability	Method of Breaking	Factors Involving Stability
Size; Electron Change. Volume Ratio. Relative Density	Settling Centrifuge Heat Electrical	Nature of Emulsifying Agent. Viscosity of oil. Density of oil. Volume ratio.
Emulsifying Agents		Emulsifying Agents
Polyvalent soaps. Soluble colloids. Solids wet by oil	Oil Finely divided	Monovalent soaps. H_2O soluble colloid. Finely divided solids wetted by H_2O
H_2O-in-oil types		Oil-in-H_2O types
Methods of Breaking		Methods of Breaking
SPECIFIC	CHEMICAL	METHODS
Carry to inversion point by Alkali Metal Soaps		Carry to inversion pt. by Metathesis (salts of polyvalent metals)
Organic acids soluble in oil		Salting out agts. for Alkali Soaps
Frequent use of Centrifuge		Destruction of film by Mineral acid or other chemical means

General Physical Methods:

1. Film broken by physical action
2. Electrical
3. Temperature change
4. Excess phase
5. Slow agitation alone or with emulsifier
6. Distillation of one or both under pressure to prevent foaming

Note: The difference of emulsion types is by use of:

1. Inspection of size
2. Stability
3. Briggs drop test