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AN INVESTIGATION OF THE USE OF SURFACE-ACTIVE AGENTS
IN THE SECONDARY RECOVERY OF OIL BY WATER FLOODING

BY

ROBERT P. SCHAFER

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
MASTER OF SCIENCE IN MINING ENGINEERING
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1953

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Approved by -

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INTRODUCTION

The importance of producing oil cannot be emphasized enough in this modern world. Therefore, when primary methods of production seemingly exhaust the oil reservoirs, a secondary method of producing more oil is a necessity. At the present time, secondary methods of oil recovery have developed into a large industry. They are not a new development. The need of introducing compressed air or air-gas mixtures into the wells to increase production was quickly realized. Water flooding methods followed, and at first were restricted to the Eastern fields. Later, about 1935, systematic water flooding methods were developed and applied all over the country.

The system of water flooding involves applying water under pressure to oil-bearing formations by means of injection wells, generally ringed around a production well. These formations are fine-grained, tightly-packed sands, which contain oil left in the formation after the primary method of production. The mechanics of the flooding involves the formation of an oil bank ahead of the advancing water and its removal through the production well.

Water flooding at the present time is a very inefficient process, due to the fact that approximately 25 per cent of the oil is left in the formation after the flood. If this oil, or even a part of it, could be removed by a special kind of water drive it would greatly increase the income of the operator but also would reduce the amount of oil left in the formation which now is unobtainable by any present methods of production.

The use of wetting agents or surface-active chemicals has been

prominent among the methods which have been proposed to reduce the amount of residual oil by water flooding. It is theoretically possible to sweep more oil out of the sand by using surface-active chemicals to lower the surface tension of the water and the interfacial tension between the oil and water. This fact has been known for some time. The principal feature cited in argument against the use of wetting agents has been excessive adsorption onto the reservoir rock surface. The advancing water front of the flood, therefore, has been depleted of these agents before beneficial effects could be realized. The amount and cost of the chemicals required to permit an effective penetration of the reservoir has been entirely out of proportion to the value of the additional oil that might be obtained. However, almost all of the early experiments were conducted using cationic and anionic wetting agents.

During the past few years non-ionic surface-active agents have become available at a low enough price to make their use in water flooding a practical matter. In laboratory tests these chemicals have shown a negligible tendency to become adsorbed by siliceous or clay minerals. From these results, it seems that the problem of excessive adsorption has been solved by the use of non-ionic wetting agents.

Most investigators of this subject have agreed that not all reservoirs respond in the same manner to the same chemical. The reasons why a certain surface-active agent is very effective on one type of reservoir formation and only moderately so or not at all on a different reservoir formation are not known completely at the present time. Therefore, to establish the effectiveness of a certain surface-active chemical upon a particular reservoir, laboratory flooding tests as

well as a pilot flood test should be carried out.

The subject matter of this thesis is the experimental investigation of the effects which certain surface-active chemicals have upon the residual oil content after water flooding of cores taken from Shell-Saunders No. 1 Well, located in the Canary Field, Washington County, Oklahoma. All surface-active agents tested were of the non-ionic water-soluble type. To the author's knowledge, no such investigation has been made using these surface-active chemicals, nor have cores from this field been tested in this manner.

REVIEW OF THE LITERATURE

As early as 1928, flooding agents were being added to water to aid in the removal of the film of oil from the sand particles. Bartell and Miller of the University of Michigan undertook a series of researches for the purpose of determining the functions of these so-called flooding agents. ⁽¹⁾ Their work consisted of a study of the

⁽¹⁾ Bartell, F. E., and Miller, F. L., Degree of Wetting of Silica by Crude Petroleum Oils, Industrial and Engineering Chemistry, Vol. 20, pp. 738-742, July 1, 1928.

degree of wetting of sand or silica by different crude oils. Each type of crude oil exhibits a different degree of adhesion for sand; hence, different amounts of work (to overcome the force of adhesion) must be expended in bringing about the displacement of the absorbed oils* from sand. This problem necessitated the measurement of the adhesion of the crude oils against silica. These measurements were made by a series of displacement pressure determinations. It was concluded that the actual displacement of adsorbed oil from the sand grains depends upon the relative wettability of the sand by the oil, and not upon the pore size. The viscosity of the oil was found to bear no direct relationship to the degree of wetting of the solid by the oil. Although the effects of change in surface tension and interfacial tension give an indication that water will displace the oil, no

* Adsorbed oil refers to the thin film of oil which adheres to the sand grains.

absolute measure of the displacing tendency is given, but only a qualitative indication of the direction in which displacement must go.

In 1947 Terwilliger and Yuster conducted a series of experiments to test the possibilities of applying various chemical agents in water flooding. ⁽²⁾ Three different approaches to this problem were made.

⁽²⁾ Terwilliger, P. L., and Yuster, S. T., Chemical Agents in Water Flooding, World Oil, Vol. 126, No. 1, pp. 54-56, June 2, 1947.

These were: (1) the possible use of oil-soluble wetting agents, (2) the injection of reactive gases; sulfur dioxide and ammonia, and (3) the application of water-soluble surface-inactive compounds. In all the experiments conducted there was no increase in recovery when oil-soluble wetting agents were used. Large amounts of oil-soluble surface-active wetting agents are adsorbed by the sand surface, which would make their use impractical even if recoveries were increased. The reactive gases used did not give results that would encourage further investigation. There seemed to be no effect due to the presence of water-soluble surface-inactive compounds.

If a chemical or a combination of chemicals could be found to inhibit corrosion, inhibit bacteria growth and aid the water in wetting the sand, more economical water flooding methods of secondary oil recovery could be realized. This is the problem which Gregory, Groninger, and Prusick considered in a paper published in 1950. ⁽³⁾ Four tests

⁽³⁾ Gregory, V.P., Groninger, C. R., and Prusick, J. H., Chemical Treatment of Flood Waters Used in Secondary Recovery, Producers Monthly, Vol. 14, No. 7, pp. 27-31, May, 1950.

were used to determine the efficiency of each chemical and combination

of chemicals. These were: (1) a corrosion test, (2) an interfacial tension test, (3) a bactericidal test, and (4) an adsorption test. From the listed test results it was found that Arquad 2 C employed in 5 ppm concentration, sodium nitrite in 50 ppm, and Ethofat 142/15, Ethofat 242/60 or Ethomeen S/20 in 5 ppm were the most effective as well as economical combinations evaluated. The authors feel that a combination of the three chemicals is necessary for complete chemical treatment of flood waters used in secondary oil fields. An economical inorganic antioxidant; a quaternary ammonium compound; and a wetting agent are the three specific chemicals necessary.

In 1951 Prusick, of Armour and Company, reported that a new Armour fatty acid derivative, "Ethomoid HT/60" (hydrogenated tallow amide condensed with 50 moles of ethylene oxide) had been tested, and found to be a potentially useful surface-active agent for increasing the recovery of crude oil.⁽⁴⁾ Laboratory tests have shown that Ethomoid HT/60 at a

⁽⁴⁾ Prusick, J. H., Secondary Oil Recovery, Oil and Gas Journal, Vol. 50, No. 14, pp. 98-8-101, August 9, 1951.

concentration of 5 ppm gave an interfacial tension, Bradford-produced water and Bradford crude oil, of 16 dynes per cm. as against the 35 dynes per cm. obtained on the control. An adsorption test was run for six days with 5 ppm of the above and no change in surface tension was found. Other surface-active agents were tested and all were lost quite rapidly by adsorption. A California producing company in a laboratory flooding test reduced the residual oil to 10% using this chemical with a 10 ppm concentration. This company is currently using this chemical in two different pilot floods.

Breston and Johnson recently reviewed such a pilot flood operating in the Bradford field. ⁽⁵⁾ Four tests with wetting agents in flood

⁽⁵⁾ Breston, J. N., and Johnson, W. E., Experiments with Wetting Agents in the Bradford Field, Producers Monthly, Vol. 16, No. 1, pp. 24-30, November, 1951.

waters were performed in the Bradford field to determine their effect on oil recovery. In all four tests non-ionic water-soluble wetting agents were used which were introduced directly into the flood water. Three of the four tests showed definite increases in oil production rates which can be attributed to the wetting agent. The fourth test has not been operating long enough to permit drawing any conclusions (November, 1951). In two of the three tests the value of the additional production was twice the cost of the wetting agent. It appears that under certain conditions wetting agents may be used profitably to increase oil recovery, at least as far as the Bradford sand is concerned. Surprisingly, there was no significant change in the water intake rates of the injection wells after adding the wetting agents. Only insignificantly small amounts of wetting agents were found in the producing well fluids up to four months after injection. No emulsion trouble was encountered and there was no change in the physical properties of the crude oil.

Calhoun, Stahl, Preston, and Nielson, of Pennsylvania State College, recently reviewed the experiments concerning the use of wetting agents in water flooding conducted in their laboratories since 1933. ⁽⁶⁾ The

⁽⁶⁾ Calhoun, J. C., Stahl, C. D., Preston, F. W., Nielson, R. F., A Review of Laboratory Experiments on Wetting Agents for Water Flooding, Producers Monthly, Vol. 16, No. 1, pp. 15-23, November, 1951.

following observations were made from the experiments they reviewed. The use of wetting agents may reduce the residual oil saturations at times to values below 10% but not all wetting agents can be expected to lower residual oil saturation. It is not clear how much of the wetting agent action is due to wetting changes and how much is due to lowering of interfacial tension. It does appear that the latter is always desirable, but its importance apparently differs between water-wet and oil-wet systems. In oil-wet systems to which a good portion of the reviewed data applies, the lowering of the residual oil correlates fairly well with lowered interfacial tension.

In December, 1951, Torrey reported that recent laboratory research on oil recovery by water flooding, using California reservoir material, has shown a remarkable reduction in residual oil content as a result of the addition of very small quantities of non-ionic ethylene oxide condensation products to the injected water.⁽⁷⁾ Results obtained from

⁽⁷⁾ Torrey, Paul D., Recent Improvements in Water Injection Techniques, Producers Monthly, Vol. 16, No. 2, pp. 25-33, December, 1951.

similar laboratory tests on Bartlesville sand from several Oklahoma fields have shown that oil recovery by water flooding may be increased from 20 to 30 per cent by the use of the same chemicals. The results of the laboratory work have been so encouraging that pilot plant field tests have been put into operation. These field tests have not been running for a sufficient period of time to provide conclusive evidence on the effects of the chemical treatment. However, it can be stated that the results so far obtained (September, 1951) are encouraging.

The effect of non-ionic surface-active compounds should be

distinguished clearly from the generally unsatisfactory experience that has been obtained from former attempts to use many anionic compounds, which tend to become adsorbed quickly on reservoir surfaces. These non-ionic compounds have maintained their surface-active properties after long periods of contact with pulverized oil sands. In laboratory tests they have shown a negligible tendency to become adsorbed by siliceous or clay minerals.

Botset has discussed some current research concerning the secondary recovery of oil by flooding with water containing surface-active compounds, and points out that although some increased recovery by using these agents has been reported, it is not known which of many types of wetting agents is most effective, or what is the optimum amount to be used.⁽⁸⁾ It is very probable that no one wetting agent

⁽⁸⁾ Botset, H. G., An Interpretation of Some Current Research in Secondary Recovery, Producers Monthly, Vol. 16, No. 6, pp. 37-41, April, 1952.

will be found to be the best for all reservoirs, but that a certain amount of experimentation will be necessary to determine the proper material to be used on each reservoir.

Morgan, Prusick, and Torrey found it to be possible to choose specific agents for the beneficial treatment of a particular reservoir material simply because of familiarity with the known characteristics of the many surface-active chemicals available.⁽⁹⁾

⁽⁹⁾ Morgan, L. O., Prusick, J. H., and Torrey, P. D., Application of Surface Chemistry to Oil Recovery, Producers Monthly, Vol. 16, No. 9, pp. 18-24, July, 1952.

As an example, it was found that although Ethomid HT/60 (hydrogenated tallow fatty acid amide reacted with 50 moles of ethylene oxide) gave excellent results on flooding a particular producing sand of Pennsylvanian age, it did not do any good when tried on a Bartlesville sand core of approximately the same geologic age. Here it was found that a specific agent for the Bartlesville formation, at least in this case, was an ester type condensation product, Ethofat 242/60 (Tall oil fatty acids reacted with 50 moles of ethylene oxide).

In another specific case it was possible to establish the tremendous effectiveness of a combination of non-ionic agents. A particular combination of non-ionic surface-active agents increased water injection rates by over 300% as compared with the injection rates obtained in control floods with untreated water. The increase in oil recovery obtained by using this chemical combination at a total concentration of 100 ppm, was from 100 to 135% over that obtained with the untreated water. These tests were made on Lower Cretaceous sand cores under carefully controlled conditions.

Moore and Blum, of the Atlantic Refining Company, recently conducted a series of experiments to understand better the mechanisms by which surface-active agents function.⁽¹⁰⁾ This was done by both

⁽¹⁰⁾ Moore, T. F., and Blum, H. A., Importance of Wettability in Surface-Active Agent Water Flooding, Oil and Gas Journal, Vol. 51, No. 31, pp. 108-111, December 8, 1951.

visual examination of idealized porous media with aid of a microscope, and flood studies on natural and synthetic core materials. While this work was limited to a few porous media and surface-active agents, Moore and Blum believe that the concepts presented are generally applicable.

It was concluded as a result of their work that little or no additional recovery could be realized by the use of surface-active agents in water-wet reservoirs at water breakthrough. On the other hand, in oil-wet rocks, it was found that additional recovery of oil may be possible using surface-active agents in the flooding water, although it is not certain whether this would be economical. The reason that oil-wet systems can benefit by use of surface-active agents is that the oil left behind the water front is a continuous phase in contrast to the discontinuous distribution in the water-wet system. No consideration was given to the possible benefits that might accrue from using surface-active agents to increase the injection rates, to kill bacteria in flood water, or to trace injected water.

WHY SURFACE-ACTIVE AGENTS INCREASE OIL RECOVERY

When considering the recovery of oil by water flooding, it should be kept in mind that oil normally occurs in the interstices and pore spaces of porous sand or limestone formations. The oil is retained there by the action of capillary forces or as an adsorbed film on the surface of the sand grains.

It seems desirable to review briefly the fundamental concepts of surface forces, before discussing the problem of fluid flow. The surface tension of a liquid is defined physically as the force exerted on a straight line of unit length in the surface, in a direction parallel to the surface but perpendicular to the line. The surface tension operates to maintain the surface area at a minimum. It is expressed as dynes per centimeter. The term "interfacial tension" is used to refer to the tension between two liquids phases in contact or between a liquid and a solid.

The interfacial tension between a solid and a liquid generally cannot be measured. When a drop of liquid is placed on a flat solid surface, it assumes one of three shapes: ⁽¹¹⁾

(11) Andresen, K. H., Torrey, P. D., and Dickey, P. A., Capillary and Surface Phenomena in Secondary Recovery, A. P. I., Annual Meeting 24 (IV), pp. 182-188, 1943.

1. The liquid remains on the surface as a spherical drop, i.e., it will not wet the surface.

2. The drop remains lying in equilibrium with a definite angle of contact with the solid surface. Then the following relationship

exists:

$$S_{sg} = S_{lg} \cos \theta + S_{sl}; \text{ or } S_{sg} - S_{sl} = S_{lg} \cos \theta = A$$

Where:

S_{sg} = the interfacial tension between solid and gas.

S_{lg} = the interfacial tension between liquid and gas.

S_{sl} = the interfacial tension between solid and liquid.

θ = the contact angle between the solid and the liquid-gas interface measured through the water phase.

A = the adhesion tension of liquid against solid.

The difference between the interfacial tensions of the solid and gas, and solid and liquid, is called adhesion tension. It may be determined by the angle of contact between the solid and the liquid-gas interface and the interfacial tension between the liquid and gas.

3. The drop spreads over the surface, completely wetting it. In this case the contact angle is zero, and the adhesion tension is equal to or greater than the surface tension of the wetting fluid. As the contact angle approaches zero, the adhesion tension approaches the surface tension of the wetting fluid.

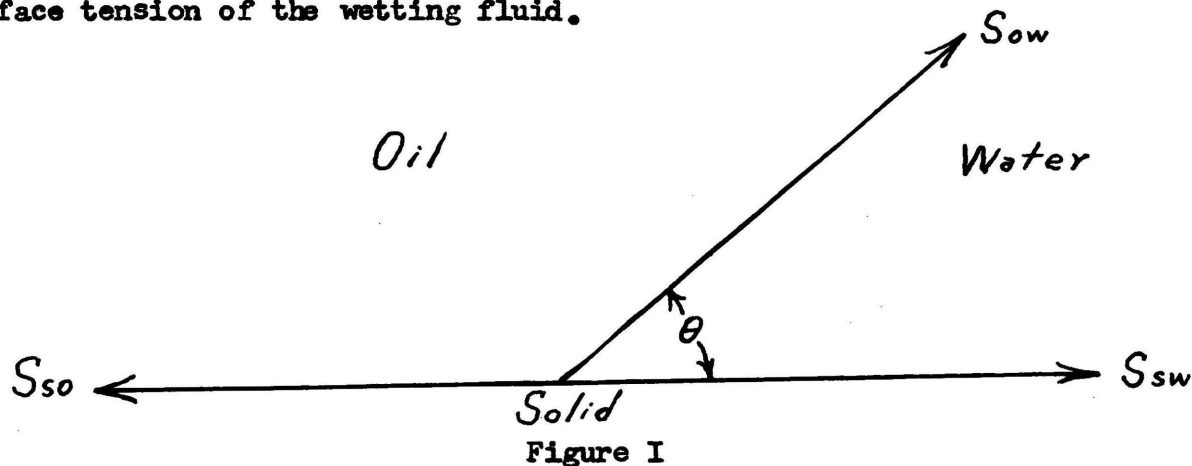


Diagram of Interfacial Forces at the Contact of
Oil, Water, and Solid

The adhesion-tension relationships under conditions where water and oil are brought in contact with the surface of a solid have been illustrated by Benner, Riches and Bartell, as shown in Figure I. ⁽¹²⁾

(12) Benner, F. C., Riches, W. W., Bartell, F. E., Nature and Importance of Surface Forces in Production of Petroleum, Drilling and Production Practice, pp. 442-446, 1938.

S_{SO} , S_{SW} , and S_{OW} represent the interfacial tension at the solid-oil, solid-water, and water-oil interfaces. If S_{SO} is greater than $S_{OW} - S_{SW}$, the water will spread over the surface of the solid, displacing the oil therefrom. If S_{SO} should be less than $S_{OW} - S_{SW}$, the system will come to equilibrium at some definite contact angle θ , measured through the water phase. Thus at equilibrium:

$$S_{SO} - S_{SW} = S_{OW} \cos \theta$$

And: $S_{SO} - S_{SW} = A_{SW} - A_{SO} = S_{OW} \cos \theta$

Where: A_{SW} = the adhesion tension of water against solid.

A_{SO} = the adhesion tension of oil against solid.

The magnitude of A_{SW} and A_{SO} determine whether a given solid will be wet to a greater extent by water or oil. As determined by Bartell and Miller, no oil investigated had an adhesion tension against pure silica greater than that of water, although there is considerable variation in the degree of wetting of silica in crude from different sources. ⁽¹³⁾ If the adhesion tension (A_{SW}) between the solid and the

(13) Bartell, op. cit., pp. 738-742.

water exceeds the adhesion tension (A_{SO}) between the solid and the oil, water will spontaneously displace oil from the solid. In like manner if the value of A_{SO} approaches that of A_{SW} , the amount of spontaneous

displacement will decrease and become zero when A_{SO} equals A_{SW} . If A_{SO} exceeds A_{SW} the oil will spontaneously displace water from the solid and the solid may be considered to be preferentially wet by oil. Therefore, it can be deduced that an oil having a low adhesion tension to the reservoir rock should react more favorably to water flooding than one having an adhesion tension approaching that of injected water.

The resultant of the forces expressed as interfacial tensions may be determined as capillary pressure. It is well known that a liquid in a capillary tube will rise or fall to a certain level above or below the level of the fluid in which the end of the tube is immersed. The equilibrium height at which the liquid will stand is proportional to the capillary pressure; it is greater, the smaller the tube. Under these conditions, capillary pressure may be defined as the pressure exerted by two immiscible liquids confined within a channel of capillary dimensions, which causes the interface to move along the channel. More generally, capillary pressure is the pressure differential across the interface between two fluid phases (oil and water, oil and gas, or water and gas). In equilibrium, the capillary pressure acts to maintain the interface in a certain position opposing any change in direction. It is determined as:⁽¹⁴⁾

(14) Leverett, M. C., Capillary Behavior in Porous Solids, Trans. Am. Inst. Mining Met. Engrs., 142, pp. 152-68, 1941.

$$P_c = S \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

Where:

P_c = the capillary pressure.

S = the interfacial tension.

R_1 and R_2 = the two principal radii of the curvature of the interface.

By definition, the capillary pressure is a pressure differential across the interface between two fluids. In the case of a porous medium fully saturated with one fluid, motion of another displacing fluid will not take place unless the applied pressure is able to exceed the capillary pressure at the interface of the two fluids.

Benner, Dodd and Bartell determined the interfacial tensions and contact angles of water and oil against silica and then calculated the "displacement pressure" for the displacement of oil when it occupies 100 per cent of the pore volume.⁽¹⁵⁾ This was determined as:

(15) Benner, F. C., Dodd, C. G., and Bartell, F. E., Evaluation of Effective Displacement Pressures for Petroleum-Oil-Water-Silica Systems, "Drilling and Production Practice, pp. 169-77, 1942.

$$P_d = \frac{2S_{wo} \cos \theta}{rg}$$

where: P_d = the displacement pressure.
 r = the effective mean pore radius.
 g = the gravitational constant.

The observed pressure required to displace oil with water from crushed compressed silica was found to check the calculated values in a satisfactory manner.

When a water-wet porous medium containing oil and connate water is water flooded, the injection water first displaces the connate water, which in turn displaces the oil. The oil left behind the water flood front is in the form of discontinuous ganglia. Since the oil is a non-wetting phase these ganglia occupy the funicular region of the pore space.

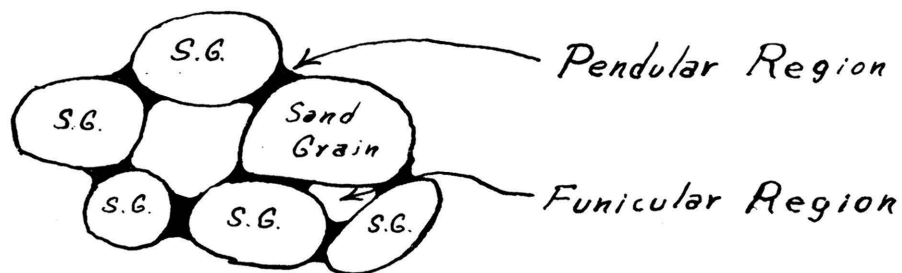


Figure II

Diagram of Fluid Distribution at the
Contacts of Sand Grains

Considering the mobility of the connate water, it is probable that no surface-active agents can be brought to a leading edge of the flood front. Since this is true, no possible benefit in the recovery of oil at water breakthrough should be expected. Therefore, to aid in the recovery of oil, the surface-active agents should be beneficial in the displacement of the bypassed residual oil ganglia.

To do this, the capillary force exerted by the water must be overcome or reduced to allow the oil to flow through the water filled openings, or the size and shape of these discontinuous ganglia must be changed. These changes may be brought about by increasing the pressure gradient thereby increasing the displacement pressure and by the addition of surface-active agents to reduce the interfacial tension. To increase the pressure gradient across a reservoir much above present practice does not seem feasible. An alternative is to reduce the interfacial tension by the use of surface-active chemicals.

When an oil-wet porous medium is water flooded, the injected water proceeds through the funicular region, leaving extensive quantities

of oil in the pendular region as a film on the matrix particles. In order that the oil may be displaced from this oil-wet system, the water must be made to penetrate the regions where oil is present. To do this, either the pressure gradient must be increased or the interfacial tension must be decreased. An increase in pressure gradient or a decrease in interfacial tension will lead to a higher recovery of oil.

DESCRIPTION OF EXPERIMENTAL PROCEDURE

Preliminary Examination of Surface-Active Agents

Several samples of commercial surface-active agents were obtained from each of the following companies:

The Dow Chemical Company.

Victor Chemical Works.

I. E. Du Pont De Ne Mours and Company.

Rohm and Haas Company.

Monsanto Chemical Company.

Union Carbide and Carbon Corporation.

Atlas Powder Company.

These surface-active agents were all of the non-ionic water-soluble type.

Solutions of each surface-active agent at a concentration of 100 ppm were prepared using distilled water as the solvent. The surface tension of these solutions was found by using a Du Nouy Tensiometer.

The surface-active agents submitted by the above mentioned companies, and the surface tension of these agents are shown in Table I and Table II.

Table I
Surface-Active Agent Data

The Dow Chemical Company

- 1.) Dowanol 33 B 27.7 dynes/cm.
- 2.) Dowanol 50 B 28.8 dynes/cm.

Victor Chemical Works

- 1.) Victawet 12 28.8 dynes/cm.
- 2.) Victawet 14 28.8 dynes/cm.
- 3.) Victamul 24 C 31.6 dynes/cm.

E. I. Du Pont De Ne Mours and Company

- 1.) Duponol 80 33.0 dynes/cm.
- 2.) Duponol G 35.0 dynes/cm.
- 3.) Alkanol DW Solution 34.0 dynes/cm.

Rohm and Haas Company

- 1.) Triton X-155 32.0 dynes/cm.
- 2.) Triton X-100 29.0 dynes/cm.

Monsanto Chemical Company

- 1.) Sterox SK 31.7 dynes/cm.

Union Carbide and Carbon Corporation

- 1.) "Tergitol" Dispersant NPG 30.0 dynes/cm.
- 2.) "Tergitol" Penetrant EH 32.0 dynes/cm.
- 3.) "Tergitol" Penetrant O8 30.0 dynes/cm.
- 4.) "Tergitol" Penetrant 4 31.0 dynes/cm.

Table II
Surface-Active Agent Data

Atlas Powder Company

| | |
|-------------------|----------------|
| 1.) Tween 21 | 37.0 dynes/cm. |
| 2.) Tween 80 | 41.0 dynes/cm. |
| 3.) G-672 Lot 104 | 35.0 dynes/cm. |
| 4.) Atlox 1045 A | 42.0 dynes/cm. |

Test Procedure

Each surface-active agent was tested in a similar manner. The test procedure consisted of the following steps:

- (1) Extraction of all oil in the core.
- (2) Saturation of the core with oil.
- (3) Flooding the core and measuring the amount of oil produced.

The oil originally present in the core was extracted by means of the Soxhlet Extraction Apparatus. The apparatus was assembled as shown in Figure III and the core was placed in the Soxhlet tube of the apparatus. The boiling flask which contained carbon tetrachloride was heated. The vapor from the heated solvent passed up through the vapor tube and into the condenser tube. Here the vapor was condensed, and the fluid dropped on the core. This condensed solvent dissolved the oil in the core. The solvent plus the dissolved oil accumulated in the lower part of the containing glass tube until it reached the overflow point of the siphon tube. When the liquid level reached this point all of the accumulated liquid was siphoned back into the flask.

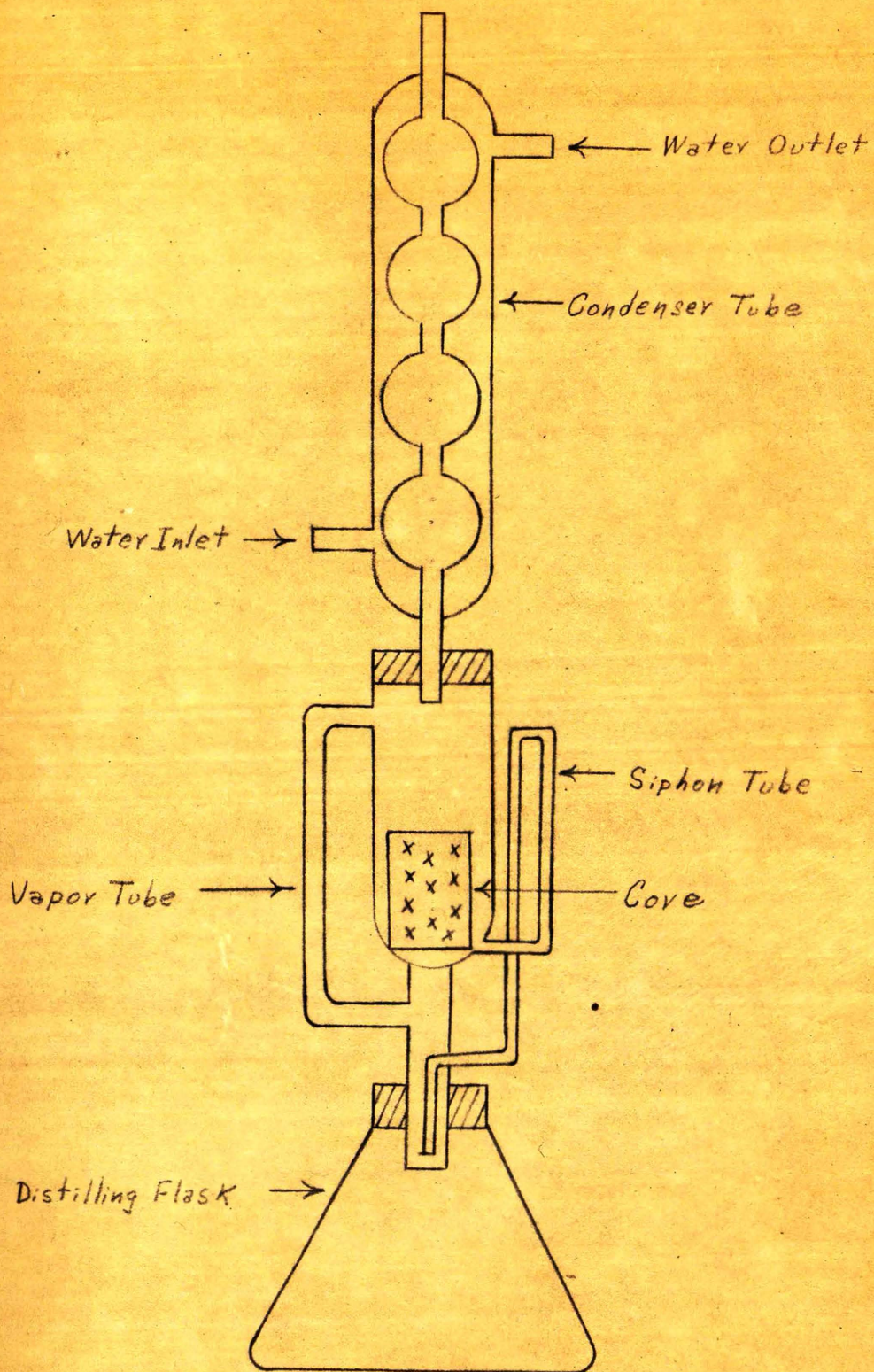


FIGURE III

SOXHLET EXTRACTION APPARATUS

This process was continued for two hours, at which time all of the oil was supposedly dissolved out of the core. The heater was removed and the apparatus allowed to cool. The core was removed and placed in an oven to dry overnight. After drying, the core was allowed to cool to room temperature in a desiccator and weighed on an analytical balance (W_1).

The core was saturated by submerging it in oil in a sealed container, evacuating the core by applying a vacuum to the system and relieving the vacuum. The core was weighed again (W_2). The weight of oil present in the core was given by $W_2 - W_1$. The specific gravity (S.G.) of the crude oil used in these tests was found with an A.P.I. hydrometer. The volume of oil present in the core was given by $(W_2 - W_1)/S.G.$

The core was mounted in the core holder as shown in Figure IV. Sealing wax was used to seal the core to the core holder to prevent by-passing of the flood water. The apparatus shown in Figure V was assembled and the oil burette attached to the core holder and filled with water. Data was obtained on the amount of oil recovery by a direct reading of the oil burette. In all tests flow was vertically upward.

A control flood for each core was made using distilled water as the flood water. Comparison of data obtained from the control flood with the data obtained from flood tests in which a surface-active agent was added to the flood water shows the effect, if any, that these chemicals have upon the residual oil content of the core. To test the reproducibility of the data two control floods were made using Core No. 1.

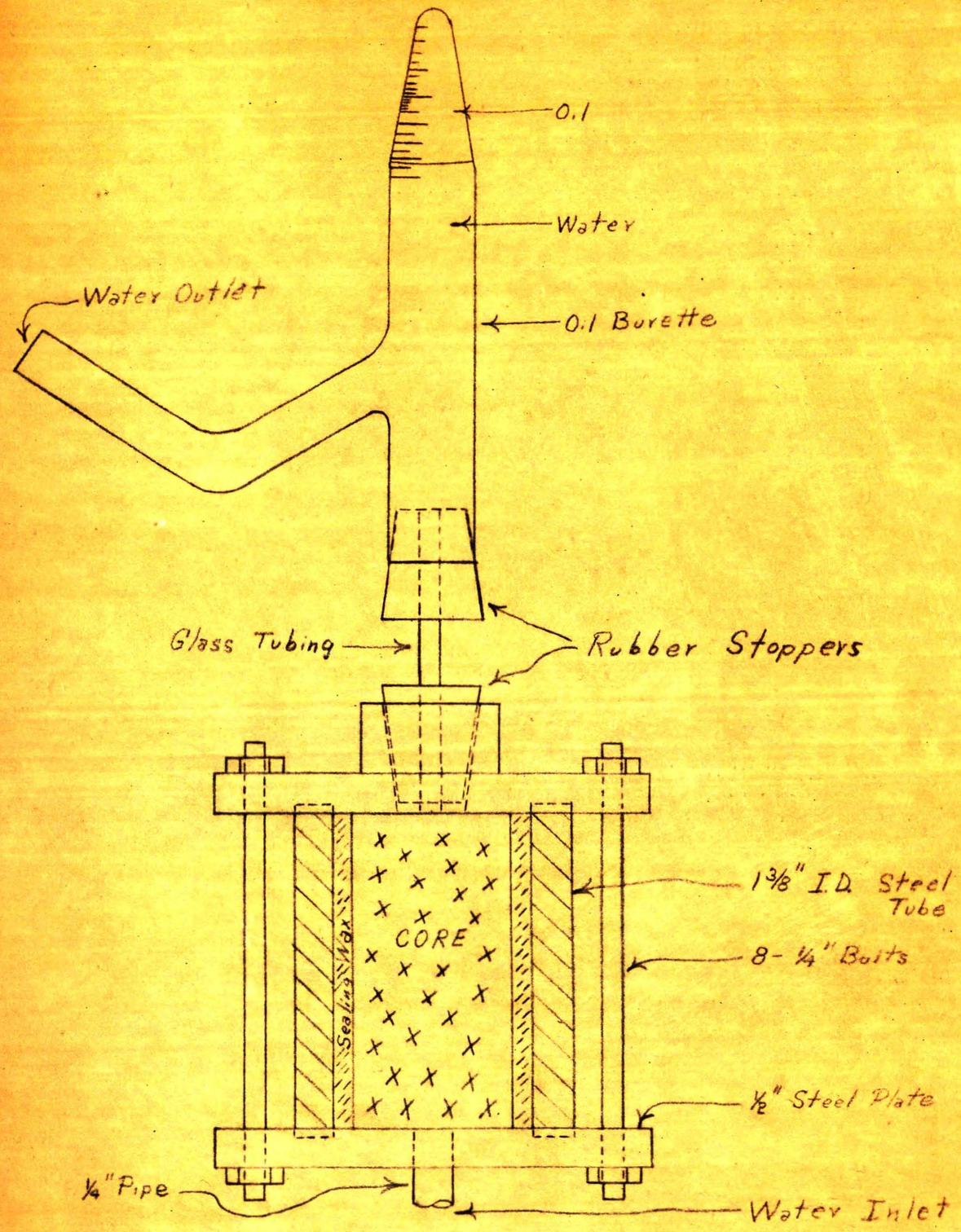


FIGURE IV
CORE HOLDER and BURETTE ASSEMBLY

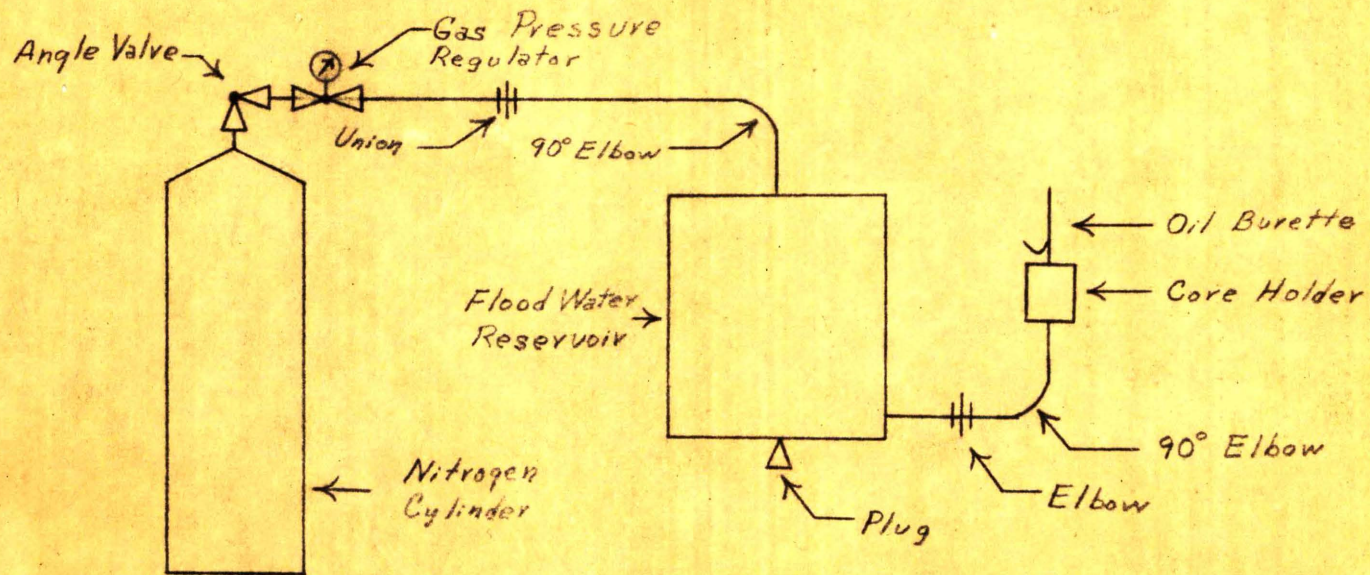


FIGURE V

SCHEMATIC DIAGRAM of FLOOD SYSTEM

Table III
Description of Core No. 1

Porosity: 0.215

Permeability: 350 md.

Core Dimensions:

| <u>Run</u> | <u>Length (cm.)</u> | <u>Diameter (cm.)</u> |
|------------|---------------------|-----------------------|
| 1 | 4.03 | 2.506 |
| 2 | 4.04 | 2.503 |
| 3 | 4.03 | 2.508 |
| 4 | 4.03 | 2.508 |
| 5 | 4.05 | 2.509 |
| 6 | 4.04 | 2.509 |
| 7 | 4.05 | 2.507 |
| 8 | 4.03 | 2.504 |
| 9 | 4.05 | 2.503 |
| 10 | 4.04 | 2.505 |
| Avg. | 4.03 | 2.506 |

$$\begin{aligned}
 \text{Volume of Core} &= \frac{\pi d^2 l}{4} \\
 &= \frac{\pi (2.506)^2 (4.03)}{4} \\
 &= 19.72 \text{ cm}^3.
 \end{aligned}$$

$$\begin{aligned}
 \text{Pore Volume of Core} &= \text{Volume} \times \text{Porosity} \\
 &= (19.72)(0.215) \\
 &= 4.24 \text{ cm}^3
 \end{aligned}$$

Table IV
Flood Test No. 1

Core: No. 1

Flood water used: Distilled water.

Surface tension of flood water: 71 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.24 cm.³

| | |
|-------------------------------------|------------|
| Weight of core after saturation | 45.4722 g. |
| Weight of core before saturation | 42.3992 g. |
| Weight of oil in core | 3.0730 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.55 ml. |
| Initial oil saturation $3.55/4.24$ | 0.838 |
| Volume of oil in separator | 2.40 ml. |
| Volume of oil remaining in core | 1.15 ml. |
| Residual oil saturation $1.15/4.24$ | 0.271 |
| Per cent recovery $(2.4/3.55)(100)$ | 67.6% |

Table V
Flood Test No. 2

Core: No. 1

Flood water used: Distilled water.

Surface tension of flood water: 71 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 4.24 cm.³

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 45.2090 g. |
| Weight of core before saturation | 42.6757 g. |
| Weight of oil in core | 2.5333 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.92 ml. |
| Initial oil saturation $2.92/4.24$ | 0.690 |
| Volume of oil in separator | 1.90 ml. |
| Volume of oil remaining in core | 1.02 ml. |
| Residual oil saturation $1.02/4.24$ | 0.241 |
| Per cent recovery $(1.90/2.92)(100)$ | 65.1% |

Table VI
Flood Test No. 3

Core: No. 1.

Flood water used: Distilled water with Victamul 24c (100 ppm).

Surface tension of flood water: 31.6 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 4.24 cm.³

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 45.0290 g. |
| Weight of core before saturation | 42.6035 g. |
| Weight of oil in core | 2.4255 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.80 ml. |
| Initial oil saturation $2.80/4.24$ | 0.655 |
| Volume of oil in separator | 1.55 ml. |
| Volume of oil remaining in core | 1.25 ml. |
| Residual oil saturation $1.25/4.24$ | 0.295 |
| Per cent recovery $(1.55/2.80)(100)$ | 55.3% |

Table VII
Flood Test No. 4

Core: No. 1

Flood water used: Distilled water with Victawet 12(100 ppm).

Surface tension of flood water: 28.8 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 4.24 cm.³

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 45.3764 g. |
| Weight of core before saturation | 42.6453 g. |
| Weight of oil in core | 2.7311 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.155 ml. |
| Initial oil saturation $3.155/4.24$ | 0.744 |
| Volume of oil in separator | 2.70 ml. |
| Volume of oil remaining in core | 0.455 ml. |
| Residual oil saturation $0.455/4.24$ | 0.1072 |
| Per cent recovery $(2.70/3.155)(100)$ | 85.7% |

Table VIII
Flood Test No. 5

Core: No. 1

Flood water used: Distilled water with Dowanol 50B (100 ppm).

Surface tension of flood water: 28.8 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 4.24 cm.³

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 45.3944 g. |
| Weight of core before saturation | 42.8071 g. |
| Weight of oil in core | 2.5873 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.99 ml. |
| Initial oil saturation $2.99/4.24$ | 0.705 |
| Volume of oil in separator | 2.60 ml. |
| Volume of oil remaining in core | 0.39 ml. |
| Residual oil saturation $0.39/4.24$ | 0.092 |
| Per cent recovery $(2.60/2.99)(100)$ | 87.0% |

Table IX
Description of Core No. 2

Porosity: 0.184

Permeability: 220 md.

Core Dimensions:

| <u>Run</u> | <u>Length (cm.)</u> | <u>Diameter (cm.)</u> |
|------------|---------------------|-----------------------|
| 1 | 3.89 | 2.499 |
| 2 | 3.90 | 2.506 |
| 3 | 3.90 | 2.498 |
| 4 | 3.89 | 2.504 |
| 5 | 3.88 | 2.502 |
| 6 | 3.89 | 2.503 |
| 7 | 3.88 | 2.502 |
| 8 | 3.88 | 2.500 |
| 9 | 3.90 | 2.503 |
| 10 | 3.89 | 2.502 |
| Avg. | 3.89 | 2.502 |

$$\begin{aligned}
 \text{Volume of core} &= \frac{\pi d^2 l}{4} \\
 &= \frac{\pi (2.502)^2 (3.89)}{4} \\
 &= 19.13 \text{ cm.}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{Pore Volume of Core} &= (\text{Volume})(\text{Porosity}) \\
 &= (19.13)(0.184) \\
 &= 3.52 \text{ cm.}^3
 \end{aligned}$$

Table X
Flood Test No. 6

Core No. 2

Flood water used: Distilled water.

Surface tension of flood water: 71 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 3.52 cm^3 .

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.8920 g. |
| Weight of core before saturation | 41.0274 g. |
| Weight of oil in core | 2.8646 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.31 ml. |
| Initial oil saturation $3.31/3.52$ | 0.941 |
| Volume of oil in separator | 2.00 ml. |
| Volume of oil remaining in core | 1.31 ml. |
| Residual oil saturation $1.31/3.52$ | 0.372 |
| Per cent recovery $(2.00/3.31)(100)$ | 60.5% |

Table XI
Flood Test No. 7

Core: No. 2

Flood water used: Distilled water with "Tergitol" Dispersant NPG (100 ppm)

Surface tension of flood water: 30.0 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 3.52 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 43.8334 g. |
| Weight of core before saturation | 41.2401 g. |
| Weight of oil in core | 2.5933 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.995 ml. |
| Initial oil saturation $2.995/3.52$ | 0.850 |
| Volume of oil in separator | 2.05 ml. |
| Volume of oil remaining in core | 0.945 ml. |
| Residual oil saturation $0.945/3.53$ | 0.268 |
| Per cent recovery $(2.05/2.995)(100)$ | 68.5% |

Table XII
Flood Test No. 8

Core: No. 2

Flood water used: Distilled water with "Tergitol" Penetrant EH (100 ppm)

Surface tension of flood water: 32.0 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 3.52 cm³.

| | |
|------------------------------------|------------|
| Weight of core after saturation | 43.9355 g. |
| Weight of core before saturation | 41.3303 g. |
| Weight of oil in core | 2.6052 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.01 ml. |
| Initial oil saturation 3.01/3.52 | 0.855 |
| Volume of oil in separator | 2.05 ml. |
| Volume of oil remaining in core | 0.96 ml. |
| Residual oil saturation 0.96/3.52 | 0.272 |
| Per cent recovery (2.05/3.01)(100) | 68.1% |

Table XIII
Flood Test No. 9

Core: No. 2

Flood water used: Distilled water with Victawet 14 (100 ppm).

Surface tension of flood water: 28.8 dynes/cm.

Pressure source: Compressed air.

Pore volume of core: 3.52 cm^3 .

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.9470 g. |
| Weight of core before saturation | 41.4033 g. |
| Weight of oil in core | 2.5437 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.94 ml. |
| Initial oil saturation $2.94/3.52$ | 0.836 |
| Volume of oil in separator | 1.70 ml. |
| Volume of oil remaining in core | 1.24 ml. |
| Residual oil saturation $1.24/3.52$ | 0.353 |
| Per cent recovery $(1.70/2.94)(100)$ | 58.0% |

Table XIV
Flood Test No. 10

Core: No. 2

Flood water used: Distilled water with Tween 80 (100 ppm).

Surface tension of flood water: 41.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.52 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 43.8730 g. |
| Weight of core before saturation | 41.4180 g. |
| Weight of oil in core | 2.4550 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.835 ml. |
| Initial oil saturation $2.835/3.52$ | 0.795 |
| Volume of oil in separator | 1.60 ml. |
| Volume of oil remaining in core | 1.235 ml. |
| Residual oil saturation $1.235/3.52$ | 0.351 |
| Per cent recovery $(1.60/2.835)(100)$ | 57.5% |

Table XV
Flood Test No. 11

Core: No. 2

Flood water used: Distilled water with Duponol 80 (100 ppm).

Surface tension of flood water: 33.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.52 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 43.9070 g. |
| Weight of core before saturation | 41.3560 g. |
| Weight of oil in core | 2.5510 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.945 ml. |
| Initial oil saturation $2.945/3.52$ | 0.838 |
| Volume of oil in separator | 1.80 ml. |
| Volume of oil remaining in core | 1.145 ml. |
| Residual oil saturation $1.145/3.52$ | 0.326 |
| Per cent recovery $(1.80/2.945)(100)$ | 61.1% |

Table XVI
Flood Test No. 12

Core: No. 2.

Flood water used: Distilled water with Tween 21 (100 ppm).

Surface tension of flood water: 37.0 dynes/cm.

Pressure source: Nitrogen

Pore volume of core: 3.52 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 43.9894 g. |
| Weight of core before saturation | 41.4102 g. |
| Weight of oil in core | 2.5792 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.975 ml. |
| Initial oil saturation $2.975/3.52$ | 0.845 |
| Volume of oil in separator | 1.80 ml. |
| Volume of oil remaining in core | 1.175 ml. |
| Residual oil saturation $1.175/3.52$ | 0.334 |
| Per cent recovery $(1.80/2.975)(100)$ | 60.5% |

Table XVII
Description of Core No. 3

Porosity: 0.215

Permeability: 345 md.

Core Dimensions:

| <u>Run</u> | <u>Length (cm.)</u> | <u>Diameter (cm.)</u> |
|------------|---------------------|-----------------------|
| 1 | 3.90 | 2.494 |
| 2 | 3.91 | 2.500 |
| 3 | 3.91 | 2.492 |
| 4 | 3.90 | 2.498 |
| 5 | 3.89 | 2.496 |
| 6 | 3.89 | 2.492 |
| 7 | 3.91 | 2.498 |
| 8 | 3.90 | 2.494 |
| 9 | 3.90 | 2.496 |
| 10 | 3.89 | 2.497 |
| Avg. | 3.90 | 2.496 |

$$\begin{aligned} \text{Volume of Core} &= \frac{\pi d^2 l}{4} \\ &= \frac{\pi (2.496)^2 (3.90)}{4} \\ &= 19.07 \text{ cm}^3. \end{aligned}$$

$$\begin{aligned} \text{Pore Volume of Core} &= (\text{Volume})(\text{Porosity}) \\ &= (19.07)(0.215) \\ &= 4.10 \text{ cm}^3. \end{aligned}$$

Table XVIII
Flood Test No. 13

Core: No. 3

Flood water used: Distilled water.

Surface tension of flood water: 71 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.10 cm^3 .

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 44.1945 g. |
| Weight of core before saturation | 41.2435 g. |
| Weight of oil in core | 2.9510 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.405 ml. |
| Initial oil saturation $3.405/4.10$ | 0.831 |
| Volume of oil in separator | 2.05 ml. |
| Volume of oil remaining in core | 1.355 ml. |
| Residual oil saturation $1.355/4.10$ | 0.331 |
| Per cent recovery $(2.05/3.405)(100)$ | 60.2% |

Table XIX

Flood Test No. 14

Core: No. 3

Flood water used: Distilled water with Triton X-100 (100 ppm).

Surface tension of flood water: 29.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.10 cm^3 .

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 44.3220 g. |
| Weight of core before saturation | 41.4533 g. |
| Weight of oil in core | 2.8687 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.315 ml. |
| Initial oil saturation $3.315/4.10$ | 0.809 |
| Volume of oil in separator | 1.90 ml. |
| Volume of oil remaining in core | 1.415 ml. |
| Residual oil saturation $1.415/4.10$ | 0.345 |
| Per cent recovery $(1.80/3.315)(100)$ | 57.3% |

Table XX
Flood Test No. 15

Core: No. 3

Flood water used: Distilled water with Triton X-155 (100 ppm).

Surface tension of flood water: 32.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.10 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 44.4020 g. |
| Weight of core before saturation | 41.5592 g. |
| Weight of oil in core | 2.8428 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.280 ml. |
| Initial oil saturation $3.280/4.10$ | 0.802 |
| Volume of oil in separator | 2.10 ml. |
| Volume of oil remaining in core | 1.18 ml. |
| Residual oil saturation $1.18/3.52$ | 0.288 |
| Per cent recovery $(2.10/3.280)(100)$ | 64.0% |

Table XXI
Flood Test No. 16

Core: No. 3

Flood water used: Distilled water with Alkonol DW Solution (100 ppm).

Surface tension of flood water: 34.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.10 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 44.2275 g. |
| Weight of core before saturation | 41.5823 g. |
| Weight of oil in core | 2.6452 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.055 ml. |
| Initial oil saturation $3.055/4.10$ | 0.745 |
| Volume of oil in separator | 1.70 ml. |
| Volume of oil remaining in core | 1.355 ml. |
| Residual oil saturation $1.355/4.10$ | 0.330 |
| Per cent recovery $(1.70/3.055)(100)$ | 55.7% |

Table XXII
Flood Test No. 17

Core: No. 3

Flood water used: Distilled water with Duponol G (100 ppm).

Surface tension of flood water: 35.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.10 cm³.

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 44.0025 g. |
| Weight of core before saturation | 41.6259 g. |
| Weight of oil in core | 2.3766 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.74 ml. |
| Initial oil saturation $2.74/4.10$ | 0.670 |
| Volume of oil in separator | 1.40 ml. |
| Volume of oil remaining in core | 1.34 ml. |
| Residual oil saturation $1.34/4.10$ | 0.327 |
| Per cent recovery $(1.40/2.74)(100)$ | 51.1% |

Table XXIII
Flood Test No. 18

Core: No. 3

Flood water used: Distilled water with Sterox SK (100 ppm).

Surface tension of flood water: 31.7 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 4.10 cm³.

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 44.4046 g. |
| Weight of core before saturation | 41.6713 g. |
| Weight of oil in core | 2.7333 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 3.15 ml. |
| Initial oil saturation $3.15/4.10$ | 0.770 |
| Volume of oil in separator | 2.10 ml. |
| Volume of oil remaining in core | 1.05 ml. |
| Residual oil saturation $1.05/4.10$ | 0.256 |
| Per cent recovery $(2.10/3.15)(100)$ | 66.8% |

Table XXIV
Description of Core No. 4

Porosity: 0.159

Permeability: 200 md.

Core Dimensions:

| <u>Run</u> | <u>Length (cm.)</u> | <u>Diameter (cm.)</u> |
|------------|---------------------|-----------------------|
| 1 | 3.87 | 2.494 |
| 2 | 3.86 | 2.498 |
| 3 | 3.86 | 2.502 |
| 4 | 3.87 | 2.500 |
| 5 | 3.88 | 2.498 |
| 6 | 3.87 | 2.496 |
| 7 | 3.88 | 2.499 |
| 8 | 3.87 | 2.497 |
| 9 | 3.86 | 2.498 |
| 10 | 3.88 | 2.498 |
| Avg. | 3.87 | 2.498 |

$$\begin{aligned}
 \text{Volume of Core} &= \frac{\pi d^2 l}{4} \\
 &= \frac{\pi (2.498)^2 (3.87)}{4} \\
 &= 18.96 \text{ cm}^3.
 \end{aligned}$$

$$\begin{aligned}
 \text{Pore Volume of Core} &= (\text{Volume})(\text{Porosity}) \\
 &= (18.96)(0.159) \\
 &= 3.014 \text{ cm}^3.
 \end{aligned}$$

Table XXV
Flood Test No. 19

Core: No. 4

Flood water used: Distilled water.

Surface tension of flood water: 71 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.014 cm^3 .

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.5591 g. |
| Weight of core before saturation | 41.2185 g. |
| Weight of oil in core | 2.3406 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.70 ml. |
| Initial oil saturation $2.70/3.014$ | 0.897 |
| Volume of oil in separator | 1.70 ml. |
| Volume of oil remaining in core | 1.00 ml. |
| Residual oil saturation $1.00/3.014$ | 0.332 |
| Per cent recovery $(1.70/2.70)(100)$ | 63.7% |

Table XXVI
Flood Test No. 20

Core: No. 4

Flood water used: Distilled water with Atlox 1045A (100 ppm).

Surface tension of flood water: 42.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.014 cm³.

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.5381 g. |
| Weight of core before saturation | 40.9933 g. |
| Weight of oil in core | 2.5448 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.94 ml. |
| Initial oil saturation $2.94/3.014$ | 0.975 |
| Volume of oil in separator | 2.00 ml. |
| Volume of oil remaining in core | 0.94 ml. |
| Residual oil saturation $0.94/3.014$ | 0.312 |
| Per cent recovery $(2.00/2.94)(100)$ | 68.1% |

Table XXVII
Flood Test No. 21

Core: No. 4

Flood water used: Distilled water with G-672 (100 ppm).

Surface tension of flood water: 35.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.014 cm³.

| | |
|---------------------------------------|------------|
| Weight of core after saturation | 43.4870 g. |
| Weight of core before saturation | 41.2475 g. |
| Weight of oil in core | 2.2395 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.585 ml. |
| Initial oil saturation $2.585/3.014$ | 0.858 |
| Volume of oil in separator | 1.60 ml. |
| Volume of oil remaining in core | 0.985 ml. |
| Residual oil saturation $0.985/3.014$ | 0.327 |
| Per cent recovery $(1.60/2.585)(100)$ | 61.9% |

Table XXVIII
Flood Test No. 22

Core: No. 4

Flood water used: Distilled water with "Tergitol" Penetrant 08 (100 ppm).

Surface tension of flood water: 30.0 dynes/cm.

Pressure source: Nitrogen;

Pore volume of core: 3.014 cm^3 .

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.5050 g. |
| Weight of core before saturation | 41.3600 g. |
| Weight of oil in core | 2.1450 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.48 ml. |
| Initial oil saturation $2.48/3.014$ | 0.823 |
| Volume of oil in separator | 1.90 ml. |
| Volume of oil remaining in core | 0.58 ml. |
| Residual oil saturation $0.58/3.014$ | 0.192 |
| Per cent recovery $(1.90/2.48)(100)$ | 76.6% |

Table XXIX

Flood Test No. 23

Core: No. 4

Flood water used: Distilled water with Dowanol 33B (100 ppm).

Surface tension of flood water: 27.7 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.014 cm³.

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.5502 g. |
| Weight of core before saturation | 41.3574 g. |
| Weight of oil in core | 2.1928 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.53 ml. |
| Initial oil saturation $2.53/3.014$ | 0.84 |
| Volume of oil in separator | 1.80 ml. |
| Volume of oil remaining in core | 0.73 ml. |
| Residual oil saturation $0.73/3.014$ | 0.242 |
| Per cent recovery $(1.80/2.53)(100)$ | 71.2% |

Table XXX
Flood Test No. 24

Core: No. 4

Flood water used: Distilled water with "Tergitol" Penetrant 4 (100 ppm).

Surface tension of flood water: 31.0 dynes/cm.

Pressure source: Nitrogen.

Pore volume of core: 3.014 cm³.

| | |
|--------------------------------------|------------|
| Weight of core after saturation | 43.5387 g. |
| Weight of core before saturation | 41.3614 g. |
| Weight of oil in core | 2.1773 g. |
| Specific gravity of oil | 0.866 |
| Volume of oil in core | 2.51 ml. |
| Volume of oil in separator | 1.70 ml. |
| Volume of oil remaining in core | 0.81 ml. |
| Residual oil saturation $0.81/3.014$ | 0.269 |
| Per cent recovery $(1.70/2.51)(100)$ | 67.7% |

Table XXXI
Summary of Results

Core No. 1

| <u>Chemical Added to Flood water</u> | <u>Surface Tension of Flood Water (dynes/cm.)</u> | <u>Initial Oil Saturation</u> | <u>Residual Oil Saturation</u> |
|--|---|-----------------------------------|------------------------------------|
| None | 71.0 | 0.838 | 0.271 |
| None | 71.0 | 0.690 | 0.241 |
| Victamul 24 c | 31.6 | 0.655 | 0.295 |
| Victawet 12 | 28.8 | 0.744 | 0.107 |
| Dowanol 50 B | 28.8 | 0.705 | 0.092 |

Core No. 2

| | | | |
|----------------|------|-------|-------|
| None | 71.0 | 0.941 | 0.327 |
| Dispersant NPG | 30.0 | 0.850 | 0.268 |
| Penetrant EH | 32.0 | 0.855 | 0.272 |
| Victawet 14 | 28.8 | 0.836 | 0.353 |
| Tween 80 | 41.0 | 0.795 | 0.351 |
| Duponol 80 | 33.0 | 0.838 | 0.326 |
| Tween 21 | 37.0 | 0.845 | 0.334 |

Table XXXII
Summary of Results

Core No. 3

| <u>Chemical Added to Flood Water</u> | <u>Surface Tension of Flood Water (dynes/cm.)</u> | <u>Initial Oil Saturation</u> | <u>Residual Oil Saturation</u> |
|--|---|-----------------------------------|------------------------------------|
| None | 71.0 | 0.831 | 0.331 |
| Triton X-100 | 29.0 | 0.809 | 0.345 |
| Triton X-155 | 32.0 | 0.802 | 0.298 |
| Alkonal DW | 34.0 | 0.745 | 0.330 |
| Duonol G | 35.0 | 0.670 | 0.327 |
| Sterox SK | 31.7 | 0.770 | 0.256 |

Core No. 4

| | | | |
|--------------|------|-------|-------|
| None | 71.0 | 0.897 | 0.332 |
| Atlox 1045A | 42.0 | 0.975 | 0.312 |
| G-672 | 35.0 | 0.858 | 0.327 |
| Penetrant 08 | 30.0 | 0.823 | 0.192 |
| Dowanol 33B | 27.7 | 0.840 | 0.242 |
| Penetrant 4 | 31.0 | 0.834 | 0.269 |

DISCUSSION OF RESULTS

The laboratory flooding tests were divided into four separate groups, with a different core used in each group. In the first group were those experiments reported in Tables I to VI inclusive.

For core No. 1 the residual oil saturation after flooding with distilled water was found to be 0.271. To determine with what accuracy the results of these tests could be reproduced, a second control flood using distilled water was made and the residual oil saturation was found to be 0.241. The first surface active agent tested was Victamul 24 C. The residual oil saturation (0.295) when this chemical was added to the flood water was greater than the values obtained for distilled water. Victawet 12 when used as a flooding agent on core No. 1 gave a value of 0.1072 for the residual oil saturation, a definite decrease from the value obtained with the control flood. The value of the residual oil saturation when Dowanol 50 B was used as the flooding agent was 0.092 which is similar to the value obtained with Victawet 12.

The results obtained using core No. 2 were reported in Tables VII to XIV inclusive. For core No. 2 the residual oil saturation after flooding with distilled water was found to be 0.372. "Tergitol" Dispersant NPG has the greatest effect on the residual oil saturation of the chemicals tested with core No. 2. This surface active agent lowered the residual oil saturation to 0.268. The effect of "Tergitol" Penetrant EH was similar to that of "Tergitol" Dispersant NPG in that it lowered the residual oil saturation to 0.272. The effect which Victawet 14 and Tween 80 had on the residual oil saturation was negligible. Duponol 80 gave a

value of 0.326 for the residual oil saturation after flooding, a decrease of 0.046 from the value obtained with the control flood. The effect of Tween 21 on the residual oil saturation was to lower it to 0.334.

The data obtained from the flood tests of core No. 3 were reported in Tables XV to XXI inclusive. The control flood, using distilled water to flood the core, gave a residual oil saturation of 0.331. The first surface active agent tested with this core was Triton X-100. It gave a value for the residual oil saturation of 0.345 which was slightly larger than the value obtained from the control flood. Two chemicals tested with core No. 3 gave results which were similar to the value obtained with the control flood. They were Alkonol DW Solution and Duponol G. Any effect which these chemicals had on the residual oil saturation can be neglected. The greatest effect on the residual oil saturation of core No. 3 was found in the flood test using Sterox SK as the flooding agent. This surface active agent lowered the residual oil saturation to 0.256.

Tables XXII to XXVIII inclusive show the results obtained when core No. 4 was flooded. A residual oil saturation of 0.332 was obtained when core No. 4 was flooded with distilled water. Atlox 1045 A and G-672 did not lower the residual oil saturation an appreciable amount. For all practical purposes the effect of these chemicals on the residual oil saturation can be neglected.

"Tergitol" Penetrant 08 had the greatest effect on the residual oil saturation of core No. 4. It lowered the residual oil saturation to 0.192. Dowanol 33 B gave a value of 0.242 for the residual oil saturation. The value of the residual oil saturation when "Tergitol" Penetrant 4 was

used as the flooding agent was 0.269, a decrease of 0.063 from the value obtained on the control flood.

A summary of the results obtained in this investigation is reported in Tables XXXI and XXXII. The surface tension of the flood water used, the initial oil saturation and the residual oil saturation are listed for each flood test.

CONCLUSIONS

It is seen from the values of 0.271 and 0.241 for the residual oil saturation of core No. 1 obtained with the control flood that the results obtained with the experimental procedure used cannot be reproduced exactly. Therefore, unless the surface active agents tested decreased the oil saturation more than 0.03 their effect may be neglected. In several flood tests the residual oil saturation was greater than in the control flood, but in no case was this increase more than 0.03. Consequently, these surface active agents may be considered to have no effect on the residual oil saturation.

In the following tabulation the results of the flood tests are grouped according to the decrease in residual oil saturation from the value obtained with the control flood.

| <u>Surface Active Agents Tested</u> | <u>Surface Tension of Flood Water</u> | <u>Decrease in Residual Oil Saturation</u> |
|-------------------------------------|---------------------------------------|--|
| Dowanol 50 B | 28.8 | 0.162 |
| Victawet 12 | 28.8 | 0.149 |
| "Tergitol" Penetrant 08 | 30.0 | 0.140 |
| "Tergitol" Dispersant NPG | 30.0 | 0.104 |
| "Tergitol" Penetrant EH | 32.0 | 0.100 |
| Dowanol 33 B | 27.7 | 0.090 |
| Sterox SK | 31.7 | 0.075 |
| "Tergitol" Penetrant 4 | 31.0 | 0.063 |
| Duponol 80 | 33.0 | 0.046 |
| Triton X-155 | 32.0 | 0.043 |
| Tween 21 | 37.0 | 0.038 |

It is seen that positive evidence of decrease in residual oil saturation was found in 11 flood tests. There was no decrease in residual oil saturation from the other 8 chemicals tested.

From the above tabulation, it can be seen that there is no relationship between the surface tension of the flood water and the decrease in residual oil saturation. In view of this condition no prediction of decrease in residual oil saturation may be made from the surface tension of the flood water.

The tests, of course, do not demonstrate that use of these chemicals will give an economical increase in recovery of oil. The concentration used in this investigation, 100 ppm, may represent too great an increase in cost per barrel of oil produced. No attempt was made to test the corrosive properties of these chemicals, nor to determine whether the flood waters tested were compatible with the connate water of the reservoir. The significant result of this investigation is the evidence that 11 of the 19 chemicals tested did decrease the residual oil saturation.

SUMMARY

A series of water flood tests were conducted on cores from Shell-Saunders No. 1 Well, located in the Canary Field, Washington County, Oklahoma. The purpose of these tests was to investigate the effects which flood waters containing certain surface active agents have upon the residual oil saturation.

Solutions of each surface active agent at a concentration of 100 ppm were prepared using distilled water as the solvent. The surface tensions of these solutions were found by using a Du Nouy Tensiometer. Any oil originally present in the cores was extracted by means of a Soxhlet Extraction Apparatus. The core was saturated with a known quantity of oil, mounted in the core holder and flooded with the solutions containing the surface active agents. The amount of oil removed by water flooding was found by a direct reading of the oil burette.

From the pore volume of the core and the amount of oil present before and after flooding, the initial and residual oil saturations were calculated for each flood test. The effect which flooding with solutions containing surface active agents had on the residual oil saturation was found by comparison with the residual oil saturation obtained when distilled water was used to flood the core.

The results of the investigation showed that of the 19 surface active agents 11 gave positive evidence of a decrease in residual oil saturation.

No relationship was found to exist between the surface tension of the flood water tested and the change in residual oil saturation.

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VITA

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