A STUDY OF WATER
IN
CRUDE OIL EMULSIONS

BY

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ABSTRACT

The research work covered by this thesis was all based on water-in-oil emulsions. Investigations were made from a production point of view to determine the flow characteristics of crude oil emulsions.

Six crude oils from different parts of the United States were chosen with gravities from 13°API to 35°API. Brines of two different salinities were used to create emulsions with increasing water contents. Studies were also made at two different temperatures, 75°F and 125°F. At 75°F all experiments were done with natural and artificial emulsions.

Rheological properties were investigated. The degree of non-Newtonian behavior was determined for both the natural and artificial emulsions made from five of the crude oils. Stability and point of inversion were studied for these emulsions. The effect of an emulsifying agent was investigated. The emulsions were also studied visually through a microscope, and photomicrographs were taken. Surface tension was measured for brine and one crude oil, and oil-water interface tension was measured with and without an emulsifier.

Difficulties were encountered when making natural emulsions of higher water content than 30-35% because of instability, and when the viscosity became higher than could be measured by the rotary viscometer.

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INTRODUCTION

The subject of emulsions has had little discussion in the literature related to oil production problems, and until recently the matter has been more or less ignored. Even today, internal publications of private companies give the best information about emulsion problems concerning the oil industry.

An emulsion is a mixture of "liquid in liquid", where the two liquids are immiscible. Generally, only two main groups of liquids are considered to form an emulsion. Those are oil and water, as almost any highly polar, hydrophilic liquid falls into the "water" category, and the non-polar, hydrophobic liquids are considered "oils". Therefore, two main groups of emulsions are considered, the oil-in-water emulsions and the water-in-oil emulsions. This study concentrates exclusively on the latter group, as this is the most likely to be encountered in the oil field. It is the purpose of this study to investigate the viscous and rheological properties of natural and artificial emulsions throughout a range of concentrations. Properties like emulsion stability, point of inversion and effect of emulsifying agents will be discussed both from physical measurements and from observations through a microscope.

THEORY BEHIND EXPERIMENT

Emulsions in general:

Emulsions have become more and more common through the last decades, especially in the commercial industries such as foods, cosmetics, paints and chemicals. The properties of those emulsions will also apply to crude oil and water emulsions to some extent.

In the past, a great deal of effort has been devoted towards mathematical formulations of energy relationships at the interfaces of emulsion systems. A number of good approaches have been devised to explain certain emulsion phenomena. In Lissant's Emulsions and Emulsion Technology(1) the emulsion performance properties are determined to be more dependent on their physical configuration than on the chemical properties of the constituents.

Lissant(1) divides the emulsions into three physical classifications; namely the low-, the medium- and the high-internal-phase-ratio type, which in our case is the water content or the volume of water divided by the total volume of liquid.

For water-in-oil emulsions, which this study concerns, the three categories can be presented as follows:

GROUP	WATER CONTENT
Low water content	<30%
Medium water content	30%-74%
High water content	>74%

It should be pointed out that these values are all theoretically chosen.

When the internal phase constitutes less than 30 percent of the total volume, the individual droplets do not significantly interfere with each other, and the physical properties of the whole system are mainly determined by the nature of the external continuous phase. As more of the internal phase is added, the droplets begin to collide and interfere, which causes the viscosity of the emulsion to increase.

Above 50 percent water content the particles of the internal phase are forced into close contact, and the emulsion will have a high shear stress value and most likely show a non-Newtonian flow behavior.

At a water content of 74 percent, another theoretical packing point is reached, and the internal particles are packed in a way that makes an unstable emulsion. Adamson(7) states that "an emulsion would have to break or invert if the internal phase exceeds 74% of the total volume, if it consisted of uniform rigid spheres", as illustrated in Fig. 1.

The system, however, is more likely to have a configuration as that in Fig. 2, and reports on oil-in-water emulsions containing 99% oil show that it is only a theoretical value. Lissant[(1)] adds that most emulsifiers lose their effectiveness above this range and inversion is likely to occur.

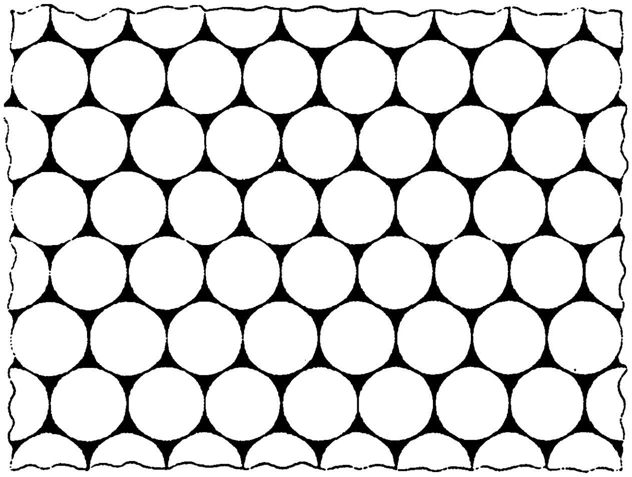


Fig. 1 - Closely packed uniform, spherical droplets take up 74% of the volume. (From Becher (2)).

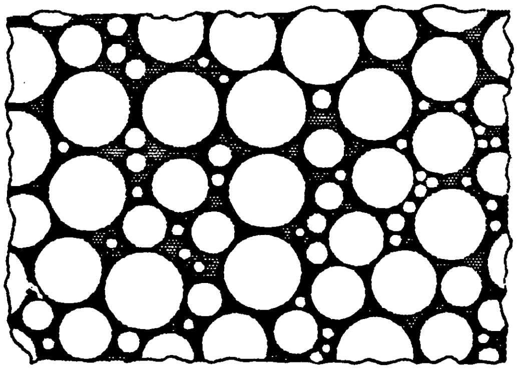


Fig. 2 - Non-uniform, spherical droplets can take up any percentage of the volume. (From Becher (2)).

Davies and Rideal(4) found that an emulsion will break or invert depending on whether the inverse emulsion is stable or unstable, as illustrated in Fig. 3.

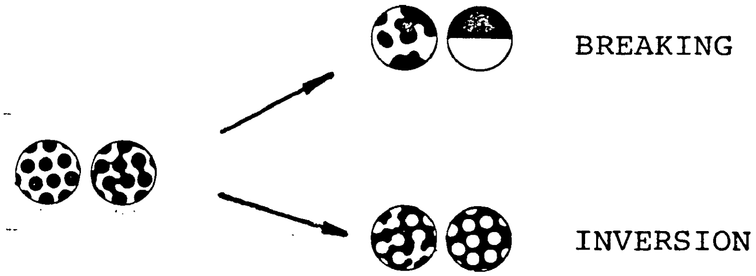


Fig. 3. - Diagrammatic representation of breaking and inversion of emulsions. Dark is oil, white is water. (From Davies and Rideal(4)).

Bikerman's(5) results show that when making artificial emulsions, the nature of the emulsifying agent affects the type of emulsion, perhaps more than anything else. He says that "agents soluble in water but not in oil, tend to produce an oil-in-water emulsion, while water-in-oil emulsions are stabilized by oil-soluble emulsifying agents".

Adamson(7) describes the inversion phenomenon as a process illustrated in Fig. 4.

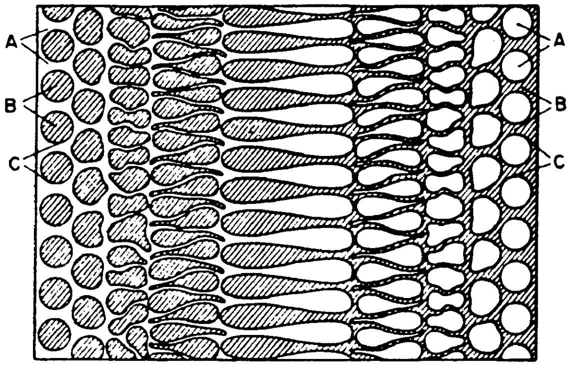


Fig. 4 - The inversion process.
A is water, B is oil, C is emulsifier.
(From Adamson(7)).

Surface activities:

Surface tension.

Becher$^{(2)}$ states that "in a bulk of liquid the molecules are sufficiently close so that the effect of attractive forces are considerable. In fact, these forces are great enough to keep all but a limited number of molecules from escaping in the vapor state". Although the forces are relatively large in magnitude, they tend to balance out in the bulk of the liquid. The molecules in the surface region, however, not being surrounded by other molecules, are subjected by an unbalanced attraction, giving a net effect into the liquid perpendicular to the surface, Fig. 5.

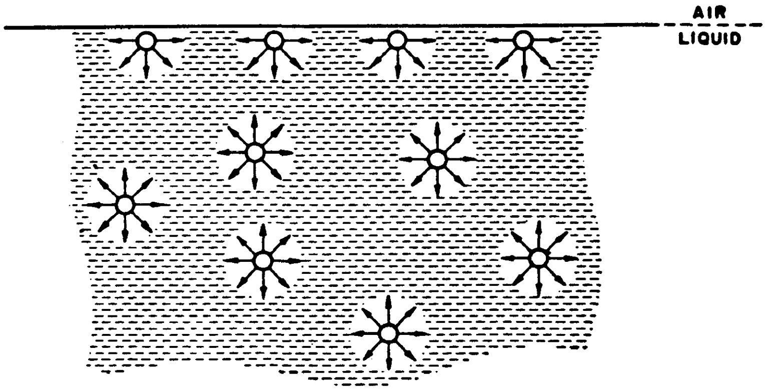


Fig. 5 - Forces acting on molecules on the surface and the interior of a liquid. (From Becher(2)).

Surface tension may be defined as: "The work in ergs needed to generate one square centimeter of surface". The units using this definition should then be ergs/cm^2, but the surface tension can also be defined in terms of a force acting along a one-cm length of surface. Since one erg is equal to one dyne-centimeter, the unit dyne/cm is used for surface tension.

Interfacial tension:

In the theory of emulsions, the previous discussion is not of very much importance. Of more interest are the boundary tensions existing between two liquids. That kind of boundary tension is called an interfacial tension.

When two immiscible liquids are placed in contact, an interface is created. Here, as in the previous example, there will be an imbalance of forces, Fig. 6.

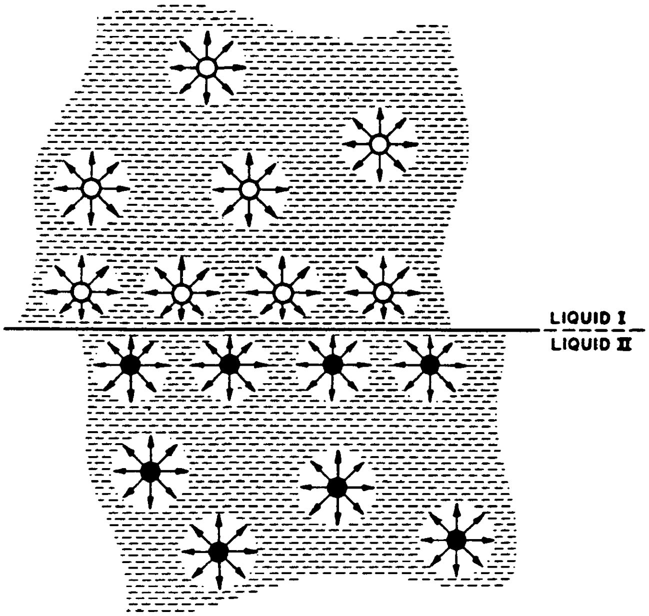


Fig. 6 - Forces acting on molecules at the interface and the interior of two liquids. (From Becher(2)).

It is therefore to be expected that the value of the interfacial tension will be between the values of the individual surface tensions of the two liquids.

The surface tension (in dynes/cm) is the work needed to create surface area and can be written as:

$$\text{work} = \gamma dA \qquad \text{..........(I)}$$

where: γ = surface tension (dynes/cm)

dA = additional area (cm^2)

For a bubble the surface energy is:

$$E_s = 4\pi r^2 \gamma \qquad \text{.........(II)}$$

where: E_s = surface energy (ergs)

r = bubble radius (cm)

A decrease in bubble radius by dr will give a change in surface energy of:

$$\Delta E_s = 8\pi r\gamma\, dr \qquad \text{.......(III)}$$

Since a decrease in bubble size decreases the surface energy, the drop in energy must be compensated by a pressure difference (Δp) across the bubble surface, or:

$$4\Delta P\pi r^2\, dr = 8\pi r\gamma\, \cancel{dV}\, dr$$

which becomes:

$$\Delta P = \frac{2\gamma}{r} \qquad \text{.......(IV)}$$

From the last equation it can be concluded that the smaller the bubble, the greater is the pressure difference between the inside and outside of the bubble. On the other hand, by decreasing the surface tension, a lower pressure drop will occur across the surface. By lowering the surface tension, it takes less energy to create surface, which means it takes less energy to make small bubbles.

Natural vs. artificial emulsions:

In this study natural emulsions are those made from two immiscible liquids. An artificial emulsion is made by using an emulsifying agent to create a film between the oil and water particles.

Most, if not all, of the commercial emulsions are artificially made and may be stable for years. Examples are hand lotions and paint.

Bikerman(6) says that "true two-phase emulsions contain droplets of one liquid in the continuous phase of another". They are relatively short-lived, but their behavior is easier to understand than that of the common emulsions which are protected by a film of emulsifying agent.

The theoretical aspects of natural vs. artificial and loose vs. tight emulsions will be discussed in the following section.

Low water content emulsions:

Lissant states the following: "Two pure liquids will not form a stable emulsion". After agitating two liquids we have a system of spheres dispersed in a liquid medium. The interfacial area is now much greater than would be between two bulk systems. Much energy has been added to create all this interfacial area, and if given a chance, the system will give it up and go back to the two bulk phases with the minimum interface. This happens by coalescence, where the droplets either fall or rise, because of gravity and buoyancy respectively. When the droplets collide, coalescence begins, the droplet size increases and the emulsion becomes looser. Coalescence, however, also occurs by the interfacial phenomenon of osmosis. Moore(15) describes how the osmotic pressure affects the coalescence between bubbles. When two bubbles of different sizes are in contact, there is a pressure difference across the semipermeable membrane between them. The pressures within the water bubbles will equalize through the membrane, and they coalesce.

A substance that can be absorbed at the interface is added to form a "skin" that keeps the droplets from actual contact can effectively prevent the coalescence between them. This substance is called an emulsifier.

From this discussion we can see that there are two basic techniques for preparing a tight dilute emulsion:

1) Making very small droplets.

2) Use an emulsifier to prevent coalescence.

The separation of the emulsion is governed primarily by Stokes' Law:

$$v = \frac{g * D^2 * (\rho_1 - \rho_2)}{18 * \mu} \qquad \text{...........(V)}$$

where: v = separation velocity of the droplet (cm/sec)

D = diameter of droplet (dispersed phase) (cm)

ρ_1 = density of dispersed phase. (g/cc)

ρ_2 = density of continuous phase (g/cc)

μ = viscosity of continuous phase (g/sec cm)

g = gravitational constant (cm/sec^2)

It is seen from this equation that the spheres of the dispersed phase will fall or rise dependent on whether ρ_1 is greater or smaller than ρ_2. Also, a larger diameter D gives a faster sedimentation, and a more viscous continuous phase will retard the movement of the droplets.

Stokes' Law is based on rigid spheres, but it is normally applicable for most practical purposes.

From Stokes' Law, the previous and the following discussion we conclude that tight emulsions, having long term stability, require small particles and the presence of an emulsifying agent. Loose emulsions are characterized by larger droplets and instability.

Woelflin(9) characterizes the emulsions as being tight, medium and loose, where in a:

-tight emulsion	no water separates out
-medium emulsion	20% water separates out
-loose emulsion	70% water separates out

Low water content water-in-oil emulsions are encountered fairly frequently in actual practice, and they usually create an undesireable situation. For example, crude oil often contains significant amounts of water or brine emulsified in the oil. Also lubricating oils and hydraulic oils may be contaminated by small amounts of emulsified water.

Medium water content emulsions:

It should be noted that the range of water content from 30% to 74% is arbitrarily chosen, and there is substantial overlap at each end of the range.

This group of emulsions is characterized by higher viscosities, non-Newtonian flow behavior, and often some difficulty in achieving long-term stability.

Lissant(1) found that at approximately 50 percent water content we can expect a rather drastic interference between droplets, even if there is an emulsifier present to prevent coalescence. The action, however, will give a non-Newtonian flow behavior and a high apparent viscosity. Also, if the emulsifier is not effective, coalescence will occur and we have an unstable emulsion. In this group the use of an emulsifier is considered the major factor in obtaining a tight emulsion, while the attainment of small droplet sizes is of secondary importance.

High water content emulsions:

High water content emulsions can only be prepared under certain special conditions. The stability of such an emulsion must be obtained by creating a film, on the surface of the dispersed droplets, that will prevent coalescence. The external phase is a continuous region, which means that any part of it can be reached from any other part without leaving the phase itself. On the other hand, the internal phase is divided into a large number of separate regions, between which one cannot travel without passing through the external phase region, as illustrated in Fig. 7.

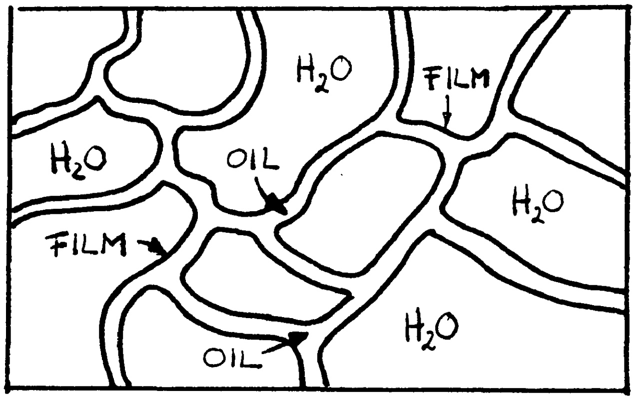


Fig. 7 - Schematic configuration in a high water content, artificial water-in-oil emulsion.

Physical properties:

Becher(2) lists six factors which affect the flow performance of an emulsion:

1) Viscosity of the external phase, (μ_o).
2) Concentration of the internal phase.
3) Viscosity of the internal phase, (μ_i).
4) Nature of the emulsifying agent and the interfacial film formed.
5) Electroviscous effect
6) Particle size distribution.

They will be discussed separately.

1) Viscocity of the external phase:

Becher(2) states that the viscosity of the external phase is the most important factor in determining the apparent viscosity of the final emulsion. There is an indication of direct proportionality between the two viscosities.

$$\mu_e = \mu_0 (x) \qquad \text{.....(VI)}$$

where (x) represents the sum of the other properties affecting the viscosity.

2) Concentration of the internal phase:

There are several theories and equations concerning this point, but common to them all is that a higher internal phase concentration results in a higher apparent viscosity of the emulsion.

3) Viscosity of the internal phase:

This term can be significant if the droplets behave as liquids. If the conditions are such that the droplets behave as rigid spheres, the chemical nature of the dispersed phase is likely to have a greater effect.

4) Interfacial film and emulsifying agents:

The film and the properties exhibited by the film are caused by the emulsifying agent itself.

The amount of emulsifier also has an effect on the point of inversion, which is where the W/O- emulsion turns to O/W-emulsion.

5) Electroviscous effect:

This effect comes from the interactions between the charges on adjacent droplets. If a system becomes more dilute, the distance between the charges increases. The interaction then drops with the inverse power of the interparticle distance. At infinite dilution the electroviscous term is zero.

6) Droplet size and size distribution:

The presence and concentration of an emulsifier has an effect on the particle size and the size distribution, both of which affect the emulsion viscosity.

A large reduction in the particle size results in a greater interfacial area, more interaction between the particles and thereby a higher viscosity.

Rheology:

Fundamentals of rheology:

Rheology is the science of the deformation and flow of matter. A Newtonian fluid is defined as a fluid whose viscosity is only dependent on pressure and temperature. At a given pressure and temperature, the relation between shear stress and the rate of shear is a constant. The constant is the viscosity, μ, and is defined by the ratio of shear stress to the shear rate. Using a rotational viscometer, the shear stress is the dial reading, and the rate of shear is the angular velocity in RPM of the viscometer cylinder. Fig. 8 shows the deformation of a fluid element.

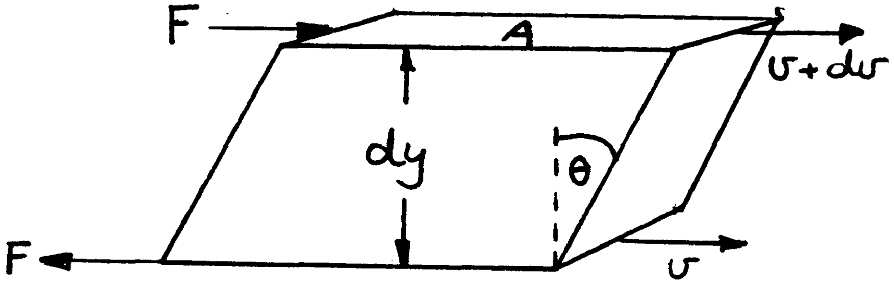


Fig. 8 - Planar shearing of a fluid element.

$$\mu = g_c * \frac{F/A}{\theta} = g_c * \frac{\tau}{dv/dy} \qquad \text{.......(VII)}$$

where: μ = viscosity (absolute)

τ = shear stress (F/A)

θ = shear rate

dv/dy = velocity gradient

All fluids which do not follow this proportionality are classified as non-Newtonian.

On a Cartesian coordinate graph, with the rate of shear (dv/dr) in RPM on the abcissa and the shear stress along the ordinate, the Newtonian fluid will always plot as a straight line passing through the origin. Any curved line or line not going through the origin will represent non-Newtonian behavior.

The major sub-group classifications of non-Newtonian fluids are:

- Ideal plastics (Bingham plastic)
- Pseudoplastics
- Dilatant fluids

On the same graph they will create curves somewhat similar to those indicated in Fig. 9.

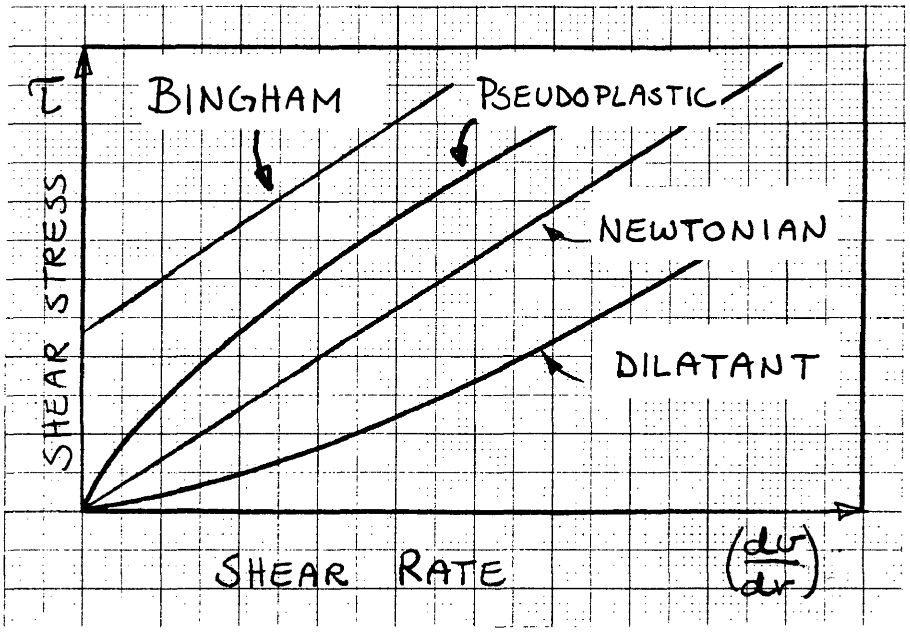


Fig. 9 - Shear stress vs. rate of shear.

The ideal plastic flow properties are specified by the plastic viscosity and the yield point only. No other parameters are needed to determine the rheological behavior. The apparent viscosity for a plastic is not a constant, but varies with applied shear stress.

All other non-Newtonian fluids are classified as "generalized non-Newtonian" out of which two main groups are the pseudoplastics and the dilatants. They have no yield point, but their apparent viscosity is a non-linear function of shear stress and shear rate. The apparent viscosity of a pseudoplastic fluid will decrease with increasing shear stress, while a dilatant fluid behaves opposite of that.

For many non-Newtonian fluids the function:

$$\tau = K^*(-\frac{dv}{dr})^n \qquad \text{......(VIII)}$$

also called the Power Law, has been found to represent the relationship between shear stress and the shear rate. It includes two constants, K and n, where n is between zero and unity for pseudoplastics, unity for Newtonians and greater than one for dilatants. K is related to the consistancy of the fluid. For Newtonians $K = \mu/g_c$.

Some non-Newtonian fluids do not follow the Power Law, or Eq. VIII, exactly since they show a significant yield point value. From this value, however, they show a Power Law behavior. The yield point term, τ_y, must therefore be added to Eq. VIII, which then becomes:

$$\tau = K^*(-\frac{dv}{dr})^n + \tau_y \qquad \text{......(VIIIb)}$$

where: τ = shear stress (lbf/ft^2)

τ_y = yield point (lbf/ft^2)

K = consistancy index $(\text{lbf sec}^n/\text{ft}^2)$

n = flow behavior index (dim. less)

$\frac{dv}{dr}$ = shear rate (sec^{-1})

The apparent viscosity is a helpful parameter, but must not be mistaken for the real viscosity. Baroid(8) uses this term simply as an indication of the shear stress that appears on the dial, by using half of the dial reading at 600 RPM. It is valuable for comparison of different non-Newtonian emulsions.

Correlation of rotational viscometer and pipe flow viscometer:

Craft, Holden and Graves$^{(3)}$ present a rheological correlation between rotary viscometer measurements and the flow characteristics in pipe, with K and n as parameters.

The equations are based on a Fann VG-meter Model 35 rotary viscometer.

General flow equation:

$$w_c = \frac{k}{2}\int_{\tau_b/\beta^2}^{\tau_b} \tau^{-1}\phi(\tau)\,d\tau \qquad \text{.........(IX)}$$

where: $\beta = r_c/r_b$

r_b = radius of stationary bob

r_c = inner radius of outer cylinder

$\tau_b = T/2\pi L r_b^2$ = shear stress experienced by fluid in contact with bob.

L = effective length of bob

T = torque transmitted to bob

w_c = angular velocity of outer cylinder

$K\phi(\tau) \Rightarrow dv/dr$ = shear rate behavior of fluid

With respect to the shear stress, τ_b, the equation can be written as:

$$\tau_b = K\gamma^n\left(\frac{2\,w_c\beta^2}{\beta^2-1}\right) \qquad \text{........(X)}$$

where n, K and γ^n are constants.

The term in the parentheses is the shear rate at the surface of the bob for Newtonian liquids. Using a rotary viscometer, the term is a constant for every speed, w_c, obtained in a non-Newtonian liquid.

By use of the following table, we get the parameters that determine the rheological flow behavior.

EXPERIMENTAL DATA		PLOTTING PARAMETERS	
Cylinder speed RPM	Dial reading θ	$\left(\frac{2w_c\beta^2}{\beta^2-1}\right)$ 1/sec	Shear stress lbf/sqft
600	$\theta 1$	1022	θ_1*0.01066
300	$\theta 2$	511	θ_2*0.01066
200	$\theta 3$	340	θ_3*0.01066
100	$\theta 4$	170	θ_4*0.01066
20	$\theta 5$	34	θ_5*0.01066
2	$\theta 6$	3.4	θ_6*0.01066

Plotting τ_b vs. $\left(\frac{2w_c\ \beta^2}{\beta^2-1}\right)$ on a log-log paper makes a straight line with slope n and intercept $K' = K\gamma^n$ on the ordinate. By obtaining different values for n, at increasing water concentrations, we get an indication of each emulsion's rheological behavior. The further n is from unity in either direction, the stronger are the non-Newtonian characteristics.

An equivalent, but more realistic way to determine the flow characters is by a pipe viscometer or a capillary tube. The general equation is somewhat similar to that of the rotary viscometer, and the expression for laminar pipe flow is:

$$\left(\frac{2v}{Kd}\right)*\tau_w^3 = \int_0^{\tau_w} \tau^2\phi(\tau)\,d\tau \qquad \ldots\ldots\text{(XI)}$$

where d = diameter of pipe

v = velocity

τ_w = stress at wall

with respect to shear stress the equation becomes

$$\tau_w = \frac{d \Delta P}{4L} f = K_p' \left(\frac{8v}{d}\right)^{n'} \qquad \text{.......(XII)}$$

where: P_f = pressure drop due to friction

l = length of pipe

Plotting τ_w vs. $(\frac{8v}{d})$ on a log-log paper makes a straight line with slope n' and intercept K_p'.

The difference, however, between the two methods turns out to be insignificant, as n' turns out to be the same while K' varies slightly. We therefore consider the results from the rotary viscometer to be valid. See Fig. 10.

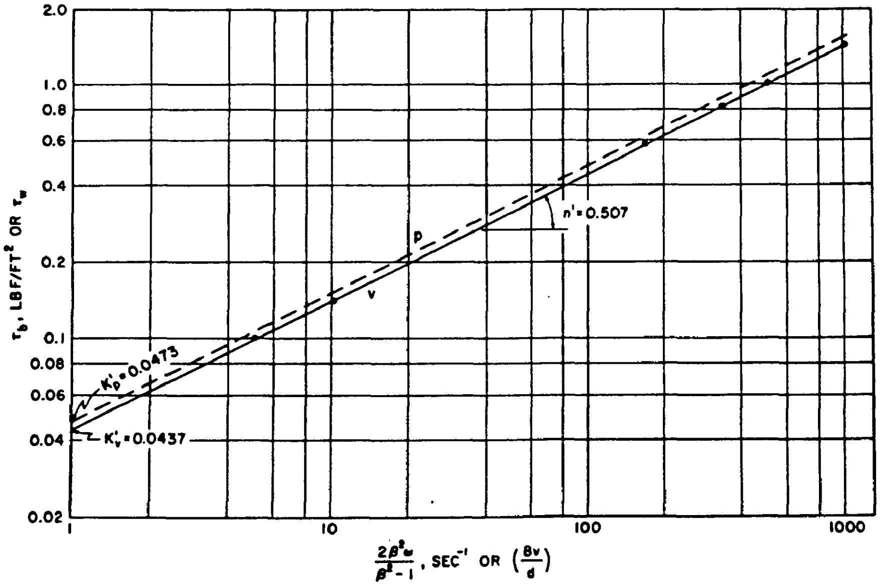


Fig. 10 - Example plot of VG-meter data (v), and resulting pipe flow curve (p). (From Craft, Holden and Graves[3]).

It should be pointed out that the same correlation applies to the variable speed rotational viscometer, as the ratio between cylinder radius and bob radius is the same as for the Model 35.

EXPERIMENTAL PROCEDURE

Crude samples and equipment used throughout the experiment are listed in Tables 1 and 2.

When measuring the salt contents of the brines, a 3-armed balance and a graded cylinder were used. A 150,000 mg/l salinity was obtained by mixing 150 grams of salt into 1000 ml of distilled water. The Hamilton Beach mixer quickly made a homogeneous solution. The 20,000 mg/l salinity was obtained by diluting 100 ml of the 150,000 mg/l brine with 650 ml of distilled water.

Preselected amounts of crude oil, water and emulsifying agent (for artificial emulsions) were measured before being mixed to form natural or artificial emulsions. The mixing was done with the Hamilton Beach mixer. The emulsion, when mixed, was poured into the rotational viscometer cup and filled up to the desired line (350 ml for the Fann VG-meter Model 35 and 400 ml for Baroid's variable speed model). Readings were taken for emulsions with 0, 9.1, 22.2, 36.4 and 50% water. Both viscometer models have a cylinder and bob arrangement, where the cylinder rotates at a certain speed around the stationary, spring loaded bob. The bob is attached to the dial, and is pulled out of balance position as the cylinder rotates. The gap between bob and cylinder is only 0.045 inches. When rotated at any certain speed,

TABLE 1

LIST OF CRUDE OILS:

No.	State	Field	Company	API @ 60F
1	Wyoming	Winkleman Dome	Amoco	13
2	Arkansas	Smackover	Phillips	19
3	Illinois	Robinson	Marathon	25
4	California	Shields Canyon	Texaco	27
5	Wyoming	Teapot Dome	DOE	29
6	Colorado	Plum Bush	Conoco	35

TABLE 2

LIST OF EQUIPMENT:

2-Speed Hamilton Beach mixer, Model 30

6-speed Fann VG-meter, Model 35

- Variable speed viscometer, Baroid, 2-720 RPM
- Plate heater
- Polaroid Land Camera, Model 3MP
- American Optical Microscope, 40, 100, 400, 1000 power
- 3-armed balance, accuracy 1/10 gram

a number is read on the dial, corresponding to the shear stress at the wall of the bob.

One set of readings was taken at the ambient room temperature. Another set of readings were taken at 125°F. A plate heater was used to raise the emulsion temperature to 125°F.

The rheological properties of the emulsions were determined using the variable speed viscometer. The same prodecure was applied as for the Fann VG-meter Model 35. Measurements were made for emulsions with water contents of 0, 4.8, 10.1, 15.8, 23.8, 33.3, 42.9 and 50.0 percent, at 16 different speeds (2-700 RPM).

Photomicrographs were taken using a microscope and a Polaroid Land Camera. To obtain good pictures at 100 power, light is essential and must penetrate the emulsion towards the film. A droplet of emulsion, natural or artificial, was squeezed between two pieces of glass. A very thin layer of emulsion was created, and the individual oil and water particles observed. The light intensity was adjusted by a transformer attached to the microscope, and the desired depth of field obtained by closing or opening the aperture between the light source and the magnifying lens. The high speed instant Polaroid film used, allowed pictures to be taken at 1/125 sec. The microscope/camera assembly is seen in Fig. 11.

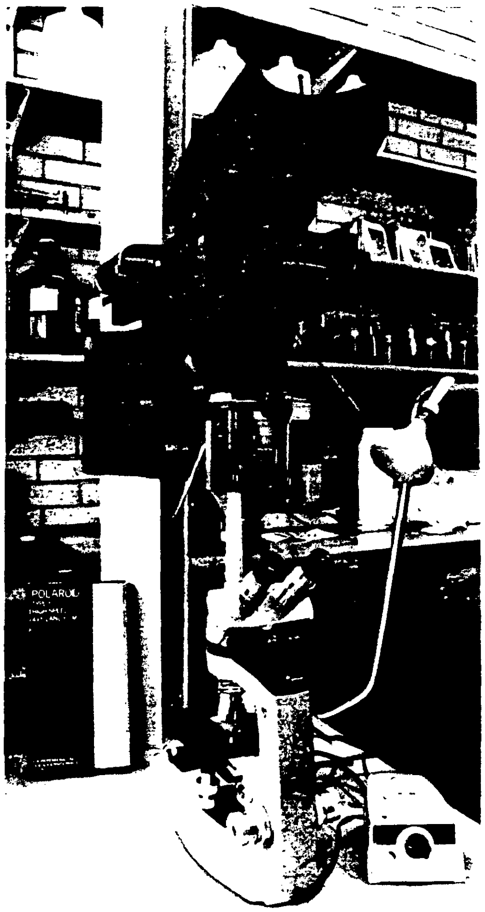


Fig. 11

The stability of the natural emulsions was determined by mixing each crude with brine at a water content of 23%, then letting the emulsion rest for one hour in a graduated cylinder to see the amount of water that separated out. Photomicrographs were also taken to observe the particle sizes of the components.

The point of inversion was approximately located for the natural emulsions during the viscosity measurements, as some of the emulsions inverted at low water contents. For the artificial emulsions, however, water and emulsifying agent were added till no more water could be mixed into the emulsion, but rather stayed as free water. Photomicrographs were taken of each sample at their maximum water content. Photomicrographs were also taken of the artificial emulsions at lower water contents, as they appeared during the viscosity measurements. Some had 36% and some had 50% water, dependent on where the maximum measurable dial reading was reached.

A couple of the measurements, the rheology test for the 35° API crude oil, were repeated to check the measurement repeatability.

One percentage by volume, 2% of emulsifying agent was used for the artificial emulsions. Two measurements using 0.5% emulsifying agent were made for comparison. Photomicrographs were taken.

To observe the effect of the amount of the emulsifier, the 27° API crude oil containing 35% water was mixed with an increasing amount of the emulsifying agent. 400 ml of crude oil, and 152 ml of 20 mg/l salinity brine were mixed with 0, 1/8, 1/4, 1/2, 1, 2, 4, 6 and 8 volume percent of emulsifier. The shear stress was read at 2, 10, 20, 100, 300 and 600 RPM using the variable speed rotational rheometer.

The emulsifying agent used, EZ-MUL, a trade mark of Baroid Division of NL Industries, was provided by NL

Baroid Industries, Denver. According to Baroid(8), it can be used at very low concentrations and will emulsify water of any salinity. EZ-MUL is primarily used for making oil based drilling fluids, where an emulsion between water and diesel oil is required.

Using a Fisher Surface (Ring-type) Tensiometer, the surface tension was measured for 150,000 mg/l brine and the 27° API crude oil. After adding 1/2%, 1% and 4% of emulsifier to the crude oil, the interface tension between brine and crude oil was measured. The tensiometer was first calibrated with distilled water. An illustration of the tensiometer is seen in Fig. 12.

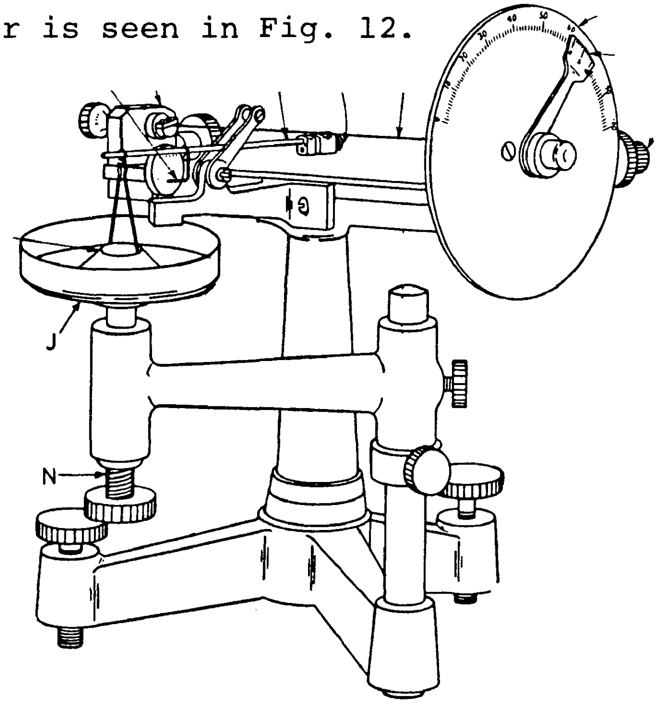


Fig. 12 - Du Noüy - Tensiometer.
(From Pirson(11)).

A ring was lowered into the liquid investigated. The force needed for the ring to break through the surface or interface upwards, was measured and converted to dynes/cm. Four measurements were taken each time, and an average was calculated. Illustrations of the surface and interface can be seen in Figs. 13 and 14.

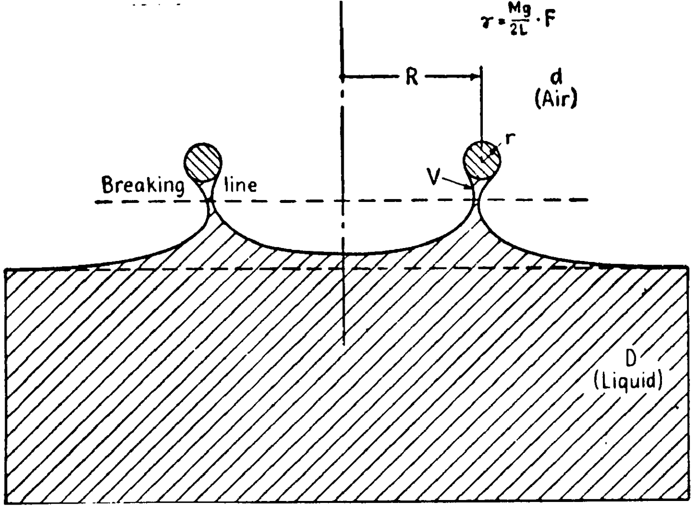


Fig. 13: Liquid surface film at breaking point. (From Pirson(11)).

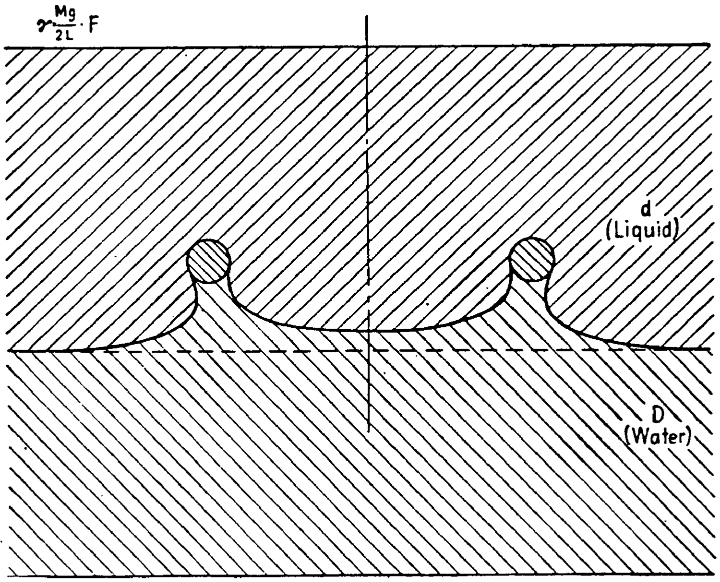


Fig. 14: Interfacial film during interfacial tension.
(From Pirson(11)).

Calibration of the surface tensiometer was made as follows:

$$\gamma = \frac{Mg}{2L} * F \qquad \text{......(XIII)}$$

where: γ = surface tension (dynes/cm).

M = weight of liquid raised above surface (g).

L = circumference of ring (cm).

F = correction factor.

g = gravitational acceleration (cm/sec^2).

The values of these parameters are:

M = weight required to bring lever arm back to neutral position.

L = 6.005 cm.

g = 980.2 cm/sec^2 (Denver 40° lat.).

F = found from tables and is a function of R^3/V and R/r.

where: R = mean radius of ring (cm)

r = radius of ring wire (cm)

V = volume of liquid lifted (cm^3)

$$V = \frac{M}{D-d} \qquad \text{....(XIV)}$$

where: D = density of water (g/cm^3)

d = density of air saturated with water vapor (g/cm^3)

Values are:

D = 0.99900 g/cm^3

d = 0.00118 g/cm^3 @ 20°C. (From Table 12.2 in Chemical Engineers Handbook$^{(12)}$).

$$R = 0.9557 \text{ cm}$$

$$R/r = 53.79$$

$$V = \frac{M}{0.99782} \text{ cm}^3$$

The value of M is measured for several experiments with water, and an average value of the surface tension is computed. This value and the corresponding dial reading is used for further measurements.

$$\gamma_x = \frac{R_x \gamma_c}{R_c} \qquad \text{......(XV)}$$

where: γ_x = surface tension of unknown (dynes/cm)

R_x = dial reading of unknown

R_c = dial reading at calibration

γ_c = surface tension corresponding to R_c (dynes/cm)

Out of the six crudes in Table 1, No. 2, 3, 5 and 6 were used for viscosity measurements. No. 1 was too viscous to be investigated with the Fann VG-meter, while No. 4 was close to both No. 3 and 5 in API gravity. All crude oils but No. 1 were used for rheology measurements, while stability and inversion were observed for all six samples.

An example of pressure drop in a pipe was calculated for the 25° API crude oil for 8 different water contents.

EXPERIMENTAL RESULTS

The results from my experiments are reported in this chapter and in the appendix. They include a general discussion on the different properties, a presentation of the specific results and a conclusion to the subject.

Shear stress as a function of water content.

Figs. 16 through 19 show the results of the viscosity measurements. Gravities are from 19° API to 35° API and water contents are from 0% to 50% by volume. Both natural and artificial emulsions are included.

An immediately noticeable characteristic of almost all the emulsions, is that the shear stress, measured with the rotary viscometer, increases non-linearly, rather exponentially, as water is added. The exceptions to this characteristic are most probably due to a very unstable emulsion.

Woelflin(9) concludes his experiments with a graph showing viscosity ratio, that is the apparent viscosity of the emulsion divided by the viscosity of the dead crude oil, as a function of percent brine in emulsion. It is used as a reference in Frick's(10) Petroleum Production Handbook, p. 6-60. Table 3 lists my equivalent results, which are plotted in Fig. 15 together with Woelflin's results. It is seen that an emulsion does not have to follow the properties shown in his graph. He used three different crude oils of two API gravities (16 and 25° API), and the curves obtained are only valid for those particular ones. The same can be said about the results of this study. It should be pointed out that Woelflin, in his experiment, included both natural and artificial emulsions, the same as in this study. The blanks in Table 3 are due to inverted emulsions. The so-called viscosity ratio is a questionable parameter as it becomes very sensitive to low values of dead oil viscosities, giving the denominator in the ratio a small value.

The effect of water salinity:

The difference in curve characteristics between the two used brine salinities is not very significant, especially when considering the two extremely different salinities used.

The results can be observed in Figs. 16 through 19.

The effect of temperature:

Figs. 16 through 19 demonstrate the expected effect of increased temperature on natural emulsion viscosity. All shear stress readings are significantly lower at 125°F than for those at room temperature. Woelflin's(9) part of

TABLE 3

$$\text{VISCOSITY RATIO} = \frac{\text{VISCOSITY OF EMULSION}}{\text{VISCOSITY OF DEAD OIL}}$$

^{o}API	Water %	Nat.Em.75 F	Nat.Em.125 F	Art.Em.75 F
19	9.1	1.37	1.67	1.29
"	22.2	2.11	2.81	2.02
"	36.4	3.8	5.30	3.33
"	50.0	-	-	-
25	9.1	1.16	1.39	1.11
"	22.2	1.37	2.00	1.77
"	36.4	-	-	3.15
"	50.0	-	-	-
29	9.1	1.37	1.60	1.68
"	22.2	2.32	2.60	3.10
"	36.4	4.26	4.3	5.68
"	50.0	7.58	6.3	9.74
35	9.1	1.4	1.57	1.73
"	22.2	2.53	3.0	3.27
"	36.4	4.67	6.14	6.53
"	50.0	7.6	12.43	12.0

Fig. 15 - A GRAPHICAL PLOT OF THIS PAPER'S RESULTS VS. WOELFLIN'S(9) RESULTS.

- - - - - - - - - - - - WOELFLIN'S RANGE

———————— RESULTS FROM THIS PAPER

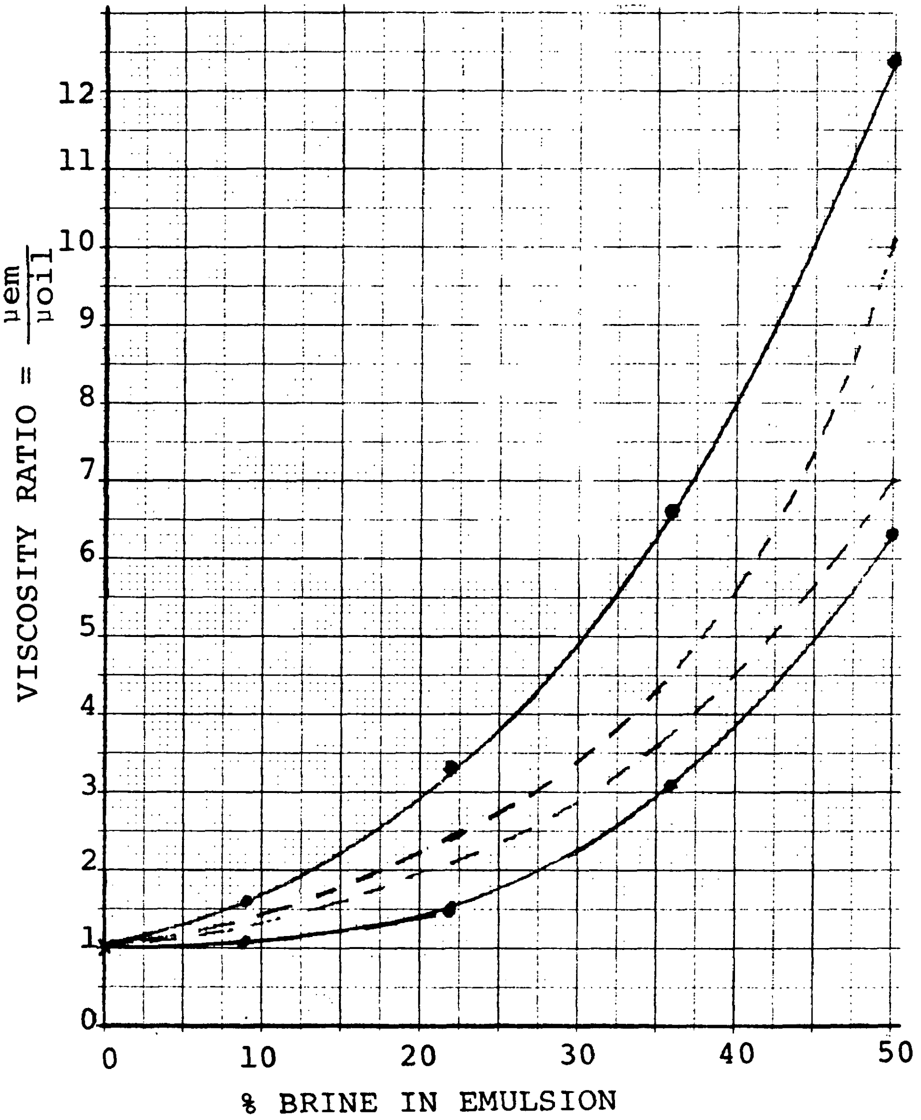


Fig. 16 - APPARENT VISCOSITY VS. WATER CONTENT

19° API CRUDE

1 - Natural @ 75°F, 20,000 mg/L
2 - Natural @ 75°F, 150,000 mg/L
3 - Natural @ 125°F, 20,000 mg/L
4 - Natural 125°F, 150,000 mg/L
5 - Artificial @ 80°F, 20,000 mg/L
6 - Artificial @ 80°F, 150,000 mg/L

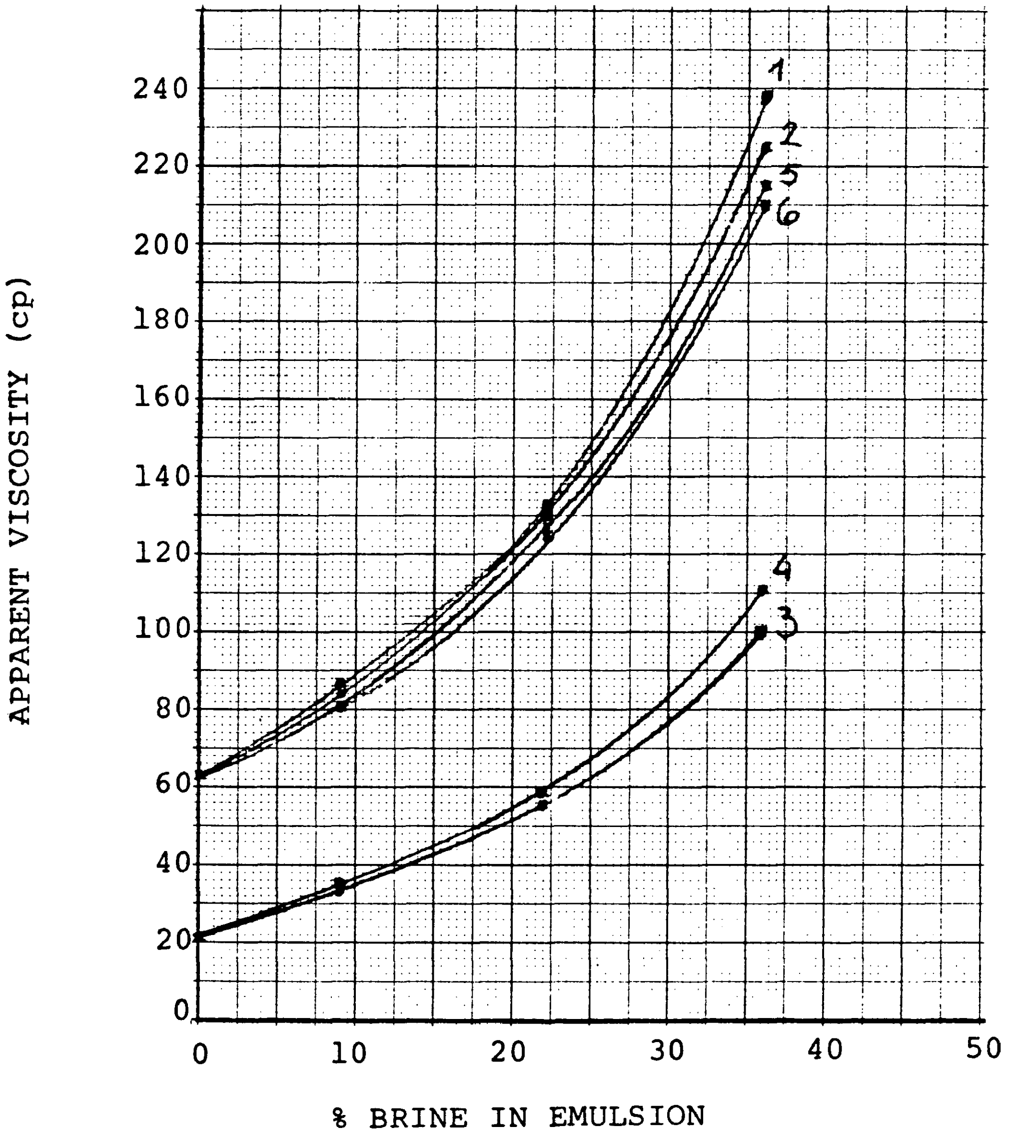


Fig. 17 - APPARENT VISCOSITY VS. WATER CONTENT

25° API CRUDE

1 - Natural @ 71°F, 20,000 mg/L
2 - Natural @ 78°F, 150,000 mg/L
3 - Natural @ 125°F, 20,000 mg/L
4 - Natural @ 125°F, 150,000 mg/L
5 - Artificial @ 80°F, 20,000 mg/L
6 - Artificial @ 80°F, 150,000 mg/L

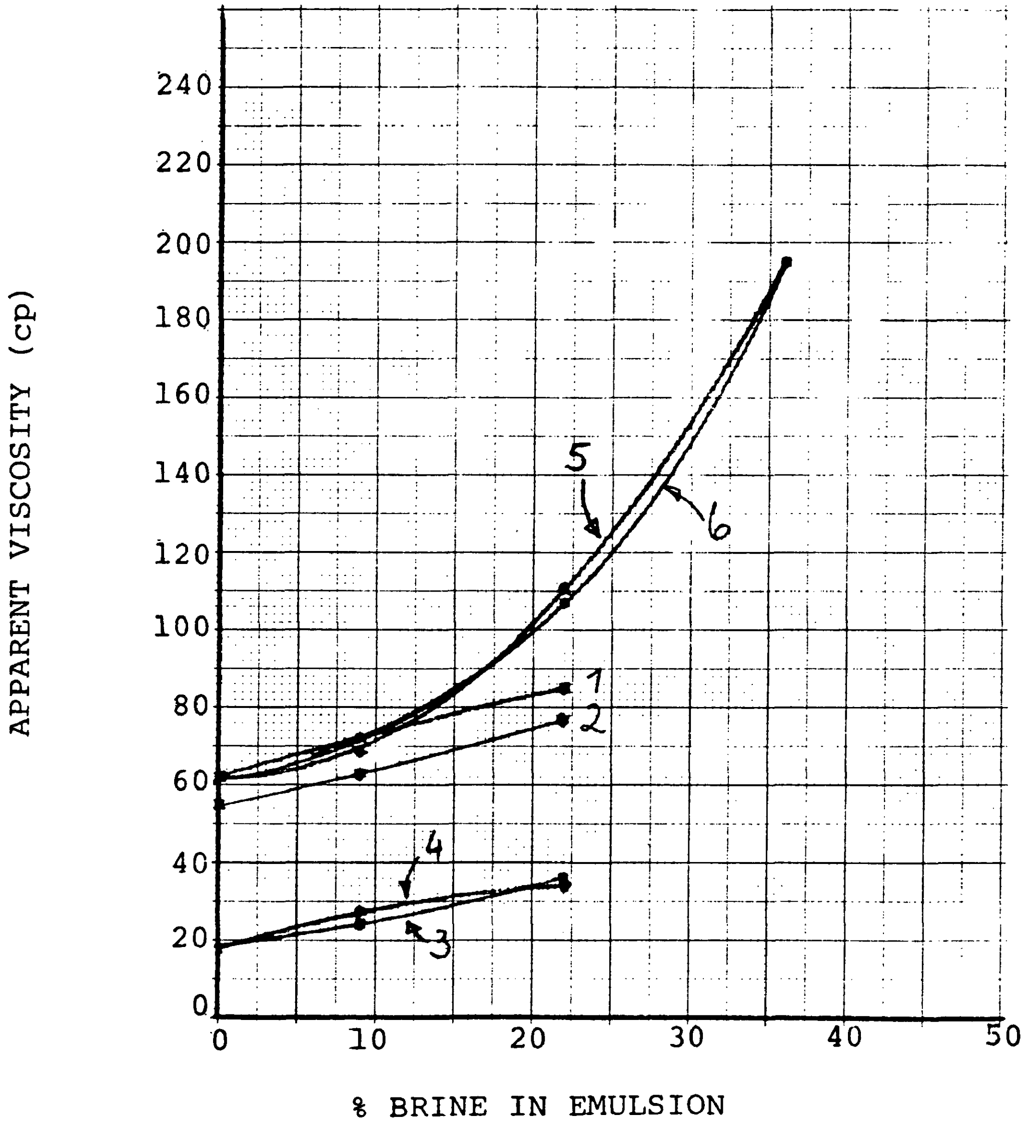


Fig. 18 - APPARENT VISCOSITY VS. WATER CONTENT

29° API CRUDE

1 - Natural @ 70°F 20,000 mg/L
2 - Natural @ 70°F, 150,000 mg/L
3 - Natural @ 125°F, 20,000 mg/L
4 - Natural @ 125°F, 150,000 mg/L
5 - Artificial @ 80°F, 20,000 mg/L
6 - Artificial @ 80°F, 150,000 mg/L

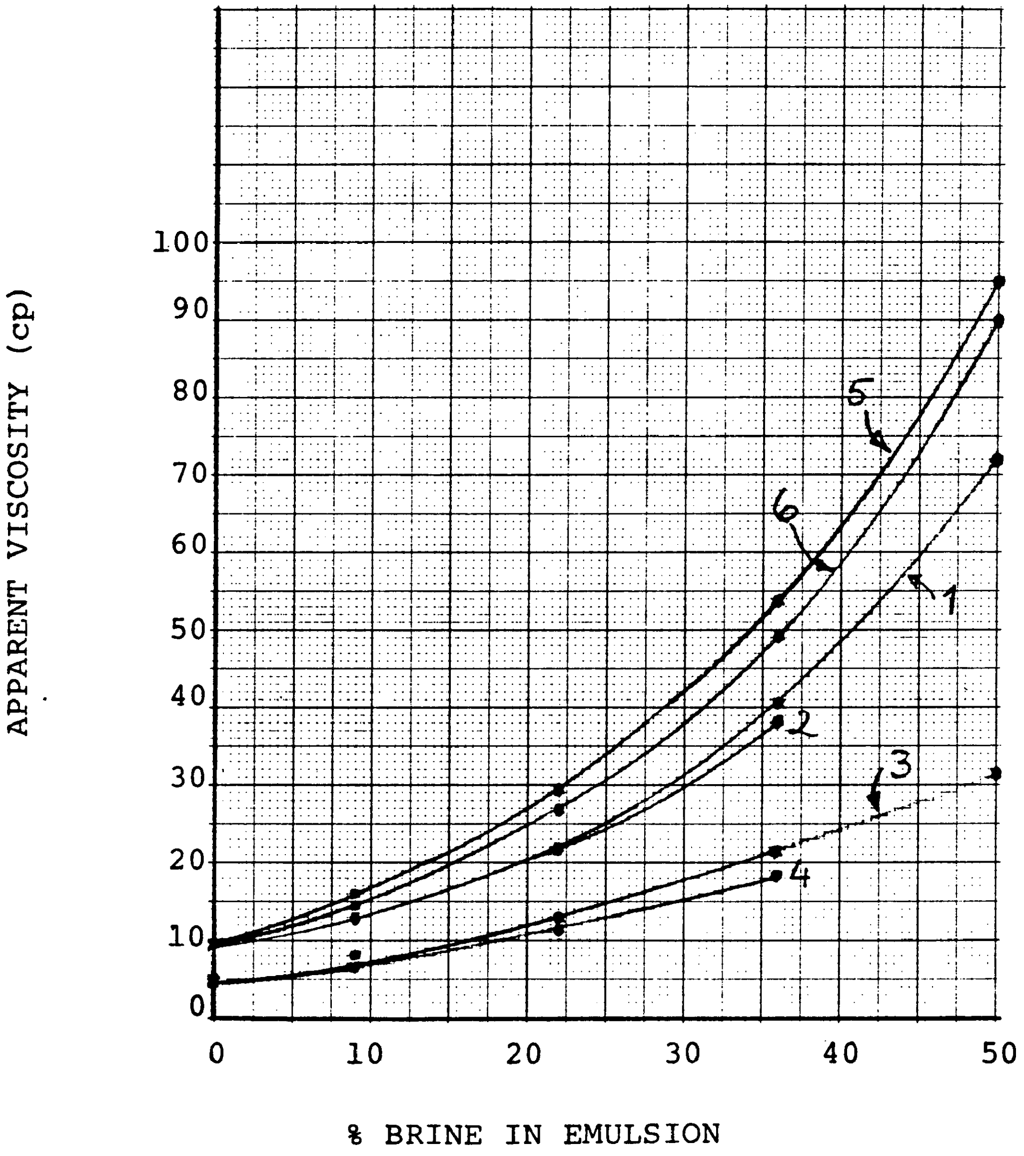


Fig. 19 - APPARENT VISCOSITY VS. WATER CONTENT

35° API CRUDE

1 - Natural @ 75°F, 20,000 mg/L
2 - Natural @ 75°F, 150,000 mg/L
3 - Natural @ 125°F, 20,000 mg/L
4 - Natural @ 125 , 150,000 mg/L
5 - Artificial @ 80°F, 20,000 mg/L
6 - Arfitifial @ 80°F, 150,000 mg/L

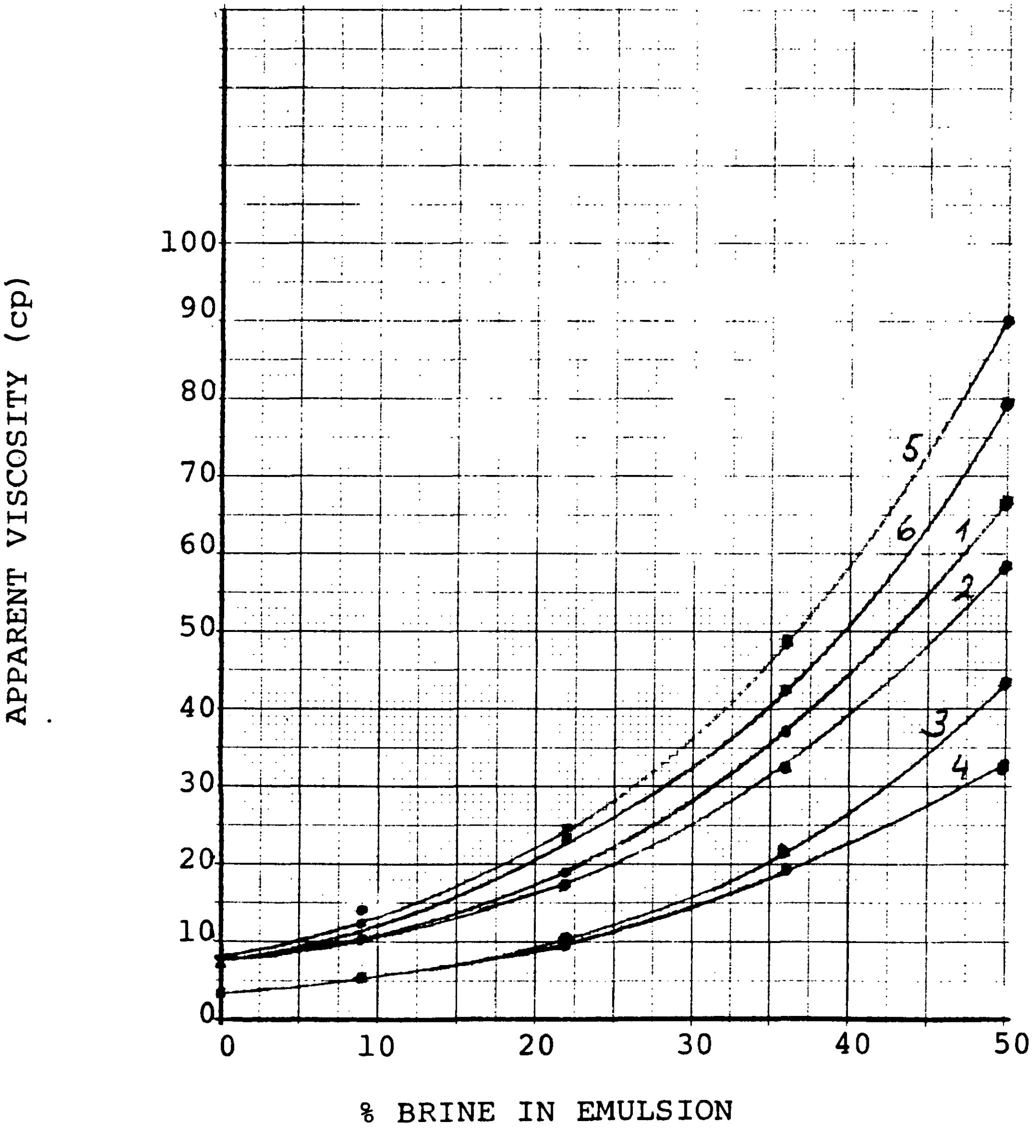


Fig. 15 also includes results at elevated temperatures, and he says that "it is apparent that the viscosity ratio for a given brine content is independent of the temperature". My results in Table 3 show that the temperature definitely affects the viscosity ratio, which is always higher at a higher temperature, probably because of the reduction in dead oil viscosity in the denominator of the ratio.

The effect of API gravity:

Figs. 20 and 21 show a comparison between the different crude oils in natural and artificial emulsions respectively. It can be seen from these charts that viscosity vs. API gravity of dead crude oils did not form a smooth curve. The 19° API and 25° API have approximately the same viscosity of about 62 cp at 75°F, while the two other ones, the 29° API and the 35° API, are both around 8 cp at the same temperature. This means that the gravity and the viscosity of crude oils are independent of each other.

The effect of the emulsifier:

Except for the 19° API crude oil, which makes a very tight and stable natural emulsion, higher values of apparent viscosity are obtained when using an emulsifier. The emulsifier, however, has a very significant effect on the rheological behavior, as seen in Tables 5 through 9.

Fig. 20 - APPARENT VISCOSITY VS. WATER CONTENT

NATURAL EMULSIONS

1 - 19° API
2 - 25° API
3 - 29° API
4 - 35° API

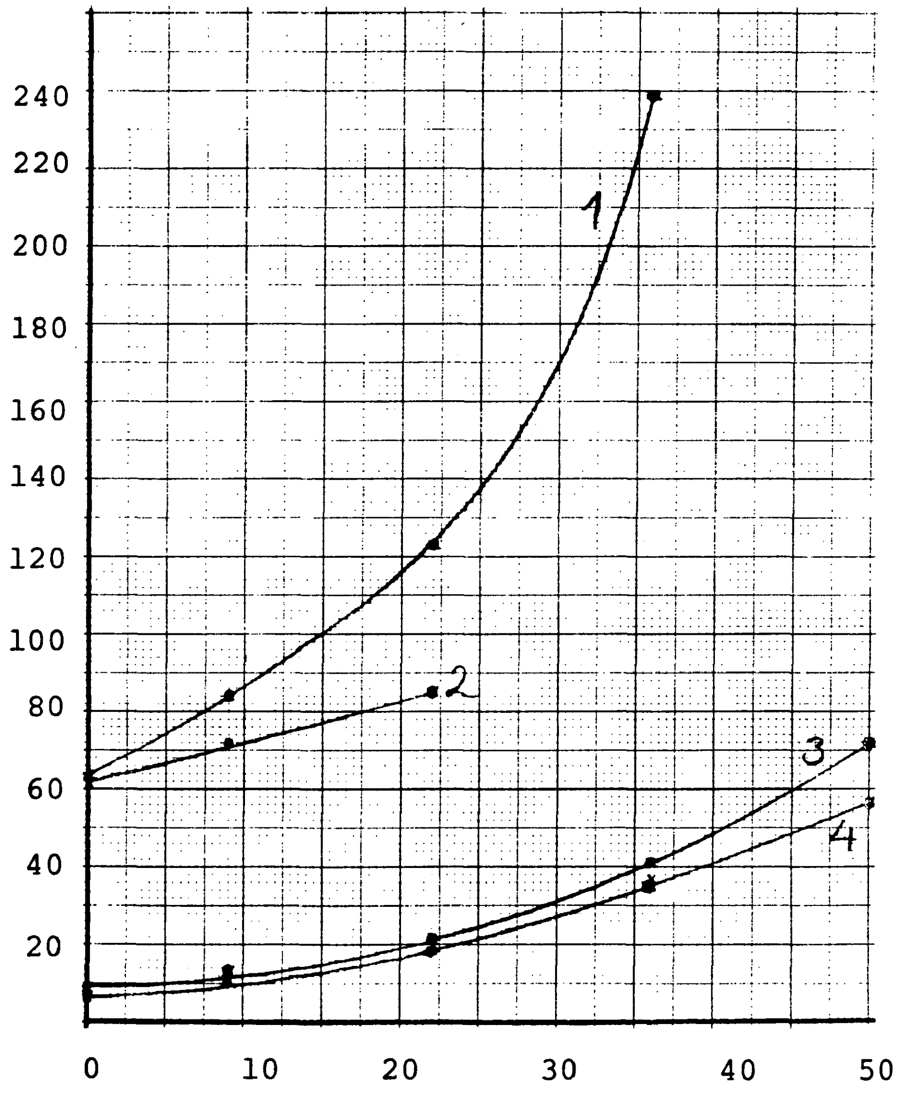
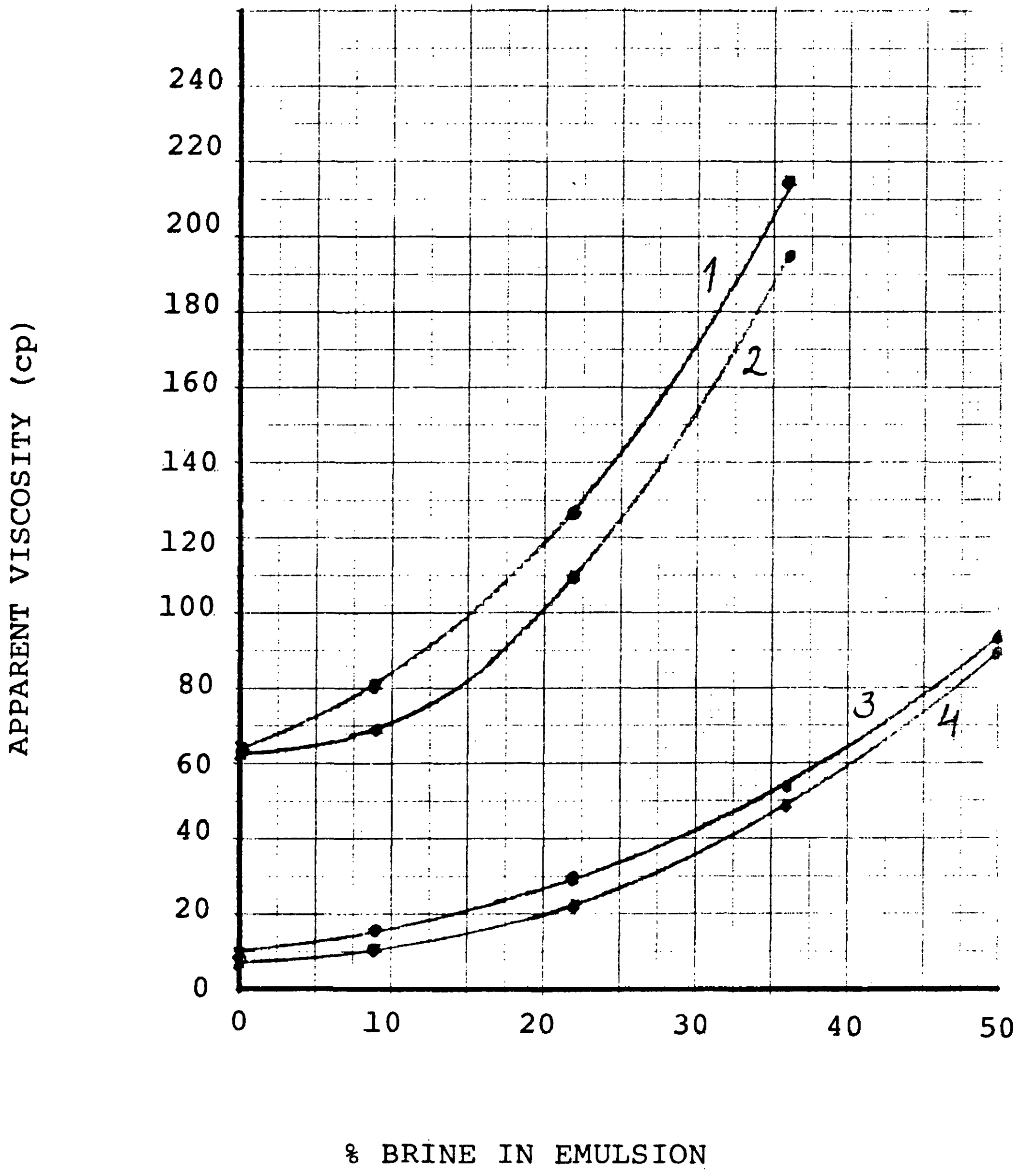


Fig. 21 - APPARENT VISCOSITY VS. WATER CONTENT

ARTIFICIAL EMULSIONS

1 - 19° API
2 - 25° API
3 - 29° API
4 - 35° API



The degree of non-Newtonian behavior increases dramatically into the plastic region as water is added together with the emulsifier. This will be discussed further in the results concerning rheology.

From the test using different amounts of emulsifier and 35% water content, the following results were obtained.

From zero percent to ½ percent by volume, there is a significant change in apparent viscosity and rheological behavior of the emulsion. The change is very noticable at low RPM's, where the readings are indicating an increasing yield point. The effect can best be seen in Fig. 22.

From 1 percent up to 8 percent content of emulsifying agent essentially no change in flow characteristics is observed. This should mean that, when using less than ½ percent of emulsifier, it is not certain that the emulsion is stable. On the other hand, using more than 2 percent in this case is most probably a waste of emulsifier.

Surface and interface tension:

The following results were obtained from the interfacial measurements and are listed in Table 4.

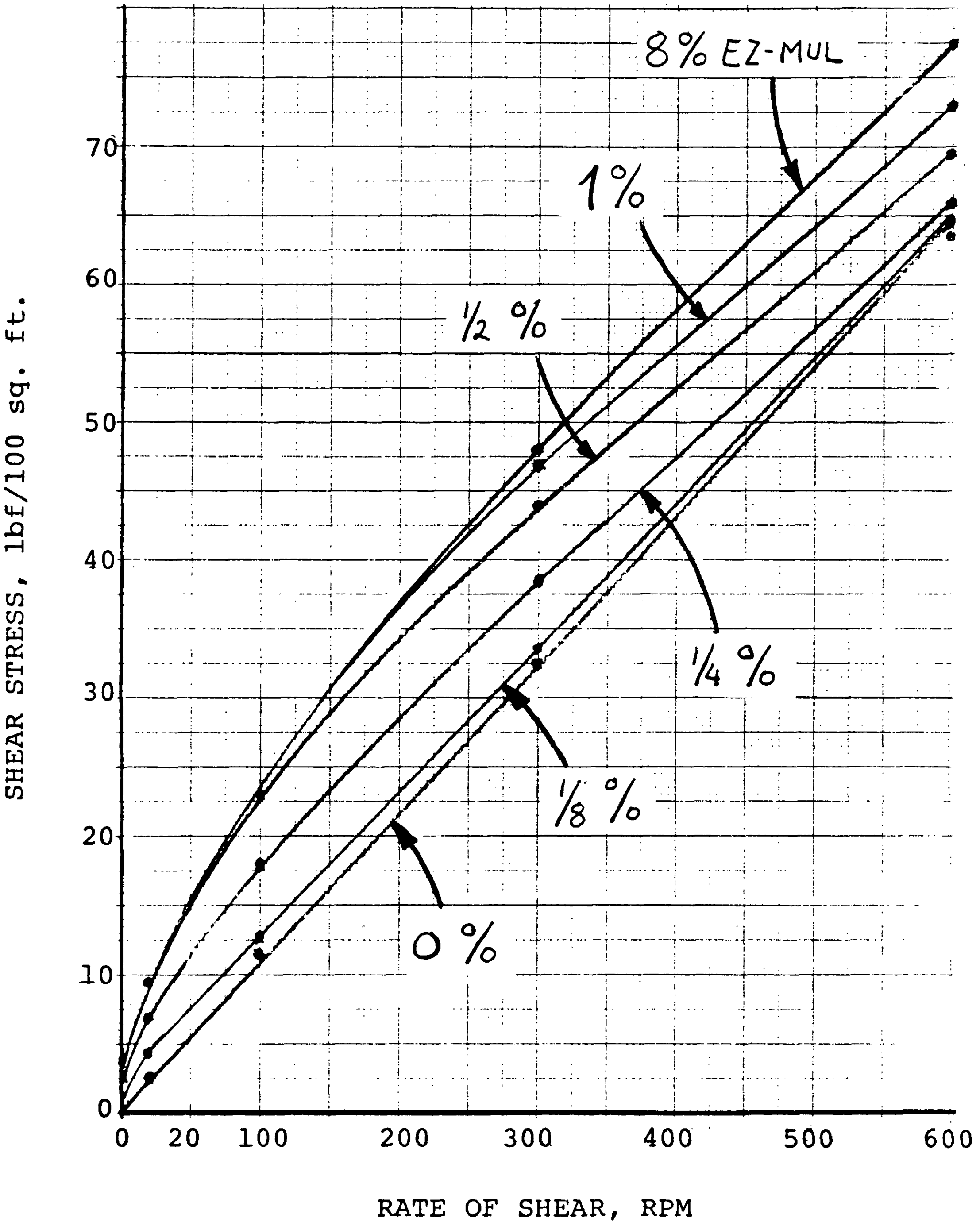
γ_s = surface tension (dynes/cm)

γ_i = interface tension

The temperature during measurements was 21°C.

The expected surface tension for pure water can be

Fig. 22 - EFFECT OF EMULSIFIER; 27° API CRUDE OIL, 35% WATER.



The expected surface tension for pure water can be calculated from the following equation:

$$\gamma_s = 75.796 - 0.145t - 0.00024t^2 \qquad \text{.....(XVI)}$$

where: t = temperature in °C

$$\gamma_s = 75.796 - 0.145 \times 21 - 0.00024 \times t^2 = 72.64 \text{ degrees/cm}$$

TABLE 4

SURFACE - AND INTERFACIAL TENSION MEASUREMENTS

Liquids	γ_s/γ_i (dynes/cm)
Distilled water	72.48
Brine, 150,000 mg/L	75.58
Crude oil, 27° API	27.41
Brine/Crude oil	19.26
Brine/Crude oil w/0.5% emulsifier	5.12
Brine/Crude oil w/1.0% emulsifier	3.43
Brine/Crude oil w/4% emulsifier	1.00

From Table 4 it is observed that the value of the interfacial tension between brine and crude oil does not fall between the individual values for surface tension, as indicated in the theory, but is lower than both. Also is seen the significant decrease in interfacial tension as an emulsifying agent is added to the crude oil. From this follows that less energy is required to form smaller particles when an emulsifier is present.

Rheology of the emulsions:

Tables 5 through 9, giving the Flow behavior index (n'), the consistancy index (K_V') and the yield point (τ_y) and Figs. 23 through 32 presenting the shear stress vs. shear rate relationship, all indicate something about the rheological properties of the natural and artificial emulsions tested.

From Tables 5 through 9, the effect of the emulsifying agent is clear. An increasing non-Newtonian (plastic) behavior is observed for all the crude oils as water is added. This is because of the large number of water particles interfering with each other, but prevented from coalescing by the emulsifying agent.

All the artificial emulsions do not show the same magnitude of non-Newtonian behavior with increasing water content, which probably is a result of the different chemical composition of the naturally occurring emulsifier.

The artificial emulsions created can generally be considered pseudoplastics. From Figs. 24, 26, 28, 30 and 32 presenting shear stress vs. shear rate, it is seen that at higher water contents, the emulsions do have a yield point, a characteristic recognized to be zero for pseudoplastics. These emulsions will therefore be classified as pseudoplastics having a yield point.

The natural emulsions are generally Newtonian, Tables 5 through 9, except the 27° API crude oil emulsion, which appears dilatant before it inverts. A reason for this may be a chemical reaction between the crude oil and the brine. The other natural emulsions stay very close to the ideal Newtonian behavior, but they are all in the plastic region, nor do they show any significant values for yield point.

The measurements shown in Fig. 32 were repeated and the same results were obtained, as seen in Fig. 33.

A calculation example of pressure loss in pipe is worked out in the Appendix for natural and artificial emulsions made from 19° API crude oil and water contents from zero to fifty percent.

Stability:

The results from the stability test for the natural emulsions are as follows:

13°API: Because of the very high viscosity, around 1000 cp at 70°F, more time was needed for the water to separate. Seventy-five percent of the water separated.

19°API: The oil and water did not separate at all. Zero percent of the water separated.

25°API: Through all experiments this crude oil showed a very low emulsion stability. One hundred percent of the water separated.

27°API: This one also was an unstable natural emulsion.

TABLE 5

RHEOLOGICAL PARAMETERS, 19°API

NATURAL EMULSIONS

% water	τ_w	τ_y	$\tau_w-\tau_y$	n'	K_v'
0	94.5	0	94.5	0.985	0.0011
4.8	107.5	0.4	107.1	0.971	0.0014
10.1	126.5	0.5	126	0.964	0.0017
15.8	156	0.7	155.3	0.965	0.0020
23.8	213.5	0.9	212.6	0.913	0.0040
33.3	310	1.3	308.7	0.953	0.0047
42.9	267*	1.5	265.5	0.961	0.0070
50.0	270**	2	268	0.990	0.0088

ARTIFICIAL EMULSIONS

% water	τ_x	τ_y	$\tau_w-\tau_y$	n'	K_v'
0	89.5	0	89.5	0.987	0.0010
4.8	110	1	109	0.885	0.0026
10.1	131.5	1.2	130.3	0.846	0.0038
15.8	160	1.5	158.5	0.843	0.0049
23.8	208	2.2	205.8	0.841	0.0063
33.3	298.5	4	294.5	0.816	0.0110
42.9	247*	8	239	0.777	0.0210
50.0	257**	12	245	0.739	0.0345

*) @ 300 RPM
**) @ 200 RPM

TABLE 6

RHEOLOGICAL PARAMETERS, 25^{o}API

NATURAL EMULSIONS

% water	τ_w	τ_y	$\tau_w-\tau_y$	n'	K'_v
0	100	0	100	0.970	0.0012
4.8	108	0.5	107.5	0.996	0.0011
10.1	121.5	0.7	120.7	0.967	0.0016
15.8	131	0.7	130.3	0.964	0.0017
23.8	149	1.0	148.0	0.939	0.0024

ARTIFICIAL EMULSIONS

% water	τ_x	τ_y	$\tau_w-\tau_y$	n'	K'_v
0	96.5	0	96.5	0.961	0.0013
4.8	112	0.7	111.3	0.914	0.00-2
10.1	134.5	1.0	133.5	0.882	0.0032
15.8	157.5	2.5	155.0	0.843	0.0047
23.8	231	4.0	227	0.780	0.0109
33.3	286	14.5	271.5	0.635	0.0355
42.9	271*	38	233	0.505	0.1065
50.0	300**	59	241	0.407	0.2393

* @ 300 RPM
** @ 200 RPM

TABLE 7

RHEOLOGICAL PARAMETERS, 27^{o}API

NATURAL EMULSIONS

% water	τ_w	τ_y	$\tau_w-\tau_y$	n'	K_v'
0	20	0	20	1.000	0.00021
4.8	23.5	0	23.5	0.981	0.00029
10.1	28	0	28	1.010	0.00029
15.8	33	0	33	1.099	0.00018
23.8	42.5	0	42.5	1.195	0.00011
33.3	55	0	55	1.230	0.00011

ARTIFICIAL EMULSIONS

% water	τ_w	τ_y	$\tau_w-\tau_y$	n'	K_v'
0	16.5	0	16.5	0.993	0.00018
4.8	21.5	0.1	21.4	0.938	0.00034
10.1	37.5	0.3	37.2	0.927	0.00066
15.8	45.5	0.4	45.1	0.846	0.00014
23.8	60.5	2.0	58.5	0.706	0.0047
33.3	88.5	6.0	82.5	0.626	0.0115
42.9	143	13.0	130.0	0.543	0.0322
50.0	200	20	180.0	0.525	0.0505

TABLE 8

RHEOLOGICAL PARAMETERS, 29°API

NATURAL EMULSIONS

% water	τ_w	τ_y	$\tau_w - \tau_y$	n'	K'_v
0	16.5	0	16.5	0.986	0.00020
4.8	20.5	0	20.5	0.904	0.00041
10.1	25	0	25	0.913	0.00046
15.8	31	0	31	0.909	0.00060
23.8	41.5	0	41.5	0.929	0.00068
33.3	62.5	0.1	62.4	0.940	0.00095
42.9	95	0.4	94.6	0.970	0.00110

ARTIFICAL EMULSIONS

% water	τ_w	τ_y	$\tau_w - \tau_y$	n'	K'_v
0	17	0	17	0.993	0.00017
4.8	20.5	0.3	20.2	0.892	0.00044
10.1	25	0.4	24.6	0.911	0.00067
15.8	36	0.6	35.4	0.855	0.00095
23.8	49	0.8	48.2	0.776	0.0023
33.3	74	5.0	69.0	0.626	0.0096
42.9	113	11.0	102.0	0.549	0.0242
50.0	155	14.0	141.0	0.525	0.0395

TABLE 9

RHEOLOGICAL PARAMETERS, 35°API

NATURAL EMULSIONS

% water	τ_w	τ_y	$\tau_w-\tau_y$	n'	K_v'
0	15	0	15	0.939	0.00026
4.8	15.5	0	15.5	0.985	0.00018
10.1	21	0	21	0.884	0.00050
15.8	27	0.1	26.9	0.871	0.00066
23.8	40	0.2	39.8	0.905	0.0008
33.3	64	0.3	63.7	0.928	0.0011
42.9	99	0.7	98.3	0.828	0.0034
50.0	140	1.0	139.0	0.852	0.0040

ARTIFICIAL EMULSIONS

% water	τ_x	τ_y	$\tau_w-\tau_y$	n'	K_v'
0	13	0	13	0.819	0.00045
4.8	18	0.1	17.9	0.840	0.00056
10.1	23	0.3	22.7	0.840	0.00068
15.8	34	0.6	33.4	0.783	0.00157
23.8	50	2.5	47.5	0.714	0.00360
33.3	77	7	70	0.567	0.01467
42.9	121	14	107	0.493	0.03745
50.0	165	14	151	0.429	0.08235

Fig. 23 - NATURAL EMULSIONS FROM 19°API CRUDE

SHEAR STRESS VS. RATE OF VS. RATE OF SHEAR.

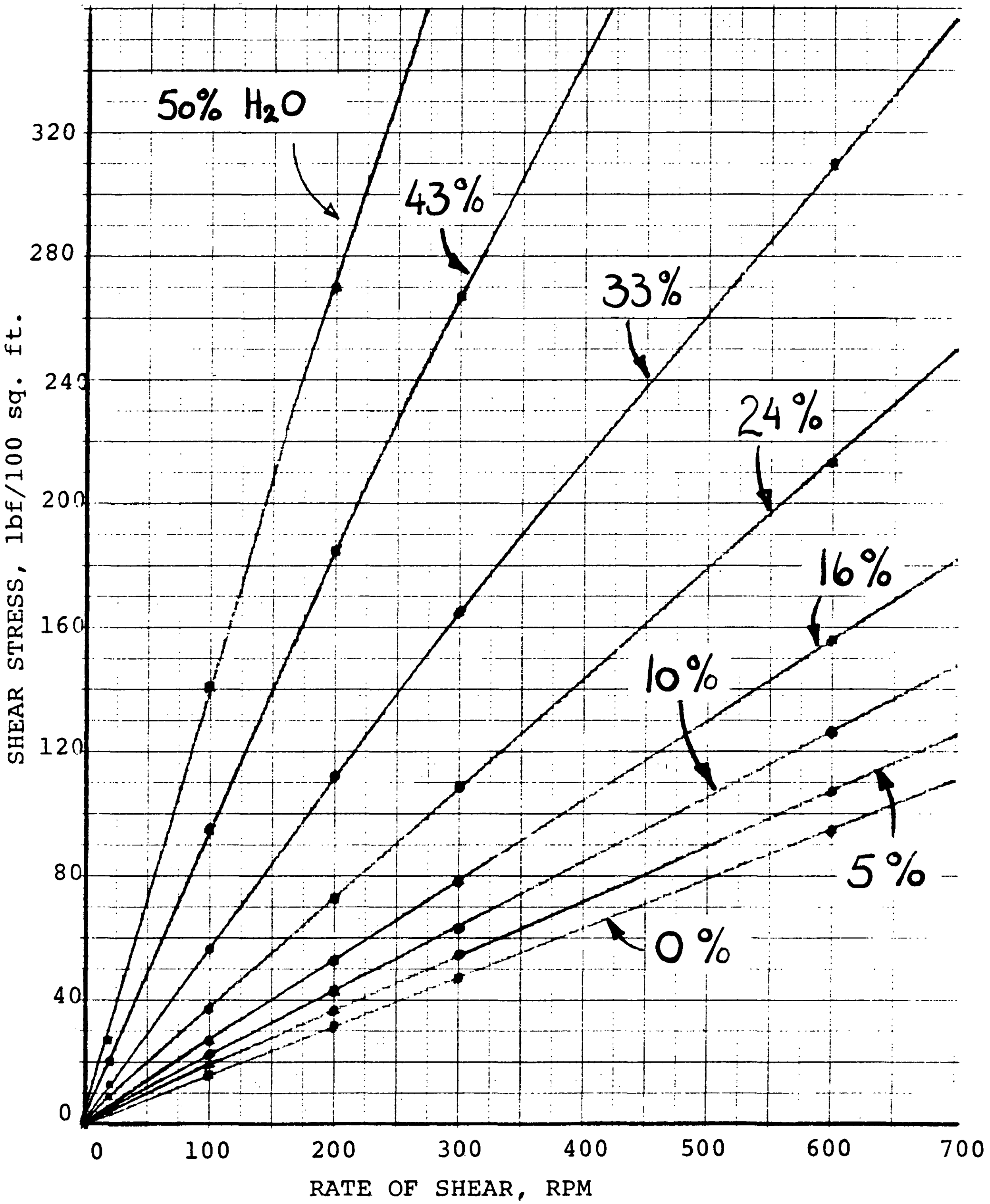


Fig. 24 - ARTIFICIAL EMULSIONS FROM 19°API crude

SHEAR STRESS VS. RATE OF SHEAR.

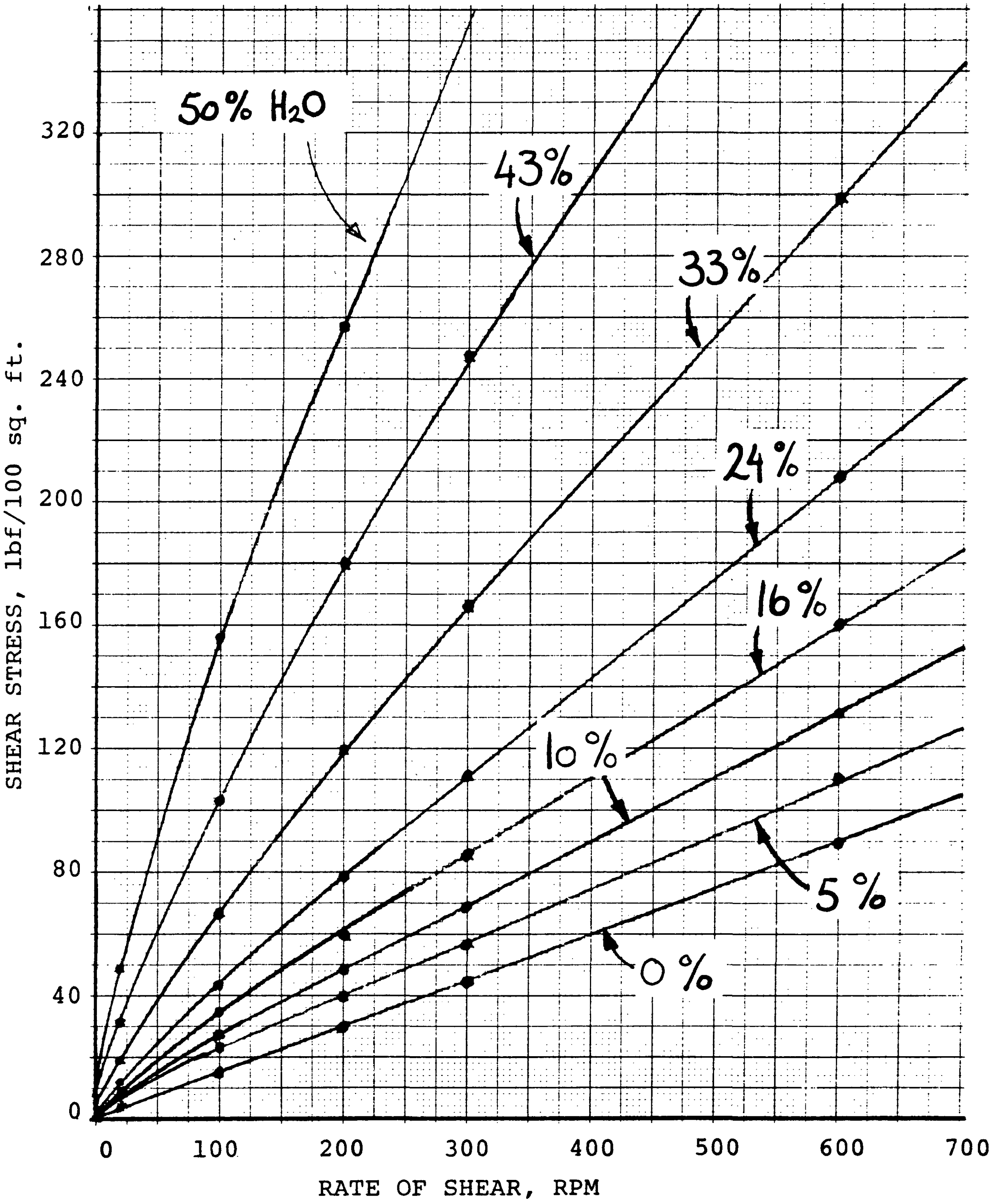


Fig. 25 - NATURAL EMULSIONS FROM 25°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

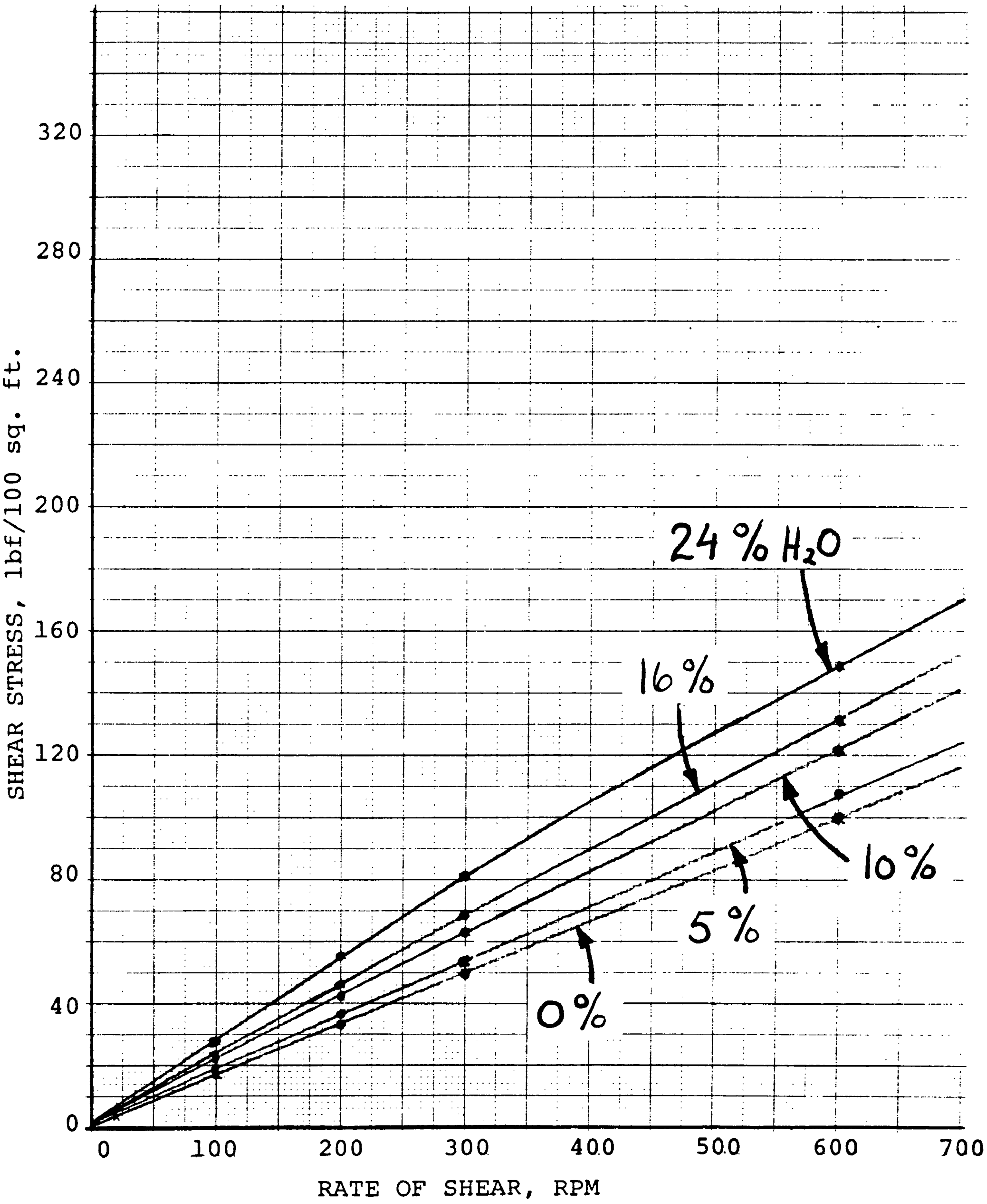


Fig. 26 - ARTIFICIAL EMULSIONS FROM 25°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

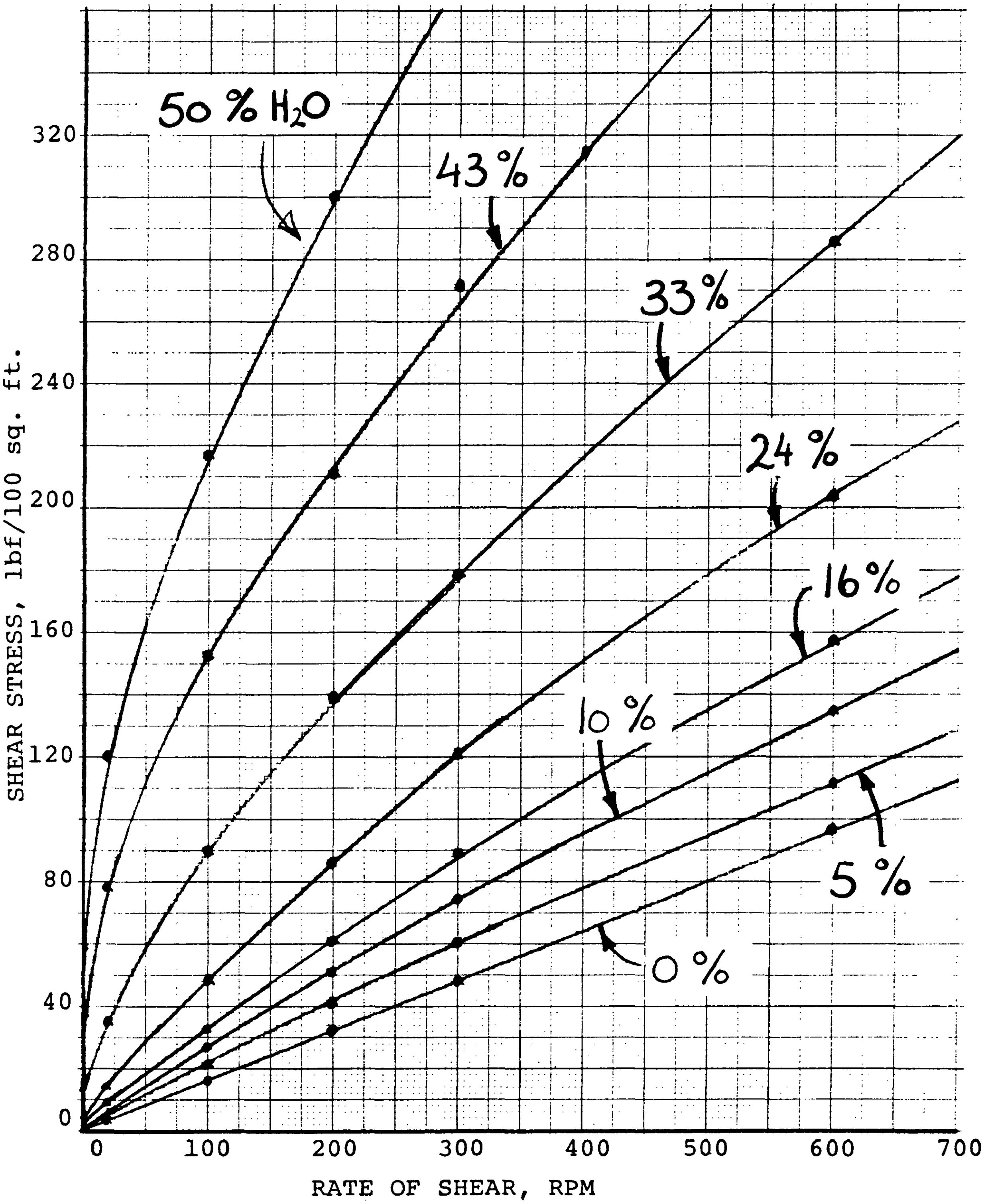


Fig. 27 - NATURAL EMULSIONS FROM 27°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

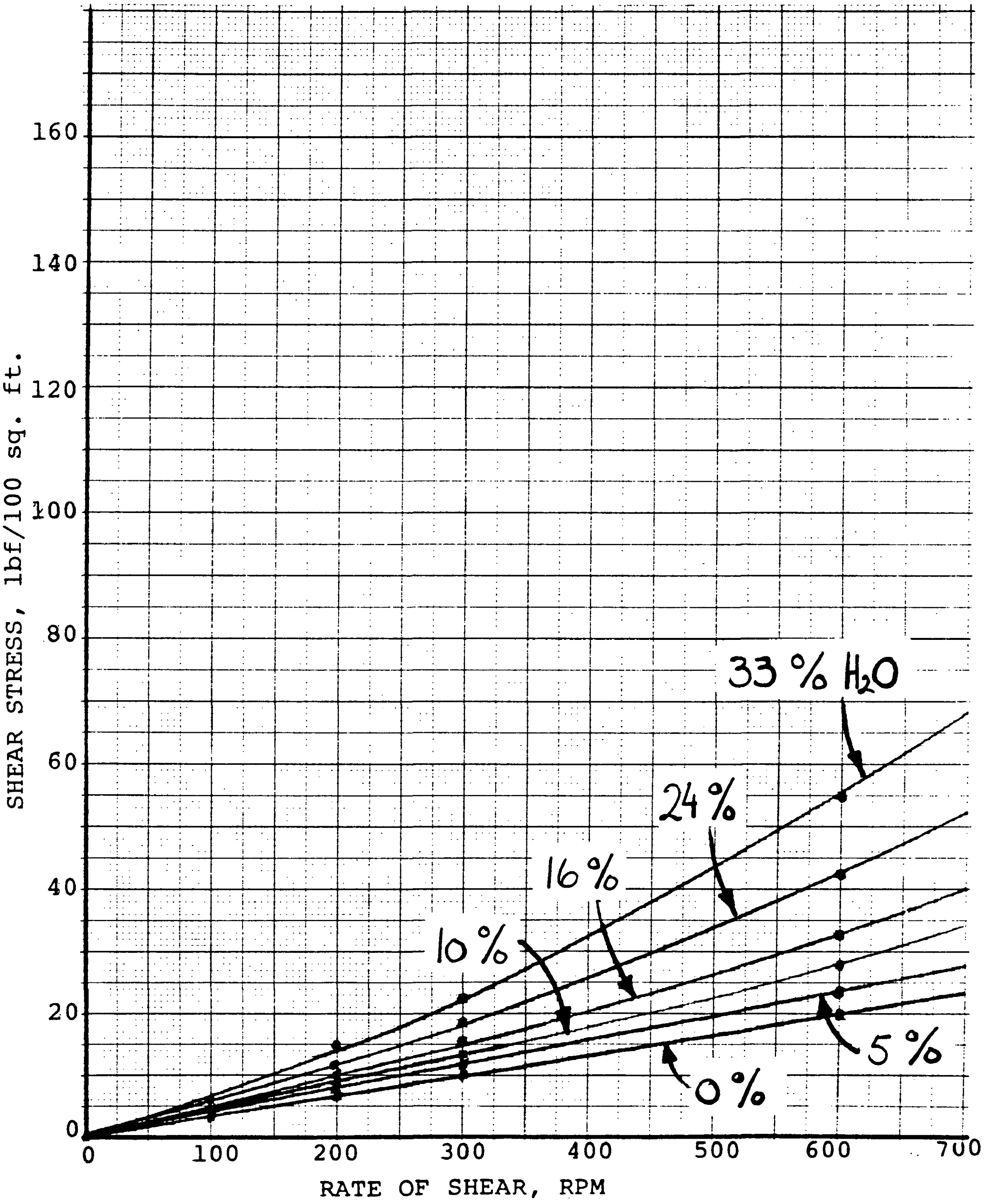


Fig. 28 - ARTIFICIAL EMULSIONS FROM 27°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

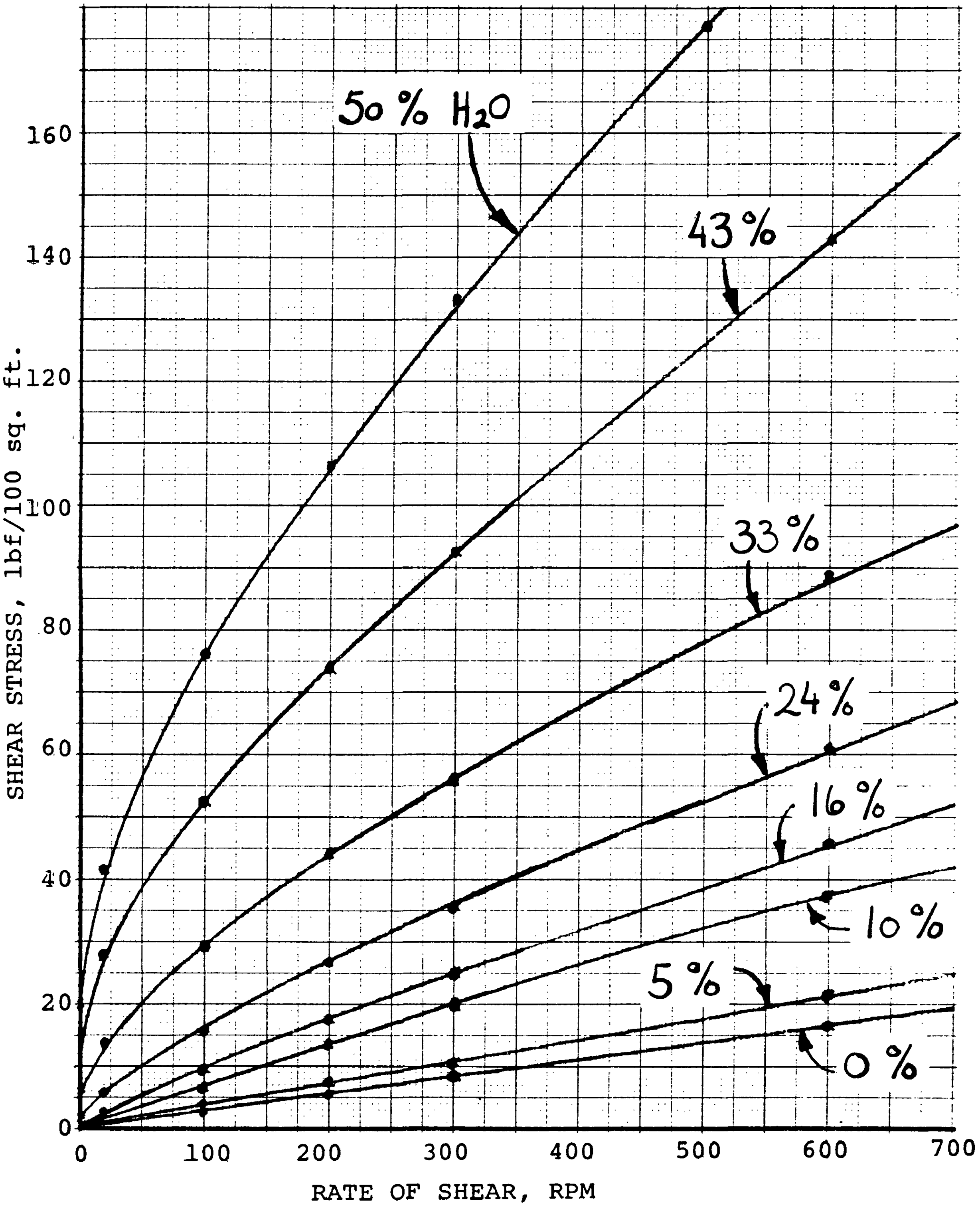


Fig. 29 - NATURAL EMULSIONS FROM 29°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

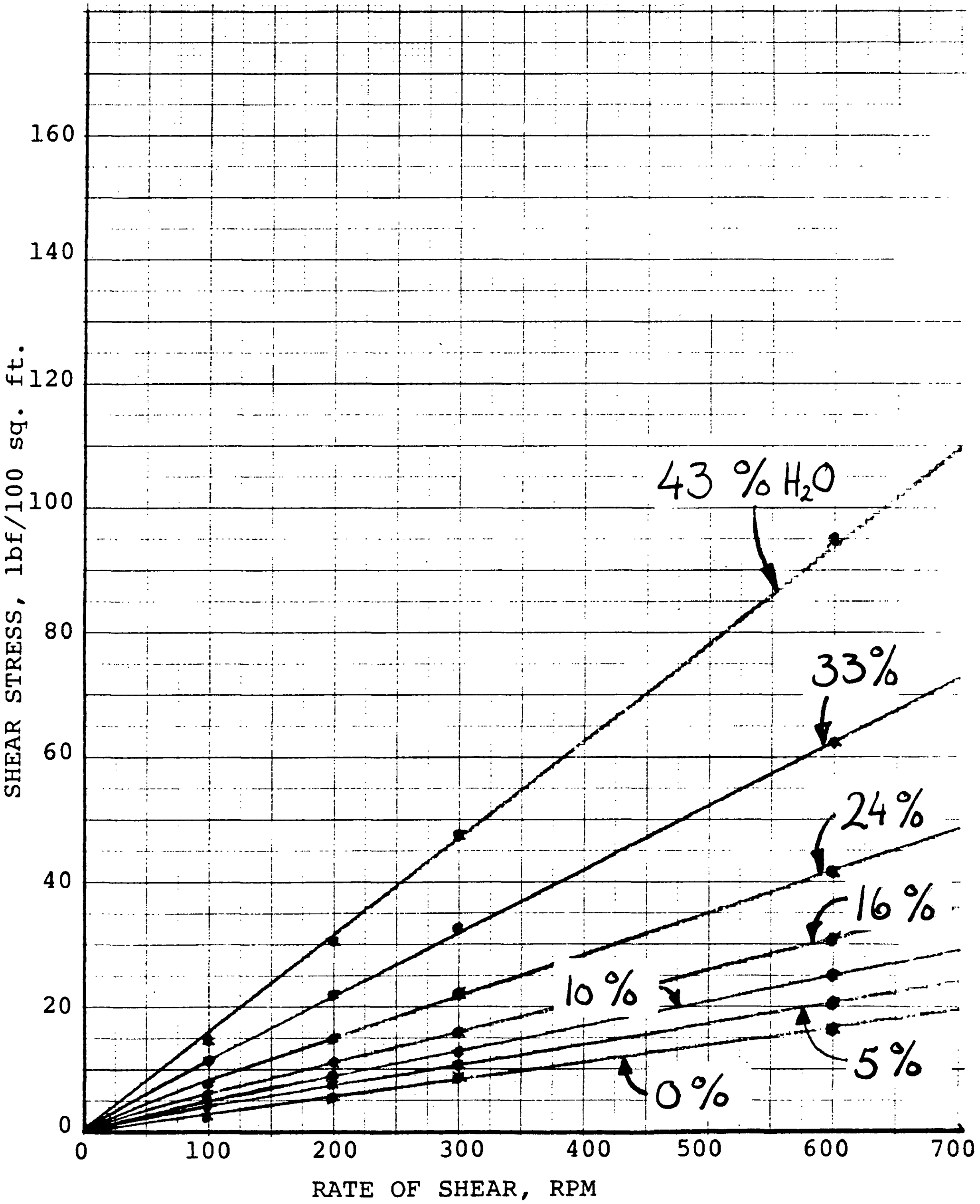


Fig. 30 - ARTIFICIAL EMULSIONS FROM 29°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

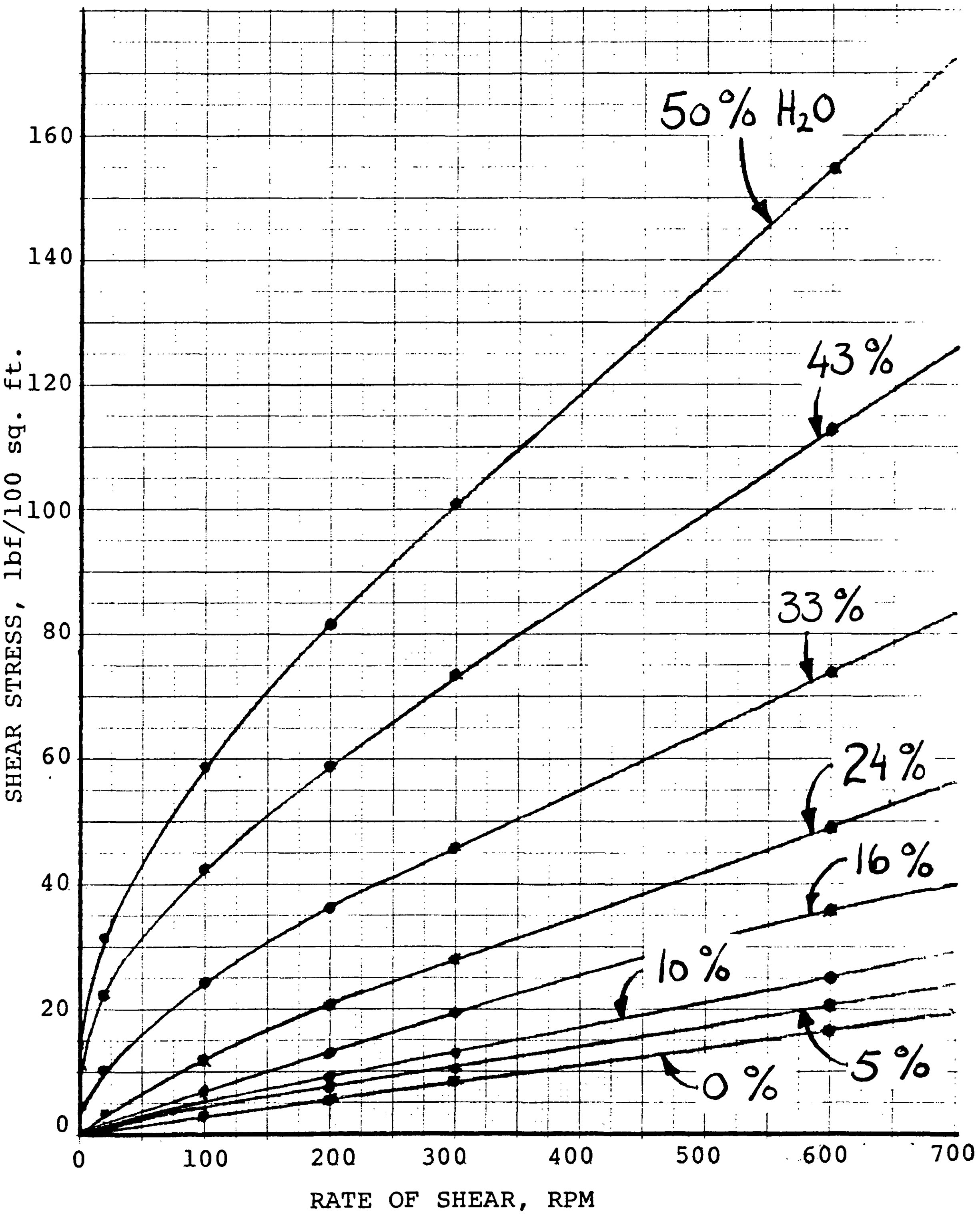


Fig. 31 - NATURAL EMULSIONS FROM 35°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

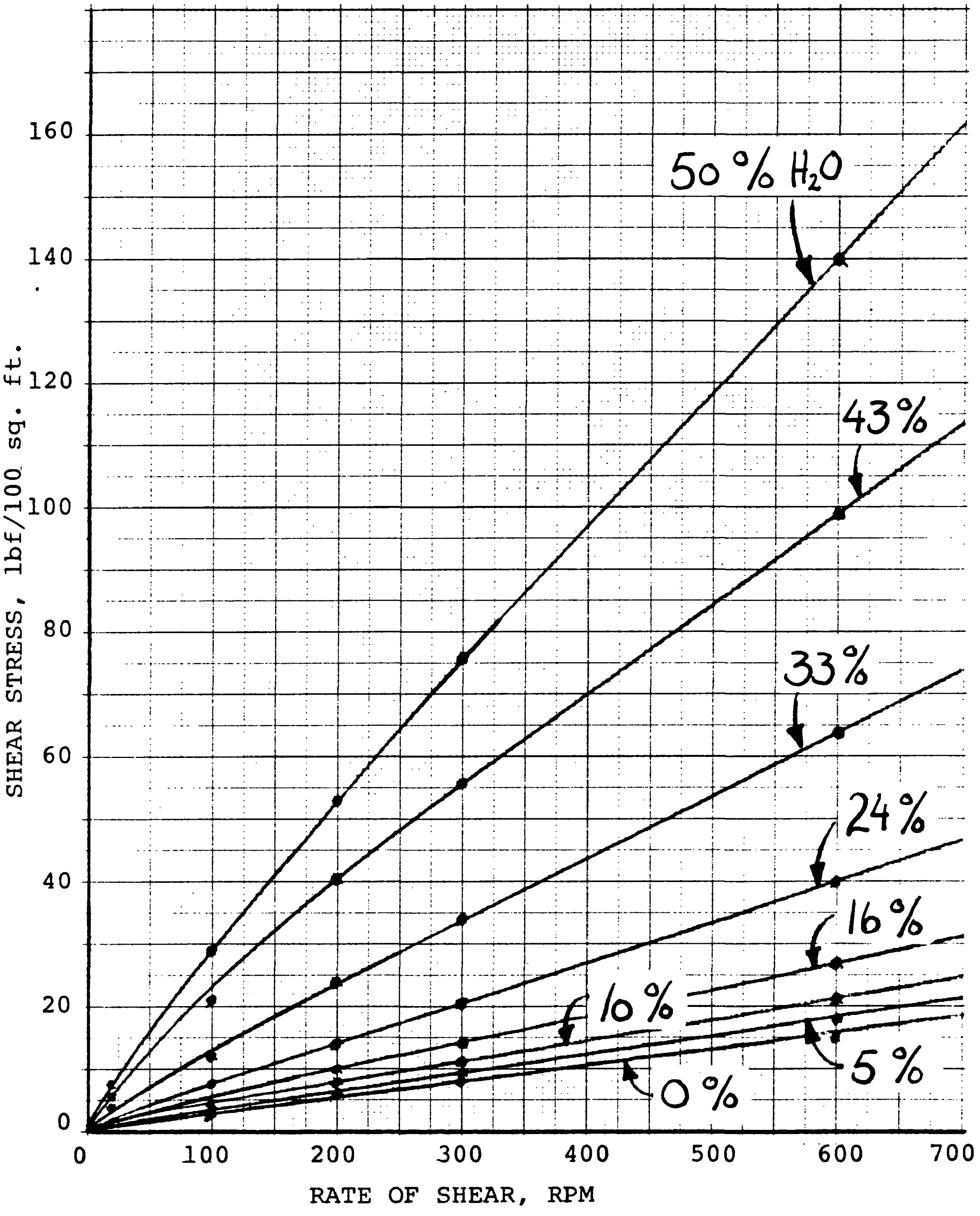


Fig. 32 - ARTIFICIAL EMULSIONS FROM 35°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.

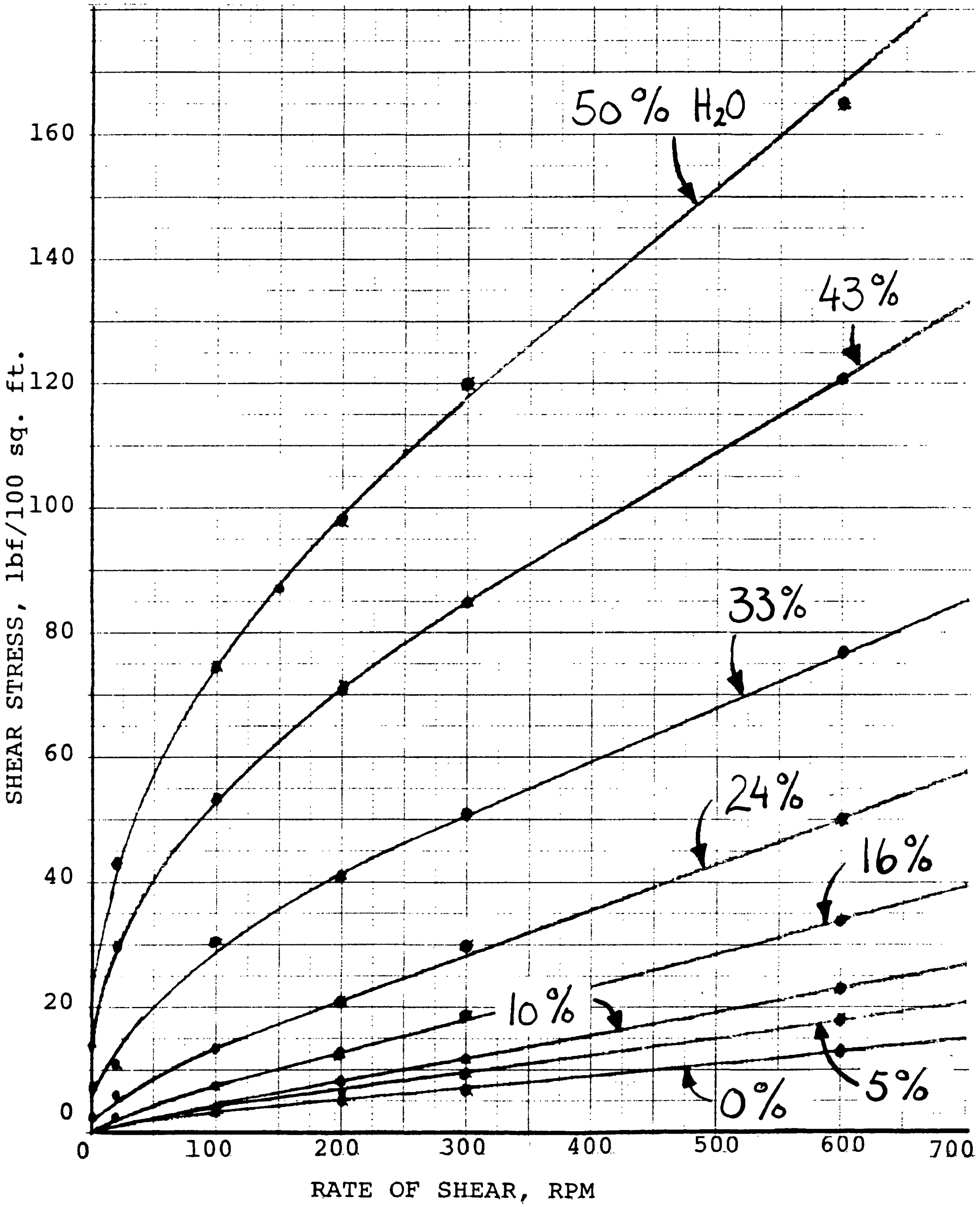
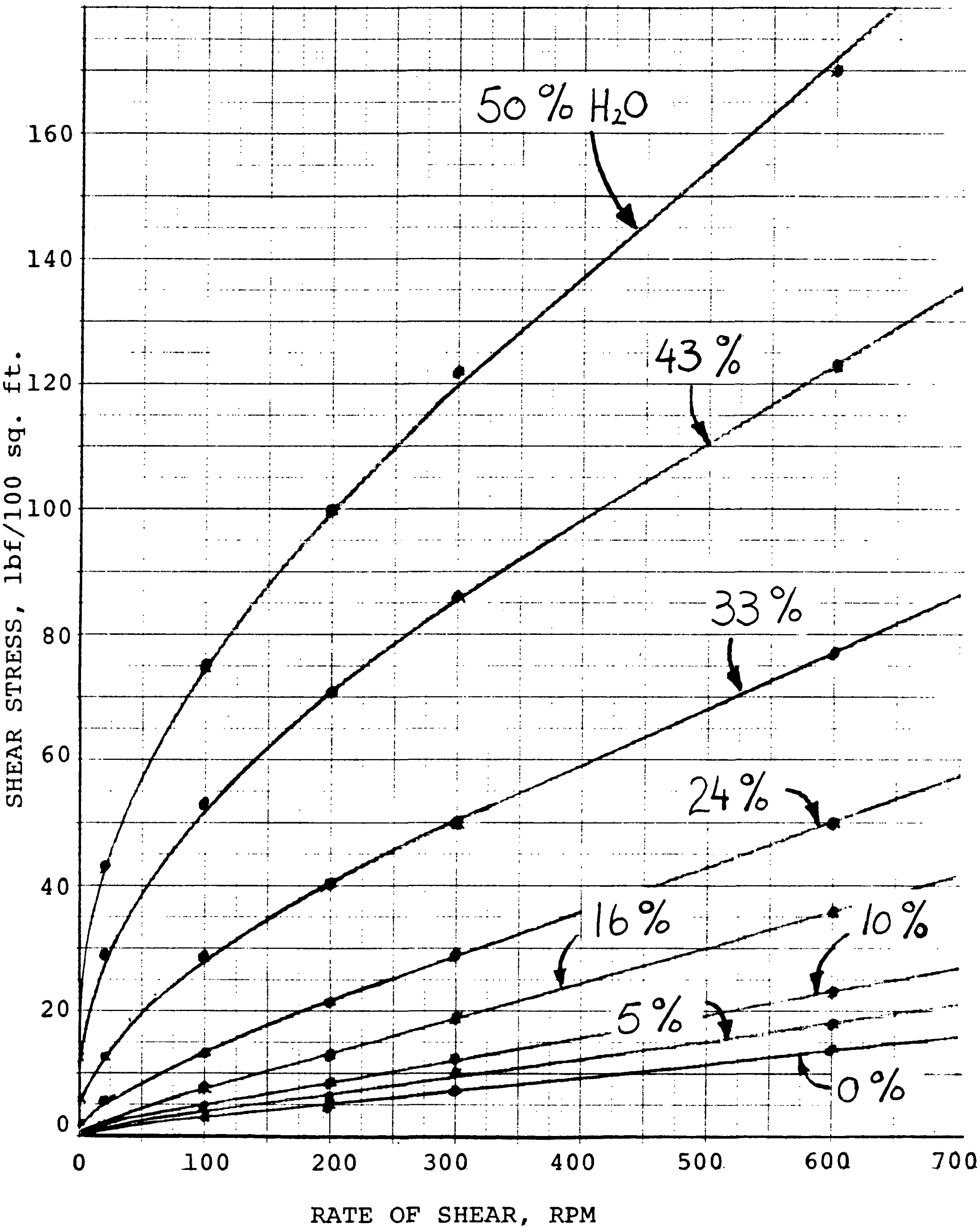


Fig. 33 - ARTIFICIAL EMULSIONS FROM 35°API CRUDE

SHEAR STRESS VS. RATE OF SHEAR.



29°API: One hundred percent of the water settled out.
Thirty-three percent of the water separated out.
35°API: Again a good emulsifying crude oil.
Zero percent of the water settled out.

Why do some crude oils make more stable emulsions than others? A reasonable explanation to this quesiton is that some of the crudes have a chemical composition which, when they are mixed with water, produce an agent having emulsifying properties. In other words, there is a natural occurance of an emulsifying agent. The varying amount and quality of the agent present create a spectrum from very good to total lack of stability.

The stability of an artificial emulsion is definitely higher than for the natural ones. There was never any tendency of water to settle out, but rather for oil droplets to migrate to the top. After 25 days, a layer of pure crude oil could be observed on the top of the emulsion.

As can be seen from the photomicrographs later in the results, some of the same properties are present in the artificially made emulsions as in the natural ones, especially the particle sizes. Despite the presence of the emulsifier, the effect of the natural emulsifying agent is not eliminated. This should mean that the naturally occurring agent, can be better than the synthetic one.

From Figs. 45 and 46, showing the particle sizes when using only ½% of emulsifying agent instead of 2%, its effect is clear. The droplets are significantly smaller than in the natural emulsions, but still much larger than for the higher concentration of emulsifier.

The photomicrographs following (Figs. 34 through 39), are of natural emulsions with 23% water content, and artificial emulsions (Figs. 40 through 45), at 36 and 50% water content. Two artificial emulsions at 50% water content and ½% emulsifier are also included (Figs. 46 and 47). Comments follow each picture.

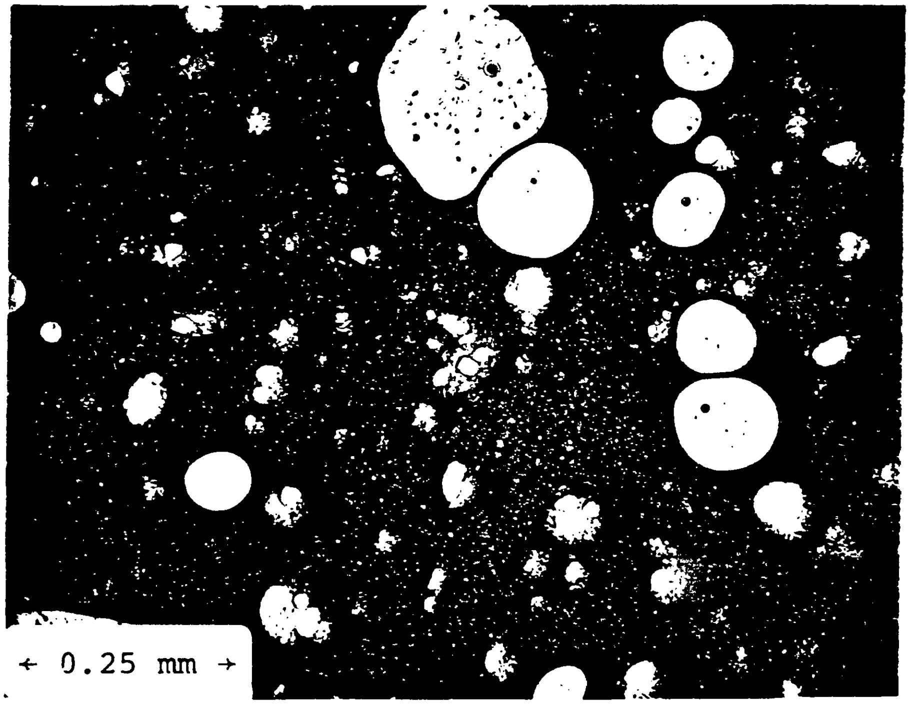


Fig. 34 - 13^{O}API, 23% water, 100 power, natural emulsion.

In Fig. 34, we can see how water particles were spread throughout the emulsion. Between some of the larger droplets was a film of oil preventing coalescence. However, observing them for awhile, it was seen that the film was not strong enough to keep the droplets separated.

Fig. 35 - 19°API, 23% water, 100 power, natural emulsion.

The presence of a natural emulsifying agent in this crude oil (Fig. 35) helped create a tight emulsion. The particles are very small, and almost no free water can be traced. The white area is air outside the emulsion.

The darker area in Fig. 36 was crude oil with large water particles dispersed in it, while the lighter area is free water. The total lack of natural emulsifier makes this emulsion very unstable, as discussed in experimental results.

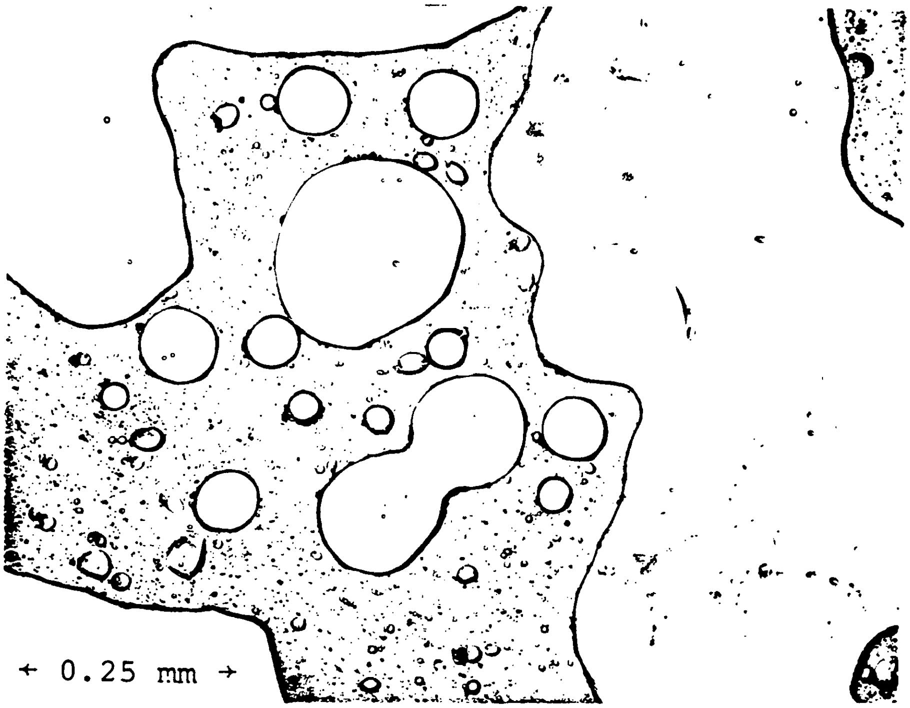


Fig. 36 - 25°API, 23% water, 100 power, natural emulsion.

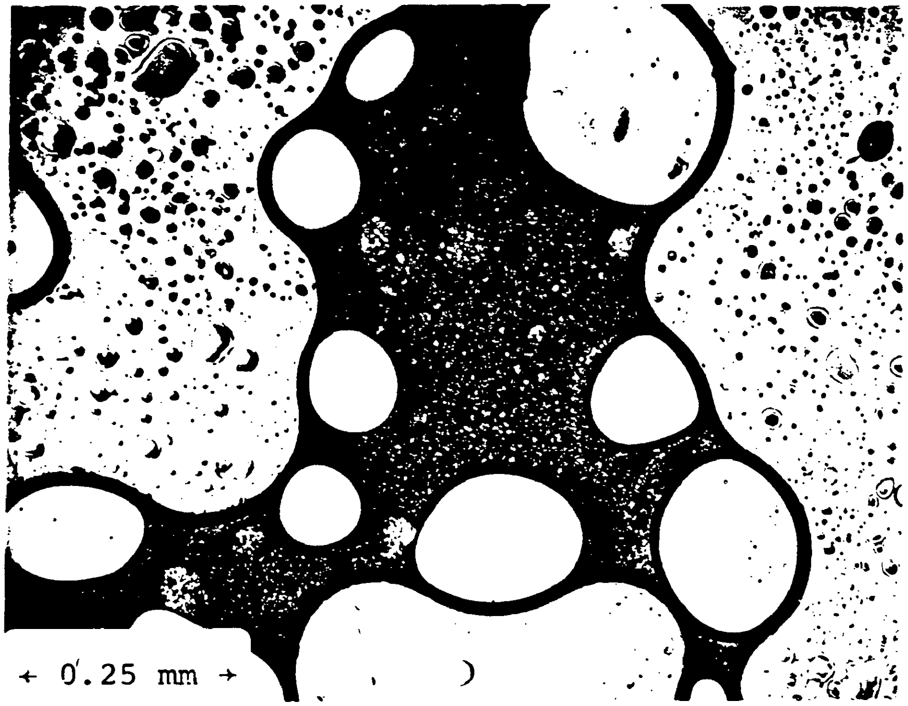


Fig. 37 - 27°API, 23% water, 100 power, natural emulsion.

Some of the emulsion in Fig. 37 was inverted. The center dark part was the continuous oil phase with large water particles dispersed, while the sides of the picture show water as the continuous phase with oil particles spread in it.

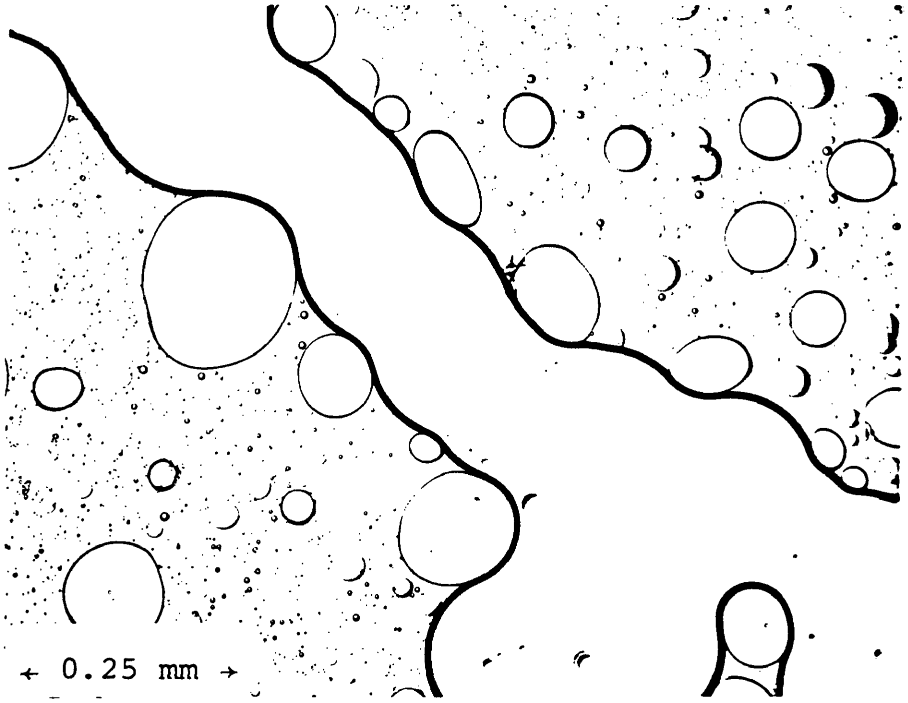


Fig. 38 - 29°API, 23% water, 100 power, natural emulsion.

Also in Fig. 38, some emulsion had inverted. The diagonal channel is free water containing small oil particles, while the surrounding solution is a continuous oil phase having water particles of all sizes. The very small water particles probably cause the partial stability observed in the stability test. Small amounts of natural emulsifier could be present, strengthening the film separating the two phases, (the thick black line).

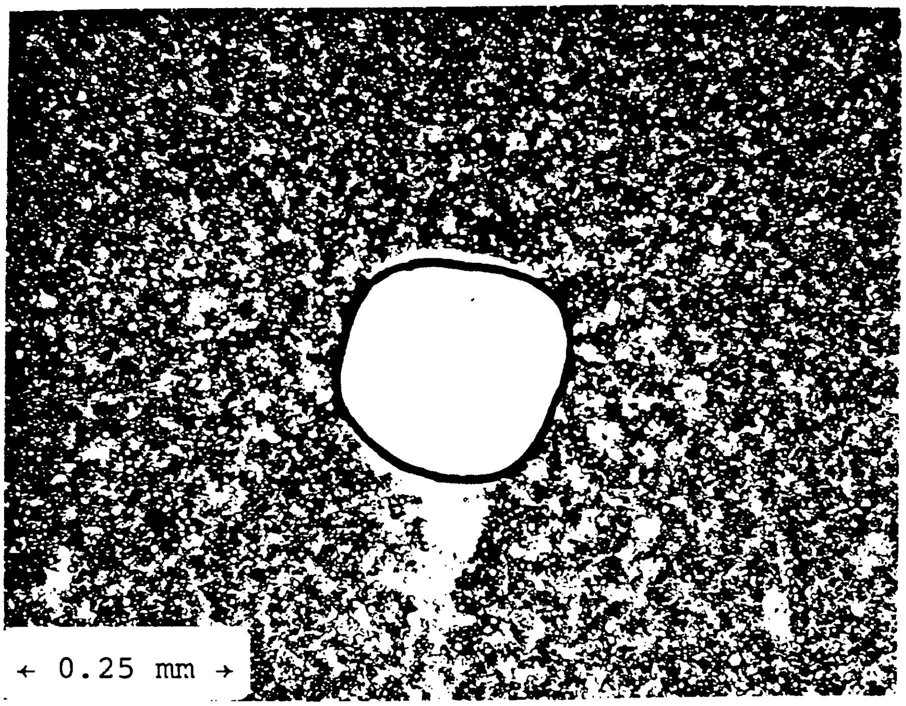


Fig. 39 - 35°API, 23% water, 100 power, natural emulsion.

To find a contrast to the otherwise well mixed emulsion in Fig. 39, this water droplet was photographed. Large water droplets were few in number in this emulsion. The water seemed to be very homogeneously spread over the entire sample area. A natural emulsifier is most probably present.

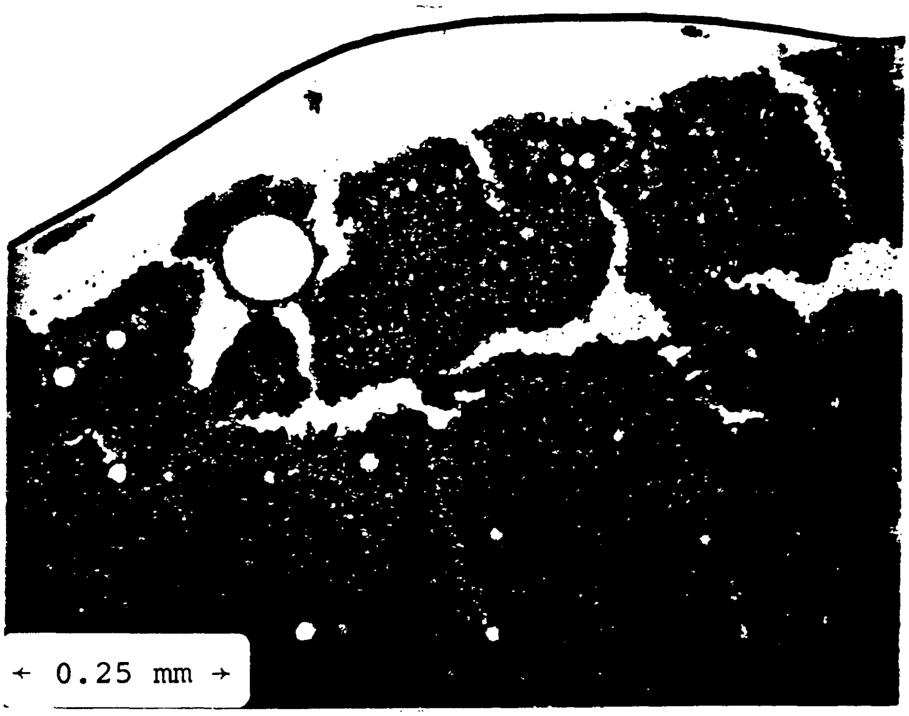


Fig. 40 - 13°API, 50% water, 100 power artificial emulsion.

Two percent synthetic emulsifier was added, Fig. 40, and a much tighter emulsion was obtained than in Fig. 11. The dark part is tight emulsion, the light areas inside the borderline are water, and outside the line is air. Significant amounts of free water are present.

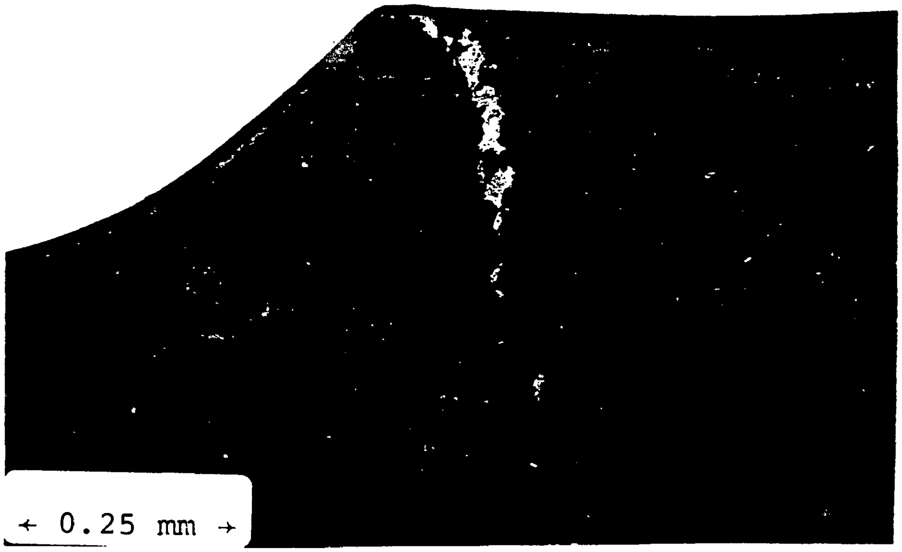


Fig. 41 - 19°API, 36% water, 100 power, artificial emulsion.

Again it is seen in Fig. 41, that this crude oil makes a very tight emulsion. Except for a few water spots, the mixture is homogeneously made up of minute particles that can hardly be seen on the photomicrograph. The white area is air outside the emulsion.

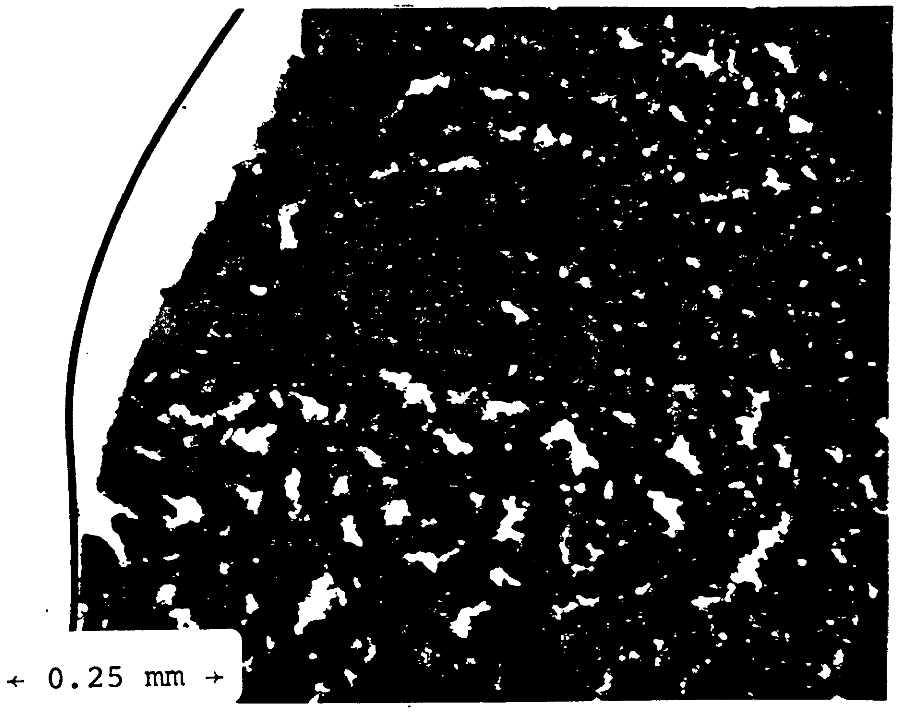


Fig. 42 - 25^{o}API, 36% water, 100 power, artificial emulsion.

The tendency toward instability of this emulsion is seen in Fig. 42, from the rather large amounts of free water which have escaped to the edge of the emulsion. To the left of the black line is air.

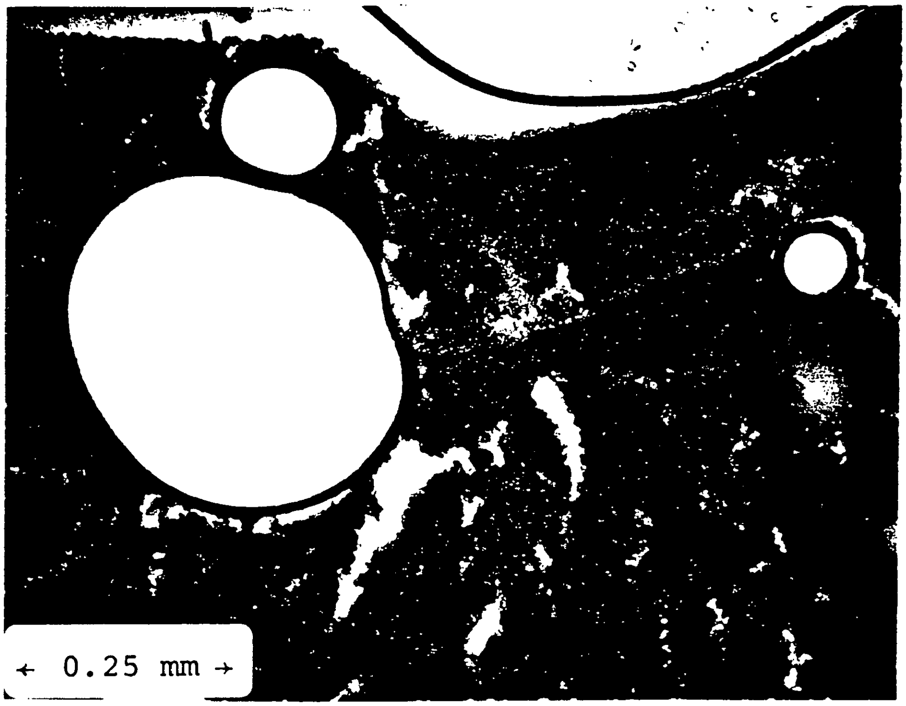


Fig. 43 - 27°API, 50% water, 100 power, artificial emulsion.

The large free water particles in Fig. 43, show that the emulsion is not perfectly homogeneous. Water separates out, though the properly emulsified parts seem to be quite stable. In the large water particle partially seen in top of picture, small oil droplets are dispersed.

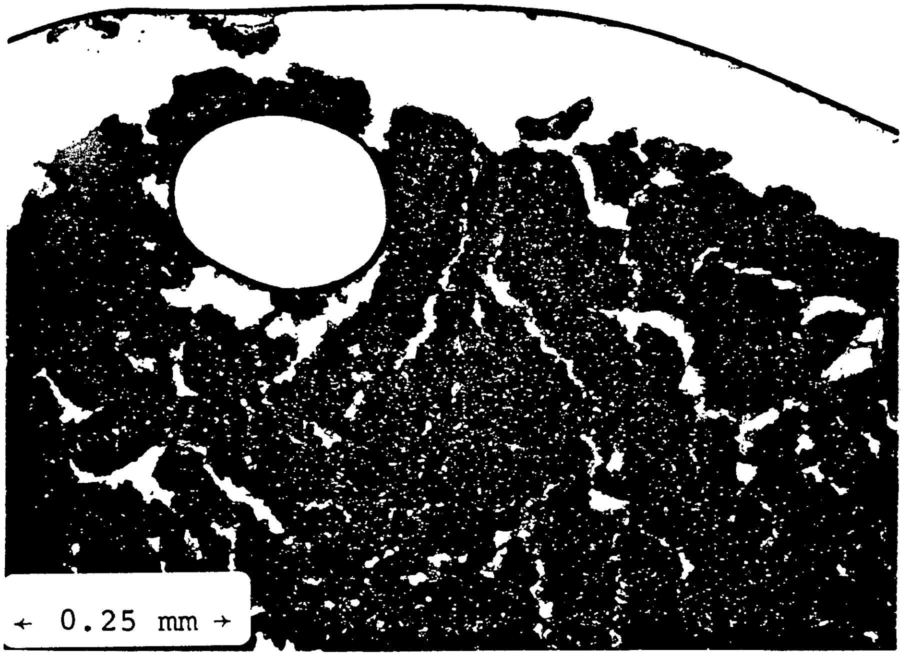


Fig. 44 - 29^{9}API, 50% water, 100 power, artificial emulsion.

The same properties are seen in Fig. 44, as for the 13^{o}API crude oil in Fig. 40. Flakes of well emulsified oil and water are floating around in rather significant amounts of free water. Outside the black line is air.

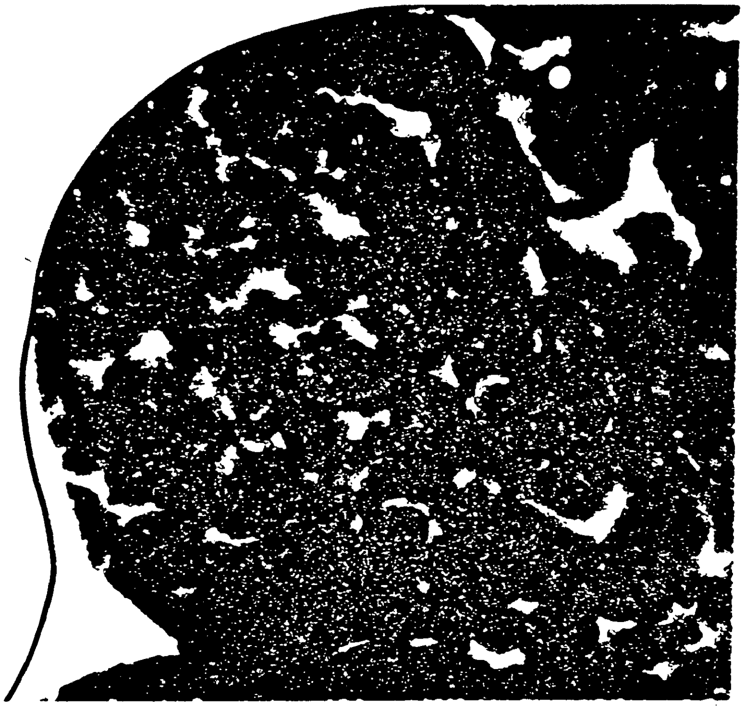


Fig. 45 - 35°API, 50% water, 100 power, artificial emulsion.

The same characteristics are observed from the picture in Fig. 45, as from most of the other artificial emulsions. As this crude oil made one of the better natural emulsions, it is possible that the crude's natural emulsifier is of higher quality than the synthetic one.

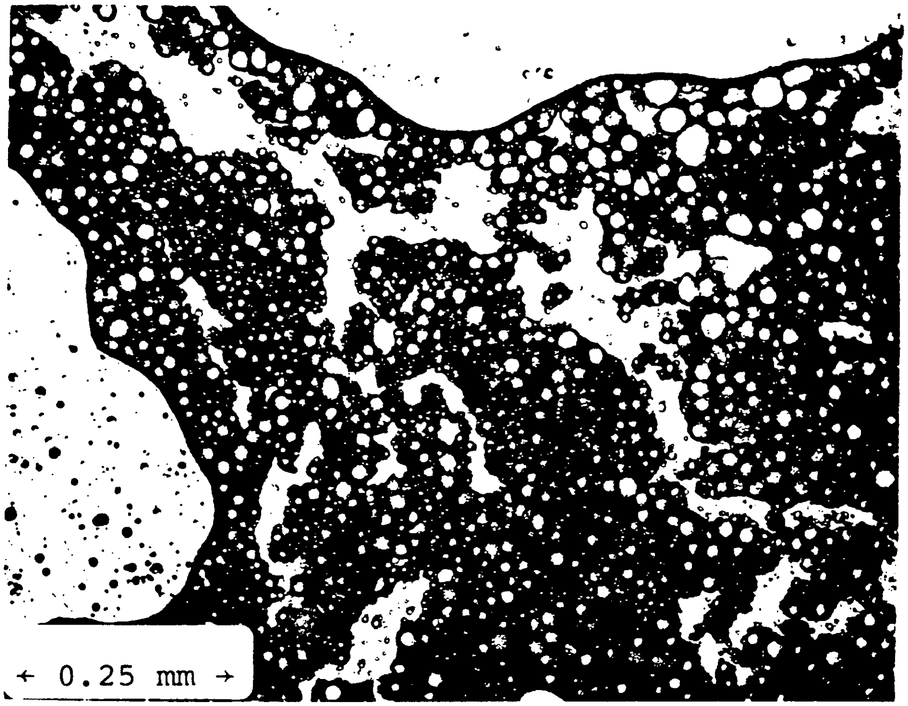


Fig. 46 - 27°API, 50% water, 100 power, artificial emulsion, ½% emulsifier.

The effect of the added emulsifier becomes clear when observing the pictures in Figs. 46 and 47, together with the corresponding photos of natural and 2% artificial emulsions in Figs. 37, 38, 43 and 44. The water particles attain an average size between those in Figs. 37/38 and 43/44. No, or little natural emulsifier is assumed to be present in these crude oils. Areas of inverted emulsion, free water with oil droplets dispersed, can be traced.

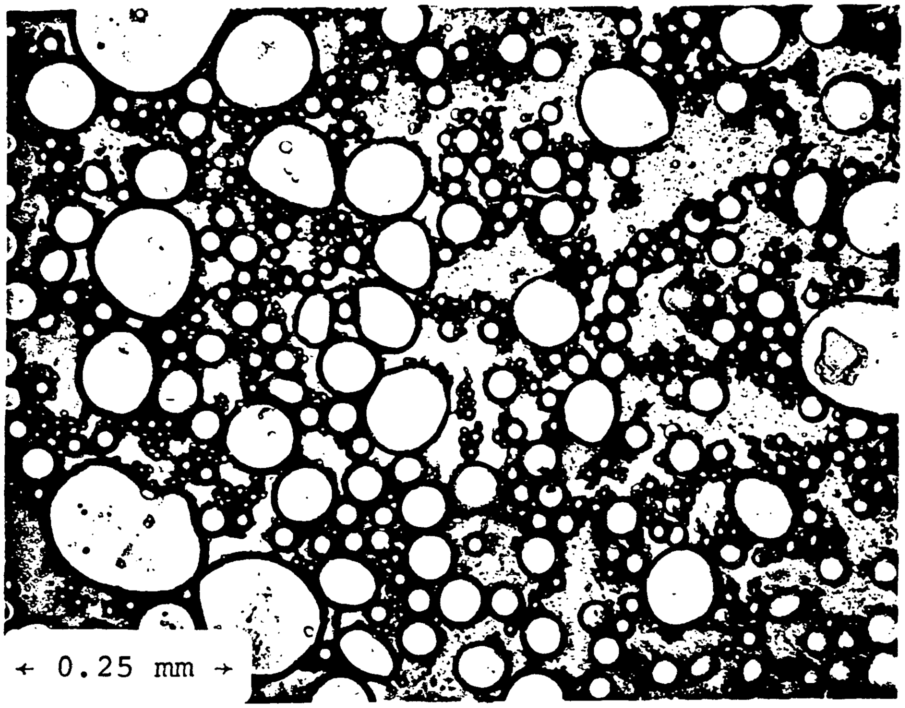


Fig. 47 - 29°API, 50% water, 100 power, artificial emulsion, ½% emulsifier.

Inversion:

The following results were obtained for the natural emulsions:

CRUDE	INVERTED
19°API	>50% water
25°API	24%-33% water
27°API	33%-43% water
29°API	43%-50% water
35°API	>50% water

These results fit fairly well with the results from the stability test. However, since, during measurements, the emulsion is not allowed to come to rest, it will stay emulsified for a longer time.

For the artificial emulsions the results were:

CRUDE	INVERTED
13°API	74% water
19°API	88% water
25°API	83% water
27°API	89% water
29°API	90% water
35°API	88% water

Basically no difference in consistancy was found between the crudes when the water content became very high. A reason for this must be that the effect of the natural emulsifier becomes insignificant.

Photomicrographs taken of each sample follow:

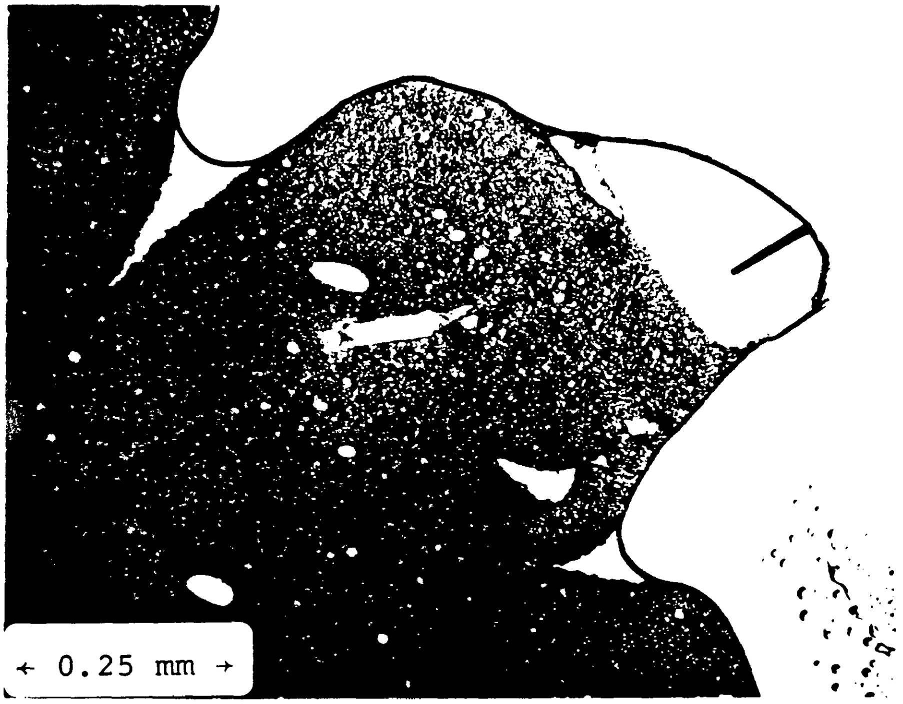


Fig. 48 - 13°API, 74% water, 100 power, artificial emulsion.

In Fig. 48, large water concentrations are shown, indicating that the point of inversion is close. Three separate zones can be seen, one having few water particles, being the darker area, followed by a part containing many water droplets, and finally the free water being the lightest area inside the border line. Outside the line is air.

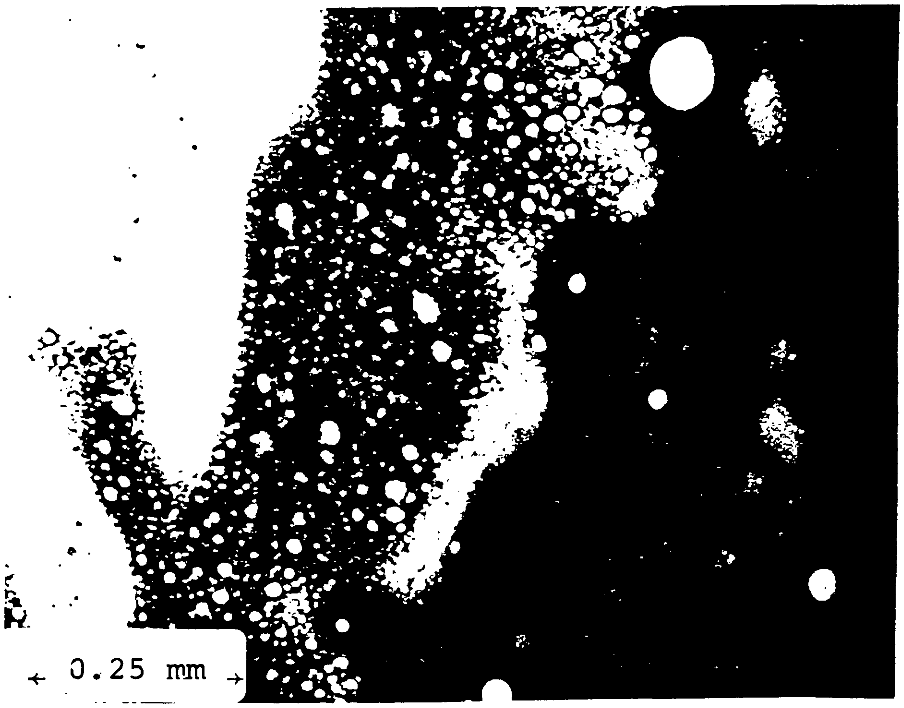


Fig. 49 - 19°API, 88% water, 100 power, artificial emulsion.

The same three zones appear clearly in Fig. 49. A free water zone, a loose emulsion zone containing rather large water particles, and a tight emulsion zone. This indicates that additional water will probably go to the free water zone and not be emulsified. It is clear, though, that the oil is still the continuous phase.

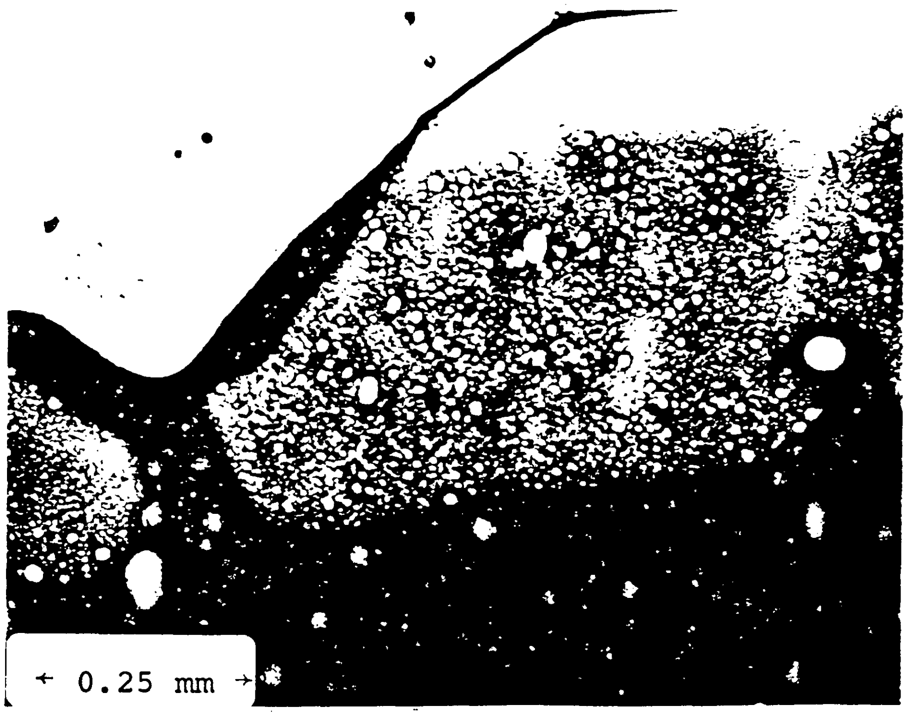


Fig. 50 - 25°API, 83% water, 100 power, artificial emulsion.

The same characteristics as in Fig. 49, are seen in Fig. 50.

The white area outside the black line is air.

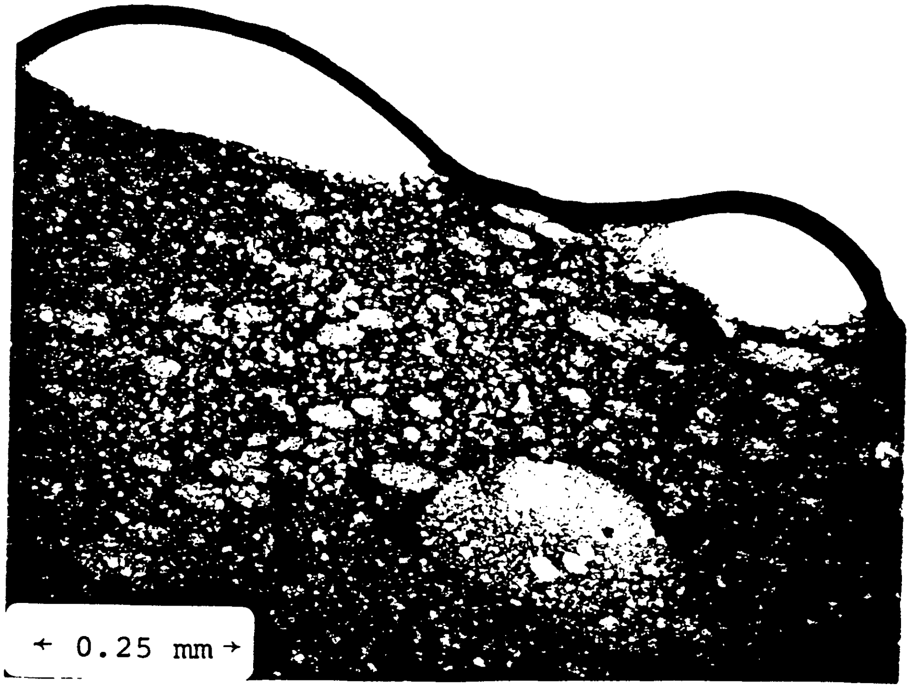


Fig. 51 - 27°API, 89% water, 100 power, artificial emulsion.

Only 11% of the emulsion in Fig. 51 is crude oil. Two zones are found, free water and emulsion. Additional water will join the free water part.

Fig. 52 - 29°API, 90% water, 100 power, artificial emulsion.

Only 10% of the emulsion in Fig. 52 is crude oil, and this is mainly surrounding the water particles together with the emulsifying agent. Two zones are found, the tight emulsion being dark and the loose emulsion being lighter. The free water part is not significant in this picture. The area outside the border line is air.

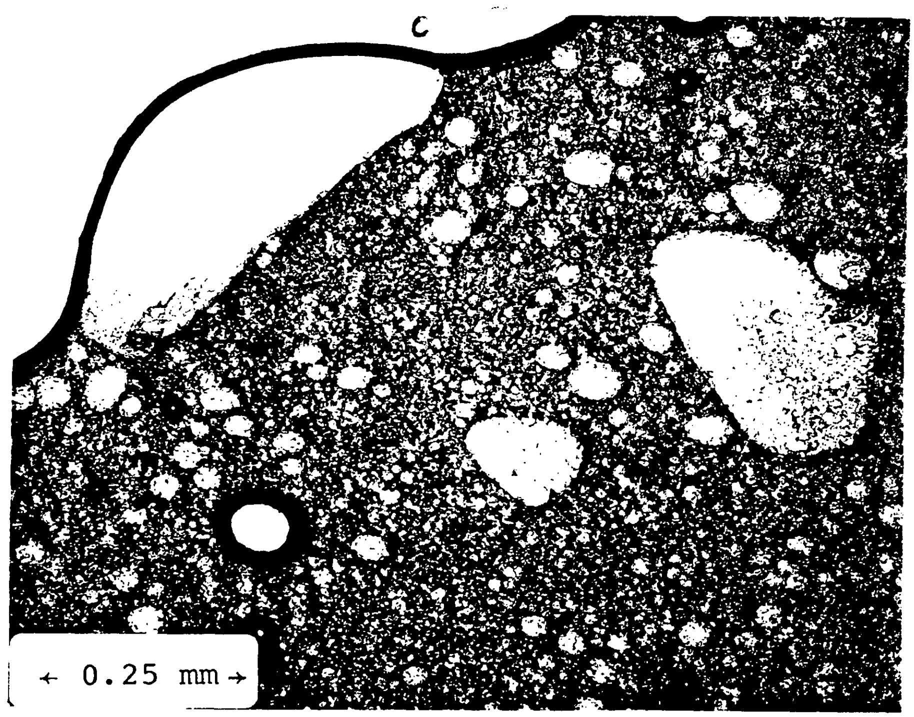


Fig. 53 - 35°API, 88% water, 150 power, artificial emulsion.

The amount of water in Fig. 53 is clear from the picture. There is very little light restriction because the oil is so diluted. However, we still get an indication of three zones, the tight emulsion in the lower right corner, looser emulsion moving up and left, ending in the free water pocket. The area outside the dark line is air.

CONCLUSIONS

1) The apparent viscosity of an emulsion increases as water is added until inversion occurs.

2) The brine salinity is not a critical factor on emulsion viscosity

3) The emulsion viscosity is very sensitive to temperature.

4) The emulsion viscosity is not very sensitive to whether an emulsifying agent is present or not.

5) The concentration of emulsifier quickly reaches a value where it no longer affects the rheological properties of an emulsion. Up to this value the rheological behavior changes dramatically.

6) The natural emulsions are generally less stable than the artificial ones.

7) There is no relationship between stability and ^{o}API gravity.

8) Natural emulsions generally show a close to Newtonian flow behavior.

9) Artificial emulsions show an increasing pseudoplastic flow behavior as water is added.

10) There is no relationship between an emulsion's degree of non-Newtonian flow behavior and the crude oil's ^{o}API gravity.

11) All the tested pure crude oils were Newtonian.

12) Some crude oils have a naturally occurring emulsifying agent.

13) At high water contents, the naturally occurring emulsifier loses its effect.

14) An emulsifying agent reduces the interface tension between brine and crude oil, thereby making the two liquids miscible.

15) A general correlation between viscosity and water content will be difficult to obtain, even if hundreds of emulsions were investigated.

16) Crudes having a natural emulsifier will cause more problems during production. This is because the oil and water are difficult to separate during processing.

17) The interfacial tension between water and crude oil decreases with increasing amount of emulsifier.

POSSIBLE FUTURE EXPERIMENTS

- A chemical analysis of the crude oils would give a a better understanding of why they behave so differently when applied to emulsions.
- Use of different synthetic emulsifiers might give some valid data.
- Rather than using °API gravity as a parameter, a geological or geographical reference could be of interest. Crude oils from the same environment might have some common properties.
- An extensive investigation using a pipe viscometer might give better data.

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APPENDIX

CALCULATION OF PRESSURE LOSS IN PIPE

Crude oil: 19^{o}API - $\rho = 7.83$ ppg

Water salinity: 150,000 mg/L - $\rho = 9.16$ ppg

Flow rate: $Q = 2{,}000$ bbl/day = 1.39 bbl/min.

Pipe diameter: $d_i = 2.992''$

Length of pipe: $L = 5{,}000$ ft.

a) Pressure loss for 0, 5, 10, 16, 24, 33, 43, and 50 percent water content, natural emulsions?

b) Pressure loss for 0, 5, 10, 16, 24, 33, 43, and 50 percent water content, artificial emulsions?

For a power-model fluid with a yield point the equation is:

$$\tau_w = K\left(-\frac{dv}{dr}\right)^{n'} + \tau_y \qquad \text{.......(VIIIb)}$$

where: τ_w = shear stress at pipe wall (lbf/100 ft.^{2})

τ_y = yield point value of fluid (lbf/100 ft.^{2}).

K = consistancy index (lbf sec$^{n'}$/ft.^{2}).

n' = flow behavior index (dim. less).

(dv/dr) = shear rate. (sec^{-1}).

τ_w is measured or read from Figs. 23 and 24.

τ_y is measured or read from Figs. 23 and 24.

(dv/dr) is measured or read from Figs. 23 and 24.

n' is found from log-log data as described in the theory.

$$K = \frac{\tau_w - \tau_y}{(-\frac{dv}{dr})^{n'}}$$

In equation XVII τ_w and τ_y have to be multiplied by a conversion factor of 0.01066 (see theory) and (dv/dr) is the RPM of the rotary viscometer times a conversion constant of 1.703 (see theory). The results are listed in Table 5. Calculations were done for 600 RPM data.

To determine whether the flow is laminar or turbulent eq. 1.77a in Craft, Holden and Graves(3) is used.

$$N_{Re} = 1.86 \frac{(d/96)^{n'} * L * v^{(2-n')} * \rho}{K_p'} \qquad \text{.......(XVII)}$$

where: N_{Re} = Reynolds number (dim. less)

d = inside diameter (inches)

L = length of pipe (ft.)

v = flow velocity (ft./sec.)

ρ = fluid density (ppg)

The flow velocity in the pipe is:

$$v = 4Q/\pi d^2 = 2.66 \text{ ft./sec.} \qquad \text{(XVIII)}$$

The density of the emulsion is determined from:

$$\rho = (f_o * 7.83 + f_w * 9.16) \text{ ppg} \qquad ......XIX$$

where: f_o = fraction of oil

f_w = fraction of water

The consistancy index for pipe flow, K'_p is converted from K'_v by use of Fig. 54.

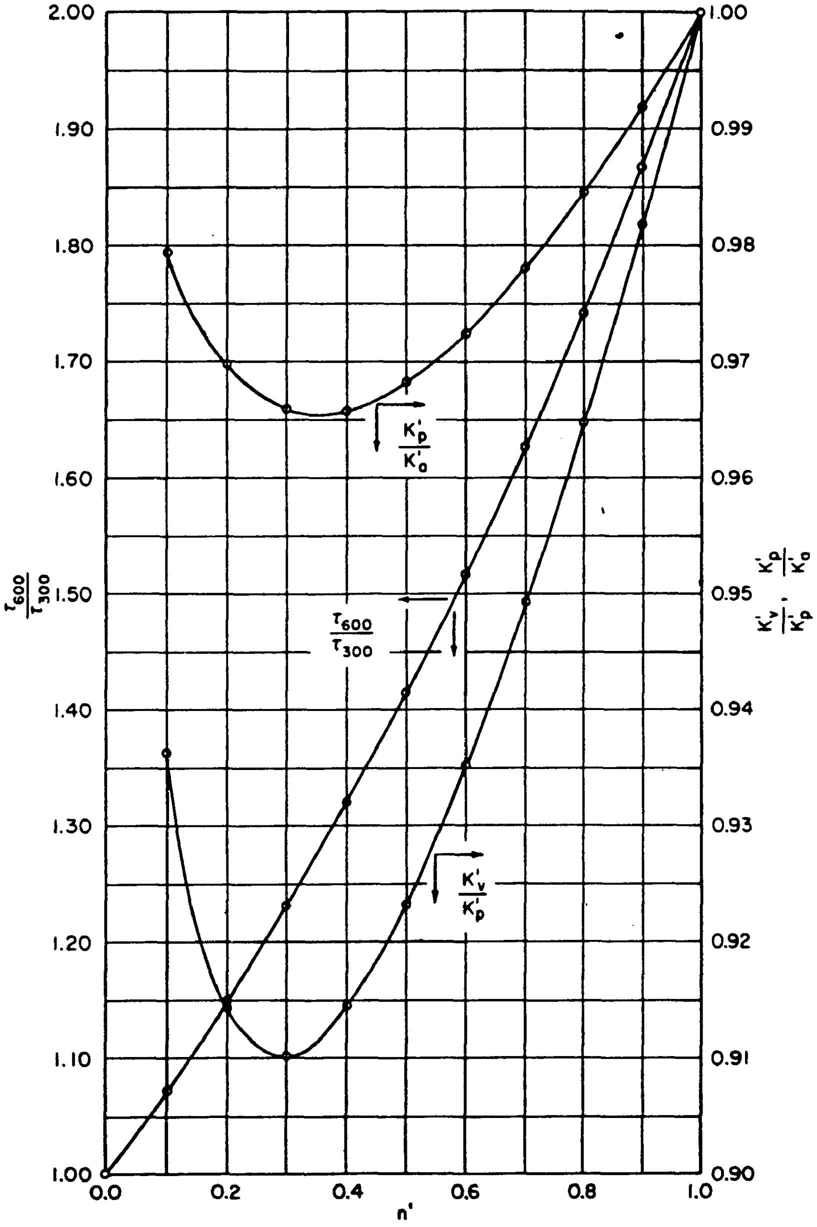

Fig. 54 - Correlation diagram for pipe-,annular-and rotational viscometer data. (From Savins(13)).

The pressure loss in the pipe is calculated from eq. XX (API-RP39).(14)

$$\Delta P_f = 0.333\ (1647)^{n'} * L * K'_p * Q^{n'}/d^{(1+3n')} \qquad \text{........XX}$$

The results from the calculations are listed in Table 10.

TABLE 10

RESULTS FROM CALCULATIONS OF PRESSURE LOSS IN PIPE

WATER CONTENT %	DENSITY ppg	NATURAL N_{Re}	EMULSIONS ΔP_f psi	ARTIFICIAL N_{Re}	EMULSIONS ΔP_f psi
0	7.83	1173	48.9	1279	44.9
5	7.90	990	58.5	767	75.6
10	7.96	847	68.9	624	93.5
16	8.04	724	81.4	498	118.3
24	8.15	451	132.4	392	152.4
33	8.27	331	183.3	253	239.2
43	8.40	219	281.9	159	386.3
50	8.50	156	400.3	116	537.7

It is seen that the pressure loss increases dramatically as the water content increases for both the natural and the artificial emulsion.