

A STUDY OF THE VISCOUS PROPERTIES
OF A PETROLEUM SULFONATE SYSTEM

By

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering.

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ABSTRACT

Investigations were made of the viscous properties of a petroleum sulfonate emulsion system to determine if the classical theories on emulsion viscosity could be extended to include this emulsion system. The constituents of the investigated emulsion system were a Gulf coast crude for the oil, Santolube 290*, a synthetic petroleum sulfonate, for the surfactant, and distilled water. Measured viscosity sets for thirty mixtures of varying compositions were determined for a temperature range of 80°F to 180°F. The test data indicated that the extension of classical viscosity theories to include the investigated emulsion system is valid and that the emulsion viscosity can be calculated using a mathematical relation similar to the Richardson equation presented by Becher (1965, p. 63).

Interpretation of the test data showed that the emulsion viscosity, μ , is a function of the crude oil and surfactant viscosity, μ_{OS} , dispersed phase concentration, C_w , surfactant concentration, C_s , time allowed for the surfactant to disperse in the crude oil and temperature. A 50 percent change in the crude oil and surfactant viscosity resulted

*Registered trademark of Monsanto Company

in as much as a 150 percent change in emulsion viscosity. Changing the dispersed phase concentration from 10 to 70 percent increased the emulsion viscosity by as much as a factor of 30. The crude oil viscosity was found to increase by 200 percent with the addition of 20 percent surfactant. A study of time required for the surfactant to disperse in the crude oil proved that the surfactant did not readily dissolve in the crude oil but required at least five days to completely disperse.

Other parameters investigated, which were felt would affect emulsion viscosity but proved not to, were mixing time of the emulsion, dispersed phase concentration and dispersed phase particle size. The test data was also reviewed to determine what parameters tested effected the general stability of the emulsion. The emulsion stability was found to be a function of dispersed phase concentration, surfactant concentration and temperature.

Flow tests of the emulsion system through a porous media showed that emulsion generation by flowing crude oil and surfactant into a water saturated sand pack was not possible at the rates and for the sand pack lengths of the test. Emulsion stability was not effected by flow through the porous media and the emulsion appeared to give a piston like displacement and maintain a constant displacement front.

CONTENTS

	<u>Page</u>
ABSTRACT	iii
ACKNOWLEDGMENTS	vii
INTRODUCTION	1
LITERATURE REVIEW	3
EXPERIMENTAL APPROACH	9
Components	9
Measuring and Reported Composition	9
Equipment	9
Test Procedure	10
EXPERIMENTAL RESULTS	13
Mixing Time	13
Dispersion Time for the Surfactant	14
Dispersed Phase Particle Size and Distribution	15
Temperature	16
Relative Concentration of the Phases	17
Surfactant Concentration	17
Phase Viscosity	18

CONTENTS (continued)

	<u>Page</u>
Stability and Inversion	18
Flow Tests.	19
Comparison with Theory.	20
SUMMARY AND CONCLUSIONS.	24
APPENDIX	27
BIBLIOGRAPHY	50

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INTRODUCTION

Recently attention has been given in the technical literature to the possibility of utilizing a water-oil emulsion or micellar solution as the driving phase in secondary recovery processes. The advantages of such a drive process would be accessibility of components, partial miscibility with reservoir fluids, and, most important, the ability to approach or exceed the viscosity of the reservoir fluids and hence obtain a favorable mobility ratio. This ability to control the mobility ratio should result in improved volumetric efficiencies of the drive process and yield a higher percent recovery of oil in place.

The composition of this driving phase will determine the driving properties. Gogarty (1967, p. 9) stated that Marathon Oil Company used a water-in-oil petroleum sulfonate-micellar solution in their studies. To achieve the stability desired, they use isopropyl alcohol as a co-surfactant. Petroleum sulfonate, the surfactant, is a waste product of refineries which until recently was considered to have no market value. The displacement mechanism of Marathon's drive process is shown in Figure 1. The process utilizes three driving phases, the micellar slug, the mobility buffer, and water. The mobility buffer phase is required to allow the final water drive to displace the micellar

without destroying it or bypassing it. This mobility buffer phase is similar in composition to the micellar slug but has a viscosity between that of the micellar slug and the drive water. The mobility buffer Marathon uses is a water which contains a polymer additive to increase the viscosity of this drive phase. Gogarty (1967, p. 10) reported percentage recoveries of between 67.5 and 94.5 percent with Maraflood* as compared to 56.7 and 62.7 percent by water flood only.

It is the purpose of this study to investigate the viscous properties of a petroleum sulfonate emulsion and to correlate the results to classical emulsion theories. To date, most of the published literature on emulsions has come from the drug, cosmetic, paint, and chemical industries. Many of their studies were based on water-oil emulsions; however, they worked with low concentrations of emulsifiers, surfactants, none of which were petroleum sulfonate. For the proposed investigation, the surfactant concentration will range from 5 to 20 percent. Hence, the classical equations for viscosity determinations based on the lower surfactant ranges, less than 5 percent, may not apply to the higher surfactant concentration ranges.

*Registered trademark of Marathon Oil Company

LITERATURE REVIEW

Viscosity is defined by Webster's Dictionary as "*That property of a body in virtue of which, when flow occurs inside it, forces a rise in such a direction as to oppose the flow.*" Viscosity, μ , is then a resistance to flow and may be defined as the shear stress, τ , exerted on an area where a unit velocity gradient in the X direction, du/dy , is acting normal to the area.

$$\tau = \mu (du/dy) = \mu D \quad *$$

D may also be written as the time rate of shear, $d\sigma/dt$, and

$$\tau = \mu (d\sigma/dt) = \mu D$$

Newtonian fluids obey these equations and are independent of the velocity gradient. However, emulsions usually do not act as Newtonian fluids. Figure 2 shows the flow behavior of four types of fluids: Newtonian, Bingham plastic, Pseudoplastic, and dilatant. The Newtonian curve is a straight line passing through the origin and is defined by a single measurement of absolute viscosity. The remaining three curves illustrate non-Newtonian fluid behavior.

*All symbols are based on SPE-AIME nomenclature except where specifically defined.

The Bingham plastic fluids were proposed by E. C. Bingham. They show a linear relation between rate of shear, du/dy , and shear stress, τ , after a minimum shear stress, τ_y , is applied. The intercept τ_y is known as the yield point. The relation of du/dy to τ is in proportion to μ_p , plastic viscosity. Unlike the Newtonian fluid two parameters, τ and μ_p , are required to define the curve for the Bingham plastic. The apparent viscosity, μ_A , of this type fluid is often useful in experimental work. Craft (1962, p. 31) explains how μ_A is obtained:

" μ_A can be obtained from the slope of a straight line drawn from the origin and terminating at some point on the flow curve whose position coincides with a given value of shear stress."

Correlations in this study will be made utilizing μ_A as the base parameter.

The remaining two fluid types, pseudoplastic and dilatant, do not have yield points, but their apparent viscosity is a nonlinear function of shear stress and possible duration of applied shear. From Figure 2, it can be observed that the apparent viscosity of the pseudoplastic fluids decrease with increasing shear stress. The dilatant fluids show the opposite behavior. The Maraflood mobility buffer with the polymer additive behaves as a dilatant fluid.

Becher (1965, p. 61) presented Sherman's list of parameters that effect the viscous properties of emulsion. These parameters are

1. Viscosity of the external phase (μ_o).
2. Volume concentration of the disperse phase (C_w).
3. Viscosity of the internal phase (μ_w).
4. Nature of the surfactant and the interfacial film

formed at the interface. This includes surfactant concentration, C_S , and viscosity, μ_S .

5. Particle-size distribution.

The external or continuous phase is generally meant to include the surfactant as it is usually a part of this phase and will be so used throughout this paper. Most published equations are of the form

$$\mu = f(C_W, \mu_W, C_S, \mu_S, \mu_O, T)$$

or

$$\mu = g_1(\mu_S, \mu_O) \cdot g_2(C_W, \mu_W, C_S, T)$$

where g_2 is a function of the properties shown as well as any others which might effect the emulsion viscosity, μ . The above equations indicate that $g_1(\mu_O, \mu_S)$ is the prime parameter to be considered in any correlations.

The importance of water concentration has been studied extensively and found to be a major factor in emulsion viscosity. Becher (1965, p. 62-69) presented several forms of equations for viscosity determinations. Most of these equations were based exclusively on μ_O and C_W . Table I presents eight of these equations and their limitations.

Becher (1965, p. 70) summed up the effect of μ_W as::

"the viscosity of the internal phase 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."

After extensive investigation on water-in-oil emulsions, Sherman (1955, p. 11) concluded μ_W , even at high values of C_W , had negligible effect on the emulsion viscosity as the droplets of water acted as rigid spheres.

It has been established by many authors that the viscosity of

emulsions depends on the nature of the surfactant. Becher (1965, p. 70) discussed a number of investigations of oil-water emulsions which related emulsion viscosity to the chemical properties of the surfactant. Sherman (1950, p. 571-573) derived empirically the equation

$$\ln(\mu/\mu_{OS}) = a C_S C_W + b$$

C_S = surfactant concentration

a and b = constants for an emulsion

which relates emulsion viscosity to surfactant concentration and the viscosity of the oil and emulsifier. This equation is very similar to the Broughton-Squires equation in Table I.

$$\ln(\mu/\mu_{OS}) = K C_W + a$$

where K and a are constants for an emulsion.

Considerable investigation has been done on the dispersed phase particle size effect on emulsion viscosity. Becher (1965, p. 77-83) presented the results of several authors' research and described this effect as being due to the mutual attraction between droplets. Sherman (1963, p. 2537) suggested particle size might be an excellent parameter with which to correlate viscosity. Becher (1965, p. 80) presented Sherman's equation which relates emulsion viscosity to dispersed phase particle size

$$\mu = a(1/dm) + b ,$$

where a and b are constants and dm is the average particle diameter.

Eveson (1959, p. 61-75) concluded that the properties of an emulsion can be greatly effected by the particle size distribution.

The phenomenon of inversion has been noted by many researchers. Inversion is the physical change in an emulsion system when the internal phase becomes the external phase. Becher (1965, p. 74) commented on

results presented by Sherman (1950) for the water-in-oil change to oil-in-water. Sherman found inversion theoretically should take place at 0.74 volume fraction water for all emulsion systems. Becher also quoted other authors' studies which found inversion points at other values of C_w .

Breaking of emulsions has long been a problem of the petroleum industry. Roberts (1926, p. 321-334) studied the effect of special chemical compounds on emulsions of mid-continent crudes and water. Brandenthaler (1927, p. 41-48) worked on the problem of emulsions formed by the producing practice of gas lifting. Viscous California crudes readily form emulsions which are hard to break and have been the subject of studies by Abozeid (1930, p. 340-358), Fisher (1930, p. 359-375), and many others. Bennett (1943, p. 145-196) detailed many of the common oil field emulsions and how they can be broken.

Only recently has a positive use of emulsions in the petroleum industry been under study. This thesis deals with one aspect of the overall study, viscous properties, and investigates the following parameters

1. mixing time
2. dispersion time of the surfactant in the oil
3. temperature
4. relative phase concentrations
5. surfactant concentration
6. phase viscosity
7. dispersed phase particle size
8. inversion and stability

General flow characteristics of the tested emulsion are also included. Stability of the emulsion during flow in a sand pack and possibility of natural mixing of the emulsion in the sand pack were investigated.

EXPERIMENTAL APPROACH

Components

The emulsion system under study is a water-in-oil emulsion using Monsanto Santolube 290 as the surfactant. Santolube 290 is a synthetic petroleum sulfonate similar to the natural petroleum sulfonate used in the Marathon study. The oil used was a 33.35° API Gulf Coast crude, which is very similar to a majority of the oil produced throughout the mid-continent and Rocky Mountain areas. Distilled water was used for the third constituent.

Measuring and Reported Compositions

All measurements were made volumetrically because all components were liquid. All reported concentrations are volume fractions of the total mixture.

Equipment

Blending of the emulsion was done in a commercial laboratory blender. All parts in contact with the emulsion were stainless steel.

Temperature was controlled by a constant temperature oil bath

capable of 220°F, which is above the emulsion boiling point at atmospheric pressure.

Viscosity measurements were made using a Fann VG meter. This is a rotation, variable-speed viscometer which is correlated to give apparent viscosity. The viscosity of mixtures of varying concentrations was measured over a preselected temperature range, room temperature to approximately 180°F.

All timing was controlled by commercial electronic timers. The blenders were automatically controlled by the timers.

Microscopic studies were made of all emulsion mixtures and microphotographs were made of critical mixtures or conditions. A commercial Polaroid MP - 3 camera with microscopic attachment was employed. The MP - 3 allowed reasonable photos to be taken up to 970 power.

The flow test sand pack was made of one inch internal diameter plexiglass tubing and was 23.9 inches long. It was packed with 20-40 mesh sand and had a porosity of 33 percent.

The pump used in flow testing was a variable speed piston pump. Testing was conducted at volume rates of 100 to 200 ml per minute.

Test Procedure

The effect of many of the parameters investigated were tested simultaneously. The effect of mixing time and dispersed phase particle size is an example. Therefore, there is some overlapping in the following discussion.

The effects of the duration of mixing time and dispersed phase

particle size on the viscous properties of the emulsion were evaluated by

1. mixing for given periods
2. testing viscosity
3. using the photomicroscope to determine dispersed phase particle size and distribution
4. discontinuously mixing for a given period of time and repeating #2 and #3.

Mixing times of 15 seconds to 15 minutes were checked by continuous mixing and discontinuous mixing procedures.

Dispersion time of the surfactant in the oil was studied by mixing the oil, surfactant and water and allowing the solution to sit for given periods of time and then testing as above. The effect of temperature on the solutions of different dispersion times was also investigated.

The effects of phase concentration, phase viscosity, temperature and surfactant concentration were investigated in the same manner. Mixtures of different concentrations were mixed, allowed to sit for one week, remixed for four minutes, and viscosity measured. Viscosity was measured for each mixture at a range of temperature from room temperature to approximately 180°F. The results were then plotted as families of curves which are discussed later.

Various samples of the previously mixed and tested mixtures were utilized in the sand pack flow tests. These mixtures were passed through the sand pack at volume rates of 100 and 200 ml per minute at room temperature, approximately 84°F. Samples were observed under the

microscope before and after passing through the sand pack to determine any change in the emulsion structure. Experimental mixtures run were

1. Oil and surfactant (10 and 20 percent surfactant)
injected into a 100 percent water saturated core;
2. An emulsion mixture with incomplete dispersion
injected into a water and oil saturated sand pack;
3. Emulsion mixtures allowed time to disperse completely
injected into a water and oil saturated sand pack.

The sand pack was flushed between runs with several pore volumes of distilled water.

EXPERIMENTAL RESULTS

Table II presents a tabulation of all mixtures tested. The results of these tests are presented in tabular form in Table III and Table IV.

Mixing Time

Three mixtures were tested to determine the effect of mixing time on emulsion viscosity. The composition of all three was the same: 10 percent surfactant, 60 percent oil, and 30 percent water. The results are presented in Table III and are plotted in Figure 3.

Mixture 27 was mixed discontinuously as shown in Table II and no change in emulsion viscosity was noted for the duration of the tests.

Mixtures 28 and 29 were initially mixed together and divided after blending. Mixture 28 was tested as Mixture 27 for the effect of discontinuous mixing. The results concur with those of Mixture 27. Mixture 29 was mixed for a period of 240 seconds and the viscosity measured. Again it was in agreement with Mixture 27 and Mixture 28. Mixture 29 was further mixed for a total mixing time of 335 seconds and 900 seconds. Agreement persisted for all durations of blending.

These three mixtures tested indicate that duration of blending from 15 seconds to 15 minutes does not effect the viscous properties of the petroleum sulfonate emulsion. It will be shown later that blending periods of four to five minutes completely mix the constituents into an emulsion.

Dispersion Time for the Surfactant

As the investigation proceeded, it became evident that Santolube 290 required time to disperse in the oil phase. The initial evidence of the need for dispersion time was the inability of Santolube 290 to mix readily with the crude oil. When poured together the two fluids separated with the Santolube 290 forming the bottom layer. It was even possible to pour off the crude oil and leave the Santolube 290 in the container. Additional evidence is demonstrated in Figures 4, 5, 6, and 7 which are plots of apparent viscosity vs. temperature for Mixtures 10, 11, 19, and 20 after various allowed dispersion times of from one to nine days. Compositions of the mixtures and test results are presented below.

Mixture Number	Composition			Dispersion Time	Viscosity at 100°F
	C _O	C _W	C _S		
10	30	50	20	5 days	10.0 cp
10	30	50	20	9 days	10.0 cp
11	35	60	5	1 day	40.0 cp
11	35	60	5	7 days	70.0 cp
11	35	60	5	14 days	70.0 cp
19	55	40	5	1 day	27.0 cp
19	55	40	5	7 days	30.0 cp
19	55	40	5	14 days	30.0 cp
20	65	30	5	1 day	16.0 cp
20	65	30	5	7 days	15.0 cp

Mixtures 11, 19, and 20 confirm that the measured emulsion viscosity of the petroleum sulfonate system is effected by the amount of time allowed for the surfactant to disperse in the crude oil. Test data of Mixtures 10, 11, 19, and 20 indicate that this time dependency is terminated after approximately five days of dispersion time. Heat did not appear to reduce the time required for dispersion as the greatest difference in measured emulsion viscosities occurred at the higher temperatures.

Dispersed Phase Particle Size and Distribution

Concurrent with the mixing time, testing the dispersed phase particle size and distribution were investigated. Each of the Mixtures, 27, 28, and 29, were studied under the microscope and microphotos taken. The particle size varied up to a mixing time of 15 seconds and stabilized for mixing times greater than 15 seconds. Figures 8, 9, 10, and 11 are microphotos taken during these tests. The size distribution for less than 15 seconds blending is presented below

Time	Size Range Observed
5-sec	0.02 to 0.04 mm
10-sec	less than 0.01 to 0.3 mm
15-sec	all less than 0.01 mm

All 29 mixtures investigated were periodically checked for any change in particle size. However, due to a standard blending time of four minutes, all mixtures appeared to be homogenous with a particle size less than that which could be measured by the scaling micrometer in the microscope. Hence, any effect of particle size and distribution

was cancelled by the constancy of mixing time. After blending for four minutes, all mixtures appeared to be completely mixed into an emulsion when observed under the microscope.

Temperature

The effect of temperature on the viscous properties of the emulsion was investigated utilizing all mixtures. In all cases the viscosity decreased as the temperature increased. Tables II, III, and IV present data that demonstrate the decrease in measured emulsion viscosity with increasing temperature. Figures 12 through 17 show graphically the nature of this emulsion viscosity-temperature relation. Figure 12 is a set of apparent viscosity-temperature plots for mixtures containing 5 percent surfactant. Similar sets of plots for 10 and 20 percent surfactant concentration mixtures are presented in Figures 14 and 16 respectively. The behavior of the emulsion viscosity-temperature relationship is further demonstrated by the isothermal lines of the plot of emulsion viscosity-dispersed phase concentration for 5, 10, and 20 percent surfactant concentration in Figures 13, 15, and 17 respectively. The isotherms for the tested concentration range, up to 70 percent dispersed phase concentration, in each figure are parallel and the isotherms of Figures 13 and 15 have approximately the same slope. The isotherms of Figure 17, however, have a slope less than the isotherms of Figures 13 and 15.

The effect of temperature on the viscosity of oil with and without surfactant is shown in Figure 18. Again the curves appear to have equal slopes and plot as nearly straight lines on semilog paper for

temperatures less than 150°F.

The temperature effects will be discussed further in the comparison with theory.

Relative Concentration of the Phases

The concentration of the water phase had a major effect on the emulsion viscosity. Increasing the water concentration caused an increase in the measured viscosity. Figures 12 through 17 all substantiate this conclusion. This increase is noted up to some given value where the additional water added does not enter into the emulsion. For 5, 10, and 20 percent surfactant concentration this maximum value of dispersed phase concentration is about 70, 70, and 60 percent water respectively. The addition of water above these concentration values resulted in free water as shown by Figures 20, 21, and 22, which are microphotographs of 10, 5, and 20 percent surfactant concentration respectively. There was no observed inversion of the emulsion even at very high dispersed phase concentration. The emulsion was always water-in-oil.

Surfactant Concentration

Emulsion viscosity for a given water concentration and a given temperature increased as the surfactant concentration was increased. This is demonstrated graphically by comparing Figures 12, 14, and 16, which are plots of apparent viscosity-temperature for different water concentrations at surfactant concentrations of 5, 10, and 20 percent respectively. The curves of Figure 16 represent viscosities higher than those of Figures 12 or 14 for the same values of C_w and temperature,

and the curves of Figure 14 represent viscosities higher than Figure 12 for the same values of C_w and temperature.

Base oil viscosity, which is plotted in Figure 19, against volume fraction surfactant, also increased as the surfactant concentration was increased. This was expected as the viscosity of Santolube 290 is over 300 cp and therefore much greater than the crude oil viscosity. The effect of surfactant concentration on base oil viscosity appears to be a straight line relationship on semilog paper up to 13 percent surfactant concentration. Above 13 percent, Figure 19 shows that incremental increases in surfactant concentration result in increasingly larger increases in base oil viscosity.

Phase Viscosity

The viscosity of the continuous phase appears to be the major parameter with which emulsion viscosities can be correlated. The parallelism of the apparent viscosity for varying dispersed phase concentration, Figures 12, 14, and 16, substantiate that the measured viscosity can be correlated to the base oil viscosity for surfactant concentrations investigated. There was no evidence found that the dispersed phase viscosity had any effect on the measured emulsion viscosities. Dispersed phase viscosity could have been over powered by the viscous nature of the three fluids or as Sherman (1955, p. 11) states not be a parameter which effects the emulsion viscosity.

Stability and Inversion

The emulsion became more stable as the volume fraction of water increased and at the higher surfactant concentrations. Stability

decreased as the temperature increased. The low C_w mixtures for 5 percent petroleum sulfonate broke down at temperatures between 150°F and 180°F.

As stated before the anticipated inversion of the system did not occur. Instead the addition of water above a given value resulted in free water. The free water made viscosity determination of Mixture 8, 80 percent water and 10 percent surfactant, and Mixture 23, 70 percent water and 20 percent surfactant, impossible at any temperature.

Flow Tests

The purpose of the flow tests was to investigate three general questions:

1. Could an emulsion be generated by flowing oil and surfactant through a sand pack?
2. Are the petroleum sulfonate emulsions stable during flow in a sand pack?
3. Would the emulsions incorporate formation water into themselves and hence change composition and viscous properties?

Mixtures 14 and 15 were used to evaluate the creation of an emulsion by flowing in a porous media. There was only a minute amount of water incorporated in the base solution and this was held as a suspension. Hence, emulsion generation in this manner does not appear feasible, at these flow rates or lengths.

Mixture 4 (40 percent water and 10 percent surfactant) and Mixture 30 (70 percent water and 5 percent surfactant) were used to study stability of the emulsion and the possibility of the emulsion incorporating formation water into the emulsion system during flow in a

porous media. The emulsions appeared as stable during flow in the sand pack as prior to flow testing. Microscopic examination of the emulsions before and after flow showed no apparent change in the emulsion structure. The emulsions displaced oil and water easily and appeared to maintain even fronts. Water flushed through the sand pack to remove the emulsions also appeared to maintain a constant front and displace most of the emulsion with four to five pore volumes of water. Again, as in the study of emulsion generation, the drive emulsions did not appear to change concentration but did hold some water as a suspension. Mixture 30 was not allowed time for the surfactant to completely disperse into the oil before mixing and flow testing, but did not appear to be less stable than Mixture 4 which had the benefit of more than 5 days for the surfactant to disperse in the oil.

Comparison with Theory

Nowhere in the researched literature were there theories or comments pertaining to mixing time or dispersion time for the surfactant. However, it was felt that these two parameters could cause erratic results or misinterpretation of the results if these effects were not investigated and understood. The effects they showed appear logical due to the chemical and physical nature of the components.

Sherman (1963, p. 2537) suggested that for water-in-oil emulsions the dispersed phase particle size might be a correlatable parameter. These results do not tend to uphold this concept. However, due to the lack of variance in the particle size at a measurable size range, these data do not disprove this concept either. This concept does not seem to apply to this system.

Table I lists several equations from the literature for relating emulsion viscosity to the parameters investigated. The Einstein, Guth-Gold-Simha, and Eilers equations are all too limited to apply to the petroleum sulfonate emulsions. The Richardson and Broughton-Squires equations do apply to systems of high internal phase concentration, however, they have not been tested for surfactant concentrations of greater than 5 percent. The experimental data is plotted in the form suggested by the Richardson equation in Figures 23, 24, and 25 for 5, 10, and 20 percent surfactant concentration respectively. By comparing Figures 23 and 24, it is found that the curves are coincident. The curves for 20 percent surfactant, Figure 25, also become coincident with the other curves when shifted to the right 0.65 cp. The determination of the slope of these families of curves was made using Figure 26, which is a plot of slope of the viscosity curves of Figures 23, 24, and 25 against volume fraction water. Using this slope, which has the general form of $e^{4.8C_w}$, and Figures 23, 24, and 25 the following equations were derived. An error analysis is presented on page 26.

For 5 and 10 percent surfactant

$$\mu = (\mu_{OS} - 0.65) e^{4.8C_w}$$

For 20 percent surfactant

$$\mu = \mu_O e^{4.8C_w}$$

which are of the same form as the Richardson equation.

In determining this family of curves only data points on the straight line portions of Figures 13, 15, and 17 were used. Curves of other values of water concentration are not included in these curve families as the derived equations would not apply to these measured

emulsion viscosities. Also it was found that for μ_{OS} at temperatures greater than approximately 175°F the curves of Figures 23, 24, and 25 became non-linear. The derived equations are limited to a temperature range of below 175°F and a dispersed phase concentration range of 10 to 70 percent water, 15 to 60 percent water, and for surfactant concentration of 5, 10, and 20 percent respectively, which are the linear portions of Figures 13, 15, and 17.

Because the curves in Figure 19 become non-linear above 13 percent surfactant concentration, the above differences in the equations could have been expected.

Sherman's equation for viscosity based on surfactant concentration, C_S , and dispersed phase concentration, C_W ,

$$\ln(\mu/\mu_{OS}) = aC_W C_S + b$$

where a and b are constants, does not appear to fit this system. However, from Figure 19, it was possible to derive an equation which relates μ_o to the surfactant concentration and the viscosity of the oil at a given temperature. This relation is

$$\mu = e^{.27C_S} \mu_{oil}$$

where C_S is the surfactant concentration. This relation is valid up to 0.13 volume factor surfactant. This can be substituted into

$$\mu = (\mu_{OS} - 0.65) e^{4.8C_W}$$

to get

$$\mu = (e^{.27C_S} \mu_{oil} - 0.65) e^{4.8C_W}$$

or

$$\mu = \mu_{oil} e^{.27C_S + 4.8C_W} - 0.65 e^{4.8C_W}$$

This equation is subject to the same limitations as the previously derived equations.

The nature of the surfactant, petroleum sulfonate, did not allow the system to invert. Further, it appeared to limit the amount of water which could be incorporated into the emulsion system. This does not follow the theories pertaining to ionic surfactants nor the results of the Marathon study. Marathon's micellar solutions inverted at about 50 percent water concentration. The ability to invert is dependent on the surfactants' compatibility with water. Santolube 290 is completely immiscible with water. Marathon's petroleum sulfonate and isopropyl alcohol appears to be miscible with water.

Error Analysis of Derived Equation

To test the accuracy of the derived equations, the viscosities of different mixtures were calculated using the equations and compared with the experimentally measured viscosities. The average error in the calculated viscosities was 9.92 percent. The maximum error was 27.3 percent. The viscosity of the base oil ranged from approximately 2.2 cp to 8.0 cp as shown in Figures 18. The accuracy of the viscometer is plus or minus 0.25 cp. The error range of the viscometer readings was from 3.1 percent to 11.0 percent.

SUMMARY AND CONCLUSIONS

This study of a petroleum sulfonate emulsion system investigated the following eight parameters

1. Mixing time
2. Dispersion time of the surfactant in oil
3. Temperature
4. Relative phase concentration
5. Surfactant concentration
6. Phase viscosity
7. Dispersed phase particle size
8. Inversion and stability

Mixing time and dispersed phase particle size proved to have negligible effect on the system for mixing times greater than 15 seconds.

The effects of temperature and surfactant concentration were determined to be substantial. A temperature change of from 100 to 200°F caused a threefold change in measured emulsion viscosity, and a surfactant concentration change of from zero to 20 percent caused a change in measured emulsion viscosity of over twofold. However, by defining μ_{os} as viscosity of the base fluid, oil and surfactant, at a

given temperature the derived equation

$$\mu = (\mu_{OS} - 0.65) e^{4.8C_w}$$

allowed for these parameters.

Relative phase concentration was also represented in the derived equation in the form of both water volume fraction and surfactant concentration. The surfactant concentration is incorporated into μ_{OS} . A change in dispersed phase concentration of from zero to 70 percent caused approximately a 20 fold increase in emulsion viscosity for 20 percent surfactant concentration.

Dispersion time of the surfactant in oil does not appear in the derived equation but would cause μ_{OS} to vary as much as a 2.5 multiple for a period of time of one week at a given temperature and surfactant concentration.

The μ_{OS} of the derived equation also represents the effects of the oil and surfactant phase viscosity which allowed μ to vary by a factor of two for a change in surfactant concentration of from zero to 20 percent. Water viscosity effects appear to be negligible.

The inversion did not occur for this system as was predicted by classical theory. The stability depends on the water volume factor, surfactant concentration, and temperature. Stability increases as C_w and C_s increase and decreases as temperature increases.

Flow tests of the petroleum sulfonate system cover the questions of the emulsion stability during flow, the emulsion's ability to incorporate fluids, and the ability to generate an emulsion in a sand pack. The flow process did not appear to affect the stability of any emulsions at the flow rates and lengths tested. The emulsions did not readily

incorporate sand pack fluids or change concentration. The sand pack fluids which were picked up were carried as a suspension. The drive process appeared to maintain a constant front during flow testing.

The possibility of generating the emulsion by flowing the base fluid through the sand pack does not appear feasible at flow rates and lengths tested. Much greater agitation is required than the flow test could supply.

APPENDIX

		<u>Page</u>
Tables	I Viscosity Relations From Becher (1965)	29
	II Tested Sets.	31
	III Mixing Time Test Sets.	33
	IV Measured Viscosities	34
Figures	1 The Maraflood Process.	37
	2 Flow Curves of Newtonian and Non-Newtonian Fluids.	37
	3 Mixing Time Tests Curve.	38
	4 Dispersion Test - Mixture 11	39
	5 Dispersion Test - Mixture 9.	39
	6 Dispersion Test - Mixture 20	40
	7 Dispersion Test - Mixture 10	40
	8 Microphotograph at 5 Seconds Mixing Time	41
	9 Microphotograph at 10 Seconds Mixing Time.	41
	10 Microphotograph at 15 Seconds Mixing Time.	42
	11 Microphotograph at 80 Seconds Mixing Time.	42
	12 5 Percent Surfactant Viscosity - Temperature Curves.	43
	13 5 Percent Surfactant Viscosity - Volume Fraction Water Curves.	43

APPENDIX (continued)

		<u>Page</u>
Figures	14 10 Percent Surfactant Viscosity - Temperature Curves	44
	15 10 Percent Surfactant Viscosity - Volume Fraction Water Curves.	44
	16 20 Percent Surfactant Viscosity - Temperature Curves	45
	17 20 Percent Surfactant Viscosity - Volume Fraction Water Curves.	45
	18 Base Fluid Viscosity Curves.	46
	19 Base Fluid Viscosity Curves.	46
	20 Microphotograph of Free Water - Mixture 23	47
	21 Microphotograph of Free Water - Mixture 24	47
	22 Microphotograph of Free Water - Mixture 26	47
	23 5 Percent Surfactant	48
	24 10 Percent Surfactant.	48
	25 20 Percent Surfactant.	48
	26 Slope Relation of Figures 23, 24, and 25	49

TABLE I

Viscosity Relations From Becher (1965)

Einstein Equation

$$\mu = \mu_{OS} (1 + 2.5 C_W)$$

not valid for $C_W > 0.02$

Guth-Gold-Simha Equation

$$\mu = \mu_{OS} (1 + 2.5 C_W + 14.1 C_W^2)$$

not valid for $C_W > 0.06$

Eilers Equation

$$\mu = \mu_{OS} (2.5 C_W + 4.94 C_W^2 + 8.78 C_W^3)$$

valid only for low values of C_W

Sherman Equation

$$\mu = \mu_{OS} (1 + a_0 C_W + a_1 C_W^2 + a_2 C_W^3 + \dots)$$

Einstein equation modified but still restricted to low values of C_W .

Richardson Equation

$$\mu = \mu_{OS} e^{a C_W}$$

Investigated for values of surfactant concentration less than 5 percent. Valid for all values of C_W .

TABLE I (continued)

Broughton-Squires Equation

$$\ln(\mu/\mu_{OS}) = a C_w + b$$

or

$$\mu = \mu_{OS} e^{a C_w + b}$$

modified Richardson equation.

Hatschek Equation

$$\mu = \mu_{OS} (1/1 - C_w^{1/3})$$

valid for $C_w > 0.75$

Sibree Equation

$$\mu = \mu_{OS} (1/1 - (h C_w)^{1/3})$$

Modified Hatschek equation. Valid for all values of C_w .

TABLE II
TESTED MIXTURES

Primary Mixtures:

- A - Oil only (33.35° API Gulf Coast Crude)
- B - Equipment check out set (60% oil, 40% water)

Test Mixtures:

No.	Oil	Percent Water	Surfactant	Temp. Range (°F)	Comments
1	85	5	10	82-175	Checked mixing time and discontinuous mixing effect. Also first test on particle size change.
2	70	20	10	84-185	Emulsion broke up in less than 16 hrs.
3	60	30	10	95-190	
4	50	40	10	88-182	No change in particle size.
5	40	50	10	83-177	
6	30	60	10	93-167	Emulsion appeared more stable.
7	20	70	10	97-174	No free oil present.
8	10	80	10	84-	Free water present - could not test for viscosity. Only 74% water in the emulsion.
9	75	15	10	97-152	Very unstable above 130°F.
10	30	50	20	95-160	Emulsion very stable.

TABLE II (Continued)

No.	Oil	Percent Water	Surfactant	Temp. Range (°F)	Comments
11	35	60	5	91-174	Emulsion very unstable.
12	39	60	1	---	Did not run unstable.
13		Sample mismixed			
14	90	0	10	84-183	Oil and emulsifier tests.
15	80	0	20	87-187	
16	95	0	5	90-175	
17	40	40	20	95-176	Very stable emulsion.
18	50	30	20	97-191	
19	55	40	5	93-177	Very unstable emulsion.
20	65	30	5	96-170	Emulsion broke at 170°F.
21	100	0	0	66-171	Check on past oil tested.
22	60	20	20		
23	10	70	20		Free water present. Emulsion contained only about 67% water.
24	25	70	5	90-163	Free water present.
25	45	50	5	94-175	Stable emulsion.
26	20	60	20	95-160	Free water present.
27	60	30	10	80	Further check on mixing time effect. Run after mixture 2.
28	60	30	10	82-115	Mixing time test.
29	60	30	10	90-120	Mixing time test.
30	25	70	5	---	Flow test only.

TABLE III

MIXING TIME TEST MIXTURES

Mixture 27			Mixture 28			Mixture 29		
Time (sec.)	Temp. (°F)	μ_A (cp.)	Time (sec.)	Temp. (°F)	μ_A (cp.)	Time (sec.)	Temp. (°F)	μ_A (cp.)
20	80	25.0	15	82	22.5			
40	81	24.5	60	83	25.75			
60	80	25.0	120	85	24.0			
120	80	25.0	240	95	22.0	240	90	22.5
			335	95	22.0	335	112	20.5
			600	107	19.25			
			900	115	19.5	900	120	20.0

TABLE IV (continued)

F-1187

Mixture 14	Mixture 15	Mixture 16	Mixture 17	Mixture 18	Mixture 19	Mixture 19 Rerun
Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)
μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)
84	87	90	95	97	93	98
9.5	10.0	5.0	48.5	34.5	30.0	31.0
4.75	7.5	4.25	36.5	22.0	23.25	22.5
3.75	5.75	3.5	29.25	15.5	18.5	16.0
3.125	4.5	2.75	21.0	13.0	12.25	12.75
2.625	3.625	2.5			8.5	12.0
Mixture 19 2nd Rerun	Mixture 20	Mixture 20 Rerun	Mixture 20 2nd Rerun	Mixture 21	Mixture 22	Mixture 23
Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)	Temp. (°F)
μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)	μ A (cp.)
91	96	93	90	66	89	Free water present no readings possible.
30.5	17.25	16.0	16.0	6.0	18.25	
22.0	13.0	11.75	11.0	4.5	18.0	
13.5	10.0	9.0	8.0	3.5	11.5	
	7.5	8.0		2.75	10.75	
				2.25	9.5	
				2.125	8.0	

TABLE IV (continued)

Mixture 24		Mixture 25		Mixture 26	
Temp. (°F)	μ A (cp.)	Temp. (°F)	μ A (cp.)	Temp. (°F)	μ A (cp.)
90		94	44.0	95	
108	110.5	122	32.75	119	150.0
128	86.0	146	25.0	139	130.0
150	64.0	175	20.0	148	105.0
163	57.5			160	97.5

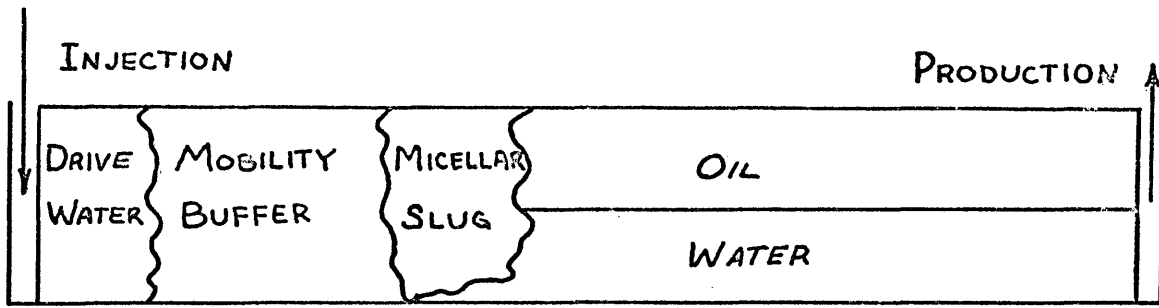


FIGURE 1

The Maraflood Process

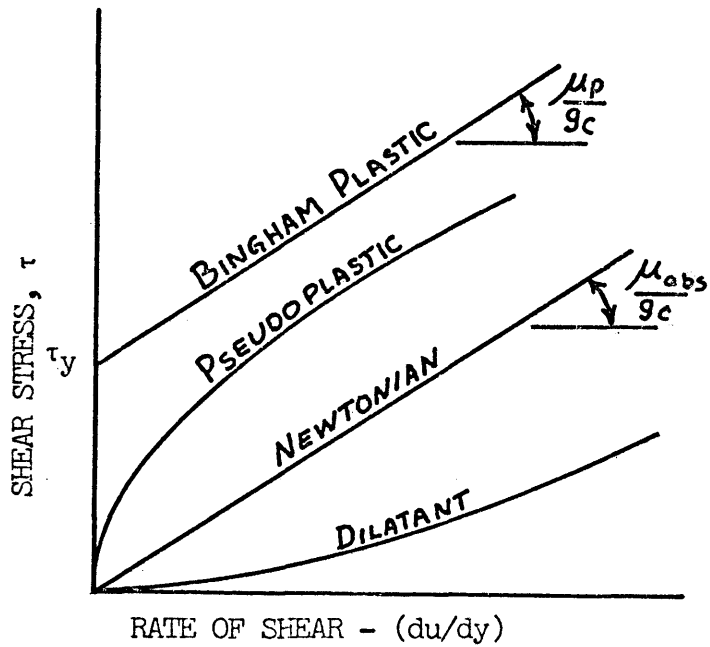


FIGURE 2

Flow Curves of Newtonian
and Non-Newtonian Fluids

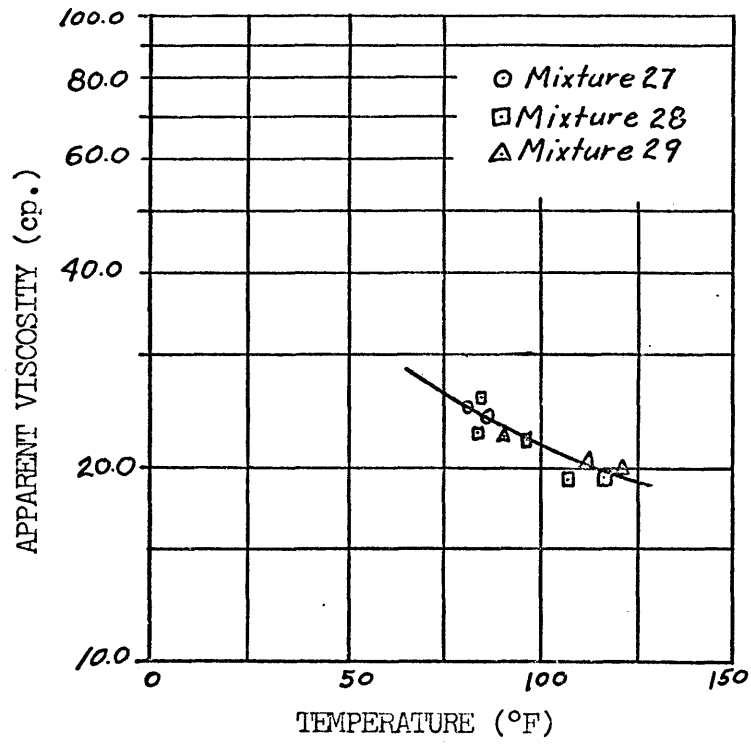


FIGURE 3
Mixing Time Tests
Volume Fraction
 $C_w = 0.30$
 $C_s = 0.10$

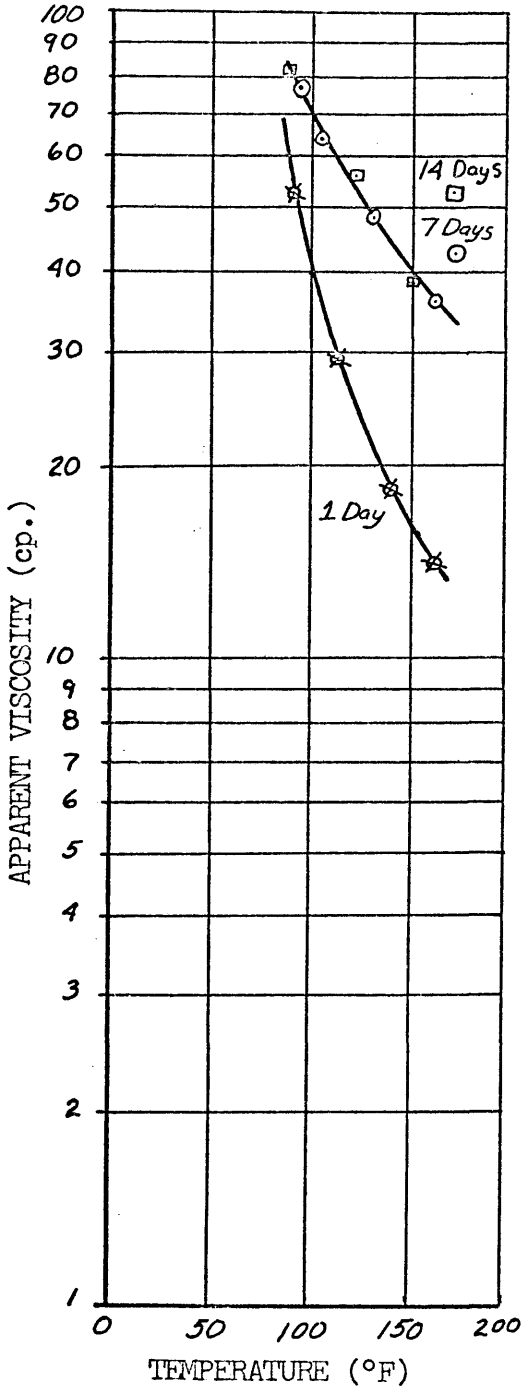


FIGURE 4

Dispersion Test
Mixture 11

Volume Fraction
 $C_w = 0.60$
 $C_s = 0.05$

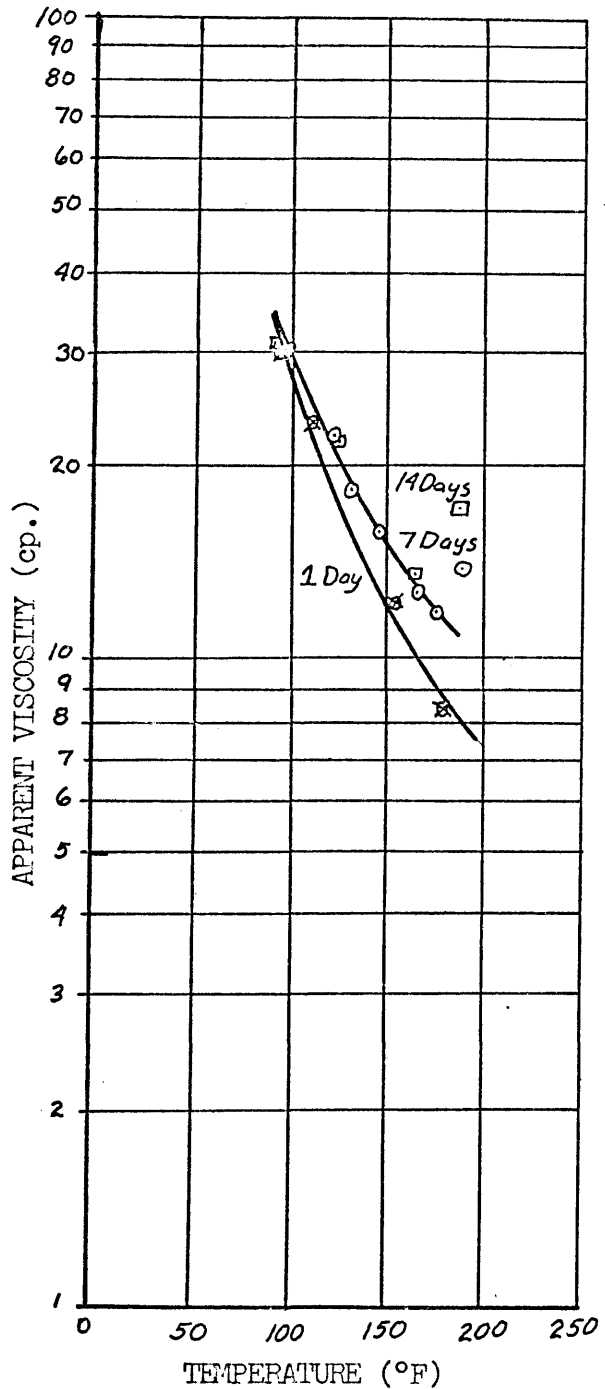


FIGURE 5

Dispersion Test
Mixture 19

Volume Fraction
 $C_w = 0.40$
 $C_s = 0.05$

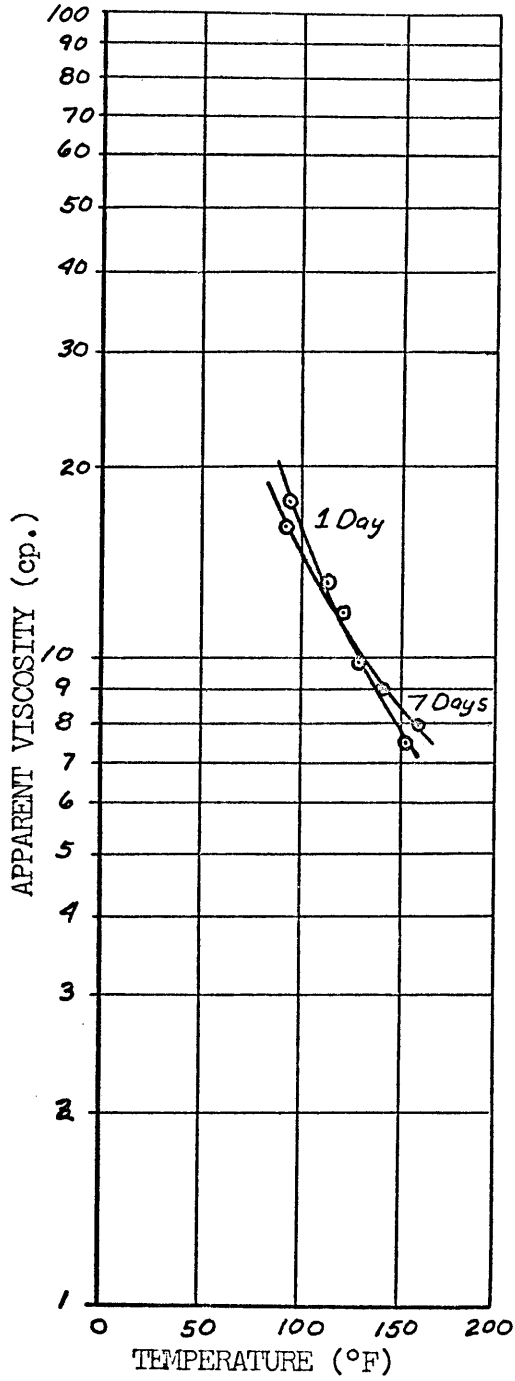


FIGURE 6
Dispersion Test
Mixture 20
Volume Fraction
 $C_w = 0.30$
 $C_s = 0.05$

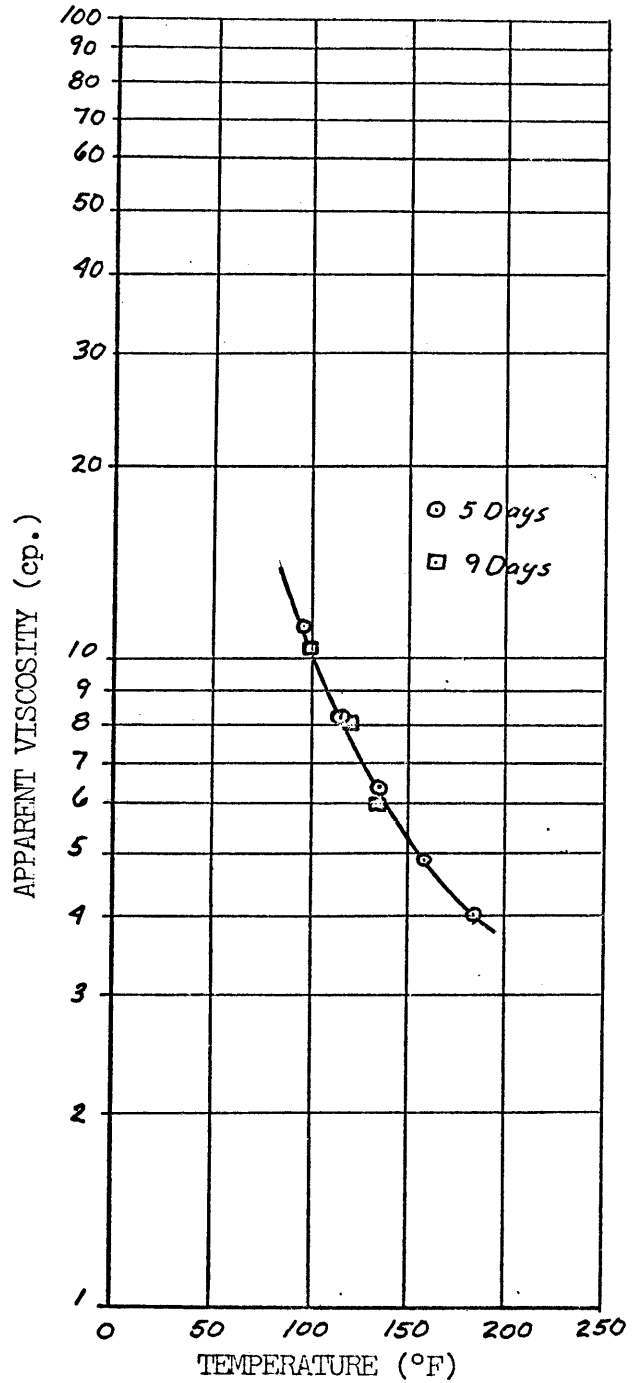


FIGURE 7
Dispersion Test
Mixture 10
Volume Fraction
 $C_w = 0.50$
 $C_s = 0.20$

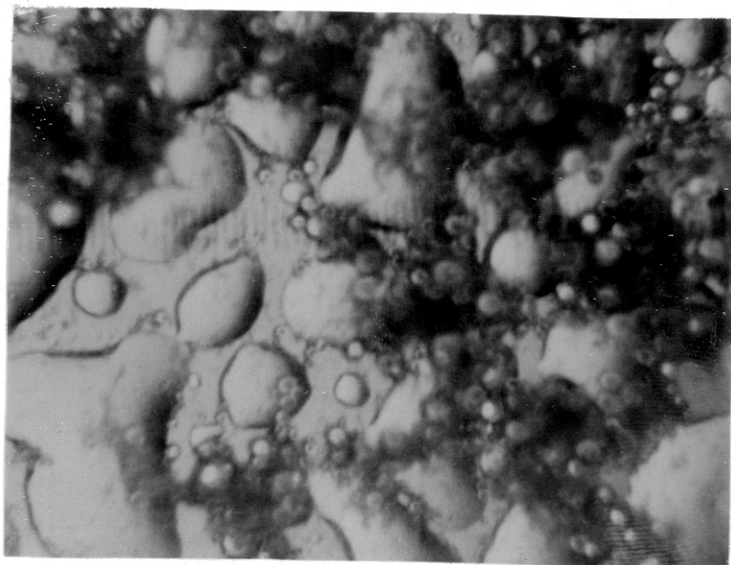


FIGURE 8

Microphotograph at 5 seconds Mixing Time

Mixture 27 80°F 100 Power

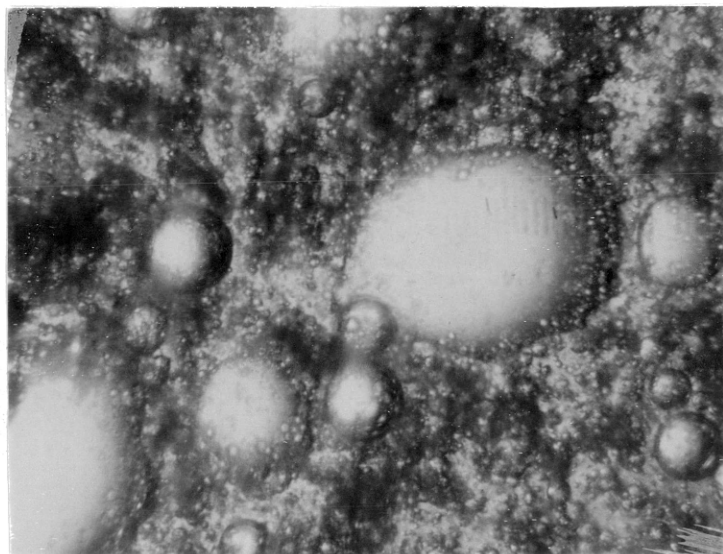


FIGURE 9

Microphotograph at 10 seconds Mixing Time

Mixture 27 80°F 100 Power

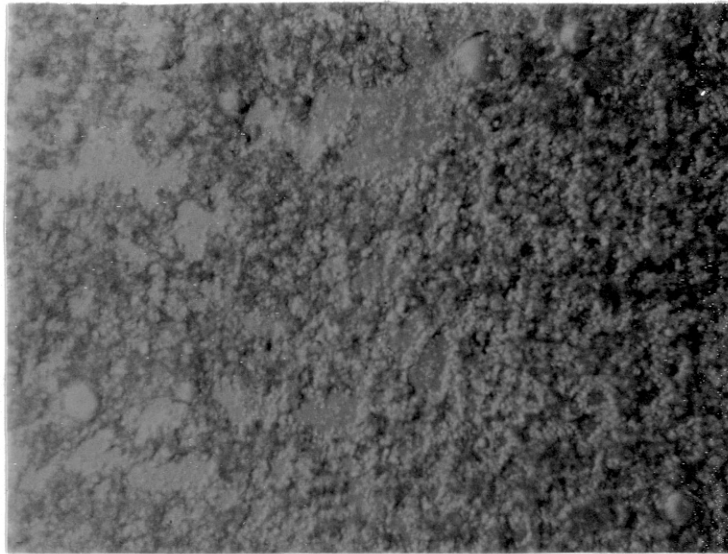


FIGURE 10

Microphotograph at 15 seconds Mixing Time

Mixture 27 80°F 100 Power

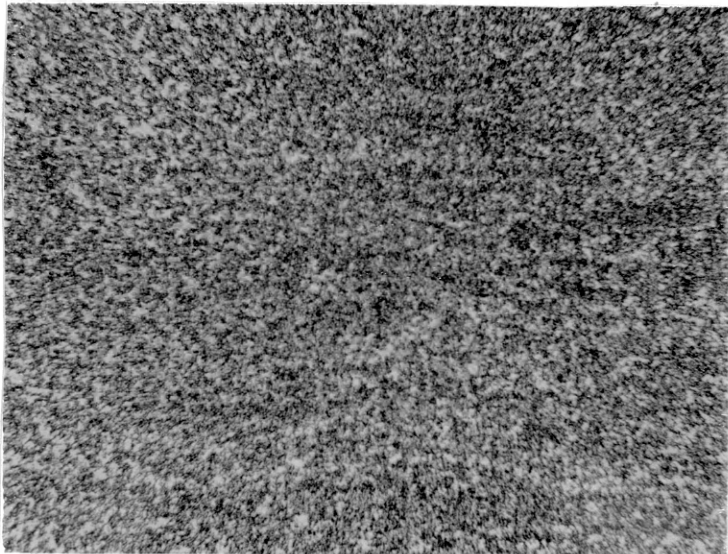


FIGURE 11

Microphotograph at 80 seconds Mixing Time

Mixture 27 80°F 100 Power

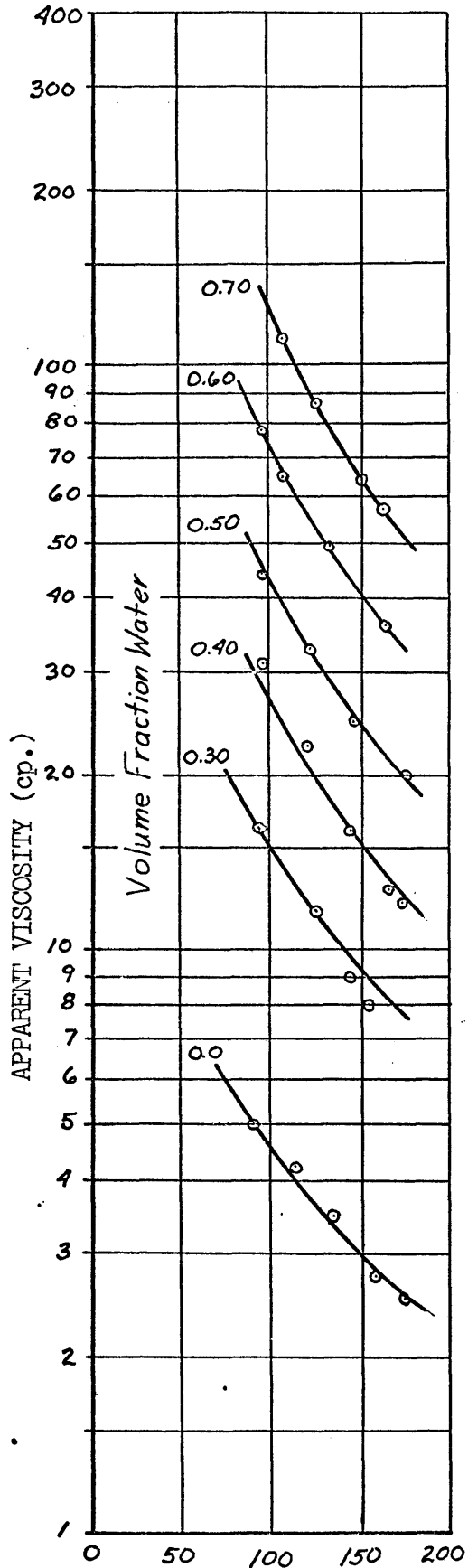


FIGURE 12
TEMPERATURE (°F)
5 Percent Surfactant
Viscosity-Temperature
Curves

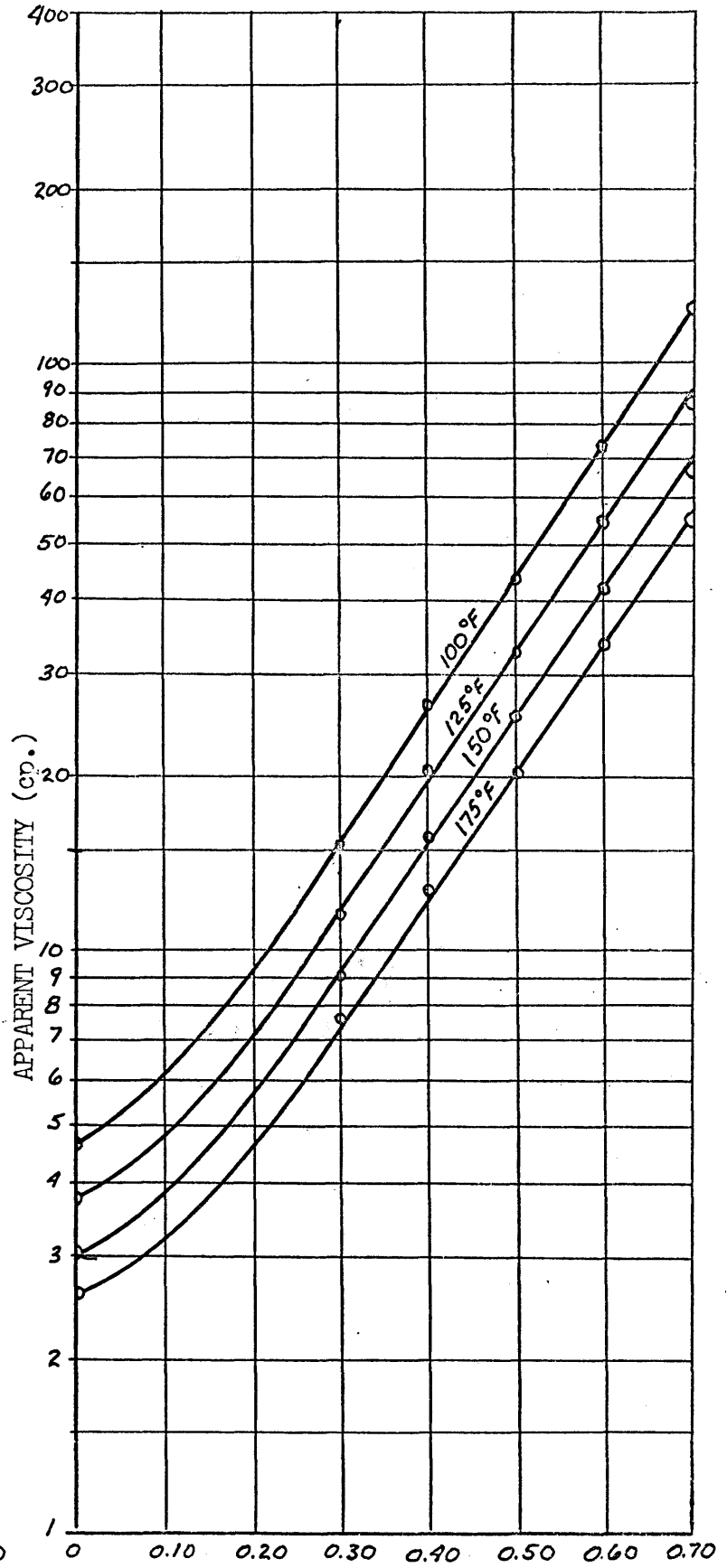


FIGURE 13
VOLUME FRACTION WATER
5 Percent Surfactant
Viscosity-Volume Fraction Water
Curves

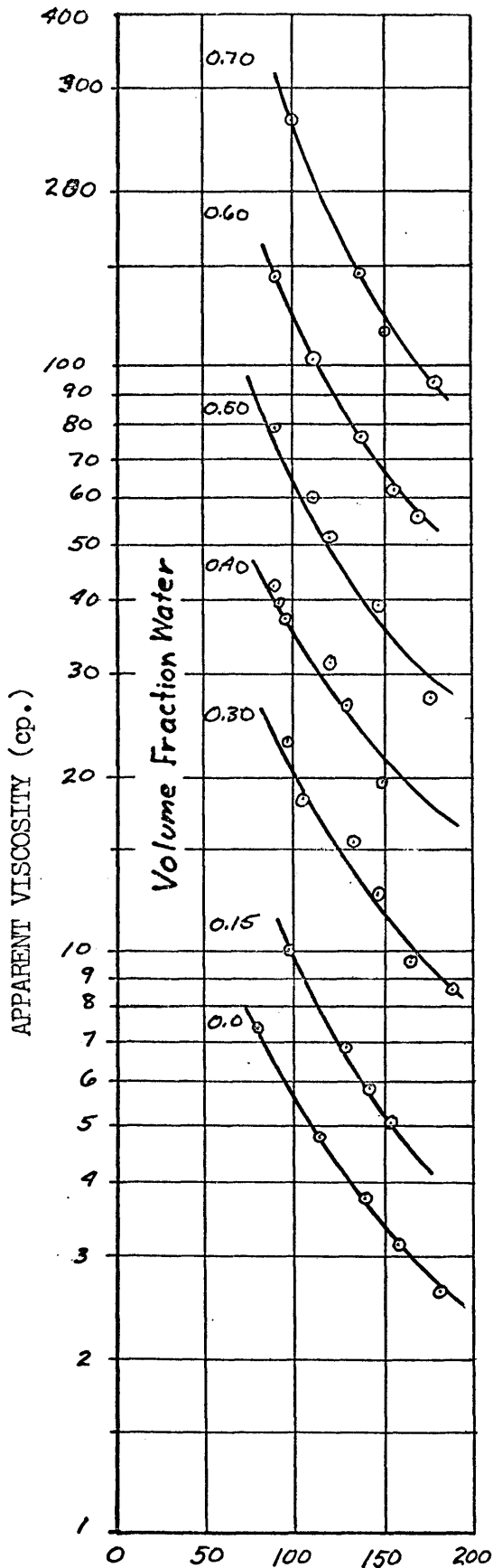


FIGURE 14
TEMPERATURE (°F)
10 PERCENT SURFACTANT
Viscosity-Temperature
Curves

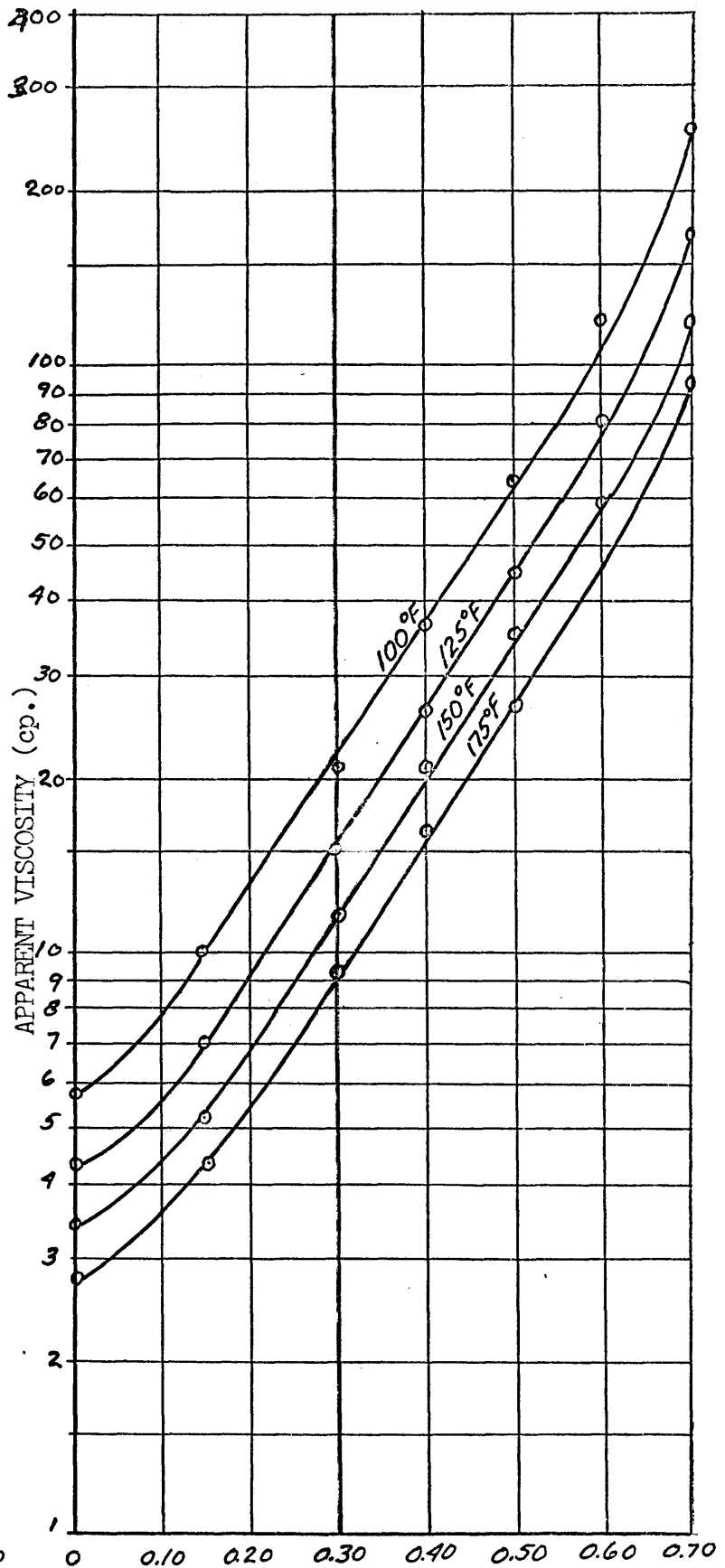


FIGURE 15
VOLUME FRACTION WATER
10 PERCENT SURFACTANT
Viscosity-Volume Fraction Water
Curves

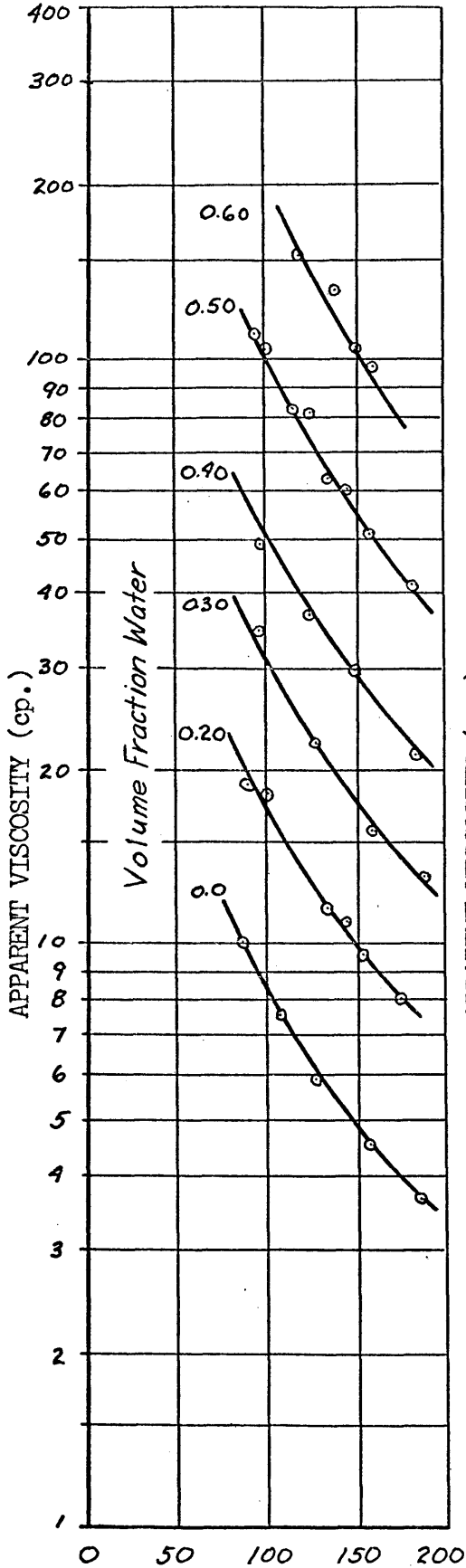


FIGURE 16
TEMPERATURE (°F)
20 Percent Surfactant
Viscosity-Temperature
Curves

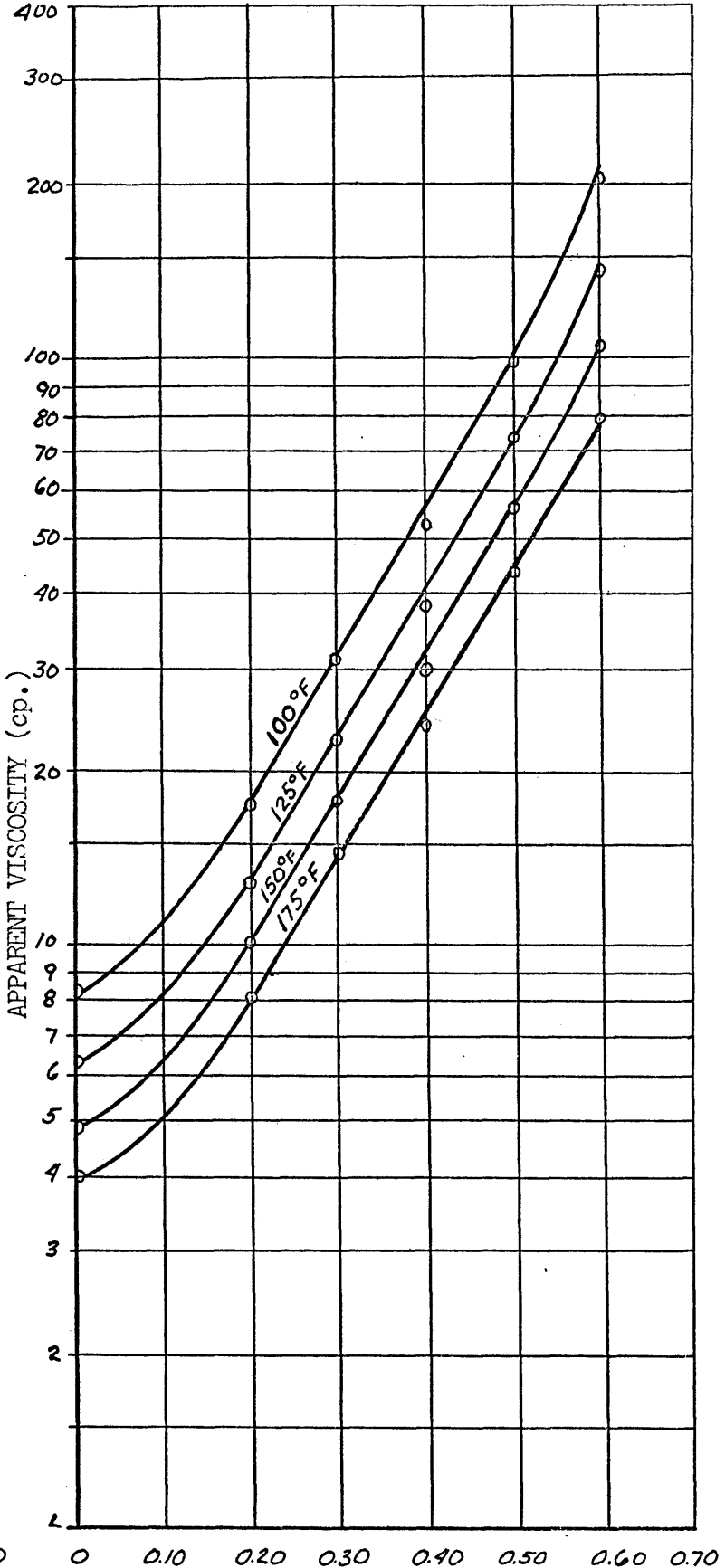


FIGURE 17
VOLUME FRACTION WATER
20 Percent Surfactant
Viscosity-Volume Fraction Water
Curves

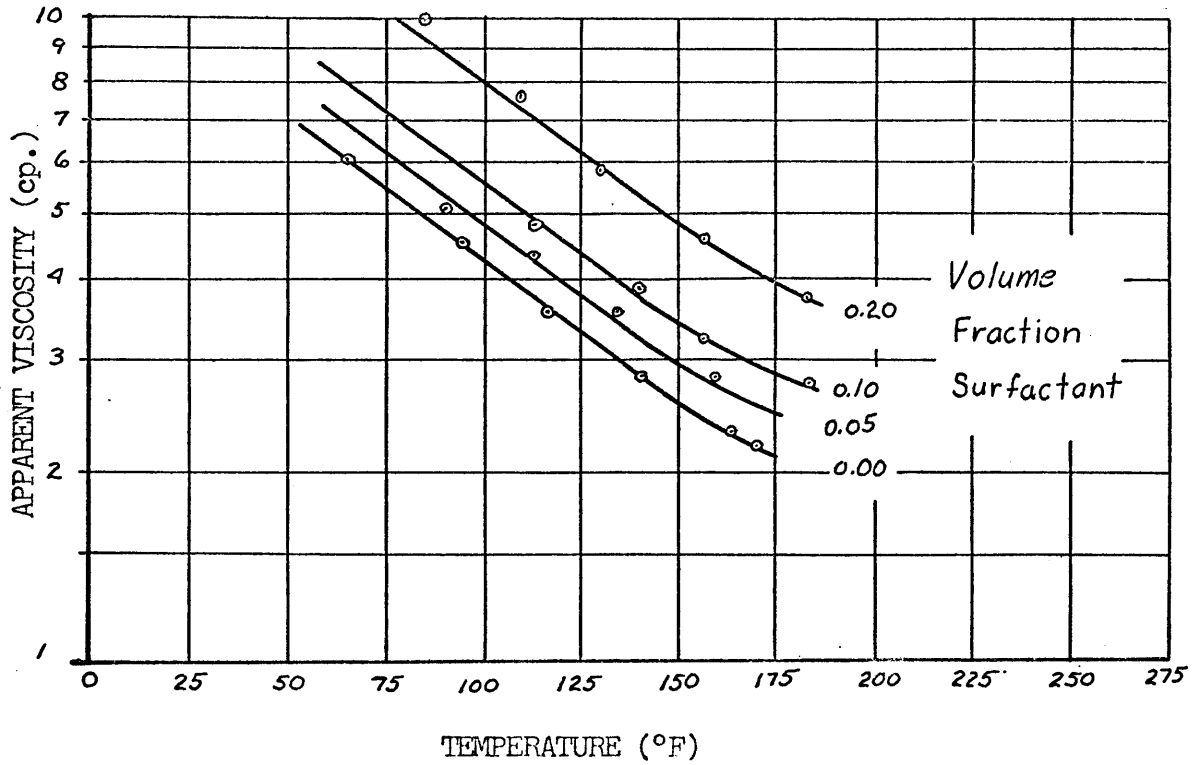


FIGURE 18

Base Fluid Viscosity Curves

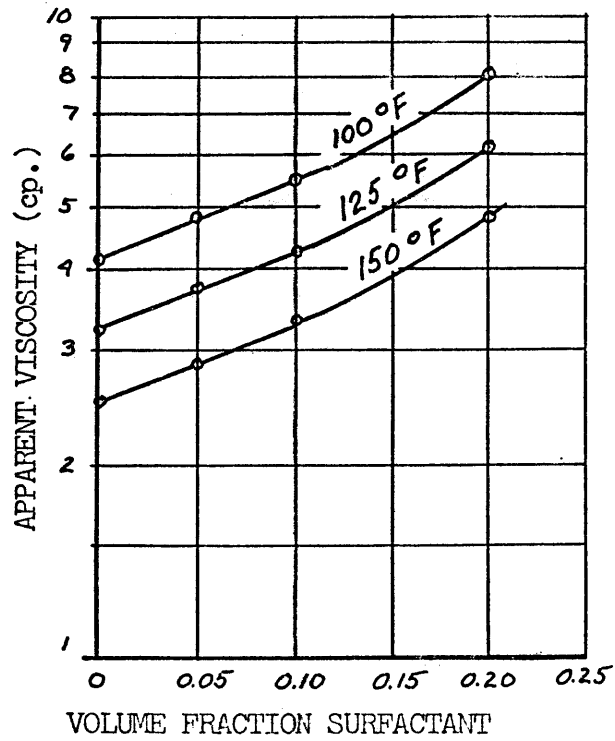


FIGURE 19

Base Fluid Viscosity Curves

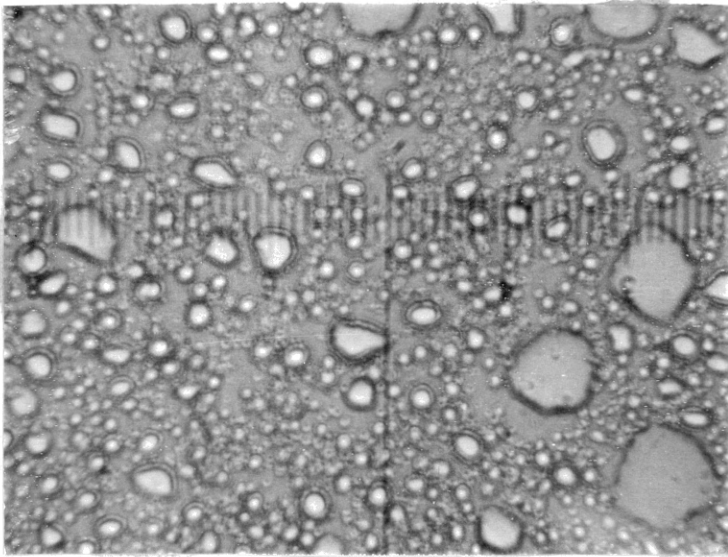


FIGURE 20

Microphotograph of Free Water
Mixture 23 $C_W = 0.70$ $C_S = 0.10$
85°F 100 Power

FIGURE 21

Microphotograph of
Free Water
Mixture 24 $C_W = 0.70$ $C_S = 0.05$
90°F 100 Power

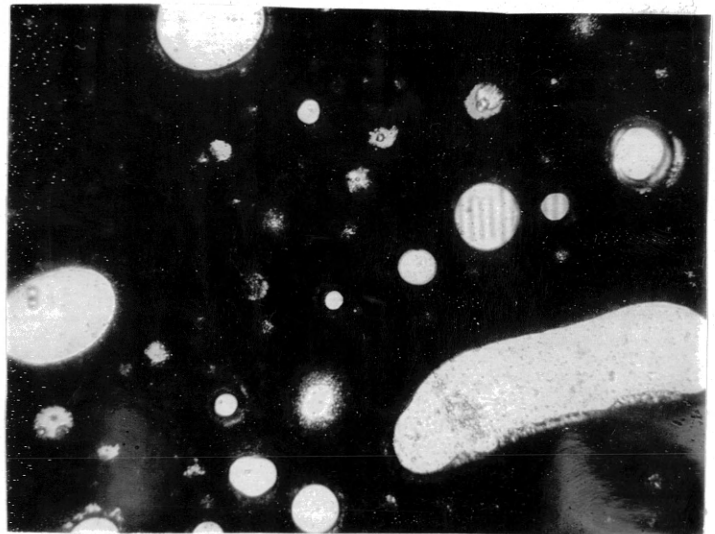
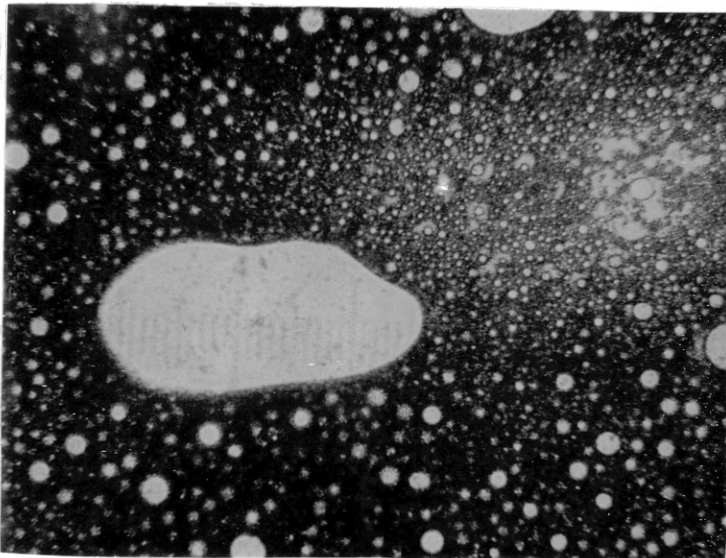


FIGURE 22

Microphotograph of Free Water
Mixture 26 $C_W = 0.60$ $C_S = 0.20$
95°F 100 Power



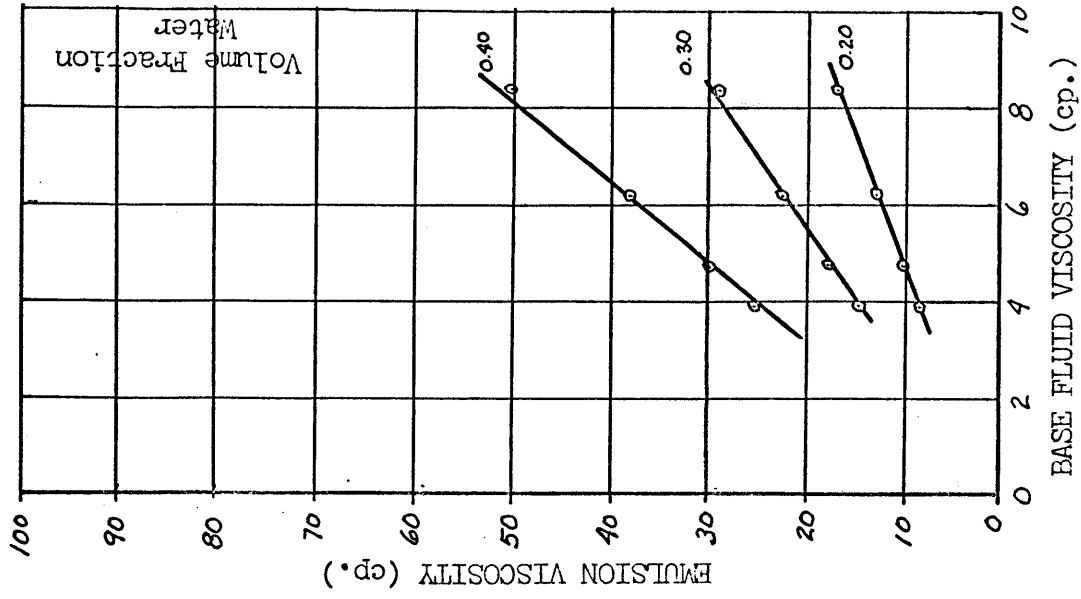


FIGURE 25

20 Percent Surfactant

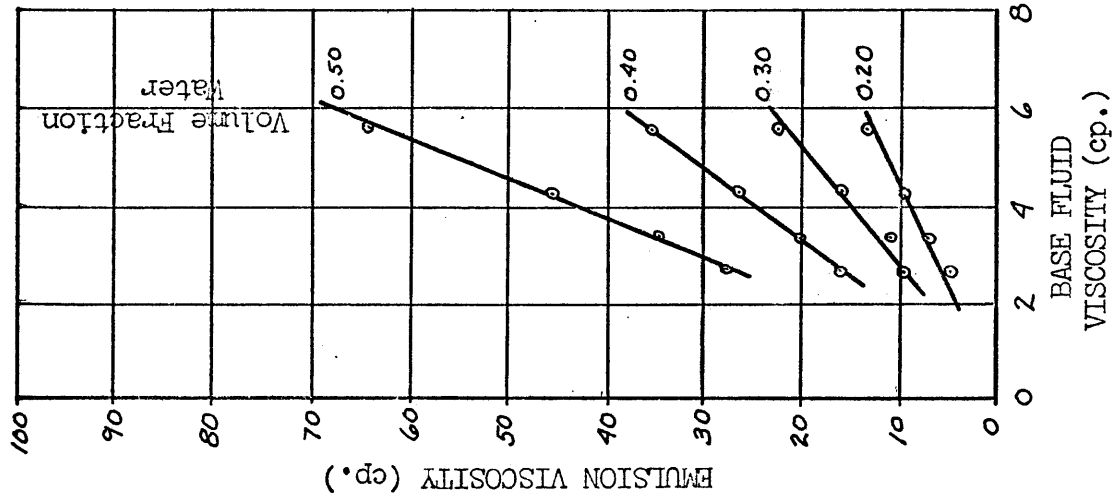


FIGURE 24

10 Percent Surfactant

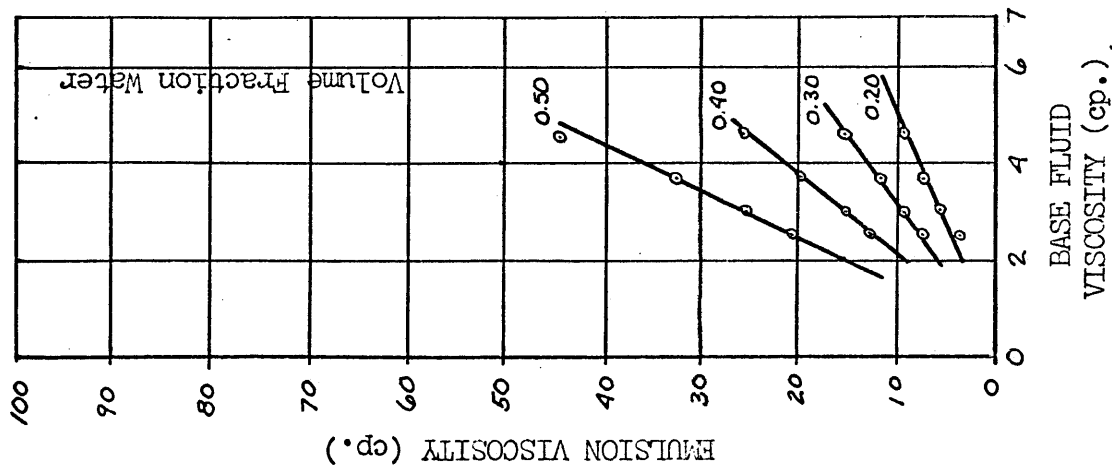


FIGURE 23

5 Percent Surfactant

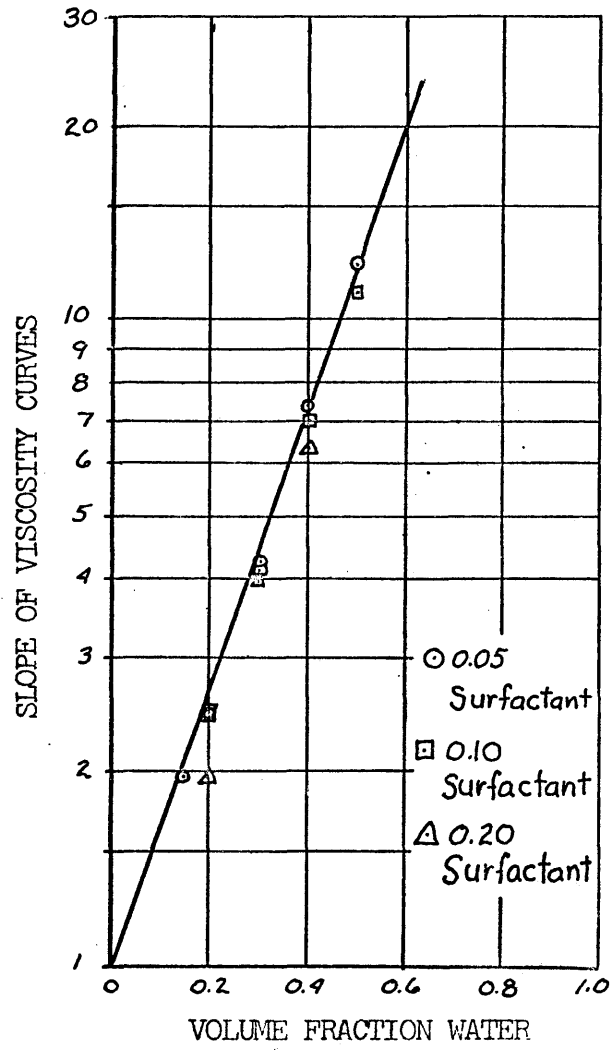


FIGURE 26

Slope Relation of
Figures 23, 24, and 25

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