# THE UNIVERSITY OF MICHIGAN INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

### RHEOLOGY OF PHARMACEUTICAL EMULSIONS

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#### INTRODUCTION

Emulsions are an important class of pharmaceuticals. They represent a useful dosage form for drugs, especially those which are insoluble liquids. Being fluids, emulsions for oral administration are frequently more readily accepted by the patient who finds tablets or capsules difficult to swallow. Emulsified ointments are commonly preferred to those with petrolatum base because of more rapid release of medicament to the skin as well as greater ease of removal from the skin and clothing. Flavors are frequently prepared in emulsion form in order to have sufficient concentration of oil in the aqueous medium. Further, emulsions are used almost exclusively as the base for cosmetic lotions, shampoos and facial creams.

The usefulness of an emulsion is strongly dependent upon its flow properties. Emulsions for internal use must have sufficient viscosity to prevent sedimentation and at the same time flow readily so as to be easily poured and swallowed. Those for parenteral use must be easily forced through a hypodermic needle. Emulsified lotions and ointments must behave as solids when undisturbed and yet be soft enough to be readily spread upon the skin.

In spite of the importance of rheological properties of emulsions little knowledge of their flow properties is available. No correlation between rheological properties and ultimate applications of emulsions has been proposed. Thus, one who is preparing a new emulsion must depend upon the sense of touch to evaluate his efforts, and a laboratory marketing an emulsion must depend upon some arbitrary control procedure or simply hope that

variations in mixing, milling and other phases of the process will be so small as to furnish a uniform product.

It appears, therefore, that the development of more logical approaches to formulation as well as the establishment of better control of product uniformity for emulsions will depend, to a large extent, upon the extension of knowledge of their flow properties.

#### LITERATURE REVIEW

#### RHEOLOGY OF EMULSIONS

### Equations for Non-Newtonian Flow

Emulsions have been found to exhibit both Newtonian and non-Newtonian flow, depending upon concentration of internal phase and composition of the suspending medium, but those of greatest interest to pharmacy, i.e., with concentration of dispersed phase above five percent, exhibit non-linear flow. In such case, the simple equation for viscosity:

$$F/S = \eta$$
,

where  $\underline{F}$  is stress,  $\underline{S}$  is shear and  $\underline{\underline{N}}$  is coefficient of viscosity, no longer is applicable. The equation of Bingham for plastic flow:

$$(F-f)/S = \eta_{pl}$$

where  $\underline{f}$  is yield value and  $\underline{\eta}_{\underline{pl}}$  is the coefficient of plastic viscosity, is equally inappropriate, since it demands linear flow beyond a fixed value of stress.

Non-linear flow has been the subject of much investigation 1,2,3,4,5, but only three equations have emerged which are generally useful in describing experimental data; these are the Williamson equation, the Structure equation and the Ree-Eyring equation. The three equations have in common the property of reducing to the Newtonian expression under suitable conditions, and the first two may reduce to the Bingham equation as well. Thus, these may be considered as generalized flow equations and not applicable exclusively to non-linear systems.

### The Williamson Equation

Williamson<sup>6</sup> proposed that the total stress,  $\underline{F}$ , consists of two components,  $\underline{F_1}$ , due to plastic resistance, and  $\underline{F_2}$ , due to ordinary viscous resistance. He found that the relationship of  $\underline{F_1}$  to shear,  $\underline{S}$ , could be described adequately by a simple hyperbola and thus obtained the following equation:

$$F = F_1 + F_2 = \frac{fS}{s + S} + \sqrt{s},$$

where <u>s</u> and <u>f</u> are constants defining the curvature and  $\frac{N}{\infty}$  is a constant describing the ultimate viscosity approached by the system at high rates of shear.

It is readily seen that  $\underline{F_1}$  will become zero for linear flow so that the equation becomes the simple linear expression for Newtonian systems with equal to  $\underline{\gamma}$ . Also, for plastic flow  $\underline{s}$  is zero and the equation becomes that for a Bingham body.

Williamson used the ratio, f/s, as an index to plasticity and the ratio,  $f/s \eta_{\infty}$ , as a "false body constant" and was able with these terms to define the brushing qualities of paint in a useful manner. He also noted that the viscosity at extremely low shear or limiting viscosity,  $\gamma_{\infty}$ , could be expressed as:

$$\gamma_0 = f/s + \gamma_0$$

Shangraw<sup>8</sup> noted that although the Williamson equation had been used successfully by Williamson and had been praised as the best equation available at that time for non-Newtonian flow curves<sup>9</sup> it had not been used widely by others. On the basis of his own results, Shangraw presumed that

limited use had been made of this equation because of the large errors involved in estimation of the constants by Williamson's methods. The first of these methods was graphical and would be expected to result in large errors unless data were available for extremely high rates of shear. Williamson's instrument was unusual in that it did furnish extremely high shear. The second method for estimation of the constants for the Williamson equation utilized three data points to estimate three constants, a procedure likely to involve large errors.

To estimate the constants more accurately, Shangraw converted the equation to the linear form:

$$F = f + \eta_{\infty} s + \eta_{\infty} S - (F/S)(s),$$

which may be expressed as:

$$F = b_0 + b_1 S + b_2 F/S,$$

where  $b_0 = f + \eta_\infty s$ ,  $b_1 = \eta_\infty$  and  $b_2 = -s$ . This expression could be evaluated by least squares and thus could be fitted with any number of data points. By this means Shangraw obtained constants for the Williamson equation which gave predicted values generally within one percent of experimental when applied to methylcellulose solutions.

Shangraw also found that plasticity constants,  $\underline{f/s}$ , and false body constants,  $\underline{f/s} \underline{\eta_{\infty}}$ , could be related to concentration of methylcellulose by log-lcg expressions. He utilized the values of limiting viscosity,  $\underline{\eta_{\infty}}$ , to calculate specific viscosity,  $\underline{\eta_{\infty}}$ , which fitted the common form of plot used to obtain intrinsic viscosity, i.e.,  $\underline{\log \eta_{\infty}/c}$  vs. c, where c is concentration.

#### The Structure Equation

Grim<sup>10</sup>, using the method of Shangraw, applied the Williamson equation to data on suspensions of salicylamide in methylcellulose solution. He found the equation to fit flow curves in an acceptable manner but was unable to find any consistent relationship between constants of the equation and concentration of suspended material. Grim noted that the hyperbolic portion of the equation was arbitrarily selected as being suitable for describing flow data and that the portion of the flow curve most dependent on this function, that at low shear rate, showed the greatest deviation from the equation. Examining this part of the Williamson equation in detail, Grim isolated values for viscoelastic flow:

$$F_1 = F - \% S = fS \over s + S$$

Converting this to linear form, he obtained:

$$1/F_1 = 1/f + (s/f)(1/S),$$

so that a plot of  $1/F_1$  versus 1/S should be linear. Values plotted in this manner demonstrated a definite non-linearity at low and high values of S; thus Grim concluded that the simple hyperbolic function was not a correct representation of the viscoelastic resistance.

Grim proposed that the total resistance to flow was composed of two components, as stated by Williamson, and that one of these is viscoelastic. The second component was said to be plastic, rather than Newtonian, since the flow curve at high rates of shear, though linear, has a positive intercept on the stress axis; thus:

$$F_p = f + \gamma_s S,$$

where  $\underline{F_p}$  is plastic resistance,  $\underline{f}$  being the intercept on the stress axis obtained by extrapolation of the linear portion of the curve and  $\underline{\mathbb{F}_p}$  being the slope of the linear portion. Grim stated that the viscoelastic resistance decreases with rate of shear, becoming zero when the flow curve becomes linear, and that the decrease in viscoelastic resistance with shear is proportional to the resistance remaining:

$$dF_v/dS = -aF_v$$

where  $\underline{F_V}$  is viscoelastic resistance and  $\underline{a}$  is a constant of proportionality. Integration yielded:

$$ln F_v = -aS + lnI,$$

<u>lnI</u> being the constant of integration. Grim expressed this in the form:

$$F_v = b_v e^{-aS}$$

where  $\underline{b_V}$ , called the viscoelastic constant, is  $\underline{I}$  from the previous expression. Thus, the final equation, called the structure equation, is:

$$F = f + \eta_o S - b_v e^{-aS}$$
.

Putting the expression for viscoelastic resistance in the form:

$$F_v = f + \gamma_o S - F = b_v e^{-aS}$$

and plotting calculated values of  $\underline{F_v}$  versus  $\underline{e^{-aS}}$ , using the arbitrary value of 0.001 for  $\underline{a}$ , Grim showed that this equation fitted experimental data better than the Williamson equation. Further, he found the slope of the linear portion,  $\underline{h}$ , fitted experimental curves better than that calculated from the Williamson equation.

Applying the structure equation to suspensions, Grim found the reciprocals of  $\underline{f}$ ,  $\underline{b_v}$  and  $\underline{\gamma_{\infty}}$  to be linear functions of the volume

concentration. Intercepts of these lines, representing infinite resistance, were judged to be a function of ultimate settling volume of the suspensions.

#### The Ree-Eyring Equation

Eyring<sup>11</sup> considered the flow of a liquid as a rate process and applied the theory of absolute reaction rates to the problem of viscosity. A liquid is considered to be made up of holes moving about in matter, these holes playing the same part in a liquid as molecules in the gas phase. Eyring considered two layers of molecules in a liquid, at a distance  $\Lambda_1$  apart, where one layer slides past the other under an applied force. If  $\underline{\mathbf{f}}$  is the force per square centimeter tending to displace one layer with respect to the other, and  $\underline{\Lambda}\underline{\mathbf{U}}$  the difference in velocities between the two layers, then, by definition,  $\mathbf{N} = \mathbf{f} \lambda_1 / \Delta \mathbf{U}$  where  $\underline{\mathbf{N}}$  is the coefficient of viscosity. The motion is assumed to involve the passage of a molecule from one equilibrium position to another in the same layer. In order for this to occur, a suitable hole or site should be available and the production of such a site would require expenditure of energy, since work must be done in pushing back other molecules. Thus the motion of the molecule may be regarded as being equivalent to the passage of the system over a potential energy barrier (Fig.

### 1). Eyring defined the dimensions of the system as:

<sup>&</sup>gt; = the distance between two successive equilibrium positions in the direction of motion,

 $<sup>\</sup>lambda_3$  = the distance between molecules in the direction of motion  $\lambda_2$  = the mean distance between two adjacent molecules in the moving layer in the direction perpendicular to the direction of motion.

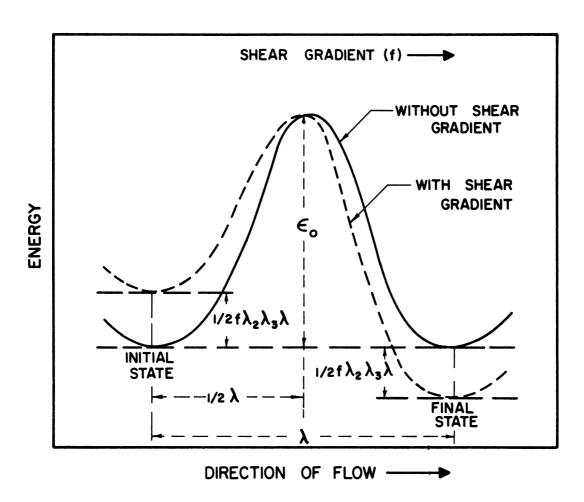


Fig. 1. Potential-Energy Barrier for Flow, with and without Shear Gradient

The potential energy barrier is considered to be symmetrical, so that the distance between the initial equilibrium position and the activated state is  $1/2 \lambda$ . The applied force acting on a molecule in the direction of flow is  $f \lambda_2 \lambda_3$  and, therefore, the energy acquired by a moving molecule when it has reached the top of the potential energy barrier is  $1/2f \lambda_2 \lambda_3 \lambda$ . The force causing the flow thus reduces the height of the potential energy barrier in the forward direction by an amount  $1/2f \lambda_2 \lambda_3 \lambda$ , the height in the opposite direction being increased by the same amount. From the theory of absolute reaction rates, the number of times a molecule passes over the energy barrier, and hence moves in any direction, per second, is given by:

$$k' = \frac{\kappa T}{h} = \frac{F^+}{F} e^{-\frac{\kappa T}{\hbar}}$$

where  $\underline{\epsilon_o}$  is the energy of activation per molecule at 0° Kelvin,  $\underline{F}$  and  $\underline{F}^{\dagger}$  are the partition functions of the initial and the activated states, respectively,  $\underline{K}$  is the Boltzman constant,  $\underline{T}$  is the absolute temperature, and  $\underline{h}$  is Planck's constant. Therefore, the specific rate of flow in the forward direction is given by:

$$k_f = \frac{kT}{h} \frac{F^{\dagger}}{F} e^{-(\epsilon_c - 1/2f\lambda_2\lambda_3 \lambda)/KT}$$

or

$$k_f = k e^{1/2 f \lambda_1 \lambda_3 \lambda / KT}$$

and the rate in backward direction is given by:

$$k_b = ke^{-1/2f \lambda_{\lambda} \lambda_{\lambda} \lambda} / KT$$
.

The distance moved by the molecule per second, and hence the rate of motion, is given by  $\underline{k_f\lambda}$  in one direction and  $\underline{k_b\lambda}$  in the other, since the molecule

moves the distance  $\underline{\lambda}$  every time it passes over the potential energy barrier. The net rate of flow  $\underline{\Delta U}$ , is equal to  $(k_f - k_b)\lambda$ . Therefore:

$$\Delta U = k(e^{1/2 f \lambda_2 \lambda_3 \lambda} / KT - e^{-1/2 f \lambda_2 \lambda_3 \lambda} / KT)$$

or

$$\Delta U = 2 \lambda k \sinh \left[ \frac{f \lambda_2 \lambda_3 \lambda}{2KT} \right]$$

The expression for the viscosity of the liquid may then be written as:

$$\gamma = \frac{\lambda_1 f}{2 \lambda_1 \sinh(f \lambda_2 \lambda_3 \lambda / 2KT)}.$$

Ree and Eyring<sup>12</sup> applied this equation to develop a generalized theory of non-Newtonian flow. According to this theory, a system is made up of different groups of flow units. The flow rate of the system is supposed to be a function of the relaxation times of the flow units which contribute to the flow process, the distribution of these relaxation times and, in the case of thixotropic flow, the deformation of the system with stress. The mechanical model of the system is as follows:

- 1. There are  $\underline{n}$  groups of flow units differing in relaxation times and geometrical directions.
- 2. The fractional area on a shear surface of the  $n^{th}$  unit is  $x_n$ , and the shear stress per unit area acting on this area is  $f_n$ .
- 3. All units on the same shear plane move with the same shear rate.

From Eyring's viscosity equation, the rate of shear is given by:

$$S = (\lambda/\lambda)$$
 ) 2 k sinh  $\alpha_n f_n$ 

where:

$$\alpha_n = (\lambda_2 \lambda_3 \lambda_n)_n / 2 \text{ KT}$$

The force acting on the units of the  $\underline{n^{th}}$  group is  $\underline{x_n}$   $\underline{f_n}$  and the stress,  $\underline{f}$ , is given by:

$$f = \sum_{n=1}^{n} x_n f_n$$

Substituting from the equation for the rate of shear, we obtain:

$$f = \sum_{n=1}^{n} \frac{x_n}{\sqrt{n}} \quad \sinh^{-1} \beta_n S$$

where:

$$\beta_n = 1/\left[ (\lambda/\lambda_n)_n KK_n^{\dagger} \right]$$

 $\beta_n$  is a constant proportional to the relaxation time of the  $\underline{n^{th}}$  kind. The equation for viscosity may be written as:

$$\gamma = \sum_{n=1}^{n} x_n \beta_n \frac{\sinh^{-1} \beta_n S}{\beta_n S}.$$

The function, (sinh  $^{-1}$   $\beta_n {\rm S})/$   $\beta_n$  S, has the property that:

$$\beta S \rightarrow 0 \frac{\sinh^{-1}\beta S}{\beta S} = 1,$$

and:

$$\beta S \sim \frac{\sinh^{-1} \beta S}{\beta S} = 0.$$

This is the generalized viscosity formula for non-Newtonian flow developed by Ree and Eyring. To illustrate, we may consider a system with three flow groups so that the equation may be written as:

$$\eta = \frac{x_1}{4_1} \beta_1 + \frac{x_2}{4_2} \beta_2 \quad \frac{\sinh^{-1} \beta_2 S}{\beta_2 S} + \frac{x_3}{4_3} \beta_3 \quad \frac{\sinh^{-1} \beta_3 S}{\beta_3 S}.$$

The first term would represent the condition for Newtonian flow:

and:

$$(\sinh^{-1}\beta_1 S)/\beta_1 S \cong 1.$$

The second term might be thought of as representing the case where:

a condition for Newtonian flow at low rates of shear and non-Newtonian flow at high rates of shear. The third term might be thought of as representing the case where:

$$\beta_{2^{S}} >>> 1$$
,

which is the condition for non-Newtonian flow. One or more components, with appropriate values for the constant  $\beta_n$ , might be required to describe the flow properties of a given system.

The equation was applied by Ree and Eyring to the data of Saunder and Treloar  $^{13}$  for masticated rubber at temperatures from  $^{40^{\circ}}$  to  $^{140^{\circ}}$ , and to the data of Mooney on lightly milled crepe at temperatures from  $^{69^{\circ}}$  to  $^{140^{\circ}}$ . Agreement with experimental observations was found to be satisfactory. The constant  $\underline{\swarrow}$  was found to be independent of temperature because of the fact that the quantity,  $\lambda_2 \lambda_3 \lambda$ , increased linearly with temperature.

The Ree-Eyring theory represents a theoretical approach to the problem of non-Newtonian viscosity. It is based on the fundamental properties of the constituents of a system and permits the calculation of the thermodynamic quantities related to the kinetics of the flow process. It also permits a theoretical study of the temperature dependence of viscosity. The equation could be applied to calculate flow curves of reduced shear rate versus shear stress, so that viscosity data at different temperatures could be directly compared. The expression for reduced rate of shear may be written as:

$$S_r = S \exp (\Delta H^{\dagger}/RT),$$

where  $\underline{\wedge}_{\underline{H}}^{\dagger}$  is the enthalpy of activation,  $\underline{R}$  is the gas constant and  $\underline{T}$  is the absolute temperature. Ree and Eyring applied this method to the data of

Mooney<sup>14</sup>, Bestel and Belcher<sup>15</sup> and Spencer and Dillon<sup>16</sup>. Satisfactory agreement between observed values and those calculated using the reported value for heat of activation was observed.

Maron and Pierce<sup>17</sup> applied the Ree-Eyring equation to the data of Maron and  $Fok^{18}$  on the flow behaviour of synthetic latex. The equation was found to be satisfactory with the assumption of one Newtonian and one non-Newtonian component, as follows:

$$\gamma = \underline{x_1} \beta_1 + \underline{x_2} \beta_2 \quad \frac{\sinh^{-1} \beta_{2S}}{\beta_{2S}},$$

or:

$$\gamma = a + b \frac{\sinh^{-1} \beta_{2S}}{\beta_{2S}},$$

where:

$$a = x_1 \beta_1,$$

and:

$$b = x_2 \beta_2.$$

Empirical relationships of the constants,  $\underline{a}$ ,  $\underline{b}$ , and  $\underline{\beta_2}$ , with the volume fraction of the dispersed phase were described and the temperature dependence of the parameters was also determined.

Ree and Eyring extended their treatment to solutions of high polymers. They designated the solvent molecules as the zeroth group, so that:

$$\eta = \sum_{n=0}^{n} \frac{x_n}{x_n} \beta_n \quad \frac{\sinh^{-1} \beta_n S}{\beta_n S}.$$

The contribution of the solvent is taken as  $X_0 N_0$ , where  $N_0$  is  $N_0 N_0$ . Equations are then derived for the relative viscosity, intrinsic viscosity,

limiting intrinsic viscosity and the inherent viscosity, using the basic definitions of these coefficients. The data of many workers, on polymer systems, is reviewed in light of these equations.

# Effect of Concentration of Dispersed Phase on Flow Properties of Emulsions

### Fundamental Equations

Although many investigators have found empirical relationships between some function of viscosity and concentration of dispersed phase of emulsions, relatively few of these equations have theoretical foundation or promise of wide application to different types of emulsions. The first significant equation relating concentration of dispersed phase which was derived theoretically was that of Einstein. Although his equation was developed for dispersions of solid particles it served as the basis for theoretical expressions for emulsions as developed by Hatchek, Taylor, Richardson, Mooney and Oldroyd.

### Einstein's Equation

The derivation of Einstein<sup>20</sup> is quite complex and several approaches have been used to arrive at the same result. Probably the most easily understood derivation is that presented by Sadron<sup>21</sup> which utilizes the method of Burgers<sup>22</sup> and Jeffrey<sup>23</sup> in evaluating the components of flow. A resume of Sadron's presentation is summarized below. The assumptions are made that (1) the particles are rigid spheres, (2) there are no interactions between particles, and (3) all the particles in the suspension are identical and the suspension is homogeneous.

Considering a liquid in a system of laminar flow parallel to the x-z plane, the components of velocity may be stated as:

$$u = u(y), v = 0, w = 0,$$

the component  $\underline{u}$  being a function of  $\underline{y}$ , the position of the layer in the body of the liquid. The velocity gradient, or rate of shear,  $\underline{S}$ , is expressed as:

$$S = du/dy$$

When a particle is introduced into the liquid, flow is disturbed, resulting in additional components of flow,  $\underline{u}'$ ,  $\underline{v}'$ , and  $\underline{w}'$ , due to the presence of the particle. The velocity of the liquid will have new components,  $\underline{u}_1$ ,  $\underline{v}_1$ , and  $\underline{w}_1$ . These components must be evaluated by integration of the Stokes-Navier equations with the boundary conditions that there is no slip at the surface of the particle and that at infinite distance from the particle the initial flow is maintained; that is:

$$u_1 = u_1 v_1 = v_1 = v = v = 0$$

For the first condition it is necessary to know the motion assumed by the particle. For this purpose an arbitrary velocity is assumed for the particle, and expressions for  $\underline{u_1}$ ,  $\underline{v_1}$ , and  $\underline{w_1}$  are evaluated for the specified boundary conditions. Next the force and torque produced by traction on the particle are calculated. Since these must vanish for the specified boundary conditions, the relations determining the actual velocity are obtained.

In the case of an ellipsoid particle where  $\underline{a}$  is the length of the semi-axis of revolution,  $\underline{b}$  is the length of the equatorial radius,  $\underline{p}$  is a/b and  $\underline{e}$  is  $(p^2 - 1)/(p^2 + 1)$ , Jeffrey<sup>23</sup> has shown that, if the direction of the

axis of rotation is defined by the angles  $\underline{\Theta}$  and  $\underline{\Psi}$ , the corresponding angular velocities,  $\underline{\underline{\bullet}}$  and  $\underline{\underline{\Psi}}$ , would be given by:

$$\dot{\hat{\mathbf{y}}} = \mathbf{S} \, \mathbf{e} \, \sin \Theta \, \cos \Theta \, \sin \mathbf{\hat{\mathbf{y}}} \, \cos \mathbf{\hat{\mathbf{y}}} \, ,$$

$$\dot{\hat{\mathbf{y}}} = \mathbf{S} \left[ \mathbf{p}^2 / (\mathbf{p}^2 + 1) - \mathbf{e} \, \sin^2 \mathbf{\hat{\mathbf{y}}} \right] \, .$$

For a spherical particle, <u>a</u> is equal to <u>b</u> and <u>o</u> becomes zero, while  $\underline{\Upsilon}$  has the value of  $\underline{1/2S}$ . Thus, a sphere rotates around the z-axis with an angular velocity of  $\underline{(1/2)S}$ . A point on the surface of the sphere will have the velocity components:

$$u = (1/2) S y, v = (1/2) S x, w = 0,$$

and the components of additional flow may be expressed as:

$$u' = u_1 - u = -(1/2)Sy,$$
 $v' = v_1 - v = -(1/2)Sx,$ 
 $w' = w_1 - w = 0.$ 

Inserting these values into the Stokes-Navier equations, the components of additional flow are calculated to be:

$$u' = -(5/2) a^3 S x^2 y r^{-5} + (1/6) S a^5 (3 y r^{-5} - 15 x^2 y r^{-7}),$$
  
 $v' = -(5/2) a^3 S x y^2 r^{-5} + (1/6) S a^5 (3 x r^{-5} - 15 x y^2 r^{-7}),$   
 $w' = -(5/2) a^3 S x y z r^{-5} + (1/6) S a^5 15 x y z r^{-5},$ 

where <u>r</u> is the distance of the point from the origin and <u>a</u> is the radius of the particle. The second term is of the order of  $a^5 r^{-4}$ , and may be neglected if  $a^2 r^{-2}$  is small, a condition that is assumed to be fulfilled.

Considering two planes with coordinates  $y_1$  and  $y_2$ , when there are no particles in the liquid, the undisturbed flow is given by:

$$u = S_0 y, v = w = 0$$

Next, in a suspension containing  $\underline{c}$  particles per unit volume, a layer parallel to the  $x_2$  plane is considered, with ordinate  $\underline{y}$  and thickness  $\underline{dy}$  such that:

and  $\underline{x_s}$ ,  $\underline{y}$  and  $\underline{z_s}$  are the coordinates of the centre of a sphere in this layer. The additional flow due to the sphere at a point  $\underline{A}$  (x=0, y<sub>1</sub>, z=0) on the surface of the sphere would be given by:

$$u_s' = -(5/2) S_0 a^3 x_s^2 (y_1-y) r_s^{-5},$$

as already indicated. A calculation is made of the  $\underline{x}$  component of the additional flow due to all the particles contained in an element of volume around the point  $(x_s, y, z_s)$  and this is calculated to be  $(u_s^i.c.dx_s.dy.dz_s)$  for  $(c.dx_s.dy.dz_s)$  particles. This component produces a retardation of the flow, and the retardation due to all the particles,  $\underline{\delta}1$ , in the layer of thickness dy is:

$$\delta_1 = -(5/2) \, s_0 \, a^3 \, (y_1 - y) \, c \, dy \, \iint_{-\infty}^{\infty} x_s^2 \, r_s^{-5} \, dx_s \, dz_s$$

This integral is evaluated to be:

$$(2/3)\pi (y_1-y)^{-1};$$

therefore:

$$\delta_1 = -(5/3)\pi \, S_0 \, a^3 \, c \, dy$$

Similarly, the retardation at the plane (y =  $-y_{\gamma}$ ) is given by:

$$S_2 = +(5/3)\int S_0 a^3 c dy$$
.

The relative horizontal velocity of flow in the planes  $(y = y_1)$  and  $(y = -y_2)$  is now decreased from  $S_0 (y_1 + y_2)$  by the amount  $\delta$ , where:

$$\delta = \delta_1 + \delta_2 = (10/3)\pi S_0 a^3 c dy.$$

Summing up the effect of all the layers from  $-y_2$  to  $y_1$ , the relative horizontal velocity of the two planes is calculated to be:

$$S_0(y_1 + y_2) = S_0(y_1 + y_2)(1-2.5 c V),$$

where  $\underline{V}$  is the volume of one particle. Now a calculation is made of the additional shearing stress,  $\underline{\gamma}$ ', on the plane  $(y = y_1)$ . This is given by:

$$I_i = \int_0^0 \left( \frac{9\lambda}{9\Lambda_i} + \frac{9\lambda}{9\Lambda_i} \right) .$$

Since  $\underline{u}'$  and  $\underline{v}'$  are independent of  $\underline{x}$ ,  $\mathcal{T}'$  is given by:

$$T' = \sqrt{0 \frac{\partial \lambda}{\partial \Omega_1}}$$

The additional shear rate,  $\frac{\partial U}{\partial y}$ , produced by a single sphere,  $(x_s, y, z_s)$ , is calculated to be:

$$\frac{\partial U'}{\partial y} = -(5/2)(x_s^2 r^{-5} - 5 x_s^2 y_1^2 r^{-7}).$$

On integrating over all spheres in one layer, and then over all layers, the resultant value vanishes. Therefore, the effect of the presence of the particles is a reduction in the relative horizontal velocity of the liquid in the planes  $(y=y_1)$  and  $(y=y_2)$ . The total rate of shear and the total shearing stress at the planes are the same as before introduction of the particles.

It is now assumed that the planes  $(y = y_1)$  and  $(y = y_2)$  are the walls of a rotational viscometer. It should be noted that:

$$d = y_1 + y_2$$

U = Relative velocity of the two walls.

When the viscometer is filled with the dispersion medium and run with a relative velocity,  $U_{\text{O}}$ , the shearing stress,  $\Upsilon_{\text{O}}$ , is given by:

$$T_{o} = \gamma_{o}U_{o}/d = \gamma_{o}S$$
,

where  $\underline{\gamma}_0$  is the viscosity of the dispersion medium. When the particles are introduced in the dispersion medium, the planes move with a relative velocity U given by:

$$U = d S_0 (1-2.5 c V).$$

 $\underline{\tau}$ , the shearing stress at the wall, is given by:

$$\gamma = \eta U/d = \eta U_0 (1-2.5 \text{ c V})/d$$

where  $\underline{\underline{\eta}}$  is the viscosity of the dispersion. Since

therefore,

$$\gamma_0 = \gamma_{(1-2.5 \text{ e V})}$$

As c is assumed very small, this may be written as:

$$\gamma = \gamma_0 (1 + 2.5 \text{ c V}),$$

and letting  $\underline{\text{cV}} = \cancel{\phi}$ , the volume fraction of the dispersed phase,

$$\eta = \eta_0 (1 + 2.5 \phi).$$

This is the well known Einstein equation for a dilute suspension of rigid noninteracting spheres.

Hatschek's Equation

Hatschek<sup>24</sup> derived an equation for the viscosity of an emulsion with a high concentration, 50% or more, of the dispersed phase, that would take into account the sharp increase in viscosity with increasing concentration of the dispersed phase. He considered a system containing uniform spheres. If the number or size of the spheres increases until each sphere touches twelve others, the particles would occupy 74.04% of the total volume.

The twelve points of contact would be the centres of the faces of a dodecahedron, and with any further increase in concentration, flattening of the particles must occur and the faces of the dodecahedron would be developed more and more.

Two horizontal planes of the system are considered, one of which moves with a velocity <u>v</u> relative to the other; the velocity is considered to increase uniformly from one plane to the next. Since the plane would be a cross section through the dodecahedron, the particles would have hexagonal shapes in the planes. If the system is sheared, the polyhedra must slide over one another, and Hatschek proposed that the movement cannot occur without distortion of the particle shape. As the movement continues, the hexagons would assume rectangular form, and on further displacement, the particles would revert to the hexagonal form. On the basis that the particle must occupy the same volume all the time, the dimensions of the rectangular parallelepiped formed at the point of maximum distortion are calculated to be:

height = 
$$r \sqrt{2}$$
  
breadth =  $r \sqrt{3/2}$   
length =  $3r$ ,

where  $\underline{r}$  is half the distance between two parallel faces of the hexagon. These distances are measured from the middle points of successive layers of the continuous phase separating the particles.

The factor tending to cause the return of the particle from the rectangular parallelepiped to the dodecahedron form is the interfacial tension between the two phases. The factor opposing this tendency is the viscosity of the two phases. Hatschek proposed that for every system there is a critical velocity beyond which the particles would not return to their original

dodecahedral form. Hatschek's equation treats only the case where this velocity is exceeded, since the treatment below the critical velocity is considered quite complex.

Since the distortion of the particles results in an increase in the surface area, work must be done in the process. Hatschek considered an element of volume in the system having the form of a parallelepiped with a square base and height, 1, consisting of a particle of the dispersed phase of thickness d and the corresponding layer of the continuous phase around it. The work, A, required to cause displacement of the whole volume is given by:

$$A = \frac{v^2}{1} \gamma ,$$

where  $\underline{v}$  is the velocity and  $\underline{\underline{\gamma}}$  is the viscosity of the system. The work,  $\underline{\underline{A_1}}$ , required to cause displacement of the dispersed phase is given by:

$$A_1 = \frac{v^2}{d} \gamma$$
.

It is proposed that, since both terms have the same form, the quantity 1/d represents the ratio of the viscosity of the system to that of the continuous phase. That is:

$$\gamma = \gamma (1/d)$$

The ratio, 1/d, is represented by the ratio,  $\underline{f}$ , of the total volume to the volume of the dispersed phase. That is:

$$\frac{1}{d} = \frac{f^{1/3}}{1/3-1}$$
.

Therefore:

$$\eta = \eta_0 \frac{f^{1/3}}{f^{1/3-1}}$$

If the total volume is taken as 1, and the volume fraction of the dispersed

phase as  $\bigcirc$  , we may write

this being the conventional form of Hatschek's equation.

Taylor's Equation

Taylor<sup>25</sup> extended Einstein's treatment to liquids containing droplets of a second liquid in suspension. Noting that the analysis would be extremely difficult if one considered the deformation of the droplet caused by viscous forces, Taylor limited his analysis to conditions of low shear or small particle size so that the surface tension of the droplets would keep them spherical. Further, he assumed that there is no slippage at the particle surface and that any film on the surface merely transmits tangential stress from the outer fluid to the droplet. Using the analysis for slow motion of a viscous fluid presented by Lamb<sup>26</sup>, Taylor pointed out that the expression for each component of velocity contains three functions, one relating pressure distribution, the second representing an irrotational motion in a field of uniform pressure, and the third representing vortex motion. Following Einstein, Taylor chose coördinate axes parallel to the principal axes of distortion, causing the function for vortex motion to disappear. Thus, the equation for one component of velocity becomes:

 $u = \begin{bmatrix} \frac{1}{M} & \frac{r^2}{z(z^{M}+1)} & \frac{\partial Pu}{\partial x} + \frac{M}{(M+1)(z^{M}+1)(z^{M}+3)} & \frac{\partial}{\partial U} \begin{pmatrix} \frac{P}{z^{M}} & \frac{\partial}{\partial z} \end{pmatrix} + \frac{\partial D}{\partial x} \end{pmatrix},$  where  $\underline{u}$  is the component of velocity,  $\underline{M}$  is the viscosity and  $\underline{r^2} = \underline{x^2} + \underline{y^2} + \underline{z^2}$ . With unidimensional flow  $(\underline{u} = \underline{\angle y}, \underline{v} = \underline{0})$ , the irrotational flow at great distances from the droplet whose center is the origin of the coordinate axes can be represented by:

$$\oint_{2} = 1/4 \times (x^{2} - y^{2}).$$

Taylor defined the appropriate functions  $\underline{\mathbb{Q}}_n$  and  $\underline{p}_n$  for outside the droplet as:

 $\oint_2 = 1/4 \approx (x^2 - y^2), \quad \oint_{-3} = B_{-3} \text{ a}^5 \frac{x^2 - y^2}{r^5}, \quad P_{-3} = \mathcal{M}_A_{-3} \text{a}^3 \frac{x^2 - y^2}{r^5},$  and the functions for the liquid inside the droplet as:

$$\emptyset_2' = B_2(x^2 - y^2), P_2 = \mathcal{M}' A_2 a^{-2} (x^2 - y^2),$$

where  $\underline{B}_{-3}$ ,  $\underline{A}_{-3}$ ,  $\underline{B}_2$  and  $\underline{A}_2$  are constants to be determined by the boundary conditions,  $\underline{\mathcal{M}}$  and  $\underline{\mathcal{M}}'$  are the viscosities of the main body of the fluid and the droplet, respectively,  $\underline{r}^2$  is  $\underline{x}^2 + \underline{y}^2 + \underline{z}^2$ , and  $\underline{a}$  is the radius of the drop. Substituting these into the equation for velocity components the following expressions are obtained:

Outside the drop:

$$u = 1/2 A_{-3} a^{3} \times \frac{x^{2} - y^{2}}{r^{5}} + B_{-3} a^{5} - \left[\frac{5x(x^{2} - y^{2})}{r^{7}} + \frac{2x}{r^{5}}\right] + 1/2 \times x$$

$$v = 1/2 A_{-3} a^{3} y \frac{x^{2} - y^{2}}{r^{5}} + B_{-3} a^{5} - \left[\frac{5y(x^{2} - y^{2})}{r^{7}} - \frac{2y}{r^{5}}\right] - 1/2 y$$

$$w = 1/2 A_{-3} a^{3} z \frac{x^{2} - y^{2}}{r^{5}} + B_{-3} a^{5} \left(-\frac{5z(x^{2} - y^{2})}{r^{7}}\right).$$

Inside the drop:

$$u' = A_2 a^{-2} \left[ -\frac{5}{z1} xr^2 - \frac{z}{z1} x(x^2 - y^2) \right] + zB_2x$$

$$v' = A_2 a^{-2} \left[ -\frac{5}{z1} yr^2 - \frac{z}{z1} y(x^2 - y^2) \right] - zB_2y$$

$$w' = A_2 a^{-2} \left[ -\frac{2}{z1} z(x^2 - y^2) \right].$$

Since continuity of velocity requires that  $\underline{u}=\underline{u}'$ ,  $\underline{v}=\underline{v}'$ ,  $\underline{w}=\underline{w}'$ , and for the drop to remain spherical torques must be equal; i.e.,  $\underline{u}\underline{x} + \underline{u}\underline{y} + \underline{u}\underline{z} = 0$ , it can be shown that the identities:

$$1/2 A_{-3} - 5 B_{-3} = -\frac{z}{z1} A_2,$$
  
 $2 B_{-3} + 1/2 \angle = \frac{5}{z1} A_2 + zB_2$ 

and

$$1/2A_{-3} - 3B_{-3} + 1/2 = 0$$

must be satisfied. These identities furnish three equations with four unknowns, and Taylor derived a fourth equation to satisfy the demands for continuity of tangential stress on the droplet:

$$A_{-3} - 16 B_{-3} + \propto = \frac{M!}{M!} \left( \frac{16}{zl} A_2 + 4 B_2 \right)$$
.

The four equations in four unknowns were then solved to obtain:

$$A_{-3} = \frac{5 \times (\frac{M' + 2/5M}{N' + M})}{z}, B_{-3} = -\frac{1}{4} \frac{M'}{M' + M}, A_{2} = \frac{z1 \times M}{4(M' + M)}$$

$$B_{2} = -\frac{3 \times M}{8(M' + M)}$$

Einstein showed that the effect of the presence of solid spheres in suspension on the viscosity of a fluid depends only on  $p_{-3}$ , and Taylor stated the same reasoning to be true in the case of liquid spheres. With solid spheres  $\frac{A_{-3}}{7} = \frac{-5}{7}$  and Einstein's expression becomes:

$$M^* = M(1 + 2.5 \oplus),$$

where  $\underline{\mathcal{M}}^*$  is the viscosity of the suspension and  $\underline{\mathbb{Q}}$  is the volume fraction of suspended spheres, while for liquid spheres the expression becomes:

$$\mathcal{M}^* = \mathcal{N} \left[ 1 + 2.5 \right) \left( \frac{\mathcal{M}' + 2/5\mathcal{M}}{\mathcal{M}' + \mathcal{M}} \right),$$
 which may be called "Taylor's Equation."

Richardson's Equation

Richardson<sup>27</sup> proposed that there may be an increase in the space occupied by the dispersed phase by an amount  $\delta c_{\bullet}$  so that the average separation of the discreet globules is decreased by a fraction  $\frac{1}{2}$  being the distance between particles. He represented the ratio of this fraction to the change in concentration by the symbol, x:

$$x = - \frac{1}{\partial c.l},$$

where  $\underline{x}$  may be looked upon as an interphasal compressibility, whose value depends on the relative compressibility of the two phases. In simple terms,  $\underline{x}$ 

may be called the overcrowding of the dispersed phase which is resisted by the continuous phase. When flow takes place, it may be thought that the continuous medium has to move between obstacles of average separation  $\underline{1}$ , subject to viscous resistance denoted by  $\underline{\gamma}$ . If the overcrowding reduces the separation to  $\underline{(1-\delta 1)}$ , this resistance is supposed to increase to  $\underline{(1-\delta 1)}$ , and:

$$d\eta/\eta = -d1/1 = x dc$$
.

Integrating, Richardson obtained:

$$\ln \frac{\sqrt{}}{\sqrt{}} = xc,$$

or

$$\eta = \gamma_0 e^{xc}$$
.

Assuming  $\underline{x}$  to be constant, Richardson's equation may be written in conventional form as:

$$\gamma = \gamma_0 e^{k\phi}$$
.

Mooney's Equation

Mocney  $^{28}$  extended Einstein's equation to apply to a suspension of finite concentration. The analysis is limited to rigid spherical particles. Mooney's approach is partly empirical in that the interaction between parameters are left for experimental determination. The analysis merely considers the space crowding effect of the suspended spheres on each other. There is no restriction imposed on the concentration or the particle size distribution. Mooney took into account the first-order interactions between particles. In a two-component system, spheres of size  $\underline{r_1}$  and partial volume concentration  $\underline{\phi_1}$ , crowd spheres of size  $\underline{r_2}$  into the remaining free volume  $\underline{(1-\lambda_{12}\underline{\phi_1})}$ , where  $\underline{\lambda_{12}}$  is a crowding factor which may be different from unity.

Mooney first considered a monodisperse system of finite concentration where spheres, all of radius  $r_1$ , are added to a suspension in two volume fractions,  $\mathbb{Q}_1$  and  $\mathbb{Q}_2$ . The addition of the first fraction will increase the viscosity by a factor:

$$H(\phi_1) = \underline{\gamma_1},$$

where  $\underline{H}$  must reduce to Einstein's formula for small values of  $\underline{\phi}_1$ . If the second fraction,  $\bigcirc$ 2, is now added, there will be a further increase in the viscosity. Part of this increase may be considered to be caused by  $\bigcirc$  2 in the viscosity of the remaining space not occupied by  $\bigcirc_1$ . This increase will be  $H(\Upsilon_{12})$  such that:

 $\underline{\Phi}_2$  is mutual, and introducing  $\underline{\Phi}_2$  reduces the free volume accessible to  $\underline{\Phi}_1$ , the effective concentration of  $\bigcirc_1$  now being:

$$\Upsilon_{21} = \frac{\Phi_1}{1 - k \Phi_2} .$$

 $\underline{H(\emptyset_1)}$  is now replaced by  $\underline{H(Y_{12})}$ . The product  $\underline{H(Y_{12})}$ . H $(Y_{21})$  is the viscosity of a suspension of total concentration  $(\phi_1 + \phi_2)$  and is equal to  $\frac{\text{H}(\oint_1 + \oint_2)}{\text{thus}}$ ; thus:

$$\frac{2}{H(\Phi_1 + \Phi_2)} = \frac{\gamma_{12}}{\gamma_0} = H(\gamma_{12}) \cdot H(\gamma_{21}) = H\left(\frac{\Phi_1}{1 - k\Phi_2}\right) \cdot H\left(\frac{\Phi_2}{1 - k\Phi_1}\right)$$

This functional equation is satisfied if  $\underline{H}$  has the form:  $H(x) = \exp{(\frac{2.5x}{1-kx})},$ 

$$H(x) = \exp\left(\frac{2.5x}{1 - kx}\right),$$

where  $\underline{x}$  is the relative viscosity. The constant, 2.5, is chosen to agree with Einstein's equation when \_\_\_\_ approaches zero.

For a suspension of  $\underline{n}$  groups of spheres, each group of a different diameter, we may write this as:

In 
$$H(\phi) = 2.5 \stackrel{\text{n}}{\underset{\text{i=1}}{\swarrow}} \frac{\text{j}}{1 - \underset{\text{j=1}}{\swarrow}} \frac{\text{j}}{\text{j}} \phi_{\text{j}}$$

For a continuous distribution of diameters, we may write this as:

$$\ln H(\phi) = 2.5 \int_0^{\phi} \frac{d\phi i}{1 - \int_0^{\phi} \wedge ji j}$$

If  $\underline{6}$  is equal to  $\underline{(\ln r/r)}$ , we may write:

$$d\Phi = P(6) d\sigma$$

and:

$$\int_{0}^{6\eta} P(\sigma) d\sigma = 1,$$

where  $\bar{r}$  is a mean radius, and  $\underline{6_1}$  and  $\underline{6_2}$  are the upper and lower limits of  $\underline{6}$ . The equation can then be written as:

$$\ln \frac{\gamma}{\gamma_0} = \ln H = 2.5 \, \phi \int_{6_1}^{6_2} \frac{P_i \, d.6}{1 - \phi \int_{6_1}^{6_2} \lambda \, ji^P_i \, d.6},$$

which is called the Mooney equation.

Oldroyd's Equation

Oldroyd<sup>29</sup> made a calculation of the elastic properties arising from the interfacial tension between the two phases of a dilute emulsion. Following Einstein and Taylor, the individual drops and the concentration of the dispersed phase are assumed to be small, so that inertia effects and hydrodynamic interactions between drops can be ignored in calculating the behaviour of a typical macroscopic element of the emulsion. The interfacial tension is assumed to have a sufficiently large constant value to keep the suspended drops approximately spherical, although departure from the spherical shape

are taken into account. The boundary conditions of no slip and continuity of tangential stress at an interface are assumed.

A homogeneous liquid,  $\underline{L}^*$ , is envisaged with the same macroscopic rheological properties as an emulsion consisting of drops of one Newtonian liquid  $\underline{L}'$  of viscosity  $\underline{\eta}'$  in another Newtonian liquid  $\underline{L}$  of viscosity  $\underline{\eta}$ . The drop size is assumed uniform, each drop having diameter  $\underline{a}$ . Two systems are considered, one in which a single drop of  $\underline{L}'$  is surrounded by  $\underline{L}$  filling the space:

where  $\underline{r} < \underline{a}$  is referred to spherical coordinates  $\underline{r}$ ,  $\underline{\Theta}$ , and  $\underline{\phi}$ . The rest of the space,  $\underline{r} > \underline{b}$ , is filled with L\*(Fig. 2). The radius  $\underline{b}$  is chosen to give the correct volume concentration of the dispersed phase in the emulsion, so that:

$$b^3 = a^3 / c$$
,

 $\underline{c}$  being the concentration by volume of dispersed phase. The two systems are required to be indistinguishable to a given degree of accuracy, provided that observations are made at a distance  $\underline{r}$  equal to  $\underline{R}$ , sufficiently large compared to b.

A perturbation method is used, following Fröhlich and Sack<sup>30</sup>, who considered the rheological properties of a suspension of elastic particles in a viscous liquid, on the assumption that the suspended particles were solid spheres obeying Hooke's law. The following expression for the relative viscosity of the emulsion is derived:

$$\frac{\eta^*}{\eta} = \frac{40(\eta + \eta') \gamma' + a(3\eta + 2\eta') (16\eta + 19\eta') \Delta}{40(\eta + \eta') \gamma' + a(3\eta + 2\eta') (16\eta + 19\eta') \Delta} + 3c \left[ \frac{4(2\eta + 5\eta') \gamma' - a(\eta' - \eta) (16\eta + 19\eta') \Delta}{40(\eta + \eta') \gamma' + a(3\eta + 2\eta') (16\eta + 19\eta') \Delta} \right]$$
 where  $\Delta$  is equal to  $\frac{d}{dt}$ .

30

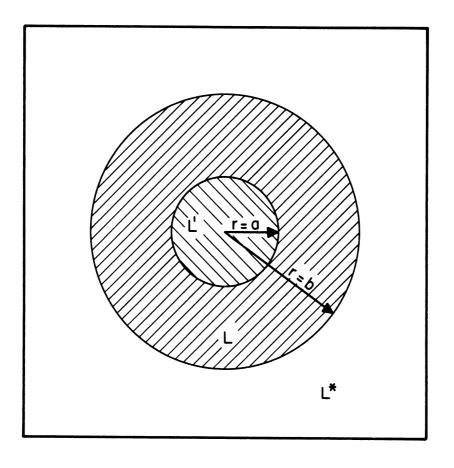


Fig. 2. Diagram Illustrating the Hypothetical System of Oldroyd

Oldroyd also made a calculation taking into account the slip due to the presence of a very thin film of the emulsifying agent at the interface and arrived at an expression similar to the one above. He concluded that the interfacial slip in a dilute emulsion should not affect the type of rheological behaviour, although it would affect the values of the rheological constants.

#### Application of the Fundamental Equations

Deviations from the theoretical Einstein factor of 2.5 have long been recognized for suspensoids<sup>31</sup>, and are usually attributed to causes such as flocculation, hydration of the particles, etc.<sup>32</sup> Several modifications of Einstein's equation have been proposed, generally by adding terms to the power series form, and by varying the value of the constant  $\underline{k}$ . An example is the equation by Guth and Simha<sup>33</sup>:

$$\eta_{\rm sp} = 2.5 \, \phi + 4.94 \, \phi^2 + 8.78 \, \phi^3,$$

where:

$$\sqrt{\text{sp}} = \sqrt{\text{rel}} - 1.$$

The additional terms are introduced to take into account higher order hydrodynamic interactions than were considered in the original Einstein treatment.

Bredee and deBooys<sup>34</sup> discussed various modifications of the Einstein equation and proposed the following equation for nonsolvated spherical particles:

$$V_{\text{rel}} = \left[1 - \frac{2.5 \, \Phi}{6 \, (1 - \varphi)}\right]^6.$$

Eilers<sup>35</sup> found this equation suitable for values of  $\bigcirc$  from  $\bigcirc$  to  $\bigcirc$  for bitumen emulsions. For larger values of  $\bigcirc$  this and other equations were found

to give values too low. From a consideration of packing of non-plastic spheres of equal diameters, Eilers postulated that the curve relating viscosity to particle size must have an asymptote at  $\Phi = 0.74$ , since beyond this concentration flow of the dispersion can no longer take place. Further, the curve must fit the Einstein formula at extremely low concentrations. On this basis, Eilers proposed the following equation:

where  $\underline{a}$  is  $\underline{1.35}$ . He found, however, that calculated viscosities were higher, and concluded that this must have been due to a deviation in the particle size of the emulsion.

Maron, Madow and Krieger<sup>36</sup> proposed an extension of the Einstein treatment, defining an apparent volume fraction as:

where  $\underline{\bigcirc}$  is the apparent volume fraction and  $\underline{\triangleleft}$  is a constant. Then:

$$Z = \frac{\Phi^{t}}{1 - \Phi^{t}} = \frac{\langle \Phi \rangle}{1 - \langle \Phi \rangle},$$

and:

$$ln \bigvee_{rel} = bZ$$
,

<u>b</u> being a constant. The factor  $\underline{Z}$  is included to obtain an analytic expression which would take into account the rapid increase of viscosity with increase in  $\underline{\mathfrak{D}}$ . The authors found that with a suitable value of  $\underline{\swarrow}$ , the equation fit the data on latex emulsions up to a concentration of  $\underline{60\%}$ . Rearrangement of the equation gives:

$$\frac{0}{\ln(\sqrt{\gamma_0})} = \frac{1}{\propto b} - 0,$$

so that a graph of  $\frac{0}{\ln(\sqrt[n]{\eta_0})}$  versus  $\underline{0}$  should be linear, with a slope of  $\underline{-b}$  and an intercept of  $\underline{1/\infty}$  b, permitting the evaluation of both  $\underline{\times}$  and b.

An interesting analysis has been presented by Oliver and Ward37 on the power series form of viscosity-concentration equations. They found that a plot of 1/ $\eta$  rel versus  $\underline{c}$  gave a linear plot for stable suspensions of spheres with volume concentrations up to 20%. The equation of the straight line may be written as:

$$\sqrt{\text{rel}} = \frac{1}{1 - \text{kc}}$$

or,

where  $\underline{k}$  is constant. For very low concentrations, this reduces to:

and if  $\underline{k}$  is 2.5 the expression becomes identical with the Einstein equation. This equation was applied to the data of several workers with the results shown in Table 1.

Leviton and Leighton 45 extended Taylor's treatment by introducing a power series of  $\Phi$ . Emulsions of milk fat in skim milk and other continuous media were used and viscosity was measured in a capillary viscometer. Taylor's equation was modified to the following:

ln rel = 
$$2.5 \left( \frac{1 + 2/50}{9 + 9} \right) \left( \frac{1}{9} + \frac{11}{3} \right)$$
.

 $\ln \ \mathrm{rel} = 2.5 \left(\frac{1}{1} + \frac{2}{5}\right) \left(\frac{1}{0} + \frac{5}{3} + \frac{11}{3}\right).$  For small values of  $\frac{1}{0}$  this reduces to the Taylor formula. The author points out that in the power series involving  $\Phi$ ,  $\Phi^{5/3}$  is included in conformity

TABLE 1

VALUES OF THE CONSTANT <u>k</u> FOR THE OLIVER-WARD EQUATION

Worker	Type of Viscometer	Size Ratio of Suspended Spheres	<u>k</u>	Range of Volume Concn, over which Equation Applies
Eirich, Buzl & Margaretha <sup>38</sup>	Capillary	2.0 : 1	2.41	0 <b>-</b> 15 plus
Broughton & Windebank <sup>39</sup>	Rotating Cylinder	1.8 : 1 1.2 : 1	2.57 2.41	0-15 plus 0-20 plus
Whitmore <sup>40</sup>	Rising Sphere	1.4:1	2.77	0-20 plus
Eveson <sup>l</sup> l	Rotating Cylinder	1.4 : 1	2.56	0-20
Nandi <sup>42</sup>	Capillary	1.4 : 1	2.42	0 <b>-</b> 35
Higginbotham43	Capillary	1.2:1	2.38	0-25
Williams <sup>44</sup>	Capillary	5.0 : 1	2.34	25 <b>-3</b> 5
Oliver & Ward37	Capillary	1.6 : 1	2.45	0-30

with the suggestion of Smoluchowsky<sup>46</sup>. The term,  $\Phi^{11/3}$ , has no theoretical significance but is included to obtain an agreement between observed and calculated values.

Sibree 47 applied Hatschek's equation to his data on emulsions of paraffins of various viscosities in water with sodium oleate as emulsifier. A concentric cylinder viscometer was used, and the viscosity was found to be independent of the rate of shear after a certain point. The Hatschek equation did not agree with experimental observations. Using observed values of  $\underline{\gamma}$  and  $\underline{\gamma}$  o, viscosities of emulsion and continuous phase, respectively, Sibree calculated the theoretical volume percent of dispersed phase by rearranging the Hatschek equation:

$$\Phi = \frac{(1 - 10)^3}{\sqrt{3}} \cdot$$

Since, in every case, the calculated value of  $\underline{\diamondsuit}$  was higher than the measured value, he calculated a volume factor, h, such that:

$$h = \emptyset$$
 calculated/ $\emptyset$  measured.

For emulsions with more than 50% dispersed phase, h was found to have a value of 1.3. According to Sibree, this apparent increase in  $\phi$  may be due to the adsorbed film which increases the size of each drop. Sibree's modification of Hatschek's equation may be written as:

$$\ln \sqrt{\frac{1}{1 + 8}} = \frac{1}{1 - 3 + \varphi} \cdot$$

 $\ln \sqrt[\gamma]{\rm rel} = \frac{1}{1 - \sqrt[3]{\rm h}\, \phi} \, .$  Broughton and Squires measured the viscosity of emulsions of Nujol, benzene and olive oil in water with sodium oleate 1%, saponin 2% and triethanolamine oleate 5% as emulsifiers. A MacMichael viscometer was used, and limiting viscosities were calculated. They proposed a modification of the Richardson equation:

$$ln \hat{l}_{rel} = a + b \hat{l}_{rel}$$

which agreed with their data. Calculated values of the volume factor, h, in Sibree's modified equation, varied from much less than 1 to much more than the 1.3 proposed by Sibree. It was concluded that neither Hatschek's equation nor its modification as proposed by Sibree, agreed with experimental observations. The yield point was found to be a function of the limiting viscosity of the emulsion.

Neogy and Ghosh<sup>49</sup> measured the viscosity of three xylene-in-water emulsions with three cationic soaps as emulsifiers, and of a water-in-benzene emulsion with magnesium oleate as emulsifier. A Couette type instrument was used, and the average values of viscosity at minimum and maximum rates of shear were calculated. Good agreement for the oil-in-water emulsions and still better agreement for the water-in-oil emulsion was obtained with the modified form of Richardson's equation, as proposed by Broughton and Squires.

In another study<sup>50</sup> on xylene-in-water emulsions stabilized with sodium oleate, myristate, laurate, caproate, and saponin, where viscosities were measured in a similar manner, these workers found that only Richardson's equation fitted their data within 5%. Sibree's modification was not satisfactory.

Toms<sup>51</sup> studied the viscosities of various organic liquids with different univalent soaps as emulsifiers. Significant variations were found in the value of the volume factor, h, in Sibree's equation, due to the nature

of the emulsifying agent and the internal phase. However, a large number of values of  $\underline{h}$  were found to be close to  $\underline{1.3}$ , indicating that Sibree's equation may give good agreement with experimental observations.

Sherman<sup>32</sup> investigated the effect on viscosity of varying the ratios of the two phases. Emulsions of mineral oil-in-water were prepared with sorbitan sesquioleate as emulsifier and a variable pressure capillary plastometer was used to measure viscosities. The results deviated considerably from values calculated with the Einstein equation and the modified equation of Guth and Simha. Hatschek's equation gave values lower than observed and the volume factor, h, from Sibree's equation was found to be 1.2 and independent of  $\dot{\Box}$ . Richardson's equation was found to be applicable only to the emulsion with 3.5% emulsifier, all other results agreeing with the modified Richardson equation.

Sherman also observed<sup>52</sup> that Richardson's modified equation and Hatschek's equation as modified by Sibree agreed with experimental observations on water-in-oil emulsions where the viscosity of the dispersed phase was varied.

Mooney<sup>28</sup> applied his equation to the data of Eilers on emulsions of bituminous materials of high softening point, such that the droplets were essentially rigid at room temperature. The diameters varied from 1.6 to 4.7 microns so that the emulsions could be considered polydisperse. Since the function  $\lambda$  ij was not known in detail, the equation was developed as a power series of  $\phi$ , yielding:

where

To the second degree in \_\_\_\_, this equation becomes:

$$\ln \frac{\eta}{\eta \circ} = \frac{2.5 \, \varphi}{1 - \sqrt{1 \, \varphi} \, 1} .$$

From Eiler's data,  $\lambda_1$  was found to have a value of 0.75.

## Effect of Particle Size of Dispersed Phase on Flow Properties of Emulsions

Jellinek<sup>53</sup> discussed a systematic treatment of distribution functions of emulsions and their average quantities. Expressions were presented for integral distributions with respect to diameter, surface area and volume. Other equations for the size distribution of emulsion particles have also been derived<sup>54</sup>,55.

The measurement of particle size has been a considerable challenge because of the special conditions that prevail in an emulsion, e.g., Brownian motion and particle diameters generally below the level for easy microscopic measurement. Many methods have been reviewed by Nassenstein<sup>56</sup>. Perhaps the most widely used is the microscopic method, utilizing a camera lucida<sup>57</sup> or microphotography<sup>58</sup>. For reducing the time involved in particle size measurement by photomicrographs, a rapid method has been developed<sup>59</sup>. Direct optical methods have also been used<sup>60</sup>,<sup>61</sup>. Various sedimentation techniques have been used as well, for measuring particle size in emulsions<sup>62</sup>.

None of the basic relationships derived for the viscosity of emulsions includes the particle size as a variable, with the exception of Oldroyd's equation, although there are many and conflicting reports on the effect of particle size and size distribution on the rheological properties of an emulsion.

It has been reported that there are significant linear increases in the viscosity of whole milk upon homogenization 63. Kremner and Soskin 64 reported that low pressure homogenization of an emulsion of benzene-in-water with 5% sodium oleate as emulsifier caused an increase in the viscosity in the ratio of 2.5:1. Since the major change upon homogenization would be greater dispersity and smaller particle size, it appears that changes observed can be attributed largely to decrease in particle size.

Traxler<sup>65</sup> considered the effect of size distribution on the flow of disperse systems. Two conditions may exist, one where the disperse phase is so large in amount that the particles are in some form of packing, another where the quantity is so small that the particles of the dispersed phase are not in contact with each other. Considering a disperse system having all spheres of the same size, the volume of the continuous phase is equal to the interstitial space of the disperse phase. The intestitial space varies with the packing arrangement and, as a consequence, the size of the individual interstice (identical with the dimension of the average film of continuous phase separating the dispersed particles) varies with the degree of packing.

The loosest packing is obtained with four points of contact between any particle and those surrounding it. As the number of contact points increases, the percent of the interstitial space and the size of the average individual interstice decreases, until twelve points of contact are formed. The percentage of interstitial space for each of several packing arrangements for spheres of uniform size is shown below:

Points of Contact	Percent Interstitial space
4	66.6
6	47.6
8	39•5
10	30•2
12	25.9

Considering two systems of the same volume concentration, one with particles of equal size, and the other containing particles of various sizes, the packing is looser in that containing various sizes. Therefore, this system is more fluid with fewer points of contact between particles and a thicker film of continuous phase separating them. Data was presented by Traxler to support this view. Two emulsions were prepared containing particles of quite uniform size. In one they were less than one micron in diameter (emulsion A), and in the other they were two to three microns (emulsion B). The viscosity of the emulsions and blends of the two were measured in a Saybolt-Furol instrument. Results were as follows:

Volume %		Viscosity at 250
Emulsion A	Emulsion B	Saybolt-Furol Units
0	100	36.0
10	90	23.0
20	80	21.5
30	70	20.0
40	60	19.5
50	50	20.5
60	40	21.5
70	30	24.5
80	20	26.0
90	10	33.0
100	0	41.5

The authors concluded that, although some of the measurements were close to or slightly below the range of sensitivity of the instrument, it was shown that blends of the two emulsions were more fluid than either emulsion alone.

Traxler<sup>67</sup> also made the point that the viscosity of an emulsion is a function of the condition of the surface of the particles as well as the size and size distribution of particles.

Using a rising-sphere method, Ward and Whitmore<sup>68</sup> measured the viscosity of suspensions of smooth spheres of methylmethacrylate polymer suspended in an aqueous solution of lead nitrate and glycerine. Various concentrations of spheres were measured with particle size ratios varying from 1.17 to 2.74 within the size range of 28 to 208 microns. It was concluded that the relative viscosity of a suspension of smooth hard noninteracting spheres is independent of the absolute size, decreasing with increasing size range to a constant value.

Sibree<sup>69</sup> reported that the viscosity of emulsions is independent of particle size and size distribution within wide limits for the same pair of liquids. Emulsions of several paraffins in water with sodium oleate as emulsifier were measured in a rotational viscometer.

Leviton and Leighton<sup>45</sup>, working with emulsions of milk fat, found the viscosity to be independent of the particle size. No measurable increase in viscosity was found with a fourfold reduction in the diameter of the dispersed globules.

In the study on the stability of emulsions using specific surface area measurements, Mullins and Becker<sup>70</sup> measured the viscosities of emulsions of peanut oil, glyceryl ricinoleate, glyceryl trioleate and cod liver oil, made with two emulsifying agents and at four homogenization pressures. An Ostwald viscometer was used. They reported that the change in specific surface

area, and consequently in particle size, did not influence the viscosity of the emulsions. A similar observation was made by Knoeckel and Wurster, who used the Drage rheometer in this study<sup>57</sup>.

Richardson<sup>71</sup> investigated the effect of particle size on the viscosity of emulsions. A falling sphere method was used to avoid continuous shearing action over a comparatively long time, as required for reading a capillary or a Couette type instrument, which might cause a breakdown of some globules in a concentrated emulsion. In the falling sphere instrument the droplets are sheared only when the solid sphere is in the vicinity of the particles. He found that as long as the emulsions were homodisperse the viscosity at high rates of shear varied inversely as the mean globule size. When a polydisperse distribution of particles was present, the system was less viscous than indicated by this relationship.

It may be seen that the relationship of viscosity to particle size is not yet clear. There are several factors causing difficulty that need to be considered. Perhaps the major difficulty is isolation of the size and size distribution effect from other factors affecting the rheological properties. It is hardly possible to avoid interaction between emulsifier and disperse phase which determines the nature of the particle surface, and this factor might make all other effects obscure. The use of several different diameters to describe the particle size creates further difficulty when comparison of results is attempted.

It would appear that there are definite differences in viscosity between homogenized and non-homogenized emulsions. In this connection a

report by Axon<sup>72</sup> may be mentioned. Axon developed a microscopic cell to examine semi-solid oil-in-water emulsions during flow. He observed two types of dispersions. In one, globules were associated in loose clusters in which each globule was free to move independently of its neighbours. In the other, a compact type of floccule occurred, where the globules were surrounded by a hydrated layer restricting their movement and presenting a mechanical barrier to deformation.

It must be pointed out that the methods used for measuring viscosity were often inadequate for evaluating non-Newtonian flow. Since homogenization is generally one of the steps in the manufacture of industrial emulsion, practical systems may be of such narrow range of size distribution that this factor may have little significance.

### Effect of Viscosity of Dispersed Phase on Flow Properties of Emulsions

Of the equations derived for the viscosity of an emulsion, only those of Taylor and Oldroyd include viscosity of the internal phase as one of the factors to be considered.

Sibree<sup>47</sup> prepared emulsions of two paraffins with a viscosity ratio of 38: 1 and found that the emulsions had a viscosity ratio of 1.4: 1. This, he concluded, was in agreement with Hatschek's equation which considers the viscosity of an emulsion to be independent of the viscosity of the dispersed phase. A similar observation was made by Sherman<sup>52</sup> in his work with water-in-oil emulsions. The viscosity of the

internal phase was varied by addition of different alcoholic derivatives to the water phase, e.g., propylene glycol, sorbitol syrup (70%) and glycerine. The viscosities were measured in an Ostwald-type viscometer.

Broughton and Squires<sup>48</sup> stated that no generalization can be drawn as to the influence of the viscosity of the dispersed phase on that of the emulsion. They investigated emulsions of Nujol, benzene and clive oil with sodium cleate, saponin and triethanolamine as stabilizers, using a MacMichael viscometer for measurements.

Toms<sup>51</sup> carried out an extensive investigation of the effect of the internal phase and emulsifier on the viscosity of emulsions. It was found that for the same emulsifier, the viscosity of an emulsion varied widely with the nature of the internal phase. He stated that this may be explained by an alteration of the mutual solubilities of the three components of the emulsion, oil, water and emulsifier. Sherman also stated that the chemical nature of the dispersed phase may be of importance with particular reference to the emulsifier.

From a consideration of the reports of these workers, it appears that the viscosity of the disperse phase does not have a significant effect in determining the viscosity of the emulsion. However, the chemical nature of the internal phase seems to be of importance, and the interaction between the internal phase and the emulsifier may be the most significant factor affecting the viscosity of an emulsion.

### Effect of Emulsifying Agent on Flow Properties of Emulsions

In an extensive investigation, Toms<sup>51</sup> prepared emulsions of eleven organic liquids using ten univalent soaps, sodium and potassium salts of lauric, myristic, palmitic, stearic and oleic acids. He found little change due to substitution of potassium for sodium in emulsions stabilized by laurate and oleate but significant changes with myristate, palmitate and stearate. On investigating the effect of the emulsifier on the value of the factor, h, in Sibree's modification of Hatschek's equation, he found the value to be altered only about 1% upon changing the cationic part of the molecule but about 20% by changing the fatty acid part of the molecule. Another observation was an increase in viscosity with greater concentration of emulsifier.

Wilson and Parke<sup>73</sup> investigated the viscosity of emulsions as a function of emulsifier concentration. The viscosity of a 70% benzene-in-water emulsion passed through a minimum upon increase of emulsifier concentration at a concentration of 0.84% sodium oleate in the aqueous phase. As a rule, however, it was found that viscosity increased continuously with increase in emulsifier concentration.

Sherman<sup>52</sup>, in his work on water-in-oil emulsions, found that addition of finely-divided carbon black to the emulsion as a stabilizer resulted in a pronounced increase in yield value and viscosity of the emulsion. He further observed that emulsions containing greater proportions of polyhydric alcohols in the dispersed aqueous phase exhibited

lower yield values and viscosities. This was explained on the basis of the specific absorption of the two phases on the carbon black surface, which is affected by the concentration of the polyhydric alcohols in the aqueous phase, leading to a decrease in the contribution towards viscosity and yield value.

Sherman<sup>74</sup> also investigated the effect of the emulsifier on water-in-oil emulsions of high water content. Emulsions were prepared containing 6.5% glycerine and 65.5% water in the aqueous phase and 2.8% emulsifying agent and 25.2% mineral oil in the continuous phase. The composition was kept constant except that ten non-ionic emulsifiers were used. Six of the emulsions were found to have relative viscosities of the same order, but marked variations were shown by the other four.

On the basis of their results, Neogy and Ghosh<sup>50</sup> also made the point that the viscosity of an emulsion depends on the emulsifier used. Broughton and Squires<sup>48</sup> observed that for a given phase pair the relative limiting viscosity varies widely with the type of emulsifier used.

Mardles and DeWaele 75 considered the rheological behaviour of suspensions and emulsions in relation to properties of surface films adsorbed on the dispersed particles. They noted that small changes in composition of a disperse system lead to important variations in rheological properties due to changes in the character of the interfacial film. An increase in the friction between particles results in larger sedimentation volumes and higher specific viscosities. In concentrated systems, this factor outweighs the usual hydrodynamic considerations.

A fact that has been brought up by several workers is that the globule size of an emulsion decreases with an increase in the concentration of the emulsifying agent, reaching a limiting value. This would seem reasonable in that at lower concentrations there may not be enough emulsifier available to cover a large area as would occur in a finer dispersion.

Although most emulsifiers reduce the interfacial tension between the organic and the aqueous phases of the system, at lease one instance has been reported 76 of an emulsifier increasing the interfacial tension. Alkali halides were found to stabilize emulsions of water in amyl alcohol. These salts are not surface-active but rather increase the interfacial tension of the system.

Sherman<sup>77</sup> recently reviewed the effect of the concentration of emulsifier on emulsion viscosity. A change in viscosity with varying concentrations of the emulsifier, for the same value of  $\Phi$ , has been observed by several workers. However, no attempt had been made to relate quantitatively the emulsifier concentration to the viscosity of the emulsion. From the experimental observations of several workers, Sherman concluded that a change in emulsifier concentration had a greater effect on emulsion viscosity in concentrated emulsions than in dilute systems. For his data on emulsions with varying concentrations of sorbitan sesquioleate the viscosity increased with concentration up to a value of  $\Phi$  of 0.5. This was explained as due to an increase in  $\Phi$ . Beyond this value of  $\Phi$  much larger changes in viscosities were observed.

Sherman proposed an equation relating emulsion viscosity to the volume concentration of the oil as well as emulsifier concentration as follows:

$$ln \gamma_{rel} = aC + G$$

where  $\underline{C}$  is the emulsifier concentration and  $\underline{G}$  is a constant. He pointed out that this equation is similar to the modified Richardson equation:

$$ln \bigvee_{rel} = k \varphi + A.$$

Sherman suggested that the  $\underline{k}$  in this equation is a function of emulsifier concentration  $\underline{c}$ . The equation fitted the data of Broughton and Squires<sup>48</sup>, Sibree<sup>69</sup>, and Van der Waarden<sup>78</sup>.

From the observations of these workers it appears difficult to describe the effect of the emulsifier on the rheological properties of emulsions. Sherman's equation is the only quantitative relationship proposed. However, the methods employed to measure viscosity by the workers whose data were used to prove this equation were not suitable for non-Newtonian systems. It appears that much work is yet needed to define the effects of emulsifier on flow properties of emulsions.

# Effect of Surface Charge of Dispersed Phase on Flow Properties of Emulsions

Smoluchowski<sup>46</sup> proposed that for a charged particle in an electrolyte, the electrical double layer might be expected to increase the effective viscosity of a suspension of solid particles. This increase is called the electroviscous effect. For this condition, he obtained the relationship:

$$\gamma = \gamma_0 \left[ 1 + 2.5 \, \phi \left\{ 1 + \frac{1}{\sigma \gamma_0 a^2} \left( \frac{g \epsilon}{2\pi} \right)^2 \right\} \right]$$

where is the specific conductivity of the electrolyte, a is the radius of the solid particle, is the dielectric constant of water and is the electrochinetic potential of the particles with respect to the electrolyte. This formula assumed that the thickness of the double layer was small compared to the particle radius. A similar result was derived by Krasny-Ergen 19. The increase in viscosity due to the presence of charges on the particles was qualitatively confirmed by Booth 10 in his experiments. Booth derived an expression for the viscosity of a suspension which involved all the assumptions made in the derivation of the Einstein equation. Further it was assumed that:

- 1. The thickness of the region containing the surface charge on the particle was small compared with the radius of the particle.
- 2. The ions in this region were immobile and could not move laterally over the surface.
- 3. The surface charge density at any point was fixed, and remained unchanged when the electrolyte was set in motion.
- 4. The potential across the region containing the surface charge was also unaffected by the motion of the electrolyte.
- 5. The double layer was small in thickness compared with the average distance between neighbouring particles.

The equation derived by Booth was of the form:

$$\gamma = \gamma_0 \left[ 1 + 2.5 \, \phi \left[ 1 + 2 \, a_n \, Q^n \right] \right] ,$$

where  $\underline{Q}_{\underline{e}}$  denotes the charge on each particle and  $\underline{a}_{\underline{n}}$  is the coefficient of the  $\underline{n}^{th}$  term in  $\underline{q}$ .

The electroviscous effect was also observed by Tanford and Buzzel<sup>81</sup> in a study of the viscosity of aqueous solutions of bovine serum albumin between the pH of 4.3 and 10.5, in which range the albumin molecule behaved as a compact particle similar to a sphere. The

increase in the intrinsic viscosity was found to be in fairly good agreement with Booth's equation. Electroviscous effects were observed by the same workers in a study of the viscosity of ribonuclease between the pH values of 1 and 11<sup>82</sup>. The increase in viscosity, however, was larger than predicted by Booth's equation.

van der Waarden<sup>78</sup> investigated the viscosity of oil-in-water emulsions of varying particle size and concentration prepared with the same oil, and the same emulsifier. Viscosities were measured in a British Standard Institution viscometer and particle size was measured by a light-scattering method. Values of the constant  $\underline{K}$  were calculated by the formula:

$$K = \frac{V_{r-1}}{\Phi}.$$

The limiting values of K as  $\bigcirc$  approached zero were obtained by plotting  $\bigcirc$  K versus  $\bigcirc$ . The values were found to be higher than the value 2.5 of Einstein's equation for uncharged rigid spheres. It was found that the limiting value approached 2.5 as the emulsifier content approached zero. An apparent increase in volume was calculated, and from it, an increase in the droplet radius by the equations:

$$v = \frac{4\pi (r + \Delta r)^3/4}{4\pi r^3/3}$$

and

$$\Delta r = r \left( 3 \sqrt{v - 1} \right)$$
.

The  $\triangle$ r values were found to be independent of particle size, and it was concluded that oil droplets behaved as if they were enveloped by a rigid layer, which in this case was calculated to have a thickness of 30-35  $A^{\circ}$ .

This apparent increase in the radius of the spherical particle was ascribed to the charge on the oil droplet. The increase in viscosity, however, was much larger than predicted by the equation of Smoluchowski or Booth.

In another investigation, van der Waarden, Harmsen and Schooten<sup>83</sup> demonstrated that the influence of electrolytes on the viscosity of emulsions of moderate or high concentration increased with a decrease in the particle size. Emulsions were prepared with 10% of a medicinal oil in water stabilized by sodium naphtha sulfonates, and varying concentrations of sodium chloride were added. The results are presented below:

Particle Diameter A <sup>O</sup>	NaCl Concn (meq./L.)	η <sub>rel</sub> of Emulsion	Percentage Decrease in $\eta_{rel}$
		7 1.0	
2050	0	1.42	about 1
2050	43	1.41	
585	O	1.63	
585	13	1.47	about 10
		·	
075	0	2.00	
275	0	2.00	about 20
275	17	1.60	<b>3</b> 5043 E0

It was proposed that two types of electroviscous effect might be involved. First, the classical effect caused by an interaction between particle and

medium, causing an apparent volume increase; second, the higher order effects caused by an interaction between particles, which becomes more marked as the concentration is increased. Only the classical effect has been elaborated fundamentally. The apparent increases in particle sizes were still found to be constant, 30-35 A° for particles of all sizes.

Donnet and Reitzer <sup>84</sup> studied the effects of particle charge on the viscosity of a suspension using spheres of carbon black carrying ionizable chemical groups as the charged particles. It was found that the viscosity of the suspension did not depend on the charge per particle when the latter varied from 750 to 2260 elementary charges. This conclusion was contrary to the theories of Smoluchowski and Booth. It would appear that considerably more work needs to be done in this field before any general conclusions can be made.

#### Effect of Viscosity of the Continuous Phase on Flow Properties of Emulsions

Most of the relationships derived for the viscosity of an emulsion include  $\underline{\eta_0}$ , the viscosity of the continuous phase. It may be said that  $\frac{3}{3}$ :

$$\eta = \eta_0 x$$

where  $\underline{x}$  is the summation of all other properties which may affect viscosity. The equation of Smoluchowski, for instance, includes the dielectric constant of water.

It is important the viscosity of the continuous phase be that of the complete medium and not that of the basic solvent alone. The difference may be quite significant if an agent such as methylcellulose or bentonite is present as an added stabilizer. It is reported that addition of bentonite to the continuous phase stabilized an emulsion of benzene in water with sodium oleate emulsifier. Axon found that emulsions of liquid paraffin in water containing bentonite exhibited thixotropic flow.

Knoeckel and Wurster<sup>57</sup> studied the stability of emulsions with varying viscosities of the continuous phase. The size frequency analysis technique was used to measure stability, and the viscosity of the continuous phase was varied by addition of methylcellulose. Sodium lauryl sulfate was used as emulsifier. Since only one emulsifier and one viscous agent were used the effects of interactions between these agents were not evaluated. Such an interaction would often be the most significant factor affecting emulsion viscosity, and thus their results have limited application.

Although the agents most commonly used as stabilizers for emulsions confer non-Newtonian properties upon the continuous phase and the final emulsion, few studies have utilized methods of measurement which are suitable for non-Newtonian liquids. For any relationship

between viscosity, emulsion and continuous phase to be useful, the non-Newtonian properties must be considered.

#### STATEMENT OF THE PROBLEM

The presently-available equations describing relationships of emulsion viscosity to various properties of dispersed and continuous phase have several features which limit their usefulness. First, they are based on data obtained by methods not suitable to non-Newtonian liquids, in spite of the fact that most practical emulsions are not of Newtonian character. Second, they assume Newtonian viscosity for the basic components of the emulsion as well as the emulsion, itself. Third, they are applicable, generally, to lower concentrations of dispersed phase than are commonly used. Fourth, these equations do not consider the interactions which commonly occur between emulsifier and dispersion medium or dispersed phase. Fifth, they have usually been developed from or tested with a small number of measurements on a limited type of emulsion.

Development of the M-2 and M-3 viscometers made possible the automatic recording of all types of flow curves in a relatively short period of time. Development of the Structure Equation made it possible to describe flow properties of non-Newtonian liquids accurately with three constants which can be calculated from the data by means of an electronic computer. Thus, it has become practical to measure large numbers of samples and search for general relationships which might predict the flow properties of emulsions.

It was the purpose of this investigation to determine the flow properties of emulsions containing common non-Newtonian suspension media and to attempt a correlation of rheological behavior, as defined by the Structure Equation, with several pertinent factors, such as particle size, concentration of dispersed phase and concentration of suspending agent in the continuous phase.

#### EXPERIMENTAL

## Apparatus and Materials

## The M-3 Viscometer

# Description

The suitability of a concentric cylinder rotational viscometer for measuring flow characteristics of pharmaceuticals and the development of an automatic recording viscometer for this purpose were described by Samyn<sup>87,88</sup> in previous work at The University of Michigan. Shangraw<sup>89</sup> designated this instrument the M-1 viscometer and described the development of the M-2 viscometer. The most important change in the M-2 viscometer was one of size, the overall dimensions being expanded to approximately four times those of the M-1. Grim<sup>91</sup> used the M-2 viscometer with two modifications to study the rheology of pharmaceutical suspensions. The two modifications were that the point bearing of the bob was changed from stainless steel to Carboloy to reduce wear, and that a digital print-out recording system was added.

The instrument used in this study, designated the M-3 viscometer, is similar to the M-2. It differs chiefly in having the cup drive consist of a spiral miter unit (VR 131, Boston Gear Works) and a horizontal motor, the two being connected by a double-belt pulley. It was felt that this would give better alignment of the cup and smoother operation. Another change from the M-2 viscometer is that a different make of x-y recorder is used (Model 2A, F. L. Mosely Co.).

### Calibration

Strain gauges. -- Each of the strain gauges was calibrated by loading with weights and observing the corresponding deflection on the x-axis of the tracing. The curve of deflection versus weight was linear for all gauges. Readings of standard resistors were made at the same time, so that the calibration constants might be in terms of standard resistors and thus independent of the degree of amplification. Calibration results are shown in Table 2.

TABLE 2

CALIBRATION CONSTANTS FOR STRAIN GAUGES

Gauge oz.	Weight Equivalent to S	Standard Resistor
OZ.	R <sub>l</sub> - Gm.	R <sub>2</sub> - Gm.
4 8 16 32 80	28.61 81.06 156.48 297.78 701.75	57.38 162.94 313.72 597.05 1400.78

Tachometer. -- The tachometer was calibrated by measuring the deflection on the y-axis of the recorder using the 10 volt, fixed scale, and the speed of the motor in r.p.m., using a Hasler speed indicator, (Hasler-Tel Company), at each of several settings on the speed controller. These values were plotted and found to be linear, and the slope of the line was used as the calibration factor. All measurements were made using this scale so that the calibration factor remained constant.

Cup and bob dimensions and instrument constants. -- Dimensions of the cup and bob are used for converting experimental data into units of shear and stress which represent the average values in the annulus between the cup and bob.

Equations for the shear constant,  $K_s$ , for converting r.p.m. to average rate of shear (in reciprocal seconds) are the Average equation<sup>91</sup>, the Fischer equation<sup>92</sup> and the Andrade equation<sup>93</sup>. Selection of the proper equation is important if the gap between cup and bob is not small, but it was shown that all three give identical values, within experimental error, for the cup and bob used with the M-2 or M-3 viscometer<sup>94</sup>. Calculation of the shear constant may be illustrated with the Andrade equation, which is the one of choice:

$$K_{s} = \frac{2\pi}{60} \cdot \frac{4R_{b}^{2} R_{c}^{2}}{(R_{c}^{2} - R_{b}^{2})} \ln R_{c}/R_{b},$$

where  $\frac{R_c}{L}$  is the radius of the cup and  $\frac{R_b}{L}$  is the radius of the bob. The rate of shear is then calculated by:

$$S = K_s (r.p.m.),$$

where  $\underline{S}$  is the average of shear in annulus.

Equations were presented by Samyn95 and Shangraw96 for the stress constant,  $\underline{K_f}$ , for converting experimental measurements of force into average shearing stress. It was shown that both equations give the same value with a small gap between cup and bob such as is found with the M-2 and M-3 viscometers. The Shangraw equation, which is the better of the two, is as follows:

$$K_{f} = \frac{\ln Rc/Rb}{\pi h(R_{c}^{2} - R_{b}^{2})},$$

where h is the height of the bob.

A given value of stress, F, involves the stress constant, the weight equivalent recorded from the strain gauge, the gravity constant and the length of the lever arm connecting the bob to the strain gauge; thus:

$$f = K_f \cdot 980$$
 . Lever arm  $\cdot Gm_{\bullet}$ ,

where  $\underline{F}$  is the stress in dyne/cm<sup>2</sup>. By using a wide range of gauges, it was possible to work with a constant lever arm and simplifying the conversion to multiplication by a single factor:

$$F = T \cdot Gm_{\bullet,\bullet}$$

where  $\underline{T}$  is a new constant, is the product of  $K_{\mathbf{f}}$ , lever arm and the gravity constant.

Dimensions of the cup and bob and the instrument constants for the M-3 viscometer are presented in Table  $3 \cdot$ 

TABLE 3

CUP AND BOB DIMENSIONS AND INSTRUMENT CONSTANTS

Dimension or constant	Value
Inside radius of the cup, R <sub>c</sub>	4.603 cm.
Radius of the bob, $R_{b}$	4.523 cm.
Height of the bob, h	19.431 cm.
Lever arm	17.0 cm.
K <sub>s</sub>	5•9731 <b>*</b>
$^{ extsf{K}}_{ extbf{f}}$	$3.9333 \times 10^{-4} \text{ cm.} -3$
T	6.5535 cm. <sup>-1</sup> sec. <sup>-2</sup>
	* Dimensionless

## Operating Procedure

A uniform procedure was followed in measuring rheological properties of all samples. Each sample was brought to temperature in an auxillary water bath at  $30.4^{\circ}$  where it was kept for at least one hour. It was then transferred to the cup of the viscometer, care being taken to avoid incorporation of air. The sample was allowed to stand in the viscometer bath for at least ten minutes before measurement. The viscometer bath was maintained at  $30^{\circ} \pm 0.1^{\circ}$  and the bath temperature was checked to insure that it was at bath temperature at the time of measurement.

A strain gauge was generally selected so that the maximum stress to be recorded would fall within the upper half of the range of the gauge. Both upcurve and downcurve were recorded, so that a failure to retrace would be noted. Differences in up- and downcurves would be encountered when the sample is thixotropic, air is entrapped in the sample or sedimentation occurs during measurement. Satisfactory retrace was obtained for all samples reported in this study. At least three successive flow curves were recorded for every sample. Either before or after the measurement, one of the calibrated resistors was switched into the circuit and its deflection on the stress axis marked.

The recorded flow curves represented an infinite number of experimental points, but a finite number of values were required for

mathematical treatment of the data. For convenience, equally spaced intervals on the y-axis were chosen, the range of the values on this axis being constant for all curves.

#### Materials Used

### Selection of Materials

For initial experiments cetyl alcohol was chosen as the dispersed phase, since it could be emulsified in a liquid state and then allowed to cool to form solid particles which would not change in size. Most of the experimental work dealt with an oil as the dispersed phase and corn oil was selected for this purpose. Water was used as the solvent for the continuous phase.

In the selection of the emulsifiers an effort was made to avoid those which cause extreme interactions. Two were selected: sodium lauryl sulfate and a mixture of 3 parts of sorbitan mono-oleate (Span-80) to 1 part polyoxyethylene mono-oleate (Tween-80).

Flow properties of the continuous phase were varied by addition of various suspending agents. Methylcellulose, sodium carboxymethylcellulose, Carbopol-934 (sodium salt), sodium alginate, tragacanth and acacia were selected as suspending agents commonly used in pharmaceuticals. Concentrations of suspending agents to be used were determined by estimating the maximum concentration of solution that could be conveniently added to a prepared emulsion. This and graded levels of concentration below this were used.

A mixture of three parts methyl para-hydroxybenzoate to one part propyl para-hydroxybenzoate was added as a preservative to solutions of suspending agents and basic emulsions, a concentration of 0.1% of the mixture being used. This was required to prevent microbial growth during storage of the samples.

A description of materials used is shown in Table 4.

Preparation of Solutions of Suspending Agents

Methylcellulose solutions were prepared by adding, with stirring, the powdered material to about one-half the required amount of water previously heated to 70°. The preservative was dissolved in the water prior to incorporation of the methylcellulose. The mixture was made up to volume with cold water and stirred in an ice bath until its temperature reached approximately 0-5°. It was then stored in a refrigerator for at least two days and finally at room temperature for at least two days before use.

Solutions of acacia, tragacanth, sodium alginate and sodium carboxymethylcellulose were prepared by mechanical dispersion of the powders in hot water containing the preservative. These were allowed to stand at room temperature for at least two days after solution was complete.

The sodium salt of Carbopol-934 was prepared by dispersing Carbopol-934 in methanol and adding the calculated amount of sodium hydroxide dissolved in methanol so that an aqueous solution of the salt would have a pH of 7. The sodium salt precipitated and was filtered out and dried at 125°. Sufficient salt was prepared at one time for

TABLE 4
DESCRIPTION OF MATERIALS USED

Material	Manufacturer	Control No.
Acacia, U.S.P.	S.B.Penick & Co.	
Methylcellulose, 1500 cps	Dow Chemical Co.	6702
Sodium carboxymethyl- cellulose, type 7 MP	Hercules Powder Co.	1406
Tragacanth, U.S.P.	S.B. Penick & Co.	WSB337
Sodium alginate, U.S.P.	Amend Drug and Chemical Co.	c510569
Carbopol-934	B.F.Goodrich Chemical Co.	785
Corn oil, U.S.P.	Corn Products Co.	
Sodium lauryl sulfate, U.S.P.	E.I.Dupont De Nemour & Co.	BWD-25671
Sorbitan mono-oleate (Span 80)	Atlas Powder Co.	610
Polyoxyethylene mono-oleate (Tween 80)	Atlas Powder Co.	502
Methyl para-hydroxy benzoate U.S.P.	Heyden Chemical Co.	cn3660
Propyl para-hydroxy benzoate U.S.P.	Heyden Chemical Co.	CN360
Cetyl alcohol, N.F.	Givaudan Delawanna Inc.	Emm man Come Page

the entier study. Solutions of this salt were made as needed by dispersing it in an aqueous solution of the preservative. Solutions were stored at room temperature for at least two days before use.

Solutions of suspending agents were assayed by drying at  $80^{\circ}$  until most of the water had been removed, then drying at  $105^{\circ}$  for two hours and weighing the residue.

### Preparation of Emulsions

Three series of emulsions were made. The first series contained varying concentrations of cetyl alcohol. These were prepared by dissolving sodium lauryl sulfate and preservative in the required amount of hot water (70-80°) and adding the melted cetyl alcohol with mechanical stirring. The emulsion was homogenized while hot with a Manton-Gaulin laboratory homogenizer (Model 15M8BA) at a pressure of 1000 lb/in². The homogenizer was previously heated by passing hot water through it. The basic emulsion contained 5.4% w/w of cetyl alcohol and 0.4% w/w of sodium lauryl sulfate. Emulsions of graded concentrations were prepared by dilution with water.

The second series of emulsions had corn oil as the dispersed phase, two different emulsifiers and varying concentrations of several suspending agents. A basic emulsion was prepared containing 60% w/w of corn oil and 5% w/w of emulsifier, either sodium lauryl sulfate or the Span-Tween mixture. When sodium lauryl sulfate was used it was dissolved along with the preservative in the required amount of water prior to addition of oil. When Span and Tween were used, the Tween was dissolved in water and the Span in the oil. In both cases, the emulsion was formed

by mechanical stirring as the oil was added to the aqueous phase. Homo-genization was performed at several different pressures, and the basic emulsion was then mixed with the selected quantity of suspending agent solution and water to yield an emulsion containing 40% w/w of oil.

The third series of emulsions contained corn oil and only one emulsifier, the Span-Tween mixture. Three suspending agents were used at different concentrations. The basic emulsion was prepared as previously described with 60% w/w oil and 5% w/w Span-Tween emulsifier. Only one homogenizing pressure, 3000 lb./in², was used. Selected concentrations of suspending agent and oil were obtained by dilution with water and suspending agent solution.

All emulsions were stirred carefully to avoid entrapping air and allowed to stand at room temperature for at least three days before measurement.

Solutions of the suspending agents were made having the same concentration of the suspending agent and sodium lauryl sulfate or Tween-80 as the aqueous phase of the finished emulsions. Since Span-80 is not soluble in water it was not added to these solutions.

In the experiments with emulsions containing varying proportions of cil, the amount of Tween-80 present in the aqueous phase varied with the concentration of the oil phase; therefore the effect of concentration of Tween-80 on flow properties of methylcellulose and sodium carboxymethylcellulose was examined. No effect was found, and solutions of suspending agents alone were used as blanks for this set of experiments.

The cetyl alcohol emulsions studied, series I, contained the following concentrations, % w/w, of cetyl alcohol: 5.4, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5 and 1.0.

The corn oil emulsions used for examination of effects of homogenizing pressures and concentration of suspending agent, series II, are shown in Table 5.

The corn oil emulsions prepared for evaluation of the effects of concentration of oil and suspending agent, series III, are presented in Table 6.

### Particle Size Measurement

Particle size analysis was carried out for all basic emulsions of the second series. The emulsion was mixed thoroughly and two drops were diluted to 100 ml. with a 50% solution of propylene glycol in water. A drop of this dilution was placed on a Petroff-Hauser bacteria counter (Arthur H. Thomas Co.). Measurement was performed using a microscope (Bausch and Lomb Co.) with a 10x eyepiece and a 47.4x objective. A grid in the eyepiece was calibrated with a stage micrometer, allowing direct measurement of particles. Fields from at least three slides were examined, at least 400 particles being measured.

# Flow Data

#### Series I

At the beginning of the experimental work it was thought that cetyl alcohol emulsions would be ideal for study. Since the emulsified

TABLE 5

CORN OIL EMULSIONS USED IN INVESTIGATION OF EFFECT OF HOMOGENIZING PRESSURE AND CONCENTRATION OF SUSPENDING AGENT

# SERIES II

Emulsifier	Suspe <b>ndin</b> g Agent	Concentration of Suspending Agent in Aqueous Phase (% w/w)
Sodium Lauryl	Sod. Carboxy- methylcellulose	0.84, 1.15, 1.46, 1.76, 2.07
Sulfate	Sod. Alginate	0.42, 0.57, 0.72, 0.87, 1.02
	Tragacanth	0.41, 0.56, 0.71, 0.85, 1.01
	Acacia	8.16, 11.35, 14.81, 17.02, 19.95
Homogenizin	g Pressures, lb.	/in <sup>2</sup> 2000, 2500, 3000, 4000.
Span 80- Tween 80	Sod. Carboxy- methylcellulose	
	Sod. Alginate	0.42, 0.57, 0.73, 0.88, 1.03
	Tragacanth	0.47, 0.65, 0.82, 0.99, 1.16
	Acacia	7.83, 10.68, 13.54, 16.39, 19.24
	Methylcellulos	e 0.68, 0.92, 1.17, 1.41. 1.66
	Carbopol-934 Sodium Salt	0.14, 0.18, 0.23, 0.28, 0.33
Homogenizing F	ressures, lb./in	<del>?</del> 1000, 2000, 3000, 4000, 5000.

TABLE 6

CORN OIL EMULSIONS USED IN THE INVESTIGATION OF EFFECT OF CONCENTRATION OF OIL AND SUSPENDING AGENT, SERIES III

Suspending Agent	Concn. of Suspending agent in Aqueous Phase % w/w			Co		trat: % v/-		Oil		
Methylcellulose	0•326	11,	16,	22,	27,	38,	43,	49,	54	
	0.434	11,	22,	27,	32,	38 <b>,</b>	43,	49,	54	
	0.543	11,	16,	22,	27,	32,	38,	43,	49,	54
	0.651	11,	16,	22,	27,	32,	38 <b>,</b>	43,	49,	54
	0.780	11,	16,	22,	27,	32,	38 <b>,</b>	43,	49,	54
	1.002	11,	16,	22,	27,	32,	38,	43,	49,	54
	1.170	11,	26,	22,	27,	32,	38,	43,	49,	54
	1.337	111,	16,	27,	32,	38,	43,	49,	54	
Sodium	0.281	11,	16,	22,	27,	32,	38,	43,	49,	54
Carboxymethyl- cellulose	0.562	11,	16,	22,	27,	32,	38,	43,	49,	54
	0.769	11,	16,	22,	27,	32,	38,	43,	49,	54
	0.984	11,	22,	27,	32,	38 <b>,</b>	43,	49,	54	
	1.153	11,	16,	22,	27,	32,	38 <b>,</b>	43,	49,	54
	1.265	11,	16,	22,	27,	32,	38 <b>,</b>	43,	49,	54
	1.476	11,	16,	22,	27,	32,	38 <b>,</b>	43,	49,	54
	1.687	111,	16,	22,	27,	32 <b>,</b>	38 <b>,</b>	43,	49,	54
Carbopol-934	0.187	11,	16,	22,	27,	32,	38 <b>,</b>	43 <b>,</b>	49,	54
Sodium Salt	0.125	   11	16,	22,	27,	32,	38,	43 <b>,</b>	49 <b>,</b>	54

particles would be solid at room temperature no coalescence of particles sould occur and a stable system might be expected. Also, the emulsion would not require a suspending agent for stability and thus would be as simple an emulsion as might be prepared. When flow curves were recorded, however, hysteresis loops were obtained, and it was thought at first that the emulsions were thixotropic. Accordingly, down curves were recorded to represent breakdown with time. These were obtained by running first a complete upand downcurve, then setting the speed of the cup at the highest rate, allowing shear to take place at this constant rate for a measured period of time before recording a downcurve. Shear at the top rate was thus allowed to take place for several fixed times until no further breakdown occurred and a downcurve corresponding to each time of shear was obtained. This procedure is the one proposed by Weltmann for obtaining the coefficient of thixotropic breakdown with time. A typical set of these curves is shown in Fig. 3.

It was found later that if one of these emulsions were allowed to stand in the viscometer for several hours after shearing, no build-up occurred and a flow curve would be identical to the equilibrium downcurve. Further, if a sample which had been previously measured and stored for periods up to one month were returned to the cup it would give the same curve as the equilibrium curve previously recorded. This made it appear that the original emulsions were not thixotropic but exhibited hysteresis loops due to occluded air or some permanent change taking place during measurement. In an effort to remove this effect several samples were subjected to reduced pressure for

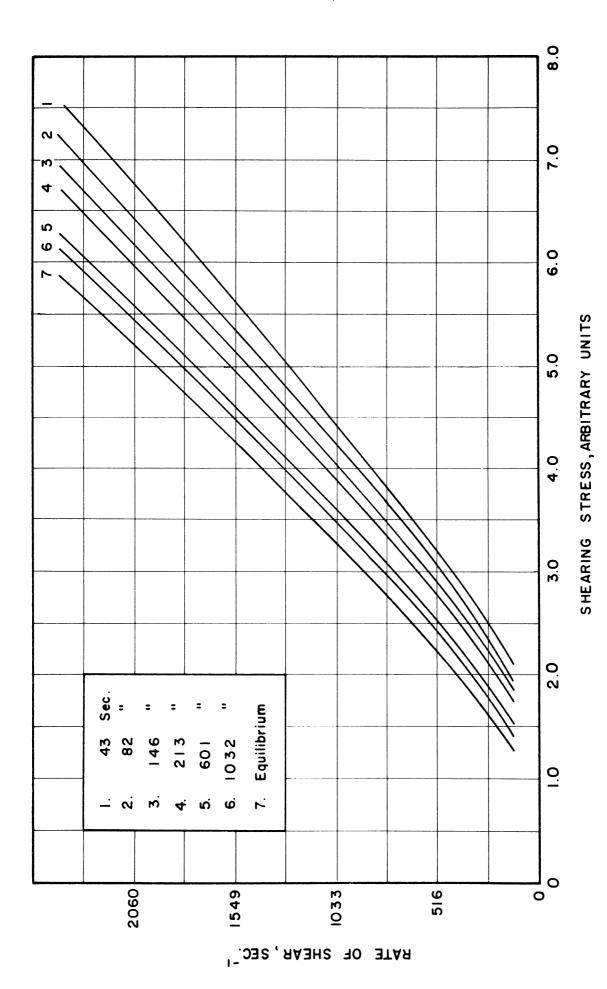


Fig. 3. Down-Curves Showing Breakdown with Time for Cetyl Alcohol Emulsions of Series I

several hours with the aim of removing air. Other samples were centrifuged to remove air. In both cases hysteresis loops were still obtained when measurements were made. Thus, the cause of hysteresis loops did not appear to be occluded air and were still unexplained. On the other hand, since the loops were not believed to represent thixotropy, only the equilibrium curves, representing a stable state of the emulsions, are presented. The equilibrium curves showed no hysteresis but were generally non-Newtonian. Equilibrium flow data are shown in Table 7.

In the presentation of data, rate of shear is shown in units of reciprocal seconds. Shearing stress is given in arbitrary units as obtained from the tracing, and the appropriate factor for converting these to absolute units of stress, dyne-cm<sup>2</sup>, is listed at the bottom of each data column.

### Series II

This group of emulsions was prepared so as to contain a fixed quantity, 40% w/w, of corn oil as the dispersed phase. The variables examined were homogenization pressure at several levels, two types of emulsifying agent and six types of suspending agent at various concentrations.

It was found that emulsions with or without suspending agent exhibited non-Newtonian flow without hysteresis loops. Acacia solution was Newtonian at all but the highest concentrations, and all other suspending agents showed non-Newtonian flow.

TABLE 7

FLOW DATA FOR SERIES I EMULSIONS CETYL ALCOHOL WITH SODIUM LAURYL SULFATE EMULSIFIER EQUILIBRIUM FLOW CURVES

		2.0 1.5 1.0	1.15 0.77 0.68	1.68 1.10 1.06	2.12 1.39 1.42	2.55 1.70 1.75	3.35 2.25 2.45	3.73 2.52 2.75	4.10 2.77 3.10	4.45 3.05 3.42	4.83 3.34 3.75	5.19 3.60 4.10	5.54 3.87 4.40	5.90 4.13 4.75	6.25 4.39 5.07	6.62 4.64 5.45	6.99 4.89 5.77	7.32 5.15 6.12	cm;2	54.4 134.0 49.7
S	(m/m %	2.5	0.90	1.25	1.50	1.77	2.26	2.49	2.70	2.92	3.15	3.36	3.77	3.98	4.19	4.39	7.60	4.80	- Dyne -	76.0
Shearing Stress	L ALCOHOL (	3.0	06.0	1.16	1.40	1.62	2.01	2.21	2,42	2.63	2.80	2.96	3.15	3.32	3.50	3.67	3.84	4.00	n Factor -	102.2
Shea	CONG. CETYL ALCOHOL (% w/w)	3.5	98.0	1.15	1.40	1.62	2.04	2.24	2.43	2.64	2.83	3.00	3.20	3.37	3.57	3.75	3.92	4.14	s Conversion Factor	128.0
		0.4	1.45	1.76	2.02	2.27	2.77	3.00	3.24	3.47	3.68	3.90	4.12	4.32	4.51	4.75	4.97	5.18	Stress	130.1
		4.5	1.80	2.16	2.50	2.79	3.34	3.60	3.87	4.13	4.36	4.62	78.4	5.10	5.33	5.57	5.81	6.05		128.0
		5.0	2.28	2.65	3.00	3.32	3.95	45.4	45.4	†8 <b>*</b> †	5.13	5.40	5.68	5.95	6.20	6.48	6.75	7.00		129.1
		5.4	2.70	3.10	3.60	3.93	02.4	5.02	5.32	5.70	6.04	6.37	69.9	7.00	7.34	2.66	7.98	8.30		123.8
	Rate	Shear Sec-1	129	258	387	516	775	406	1033	1162	1291	1420	1549	1679	1808	1937	5060	2195		

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Sodium lauryl sulfate had pronounced effect on methylcellulose, causing irregular flow curves, and on Carbopol, causing greatly reduced viscosity; hence this emulsifier was not used with these two suspending agents.

Emulsions containing suspending agents appeared to have yield values in all cases. Solutions of suspending agents, with the exception of acacia, also had yield values.

Flow data for emulsions without suspending agents are shown in Table 8, those for corresponding solutions of suspending agents are shown in Tables 9 and 14. Flow data for emulsions with sodium lauryl sulfate and the various suspending agents are presented in Tables 10-13 and data for emulsions with Span-Tween emulsifier and suspending agents are in Tables 15-20.

### Series III

This series of emulsions was prepared and measured with the aim of learning more of the effects of concentration of dispersed phase and suspending agent. Thus, one basic system with one emulsifier, Span-Tween, and with one homogenization pressure was utilized. The basic emulsion was diluted with water and suspending agent to obtain the concentration variations desired.

All of the flow curves for this series were non-Newtonian, most of them appearing to have a yield value, and none showed hysteresis.

Flow data for Series III emulsions are presented in Tables 22-29 and 31-40, and those for corresponding solutions of suspending agents are shown in Tables 21,30.

TABLE 8

FLOW DATA SERIES II EMULSIONS WITHOUT SUSPENDING AGENT

Shearing Stress

			2000	0.23	0.36	0. 84.0	) () ()	0.80	1.04	1.17	1.28	1.40	1.55	1.69 83	1.95	2.07	2.22	2.32	5.46	2.58		57.23
	0		4000	0.22	0.35	0.47	0.00	 	1.01	1.15	1.27	1.40	1.55	1.67	1.92	2.07	2.19	2.32	2.43	2.55		57.23
	Span-Tween Mixture		3000	0.22	0.33	0.40	0.0	0.89	1.03	1.16	1.29	1.42	1.57	0,1	1,95	2.08	2.20	2.34	2,48	2.60		57.67
	W	/in?	2000	0.17	0.33	0.43 2.43		0 0	0.95	1.06	1.19	1.33	1.43		1.82	1.94	2.06	2.17	2.30	2.42	Dyne - cm:2	57.76
Emulsifier		ing Pressure lb./in?	1000	0.15	0.26	0.38		70.0	0.87	66.0	1.10	1.21	1.34	+ + t	1.67	1.77	1.90	2.01	2.15	2.25	Conversion Factor Dyne	58.94
		Homogenizing	000†	0.29	0,40	0.20		0.76	0.85	0.93	1.00	1.08	1.17	1.25	24.	1.50	1.56	1.65	1.74	1.81	Stress Conv	108.1
	Sodium Lauryl Sulfate		3000	0.56	0.80	0.99	7.1	1.30	1.60	1.75	1.90	2.04	2.19	N V.	2,60	2.74	2.89	3.03	3.16	3.30		56.12
	Sodium Lau		2500	0.57	0.77	0.04	- CO	1.35	1.50	1.62	1.75	1.88	2.00	ν, ν. Στο	2.38	2.50	2.62	2.72	2.88	3.00		108.7
			2000	0.27	0.3 8.7	84.0		0.70	0.80	0.85	0.94	1.00	1.07	1. L5	1.30	1.36	7.44	1.50	1.60	1.67		107.4
	Rate of Shear	Sec:1		129	258	387	077	775	406	1033	1162	1291	1420	1549	1808	1937	2060	2195	2320	2453		

TABLE 9

FLOW DATA FOR SOLUTIONS OF SUSPENDING AGENTS CORRESPONDING TO EMULSIONS OF SERIES II WITH SODIUM LAURYL SULFATE EMULSIFIER

Flow Curves For Solutions Of Stabilizers, Series A

				8.16		•			•	•		•	•	+ ~ ひっ		•	•	•	•	•	•	• 1			72.0
		IA		11.35	١.	•	•	•	•	•	•	•	•	7.53 0.03		•	•	•	•	•	•	٠٠١		•	71.9
		ACACIA		14.81		•	•	•	•	•	•	•	•	4.25		•	•	•	•	•	•	• 1	N		71.3
			(m/m %)	17.02		•	•	•	•	•	•	•	•	6.26		•	•	•	•	•	•	• 1	- Dyne - cm:2		112.2
ing Stress	Suspending Agent		Agent,	19.95										0. 150 100 100 100 100 100 100 100 100 100								• •	on Factor		125.3
Shearing	Suspe		Conc. Suspending	0.41	0.32	0.57	0.75	16.0	1.10	1.23	1.38	1.51	1.64	1.75	200	2.13	2.25	2.38	2.50	2.60	2.75	2.85	ss Conversion		70.95
		TRAGACANTH	00	0.56	0.70	1.10	1.37	1.63	1.87	2.08	2.25	2.44	2.60	2.75	7.01 3.05	0.00	3,58	3.45	3.61	3.72	3.85	4.00	Stres		71.09
		TRAGA						•	•			•	•	3.77				•		•	•	• 1			72.32
				$ \infty$	1	٠.	$\infty$	Q	9.	6	\	<b>↑</b> .	<u>_</u>	4.92	٦.	٦,	` [-	- 6	,	$\sim$	Ċ	9			71.90
				10	1	- M		٠.	· ~	9	Ψ	0	cu	4.45	9 1	•		ι (*	)	9	[-	0			91.89
	Rate	of Shear Sec:1			129	258	387	516	949	775	+06	1033	1162	1291	1420 1510	1679	1808	1937	0907	2195	2324	2453			

TABLE 9-Continued

				_	0	.93 0.51	·	·	<u>.</u>	ri -	٠.	<u>ر</u>	ai —	ai (	N C	i a			· რ	· ń	·'n	+		Ü	79.7
		SODIUM CMC		1	0	05 0.0	H 		<u> </u>	<u>α</u>	C)	<u> </u>	<b>Υ</b>	<b>ω</b> -	† <u>-</u>		- 10	, rU	. 10	ſΩ,	9	9		1	5   79.5
		S0]		[i		<u>н</u>	•	•	•	•	•	•	•	•	•	•			•	•	•	• [		- 1	119.
			(m/m %)	1.76		1.82	•	•	•	•	•	•	•	•	•	•			•	•	•	10.50	Dyne - cm:2	- 1	120.2
ring Stress	Suspending Agent		Agent,			1.35	•	•	•	•	•	•	•	•	•	•		•	•	•	•	• 1	Factor	) L	254.0
Shearing	Susp		Conc. Suspending	0.42		0.68	•	•	•	•	•	•	•	•	•	•			•	•	•	• 1	s Conversion		60.7
		INATE	D			1.40	•	•	•	•	•	•	•	•	•	•			•	•	•	• ]	Stress		61.6
		SODIUM ALGINA			٠.	2.40	•	•	•	•	•	•	•	•	•	•			Ö	•	$\dot{\circ}$	-1		000	60.09
				$ \infty $	0	1.75	$\sim$	<u>.</u>	Q.	5	<u>ن</u>	a i	ψ.	χġι	નું ત	$\cdot^{\kappa}$	$\infty$	. 4	$\sim$	.5	۲.	0		. 00	129.1
				١.	٠.	2.50	•	•	•	•	•	•	•	•	•	•		•	•	•	•	• 1			130.0
	Rate	of Shear Sec:1			129	258	387	516	949	775	† <sub>0</sub> 6	1033	1162	1291	1470	1 1 1 1 1 1 1	1808	1937	2060	2195	2324	2453			

TABLE 10

FLOW DATA FOR EMULSIONS OF SERIES II WITH SODIUM LAURYL SULFATE EMULSIFIER ACACLA SUSPENDING AGENT

					8.16		1.36	1.56	1.75	1.34 2.10	2.27	##. 00 0	2.77	20.0	3.20	3.44	3.75	3.95		156.3
					11.35		1.62	1.95	2.25	2.85	3.14	3.43	00:4	4.27	4.70 4.85	5.11	5.68	5.95 6.23		213.6
			2500		14.81	0.00	1.46	1.76	2.05	. 60 . 60	2.86	3.14	3.65	3.90	4 t t	4.65	4.09 5.14	5.37 5.60		409.5
		5.		w/w)	17.02	1.27 1.75	2.50	2.62	3.00	3.73	4.10	74.45	5.12	5.42	5.76 6.10	6.40	7.04	7.35 7.65	- cm:2	402.3
ing Stress	Suspending Agent	Pressure lb./in. <sup>2</sup>		Aqueous Phase (%	19.95	L-73	2.10	2.45	2.76	 	3.65	3.92	7 t t t t t t t t	4.70	4. 7. 00	24.7	7.90 5.90	6.15 6.37	Facto	803.4
Shearing	Suspe	Homogenizing		Agent in	8.16	27.0	1.12	1.30	1.46	1.02	1.93	2.07	2.40	2.53	2.86	3.00	3.15	3.62	Stress Conversion	181.9
				Suspending	11.35	0.08	1.22	7.47	1.73	т у У у	24.2	2.66	3.15 3.15	3.36	3.58 81.83	4.05	4. 4. 50. 4. 50. 50. 50. 50. 50. 50. 50. 50. 50. 50	47.4		212.7
			5000															- 4 - 4 - 5 - 5 - 6 - 7		407.1
					17.02	0.89	1.60	1.94	2.25	0,0 0,0 0,0	3.14	3.45	3.75 4.01	4.31	4.57 7.07 7.00 7.00	5.10	7.39	6.95 6.20		403.1
					19.95	0. 0.	1.1	1.80	2.07	2.32 5.72	.89	3.01	3.55 52.50 54.60	3.70	3.92 9.54	4.33	4.55	4.95 5.16		798.5
			Rate of Shear	Sec:1		129	200 200 200	516	949	775 904	1033	1162	1291 1420	1549	1679 1808	1937	2060 21 95	2324 2453		

TABLE 10-Continued

				8.16	1.08	1.35		9 0 0	2.16	2.36	2.51		3.05	3.20	 	 	3.88	4.05	4.22 4.22	+ 00:		182.5
				11.35	1.20	1.55.	1.00 7.17	2.42	2.70	2.95	81.0	3.44	) in	4.17	‡ ~	† † † 6.	5.15	5.40	5.62 22	10:7		213.1
		000†		14.81	0.80	1.12	1.68	1.94	2.19	2.40	2.65	3.10		3.55	3.(5	- 02.4	04.4	4.62	4, r 6,03 6,03			405.5
	QI•		se (% w/w)	17.02	1.30	86.0	2,62	3.00	3.36	3.70	†O• †	4.40	5.00	5.31	V 10.00	6.83	6.52	6.83	7.12	7+•1	- cm2	403.1
ng Stress	Pressure lb./in?		Conc. Suspending Agent in Aqueous Phase	19.95	1.39	T 0	2.54	2.85	3.13	3.40	39. 89. 89.	 40	\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	4.68	ֆ ռ Ն․ 1 ռ	5.37	5.60	5.81	6.05	7.0	Conversion Factor Dyne	801.8
Shearing	Homogenizing		duspending Agent	8.16	1.77	200	3.07	3.42	3.80	4-15	04.4	4.0.	いせい	5.80	5 T-0	6.77	7.10	7.40	7.75	2000	Stress Conversion	97.0
Homoge		Conc. S	11.35	1.94	09:2	3.75	4.27	4.82	5.34	5.85	0.00 0.00	7.35	7.83	0.30	9.25	9.74	10.20	10.70	01.41	St	104.0	
		3000		14.81	1.24	1.80	2.76	3.25	3.69	4.10	4.55	4. r. V.v.	5.76	6.16	0.07 0.07	7.33	7.71	8.10	ωα Ο τ'α			234.0
				17.02	2.14	3.00	7.4.7	5.14	5.76	6.40	7.00	, ,	8.75	08.6	ري. ده. د	10.92	11.45	11.94	12.50	- CA-CT		234.0
				19.95	2.20	3.05	4.37	4.95	5.47	0.00	6.50	7.40	7.88	8.00 0.10	0.0 V.L	9.58	10.00	10.40	10.79	77.77		0.094
		Rate of	Shear Sec-1		129	11 00 11 00 11 00	50 ( 516	949	775	406	1033	1231	1+20	1549	7 0 C 0 0 C 0 0 0 C	1937	2060	2195	2 <b>3</b> 20 2453	5470		

TABLE 11

FLOW DATA FOR EMULSIONS OF SERIES II WITH SODIUM LAURYL SULFATE EMULSIFIER SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

				0.84	1.05	1.45	).). ·T	2.05	S. 3.	7. 7. 7.	0.0	66.0	04.60	3.62	3.82	00 <b>.</b> 4	4.22	4.4	4-80	5.00	5.18		1603	C•30T
				1.15	1.87	2.19	2.68	3.09	3.4 <u>7</u>	39.5	9T• †	t - Οα Οα	+ r	5.39	5.68	5.97	6.25	0 7 7 8 8	7.10	7.35	7.64		5 191	TO++.2
		2500		1.46	1.08	1.48	1.78	2.05	2.29	2.52	†		3.15	3.55	3.75	3.90	4.10		- t	, 4 , 8 , 8 , 8	5.00		4 7110	340.(
			se (% w/w)	1.76	1.38	1.90	2,29	2.65	2.96	3.25	3.55	ν- Ο ί	4.05	4. 70. 70.	4.00	5.02	5.25	5.50	. r	6.15	6.35	- cm:2	0 0:0	343.8
Shearing Stress	Homogenizing Pressure lb./in?		in Aqueous Phase	2.07	06.0	1.22	1.46	1.68	1.89	2.08	2.25	2,42	2.59	4,0	3.05	3.19	3.33	 	3.00	3.87	4.00	Conversion Factor Dyne		6.929
	Homogenizing I		Suspending Agent in Aqueous	0.84	1.00	1.36	1.66	1.94	2.19	2.40	2.65	2.85	3.10	3.00	3.72	3.91	4.13	4.34	+ - い。 ・ ・ ・ ・ ・ ・ ・ ・	t, 0, 1,	5.13	Stress Conversion		161.3
			Conc. St																		6.92		- 1	164.3
		2000		971 -	30	1.77	2,15	2.48	2.79	3.06	3.34	3.62	3.88	4.12	4.30	. ±	5.05	5.25	5.50	2.5	6.1.6 5.1.4			346.1
				74 1	30	1.76	21.0	2.50	2.80	3.10	3.38	3.64	3.90	4.12	4.33	10.4	5.07	5.30	5.51	5.74	6.18			342.1
				0	10.0	+ to -	- F	09.1	1.80	00.	2.16	2.34	2.50	2.65	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	٠. د د	3.25	3.40	3.54	3.65	3.00			678.1
		Rate of	Shear Sec.			100 000 000	2000	- 20.5	0.10 0.15 0.15	775		1033	1162	1291	1420	1670	1808	1937	2060	2195	2320			

TABLE 11-Continued

				0.84	1.30	2.12	2.40	δ. 8.69°2		3.20	3.67	3.90	4. 12	+ + た。 かっ	4.75	76.4	7.To	5.58	5.80		161.8
				1.15	1.95 2.55	3.07	3.52	3.90	4.27	4 4 5 0 2 5 0 5 7	5.20	5.68	00.00	6.50	6.80	7.06	75.7	7.91	8.20		163.7
		000†		1.46	1.25	2.00	2.26	2.52	2.75	76.8	3.38	3.57	3.75	1. 1. 1.5	4.30	ナナ・ ナ	4	5.00	5.15		346.7
	Q.L.		Phase (% w/w)	1.76	1.72 2.35	2.77	3.16	3.50	3.85	+ + たった たった	4.70	5.00	5.24	5.74	6.00	6.23	• • • • • • • • • • • • • • • • • • •	96.9	7.12	- cm. 2	342.7
Shearing Stress	Pressure lb./in?		t in Aqueous Pha	2.07	1.07 1.42	1.70	1.95	2.16	2,36	2.55 2.00	2.90	3.05	3.20	3.50 3.50	3.65	3.80	ω. Σ. Σ.	4.4 20.4	4.35	Factor Dyne	6.929
Shear	Homogenizing		Conc. Suspending Agent in Aqueous	1,8,0	24°T	2.30	2.65	2.97	3.26	3.55	+ O. +	4.38	4.62	4.00 7.1.4	5.38	5.63	2.00	6.34	6.59	Stress Conversion Factor	138.0
			Conc.	1.15	2.00 2.74	3.30	3.81	4.25	99•4	7.07 7.07	, r.	6.20	6.55	0.0 40.7	7.56	7.90	8 27	8.85	9.19	St	138.0
		3000		1.46	1.93	3.17	3.64	4.05	4.50	4.80	7.50	5.82	6.13	6.75	7.04	7.33	29.)	8.20	8.49		202.0
				1.76	2.27	3.69	4.23	4.72	5.16	09.0	20.00	5.77	7.15	7.00	8.18	8.52	8.87 28.0	9.50	9.83		202.0
				2.07	1.34	2.19	2.51	2.80	3.05	3.32	3.70	4.00.	4.21	# t- t- t- t- t-	4.82	5.00	5.19	7.56	5.74		458.0
		Rate of Shear	Sec:1		129 258	387	516	949	775	406	1162	1291	1420	1774 1770 1770	1808	1937	2060 2010	2320	4253		

TABLE 12

FLOW DATA FOR EMULSIONS OF SERIES II WITH SODIUM LAURYL SULFATE EMULSIFIER TRAGACANTH SUSPENDING AGENT

				0.41	0.95	1.32	1.60	1.85	2.07	2.27	84.0	2.67	2.85	00. 00. 00.	χ.τ. Στ.	0.55 C2.50		 48. %	00° <del>*</del>	4.15	4.31	64.4		6 00 5	10V·3
				0.56	1.40	1.90	2.26	2.57	2.85	3.12	3.36	3.58	3.85	† †	7 t ==	* t = -	70°+	20.	 	5.40	5.60	5.77		90	109.9
		0		0.71	1.25	1.70	2.05	2.29	2.52	2.74	2.94	3.12	3.30	3.47	٠. دوم	3.00		+ ~ + ~	4-40	4.61	77. t	4.95		1 0 1	158.7
	01•	2500	se (% w/w)	0.85	1.60	2.15	2.50	2.80	3.07	3.32	3.55	3.78	00.	4.20	0 + . + .	4.00.	00.	9.4	7. 27	7,55	5.75	5.94	- cm:2	0.02	158.9
ng Stress	Pressure lb./in?		Agent in Aqueous Phase	1.01	1.92	2.50	2.95	3.35	3.67	3.96	4.25	4.50	4.75	5.00	5.25	2.50			0. FZ	1 7 9	6.85	7.10	Dyne	- 1	160.3
Shearing	Homogenizing		Suspending Agent	0.41	0.95	1.34	1.62	1.88	2.08	2.30	2.50	2.70	2.88	3.06	3.22	3.40	3.57			- t	4.41	4.62	Stress Conversion Factor		108.7
			Conc.	0.56	1.58	1.80	2.15	2.47	2.75	3.00	3.22	3.47	3.69	3.90	4.10	4.31	4.50	4.73	4.96	7.T.	5.55	5.73	St		110.6
		2000																				4.81			164.3
																						6.10		- 1	158.7
				[0, [	06.1	20.47	2.88	3.25	3.57	3.83	4.12	7,46	4.65	06.4	5.12	5.37	5.61	5.86	80.9	200	0.22	.00.7			160.1
		Rate of	Shear Sec:1		129	1 (7)	387	516	04.0	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2060	Z195	2453			

TABLE 12-Continued

				0.41	0.85	1.19	1.46	1.69	1.91	8.12	2.33	2.50	5.69	2.85	3.05	3.22	3.40	3.56	3.72	%. %. %.	4.06	4.25	4.38		109.3
				0.56	1.23	1.67	2.00	2.32	2.60	2.85	3.10	3.34	3.56	3.76	4.00	4.20	4.47	7.62	4.83	5.04	5.25	5.45	5.64		109.9
		0007		0.71	1.12	1.52	1.83	2.09	2.32	2.54	2•7⁴	2.93	3.12	3.30	3.48	3.66	3.83	00.	4.16	4.33	4.50	4.68	4.85		158.4
	QI•		ase (% w/w)	0.85	1.45	1.95	2.29	2.62	2.88	3.13	3.39	3.60	3.84	†0 <b>.</b> †	4.25	4.45	49.4	4.85	5.05	5.25	5.43	5.64	5.85	- cm:2	158.9
ng Stress	Pressure lb./in?		Suspending Agent in Aqueous Phase	1.01	1.80	2.40	2.80	!!!!	3.50	3.76	7.08	4.32	4.58	4.83	5.07	5.32	5.55	5.77	00.9	6.25	6.47	69.9	6.95	Factor Dyne	160.1
Shearing	Homogenizing		Suspending Agen	0.41	1.45	2.05	2.52	2.95	3.32	3.67	4.03	4.35	19.4	5.00	5.30	2.60	2.90	6.20	6.48	6.79	7.08	7.37	7.68	Stress Conversion	54.7
			Conc.		1.97	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	Str	56.0
		3000		0.71	1.68	2.68	3.47	4.15	4.75	5.32	2.88	6.40	6.88	7.37	7.85	8.36	8.80	9.58	9.73	10.18	10.62	11.08	11.50		55.7
				0.85	1.62	2.23	2.67	3.08	3.42	3.74	4.05	4.35	†9 <b>°</b> †	4.92	5.20	5.45	5.72	5.98	5.24	6.50	6.75	7.00	7.25		111.0
				1.01	2.07	2.83	3.40	3.87	4.32	02.4	5.10	5.45	5.80	6.15	6.45	6.78	7.10	7.42	7.72	8.05	8.35	8.65	8.96		122.3
		Rate of	Shear Sec.		129	258	387	516	949	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2354	2453		

TABLE 13

FLOW DATA FOR EMULSIONS OF SERIES II WITH SODIUM LAURYL SULFATE EMULSIFIER SODIUM ALGINATE SUSPENDING AGENT

				+	0.82	1.16	± 4.	00. -1.	3.5	พ.ศ. พ.ศ.	2.48	2.65	2.84	9.00	3. To	3.50	3.66	3.82	3.97	4.12	4.55		158.9
				0.57	1.18	1.66	2.05	N 00	۸. د د د	٠ ر ٥	30.44	3.67	3.90	. t.	4.35	5C-+	4.97	5.17	5.38	5.56	5.75		160.6
		2500		0.72	1.66	2.37	2.89	3.32	N. (A	70.4 04.4	4.70	5.01	5.30	2.50	ر ا ا	0.40	6.65	6.92	7.17	7.42	7.65		160.6
	Z•		(% w/w)	0.87	1.12	5	1.85	7. T.	02.0	л у у у	2.99	3.15	3.33	w. o.t.	٠ د و د و	3.95	4.10	4.25	4.39	† <del>•</del> 5†	4.67	- cm:2	339.8
Shearing Stress	Pressure lb./in?		in Aqueous Phase	1.02	1.40	1.92	2.32	2.63	5. V	ν.τ. Υ.τ.ο	3.60	3.80	, t	4.18	4.05	4.70	4.88	5.05	5.20	5.36	5.52	Factor Dyne	346.1
Sheari	Homogenizing		Conc. Suspending Agent	0.42	0.80	1.10	1.38	1.60	T.02	N 0		2.58	2.75	2.94	3.LO	3.47 44	3.61	3.75	3.95	7	4.25	Stress Conversion	156.8
			Conc. S	0.57	0.97	1.38	1.70	٥٠. ٥٠. ١	22.25	2.50	2.98	3.15	3.36	3.55	3.0	マン・サ	4.33	4.51	4.70	4.90	5.07		159.1
		2000		٠.		•	•	•	•	4.40 4.75		•	•	•	•			•	•	•	•		161.3
						•	•	•	•	ი გ. ს გ. ს			•	•	•	•		•		4.39	•		339.8
						•	•	•	•	 9		•	•	•	•	•			•	•	•	1 1	345.0
		成 の か と	+ + + + + + + + + + + + + + + + + + +		01	Π (C)	23.7	(O)	040	275	1) 1 1) (1) 1) (1)	1907 1107 11	1221	O.K. T. T.	1 t 1	<u>ν</u> α ο α Η :-	1937	2060 2060	21.95	K K K C	2453		

TABLE 13-Continued

				0.42	1.00	1.70	2.22	††*O	2.87	3.07	3.4	3.58	3.76	4.10	4.25	-t	4.75		158.0
				0.57	1.45	0.4.0	3.13	3.40	3.95	4.20	4.47	4.88	5.10	7.30	5.72	ر 89.7	6.34		160.1
		000η		0.72	4Z.Z	3.32	4.20	4.56	5.25	5.55	5.04 6.12	6.39	6.65	7.19	7.43	7.64	8.17		161.3
			se (%/w/w)	0.87	1.30	& C.	n. 65 7. 65	2.89	3.	3.45	, c	3.95	4.10	t 4	4.55	4.77 1.85	4.98	- cm-2	339.8
Shearing Stress	Pressure lb./in?		in Aqueous Phase	1.02	1.75	2.72	3.36	3.62	4.10	4.29	4.49	4.85	.04	5.39	5.55	5.70	6.82	Dyne	345.5
Sheari	Homogenizing		Suspending Agent	0.42	w.w.	2.30	2.00	3.83	3.87	4.12	4.4	4.88	5.13	7.60	5.83	6.05	6.51	Stress Conversion Factor	113.0
			Conc.	0.57	1.95	3.24	2.50 2.80	4.61	  	5.72	0.00	6.70	7.00	7.60	7.88	8.19	8.75	St.	113.0
		3000		0.72	2.65	4.45	5.67	6.17	6.65 7.12	7.55	7.63	8.70	80.0		10.21	10.50	11.77		113.0
					1.75	•		•		•	•	•	•		•	•			236.0
					2.35														240.0
		Rate	of Shear	zec.	129	387	510 646	277	1000 1000	1162	1291 1420	1549	1679	1937	2060	2195	2453		

TABLE 14

FLOW DATA FOR SOLUTIONS OF SUSPENDING AGENTS CORRESPONDING TO EMULSIONS OF SERIES II WITH SPAN-TWEEN EMULSIFIER

	.ulose																				6.04 3.04	-		215.7 154.7
	Methylcellulose		1.17	0.55	0.97	1.33	1.68	1.98	2.26	2.53	2.77	3.02	3.25	3.47	3.68	•	4.10	•	•	•	4.85	• 1		357.6
	I	( M/M )	1.41	7,7,0	0.77	1.05	1.28	1.52	1.72	1.90	2.07	2.25	2.40	2.55	2.70	2.84	2.99	3.12	3.24	3.37	3.48	20.0	ġ	441.2
		Phase (%	1.66	26.0	1.65	2.17	2.64	3.05	3.42	3.77	4.07	4.38	4.65	4.90	5.15	5.39	5.62	5.85	20.9	6.27	6.47 7.47		yne - cm:2	443.1
ng Agent	enth	in Aqueous	0.47	0.35	0.56	0.73	0.85	0.98	1.07	1.19	1.27	1.40	1.49	1.57	1.68	1.77	1.84	1.93	8.00	2.10	2.18 82.0	7.50	actor Dyne	163.0
Suspending Agen	Tragacanth	Agent	0.65	99.0	0.97	1.19	1.38	1.53	1.70	1.83	2.07	2.22	2.32	24.2	2.54	2.63	2.75	2.85	2.95	3.05	3.15	7.57	Stress Conversion Factor	161.8
		Suspending	0.82	1.05	1.45	1.77	2.00	2.23	2.42	2.60	2.77	2.95	3.10	3.27	3.42	3.57	3.70	3.84	3.98	4.10	4.23	4.37	tress Con	161.3
		Conc.	0.99	1.45	2.00	2.38	2.68	2.95	3.20	3.42	3.63	3.84	4.02	•	04.4	4.57	4.73	7.96	5.05	5.20	5.35	7.10	ώ	160.6
			1.16	1.05	1.40	1.65	1.83	2.00	2.17	2.35	2.43	2.55	2.67	2.77	2.90	3.00	3.12	3.23	3.31	3.40	3.50	2.00		348.5
	СМС		0.92	94.0	0.70	0.92	1.17	1.36	1.56	1.77	1.95	2.14	2.32	2,48	2.64	2.80	2.97	3.12	3.28	3.45	3.61	0.10		9.661
	Sod.		1.25	0.54	0.97	1.35	1.70	2.05	2.38	2.68	3.00	3.28	3.55	3.82	70°†	4.33	7.60	t8.t	5.10	5.33	5.57	2.13		356.3
					•	•	•	•		•	•	•	•	•	•	•	•	•	•	•	3.44	• 1		344.9
			1 .		•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	5.67	•		682.8
				٠.	•	•		•	•	•	•	•	•	•		•	•	•	•	•	3.77	•		678.1
	Rate	of Shear Sec-1	•	129	258	387	516	9+9	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2473		

TABLE 14-Continued

			0.14	0.17	0.25	0.33	0,40	0.	0.55	0.62	0.70	0.77	0.85	0.92	0.98	1.05	1.12	1.18	1.25	1.32	1,39	1.46		97.2
	Sod. Salt		0.18	m	0.48	1,9.0	0.79	0.92	1.06	1.19	1.30	1.42	1.55	1.67	1.77	1.89	1.99	2.10	2.22	2.32	2,42	2.50		97.2
	934 -		0.23	0.33	0.85	1.07	1.27	1.47	1.66	1.84	2.00	2.16	2.32	2.47	2.62	2.75	2.90	3.05	3.18	3.32	3.45	3.60		115.0
	Carbopol	(M)	0.28	0.35	0.85	1.05	1.23	1.38	1.54	1.68	1.82	1.95	2.07	2.22	2.32	2.+3	2.55	2.67	2.78	2.90	3.00	3.12		201.5
		Phase (% w/w	0.33	1.00	1.39	1.69	1.95	2.17	2.37	2.57	2.76	2.95	3.12	3.28	3.46	3.62	3.77	3.94	4.10	4.24	•	4.53	- cm_2	201.5
Agent	late	Aqueous	0.42	0,40	0.67	0.89	1.12	1.29	1.47	1.64	1.80	1.95	2.10	2.25	2.38	2.51	5.64	2.77	2.90	3.02	3.15	3.26	or Dyne	123.3
Suspending A	Sodium Alginate	Agent in	0.57		1.15	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	5.03	sion Factor	124.5
Sus	So	Suspending	0.73	02.0	1.12	1.45	1.75	2.00	2.23	2.45	2.65	2.83	3.02	3.19	3.33	3.50	3.65	3.80	3.94	4.07	4.22	4.35	ss Conversion	196.3
		Conc. Sı	0.88	0.87	1.35	1.74	2.05	2.32	2.57	2.82	3.02	3.23	3.42	3.60	3.79	3.94	4.10	4.26	74.42	4.57	4.70	4.85	Stress	233.6
			1.03	1.15	1.80	2.27	2.68	3.04	3.36	3.65	3.90	4.16	4.39	4.60	4.80	5.00	5.19	5.35	5.55	5.70	5.87	40.9		233.6
				0.12	•	•	•	•	•	•	•	•	•									• 1		97.7
	Acacia		٠ • ١	0.17	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•		98.2
				0.28	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	• 1		98.2
			1	0.40	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	• 1		98.9
				0.23	-	-	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	• 1		222.5
	Rate of Shear	f)		니 ( 이 i ()	1 0 20 20 11 00	30,0	ر ا ا	Q+Q	775	けつか	ത്. സ് പ	1162	1831	1420	コンナン・シャン・シャン・シャン・シャン・シャン・シャン・シャン・シャン・シャン・シャ	1679	H 908	1537	20ec	71.95	2324	2453		

TABLE 15

FLOW DATA FOR EMULSIONS OF SERIES II
WITH SPAN-IWEEN EMULSIFIER
SODIUM ALGINATE SUSPENDING AGENT

				.57 0.42															7.24 5.32		.2 173.1
		3000		0.73 0			75	10	1 +	 	- 68	<u> </u>	27	 		8	- 81	.35	4.68		4.5 172.
			(-	0.88		28	.24	.55	.63	798	.62	.85	70.		. 2	.8	-10	.58	5.47		373.8 374
	1.5		Phase (% w/w)	1.03	1.30	1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	2.77	3.16	3.51	7.0.7 7.1.4	74.4	4.72	5.00			•	•	•	6.65 6.88	e - cm.2	373.8 3
Stress	sure lb./in?			0.42	0.80	1.54	1.86	2.16	N.4.	, v.	3.29	3.55	3.80	4.03	4.50	4.72	4.95	5.16	5.08	·   '	173.3
Shearing St	zing Pressure	2000	Agent in Aqueous	0.57	1.20	2.4.5	2.75	3.17	3.59	v.= 2000 2000	4.72	5.05	5.38	25	6.32	6.64	6.92	7.19	7.49	Conversion Factor	173.3
SI	Homogenizing		Suspending	0.73	0.74	1.42	1.70	1.94	3 2 2 2 1	2.66	2.84	3.02	3.80	3.53	3.75	3.92	4.07	4.25	4.52	Stress Conver	377.2
			Conc. S	0.88	1.00	1.99	2.23	2.55	78.0	3.38	3.64	3.89	4.11	4.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7.7	4.76	4.97	5.16	5.36	5.57	Str	373.8
				1.03	1.30	2.5	2.85	3.25	3.62	4.25	4.56	2.84	5.12	V . V.	5.88	6.12	6.35	6.57	6.79		1373.8
																			5.07		173.6
		1000		0.57	1.00	9.9	2.45	2.86	X. C		4.26	4.57	4.08	7. TO	5.73	%°9	6.26	6.52	6.76		173.3
																			9.76		155.2
					•		•	•	•		•	•	•			•	•	•	5.35		373.6
					•		•	•	•		•	•	•			•	•		6.57		375.1
		Rate of Shear	Sec.		120 0.00	387	516	949	~ ~~~	1033	1162	1291	1420	1679	1808	1937	2060	2195	2324 2453		

TABLE 15-Continued

				0.42	0.79	1.15	1.51	1.82	2.10	2.38	2.64	20.0 20.0	3. LV	3.62	3.85	4.07	4.2	4.47	7	5.12	5.33		173.6
				0.57	1.15	1.72	8.20	29.2	3.00	3.40	3.77	# ZI	4.43	5.07	5.38	5.68	2.30	0.0 7.0 7.0 7.0 7.0	. 8.9	7.10	7.36		172.5
		2000		0.73	0.76	1.12	1.42	1.70	76.7	2.17	8. 3.38	7.70 1.00	, v	3.15	3.33	3.51	3.00	v 4	4.17	4.33	4.49		324.5
			hase (% w/w)	0.88	1.00	1.72	1.87	2.20	2.52	2.83	89.08		0 0 0 0	10.	4.25	4. 0.7	4.04	4.0.4.0.5.0.5.0.5.0.5.0.5.0.5.0.5.0.5.0.	5.22	5.40	5.58	- cm:2	373.8
ing Stress	Pressure lb./in?		Suspending Agent in Aqueous Phase	1.03	1.33	1.92	2.39	2,80	3.19	3.54	3.87	4 - 7 - 7 -	4 . 4 7 . 4	2.00	5.25	5.50	5.72	8.0		6.62	6.84	Factor Dyne	373.8
Shearing	Homogenizing F			0.42	0.75	1.12	1.45	1.74	2.00	2.29	2.55	2.80		0.4.0	3.72	3.93	4.15	4.30	17.4	76.4	5.18	Stress Conversion Factor	173.1
			Cone.	0.57	1.17	1.72	2.15	5.60	3.00	3.37	3.75	*.08 08	4.42	5.04	5.33	5.64	5.92	. V Q	6.75	7:00	7.27	St	172.8
		000†		0.73	0.75	1.07	1.37	1.63	1.89	2.11	2.31	2.50	N 0	3.05	3.24	3.40	3.58	3.04	4,07	- 22	4.37		376.5
				0.88	0.99	1.45	1.82	2.16	2.45	2.73	3.00	3.24	3.45 0.45	3.93	4.15	4.36	4.55	\$. 50-	+ r	5.30	5.49		375.2
				1.03	1.27	1.87	2.35	2.77	3.12	3.49	3.80	4.10	4.30	76.4	5.16	5,42	5.65	2.87	0,40	6.50	6.74		373.8
		Rate of	Shear Sec.1		129	258	387	516	949	775	406	1033	1162	1420	1549	7679	1808	1937	2002 3019	シュ ユマン マュ ユ	2453		

TABLE 16

FLOW DATA FOR EMULSIONS OF SERIES II WITH SPAN-TWEEN EMULSIFIER TRAGACANTH SUSPENDING AGENT

				0.473	0.37	0.55	0.72	0.87	1.04	1.20	1.35	1.50	1.64	1.77	1.92	2.05	2.19	2.32	2.43	2.57	2.70	2.84	2,98		162.3
				9,9.0	09.0	0.88	1.14	1.37	1.58	1.80	2.00	2.19	2.38	2.55	2.72	2.92	3.07	3.24	3.40	3.58	3.75	3.92	4.08		161.8
		3000		0.818	0.92	1.35	1.70	2.02	2.32	2.58	2.84	3.09	3.33	3.57	3.82	†0 <b>.</b> †	4.25	4.41	4.68	4.89	5.10	5.30	5.50		161.3
			( M,	0.991	1.14	1.63	20.2	2.37	2.70	3.01	3.30	3.60	3.89	4.13	4.39	†9 <b>•</b> †	4.89	5.12	5.35	5.58	5.28	<sub>40</sub> .9	6.25		160.1
	1.		Fnase (% w/w)	1.163	0.70	0.99	1.22	1.43	1.61	1.79	1.95	2.10	2.24	2.39	2.52	2.65	2.79	26.2	3.05	3.17	3.28	3.40	3.52	e - cm. 2	348.5
ess	Pressure lb./in?		in Aqueous Fr	0.473	0.42	19.0	0.84	1.03	1.22	1.39	1.52	1.73	1.89	2.04	2.19	2.35	2.48	2.63	2.78	2.92	3.06	3.20	3.25	Stress Conversion Factor Dyne	163.0
Shearing Stress	ing Pressu	2000	Agent in A	9,79.0	0.75	1.14	1.45	1.74	2.01	2.29	2.54	2.77	3.00	3.22	3.44	3.65	3.87	4.08	4.27	4.48	4.68	78.4	5.07	sion Facto	161.8
She	Homogenizing		Suspending Agent	0.818	1.10	1.59	2.01	2.40	2.74	3.05	3.36	3.65	3.92	4.19	4.45	4.72	4.96	5.20	5.44	5.66	5.90	6.15	6.36	ss Convers	161.3
	#4		Conc. Sus	0.991	1.25	1.82	2.26	<b>2.</b> 66	3.05	3.38	3.73	40.4	4.34	4.62	4.90	5.17	5.44	5.70	5.95	6.20	6.45	69.9	6.93	Stre	160.6
				1.163	0.75	1.08	1.33	1.56	1.76	1.95	2.12	2.30	2.46	2.62	2.75	2.90	3.05	3.19	3.32	3.45	3.65	3.72	3.84		348.5
				0.473	0.45	0.72	16.0	1.16	1.38	1.57	1.75	1.95	2.12	2.30	2.47	2.64	2.80	2.96	3.12	3.26	3.42	3.58	3.72		162.8
		1000		949.0	0.65	1.00	1.32	1.60	1.85	2.12	2.37	2.59	2.77	3.02	3.20	3.42	3.64	3.83	4.01	4.20	04.4	4.59	4.75		161.8
							1.92																		161.3
				0.991	1.37	8.00	2.55	3.00	3.42	3.82	4.18	4.52	4.87	5.17	5.49	5.76	6.05	6.33	6.62	6.87	7.12	7.40	7.65		161.0
				1.163	82	1.17	1.48	1.72	1.95	2.15	2.35	2.51	2.70	2.85	3.01	3.16	3.32	3.46	3.61	3.77	3.87	4.00	4.14		349.6
		Rate of Shear	Sec.	•	129	258	387	516	949	775	†06	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 16- Continued

				0.473	æ. 0 °	0.00	0.83	96.0	1.10	1.23	L.30	7. 7.	1.78	1.92	2.05	2. L. C	0.40	2.55	2.68	2.80		162.3
				9,646	0.54	10°C	1.25	1.45	1.67	1.85	, v	7.66	2.57	2.72	2.83	 	23.6	3.50	3.70	3.86		162.3
		2000		0.818	0.75	07	1.69	1.95	2.20	2.45	, o o	٠٠٠ د د	3.31	3.52	3.72	3.92 20.	. t	4.5	4.69	4.87		161.5
	ત્ય•		.se (% w/w)	0.991	1.15	4.0	2.57	2.95	3.30	3.60	ν. Ον.	+ - - - - - - - - - - - - - -	4.73	4.98	5.22	5.47		6.16	6.38	09.9	.m.=2	159.8
g Stress	ressure lb./in?		in Aqueous Pha	1.163	69.0	٠. در د	1.13	1.51	1.67	1.82	76.1	71.7	2.38	2.50	2.63	2.74	- ac	88.	3.22	3.32	actor Dyne cm.	347.3
Shearing	Homogenizing Pressure		Suspending Agent in Aqueous Phase	0.473	0.36	0.54	0.87	1.02	1.17	1.32	1.47	1.02 1.75	1.89	2.02	2.15	0 0 0	. d	2.65	2.80	2.92	Stress Conversion Factor	162.8
			Conc.	949.0	0.50	0.75	0.y.	1.34	1.54	1.72	1.90	) i c	0,40	2.58	2.74	2.89	ν. Ο (	3.37	3.52	3.67	Stre	161.4
		000†		0.818	0.80	1.18	1.30	2.05	2.32	2.57	& . & .		3.47	3.69	3.89	4,10	. 4 0 0	4.67	4.88	5.07		161.3
				0.991	1.12	1.58	0,0	2.65	2.95	3.24	3.51		4 4 00.4	4.52	77.4	5.02	47.7	7.40	5.92	6.12		160.6
				1.163	1.42	2.00	, v , v	3,25	3.65	3.99	4.30	19.4	+ r.	5.40	5.75	00.9	98.00	77.9	7.02	7.26		161.1
		Rate of	Shear Sec.1	1	129	258	387	949	775	406	1033	1162	1421	1549	1679	1808	1937	7000 1000 1000	2354	2453		

TABLE 17

FLOW DATA FOR EMULSIONS OF SERIES II WITH SPAN-TWEEN EMULSIFIER ACACIA SUSPENDING AGENT

			7.8	0.36	0.0 0.00	1.16	1.41	1.66	1.92	1.0	2.65	2.89	3.12	3.38	χο. Ω ο	7. 10. 10.	4.34	4.58	48.4		
			10.7	0.59			•	•	2.85		•	•	•	•	•	•					
	3000		13.5	•			•	•	20.05 20.05		•	•	•	•	•				• 1		
		۲)	16.4	09.0	1.37	1.75	2.10	2.43	2.75	3.36	3.65	3.95	4.23	4.050	. (O	7 0	71.0	5.82	6.07		
inç		Phase (% w/w)	19.2	0.95	2.08	2.60	3.10	3.59	4.05	76.4	5.32	5.70	9.08	6.45	00.0	7 · · · · · · · · · · · · · · · · · · ·	7.83	8.15	8,48	- cm:-	Ī
ssure lb./in?		Aqueous Phe	7.8	0.36	0.95	1.24	1.53	1.82	0.00	2.64	2.96	3.19	3.45	3.74	20.4	1. t	4.78	5.06	5.32	r Dyne	
Pre	2000	Agent in Ac	10.7	0.52	1.40	1.85	2.27	2.68	3.10	3.92	4.28	4.71	5.12	5.50	200		60.2	7.45	7.85	ion Factor	
Homogenizing		Suspending Ag		0.37		•	•	•	•		•	•	•	•	•			•	•	s Conversion	
		Conc. Sus	16.4	0.55	1.45	1.88	2.31	2.70	3.12	3.87	4.27	t9°t	5.00	5.37	ン・(4 た)・(4	- t- 0.5	6.76	7.10	7.45	Stress	
			1 *1	0 0 0		•	•	•	•		•	•	•	•	•			•	•		
			1 . 1	0.26		•	•	•		•	•	•	•	•	•			•	• 1		(
	1000			0.39		•	•	•		•		•	•	•	•			•	• 1		(
			10	0.60	10	⊣,	9,	άr	٠.		0	r.	ض٠	⇒. ૦	jο	٠.	- 너	9	9		
			1 . !	0.4		•	•	•		•	•	•	•	•	•			•	•		
			100	0.62	1 4	cu ·	9,	٦,	., O.	ر س)		⊣.	7. (	v, r	• - u	, w	·	r.	$\infty$		
	Rate of	Shear Sec:1		1 V V EV V W	387	516	9+9	<i>27.7</i>	1033	1162	1631	1420	1549	16.79	1037	2050	2195	2324	2453		

TABLE 17-Continued

				7.8	0.0 74.0	0.89	٠٠. 90.	1.50	1.70	л Оу.ч Оч	2.30	0, 0, 0,0,0	2.88 88.2	3.07	. v.	3.68	3.87	10:11		158.9	
				10.7	0.00	1.22	1.57	7.8 2.84	2.58	N W	3.50	3.79	-38-	+ - - - - - -	7.75	5.47	5.74	۷.0°		160.1	
		5000		13.5	0.0	0.82	1.05	1.1	1.69	-1 v	2.27	24.7	, d , d	3.01	3.1.X	w.v.	3.70	3.0(		343.2	4
	0.1•		se (% w/w)	16.4	0.69	1.08	 8.	1.00 1.00	2.15	0 0	2.85		3.50	3.70	7. t	4.29	, o, o,	4.68	- cm:2	346.1	1.0.0
ng Stress	Pressure lb./in?		in Aqueous Pha	19.2	0.72	1.67	2.10	2.00	3.26	3.61	4.87	4.57	5,18	7.45	70,5	6.23	6.50	6.75	Factor Dyne	3777 0	7++7
Shearing	Homogenizing		Suspending Agent in Aqueous Phase	7.8	0.50	0.93	1.12	1.31	1.72	رب. دربارد	2.29	2,48	2.07	3.07		3.65	3.87	4.05	Stress Conversion Factor Dyne	0 83 1	170.5
			Conc. S	10.7	04.0 80	1.10	1.40	1.70 989	2.27	ν. 4.σ. 6.α.	3.07	. W. C.	 00.00.	4.76	7. 4. 7. 7. 7.		5.21	5.47	St	13	TOT . T
		7,000		13.5	0.30	0.74 47.0	0.93	1.14	1.52	07.1	2.05	2.20	9. v. v.	2.67	0.00 0.00 0.00	ر. الارد الارد	3.26	3.42		- 1	341.5
				16.4	0.53	ري. وي. ا	1.81	2.19	2.95 2.95	9.30	7.04	4.32	4.62	5.27	5.80	, v	6.52	6.83		0 1110	344.9
				0.01	0.71	2 00	2.12	N.54	3. W. K	3.70	4. 4. 0.4.	7·L-4	5.06	5.70	00.9	0.30	6.0	7.16			347.3
		Rate of Shear	8 8 6 6 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		129	ν κ. Σ τ	516	646 116	00°4	1033	1202	1420	1549 1549	1808	1937	7000 2005 2005	2320	2453			

TABLE 18

FLOW DATA FOR EMULSIONS OF SERIES II WITH SPAN-TWEEN EMULSIFIER SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

			0.92		•	•		•	•	•	•	•	3.50		•	•	•	•			•	5.68		
	3000		1.59	17	$\hat{\sigma}$	7	r.	. 0	·ω	9	0	, M	4.62	0	` ┌	₹.		٠.	cA	5	٠, ۲	- 0		
		(,	) •		•	•	•	•	•	•		•	•	•	•	•	•	•		•		4.57	1	
21		use (% w/w	2.26	, .	•	•	•	•	•		•		•	•								5.85	1	
ure lb./inç		Aqueous Phase	0.92	٠.	•	•	•	•	•	•	•	•	3.61	•	٠	•	•	•	•	5.47	•	•	or Dyne	
ing Pressure	2000	gent in Ac	1.25		•	•	•	•	•	•	•		2.99		•		•						sion Factor	
Homogenizing		Suspending Ae			•	•	•	•	•	•	•	•	4.34	•	•	•		•	•	•	•		ss Conversion	
I		Conc. Susp			•	•	•	•	•				3.29		•		•						Stres	,
		O											3.98											
			100	⁻₹.	9		0	4	$\tilde{c}$	₹.	9		1.92	0	Ġ	$\tilde{\omega}$	<b>→</b> .	$\dot{\circ}$		$\infty$	0	4		
	1000		1.25	•	•	•	•	•	•	•	•	•	3.00	•	•	•	•		•			•		
			1.59	•	•	•	•	•	•	•	•	•	3.65	•	•	•	•	•	•	•	•	•		
				•	•	•	•	•	•	•	•	•	3.07	•	•	•	•	•	•	•		•		
			2.26	$\overset{\circ}{\alpha}$	ĸ.		ᅻ.	_રં.		$\dot{\omega}$	ď	-† '	•	$\dot{o}$	4	r.	ů,	9	$\infty$	0	ď	3		
	ate of	หลุ ๑ ๑ ๑ ๑ • • • • • • • • • • • • • • • •	1	129	258	387	516	9+9	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2050	2195	2324	2453		1

TABLE 18-Continued

				0.92	0.75	1.10	1.40	1.70	1.98	2.24	2.50	2.75	3.0T	0. KV	3.75	3.98	4.22	0 † †	4 ~	÷ п У, г Д, г	5.37			200.0
				1.25	1.15	1.70	2.16	2.60	9. 8.	3.42	3.83	02.	4.50	+ u	5.62	5.95	6.28	0.60	0.Y	77.	7.82			199.6
		2000		1.59	0.95	1.43	1.84	2.22	2.55	2.87	3.19	3.49	00 \ 00 \ 00 \	\$ ~	+ + 109:	4.85	5.10	5.35	00.0	, o	6.28			344.4
	QI•		( % m/m ) e	1.92	69.0	1.05	1.33	1.62	1.92	2.09	2.31	2.52	2.7	S. 6	3.5%	3.44	3.60	3.76	3.92	4.C	4.38	3	- CIII:	679.3
ng Stress	Pressure lb./inệ		Agent in Aqueous Phase	2.26	0.90	1.36	1.75	2.07	2.34	5.66	2.92	3.15	w (	3.00	4.05	42.4	4.43	4.62	4.02	4. 20.4	5.33			679.3
Shearing	Homogenizing		Suspending Agent	0.92	0.77	1.12	1.42	1.72	1.98	2.24	2.50	2.75	2.99		3.73	3.95	4.17	04.4	4.04	4.85	5.30		stress conversion factor = Lyne	200.0
			Conc. Su																		7.64 7.64		,,	198.8
		0001		1.59	1.00	1.47	1,88	2.24	2.60	2.45	3.25	3.66	3.87	4.15	24.4	4.95	5.22	5.47	5.70	5.95	0.10 6.42			340.9
				1.92	0.77	1.14	7,44	1.72	1.99	2.23	2.45	2.65	2.85	3.05	3.23 100	3.60	3.77	3.93	4.10	4.26	4.42			682.8
				١,	• 1 •								•	•				•	•	•	70.7	• •		678.1
		Rate	Shear Sec:1		120	1 0 1 10 1 00	387	516	949	775	±06	1033	1162	1291	1470 1740	1679	1808	1937	2060	2195	7370 7453	27.7		

TABLE 19

FLOW CURVES FOR EMULSIONS OF SERIES OF II WITH SPAN-TWEEN EMULSIFIER, METHYLCELLULOSE SUSPENDING AGENT

				0.676		0.8∂	1.15	1.42	1.70	1.95	2.20	2.42	2.65	2.88	3.10	3.30	3.50	3.73	3.93	4.12	4.33	4.52	4.72		153.6
				0.922	0.70	1.12	1.48	1.82	2.10	2.39	2.67	2.92	3.17	3.42	3.65	3.8	4.12	4.34	4.55	4.77	4.98	5.18	5.40		214.6
		3000		1.168	19.0	1.03	1.35	1.62	1.88	2.13	2.33	2.52	₹2.5	2.92	3.10	3.27	3.45	3.63	3.80	3.95	4.12	4.27	4.42		357.6
			W/w)	1.415	0.82	1.28	1.65	1.98	2.25	2.52	2.75	2.99	3.20	3.40	3.60	3.7%	3.96	4.15	4.32	64.4	4.65	4.81	4.97		441.2
	5·		Phase (%	1.661	1.19	1.80	2.28	2.67	3.05	3.39	3.68	3.95	4.22	4.45	4.69	4.90	5.12	5.33	5.55	5.74	5.93	6.12	6.33	- cm:2	2.044
ess	Pressure lb./in?		in Aqueous	0.676	0.54	06.0	1.20	1.50	1.78	90.7	2.33	2.58	2.84	3.05	3.28	3.50	3.74	3.95	4.17	4.38	7.60	4.80	5.00	· Dyne	154.7
Shearing Stres		2000	Agent	0.922	0.70	1.14	1.50	1.85	2.16	2.45	2.75	3.02	3.22	3.54	3.76	00.	2.50	4.45	4.67	4.89	5.10	5.30	5.52	Conversion Factor	215.7
She	Homogenizing		Suspending	1.168	0.70	1.10	1.42	1.71	1.99	2.55	2,45	2.66	2.88	3,08	3.26	3.45	3.65	3.81	3.98	4.15	4.32	4.48	4.65		357.6
	Ţ		Conc.	1.415	0.85	1.30	1.42	1.99	2.27	2.54	2.79	3.01	3.23	3.44	3.63	3 3 3	0.4	4.10	4.36	4.52	4.69	4.85	5.01	Stress	441.2
				199.1	1.23	1.85	2.35	2.75	3.11	3.45	3.75	†O•†	4.32	4.57	.4 .00.	5.04	5.25	٠. ۵,	5.68	5.89	90.08	6.27	6.47		443.1
				0.676	0.54	36.0	1.28	1.62	1.93	Z. 7.4	2.51	2.80	3.06	3.31	3.57	3.82	4.05	t - 2	4.50	4.73	66.+	5.19	5.40		155.2
		1000		0.922	9.0	1.12	1.50	1.85	2.21	N.52	2.85	3.12	3.38	3.68		4.T8	4.40	+. 0.0.	#. #	5.10	5.32	5.55	5.75		216.4
				1.168	02.0	1.14	1.50	1.82	2.11	2,38	2.64	2.76	3.10	3.37	3.52	3.72	ν. Ν.	0T.4	4.30	4.46	4.69	08.4	4.98		357.5
				1.415	0.62	86.0	1.25	1.50	1.70	26.1	2.07	2.25	2.40	2.55	2.70	7.0 † 0.0	8,78	3.10	3.22	3.33	3.45	3.56	3.66		679.3
				1.661	0.50	0.80	1.00	1.20	1.37	エ・ング	1.67	08.1	1.92		Z.16	K. K. C	۶.38 ا	7.45 V 1.45	Z.5.7	2.67	2.78	2.86	2.95		905.7
		Rate of	Shear Sec.		129	1 Q	387	516	0+0	5	400	1033	7977	1291	07+T	トンキン ン・1	V 0 0 L	TO00	173C	2000	2195	2324	2453		5.1

TABLE 19-Continued

				0.676	0.55	0.93	1.25	1.63	08.1 0.5	7. C	. v. c.	(O. V	 	3.35	3.59	4.00	4.25	94.4	4.68	⊅ r. ∞ c.	12:1		153.9
				0.922	۰.۲	1.22	1.64	1.98	2.33	2 c	00.0	) T . 0	3.70	3.04	4.19	4 - 4.գ	4.87	5.09	5.3	5.50	0 - 1		213.7
		2000		1.168	0.68	1.10	1.45	1.76	2.03	2.27	N. 0	0).	3.12	3.32	3.49	3.67 2.85	 	4.17	4.34	4.50 4.50			357.6
			ase (% w/w)	1.415	0.87	1.35	1.75	2.06	2.35	0.00 1.00	2.05	m (	 	3.72	9.89	* = =	4.43 6.43	1.60	4.76	4 π ως ωα	7	- cm;2	0.444
Shearing Stress	Homogenizing Pressure lb./in?		in Aqueous Phase	1.661	1.20	1.82	2.34	2.75	3.11	3.45	3.75	÷.:	4.31	4.82	5.03		7. 50.	5.89	6.08	6.28	1+.0	Dyne	443.1
Shearin	Homogenizing P		Suspending Agent	0.676	0.58	76.0	1.30	1.62	1.92	8.20	25.40	2.72	, o	3.4	3.68	3.92	4.13 4.35	4.57	4.79	5.00	)•24	ss Conversion Factor	153.6
			Conc. S	0.922	0.70	1.14	1.54	1.89	2.22	2.52	2.80	3.05	3.36		4.05	#.28 #.	4.7%	4.95	5.16	2.38	1 66.6	Stress	213.7
		0007		1.168	0.70	7.14	1.50	1.82	2.10	2.33	2.57	2.82	9.00	3.47	3.60	3.79	) 6	+ · t	. 4 . 4 . 4	4.65	4.81		356.9
				1.415	06.0	7.40	1.80	2.12	2.44	2.70	2.98	3.17	3,40	n m	4.01	4.20	4.30	1.7.7.	7.05	5.07	5.25		437.4
				1.661	1.32	20.02	2.55	3.00	3.37	3.72	4.05	4.33	4.62	4.8.7 0.1	5.38	2.60	5.82	50.0	0.43	6.64	†8 <b>.</b> 9		430.3
		RATE	SHEAR SEC -1	1_	129	1 C	387	516	9+9	775	406	1033	1162	1291	1549	1679	1808	1737	2007 7007	2320	2453		

TABLE 20

FLOW CURVES FOR EMULSIONS OF SERIES II WITH SPAN-TWEEN EMULSIFIER, CARBOPOL-934, SODIUM SALT SUSPENDING AGENT

				0.136	0.43	0.72	96.0	1.20	7.42	1.64	1.86	2.07	2.27	2.45 7.	7.64	2.83	3.02	3.20	3.40	3.58	3.79	3.95	4.17		90.2
				0.185		1.07	1.43	1.77	2.07	2.36	2.63	2.90	3.17	3.43	3.69	3.94	4-19	4.45	4.68	$\dot{\omega}$	٦.	5.39	9		89.5
		3000		0.235	0.75	1.17	1:55	1.87	2.17	2.45	2.73	2.98	3.24	3.48	3.72	3.98	4.23	4.45	7.68	4.92	5.14	5.37	5.58		118.2
				0.285	2.77	1.17	1.47	1.77	2.02	2.29	2.52	2.75	2.98	3.18	3.41	3.62	3.8¢	†0°†	4.25	4.45	4.63	4.83	5.03		158.9
			se (% w/w]	0.334	1.10	1.62	2.05	2.42	2.75	3.09	3.39	3.68	3.96	4.2.4	4.52	22.4	5.04	5.30	5.53	5.78	6.02	6.25	6.50	- cm:2	158.7
383	Pressure lb./in?		Aqueous Phase	0.136	┌.	69.0	0.93	1.15	1.35	1.52	1.76	1.99	2.18	2.36	2.55	2.74	2.92	3.11	3,28	3.46	3.64	3.82	7,00	Dyne	90.4
Shearing Stress	g Pressur		Agent in Ag	0.185	0.70	1.09	1.42	1.75	5.06	2.35	2.62	2.90	3.16	3.41	3.69	3.94	4.19	•	•	•	•	5.40	•	n Factor	89.7
Shea	Homogenizing	2000	Suspending Ag	0.235	69.0	1.07	1.40	1.70	2.00	2.26	2.52	2.79	3.04	3.26	3.50	3.74	3.95	4.19	07.4	7.62	48.4	5.04	• 1	Conversion	118.1
	HC		Conc. Susp	0.285	0.82	1.20	1.55	1.84	2.12	8.39	2.64	2.89	3.12	3.35	3.52	3.86	7.00	4.22	††·†	•	4.85	5.06	•	Stress	1159.4
				0.334				2.48	2.82	3.15	3.46	3.76	4.05	4.34	4.62	4.88	5.16	5.42	2.67	5.93	6.19	6.42	6.88		58.2
				0.136	0.32	0.55	2.77	1.00	1.21	1.43	1.61	1.82	2.00	2.20	2.38	2.57	2.75	2.92	3.11	3.30	3.45	3.65	3.82		89.9
		1000																				5.07		;	89.3
																						7.50			89.1
				0.285	.68	1.07	1.41	1.70	1.98	2.25	2.51	2.75	2.99	3.22	3.45	3.66	3.88	4.17	4.30	4.50	4.70	4.90	5.12		159.3
				0.334	1.00	1.50	1.92	2.28	2.64	2.98	3.30	3.58	3.87	4.16	4.44	4.71	4.97	5.22	5.48	5.72	5.99	6.22	6.47		59.3
		Rate of Shear	Sec_1	1	129	258	387	516	949	775	406	1033	1162	1291	1420	1540	1679	1808	1937	2060	2195	23.24 23.24	2453		

TABLE 20-Continued

				0.136	0.48	0.77	1.05	1.29	1.51	1.76	1.98	2.20	9 9 9	00.0	%. %.	3.17	3.38	3.57 a7.77	0,0	+ - - - - -	4.35		90.2
				0.185	0.73	1.15	1.52	1.85	2.18	24.45	2.75	3.03	3.30	 	00.4	4.34	4.59	4. 4.00.	00.0	5.57	5.80		6,68
		2000		0.235	0.88	1.30	1.70	2.05	2,35	2.64	2.92	3.19	3.47			74.4	4.72	4.95 8.	OT- U	5.65	5.88		118.2
			(% m/m)	0.285	1.6.0	1.37	1.72	2.04	2.34	2.62	2.87	3.12	 	00.0	+ 0°	4.27	4.50	02.4	4 n	5.33	5.55	- cm=2	158.9
Shearing Stress	Pressure lb./in?		Agent in Aqueous Phase	0.334	1.37	1.92	2.36	2.75	3.10	3.45	3.77	60.4	04.4	\$ \$ 0 L	7. t	5.50	5.77	20.9	0 / V r	6.73	7.08	Conversion Factor Dyne -	159.4
Shearin	Homogenizing ]		Suspending Agent	0.136	0.50	0.80	1.05	1.33	1.57	1.80	2.02	2.25	2.46	20.0	70.8	3/26	3.47	3.67	3.00	+ + 0. 0.	4.45	Stress Conversion	L 000
			Conc. Su	0.185	0.77	1.20	1.62	1.95	2.28	2.60	2.88	3.17	3.46	3.73	70.4	4.55	4.80	5.05	5.32		6.05		88 7
		000†		0.235	0.92	1.38	1.75	2.10	2.42	2.73	3.02	3.35	3.58	3.85	4. TO		4.85	5.10	٠	ν. α α	6.05		0 811
				0.285	0.88	1.30	1.65	1.97	2.23	2.50	2.77	3.00	3.25	3.50	3. C	ト.・. ナ トロ・. ナ	4.38	4.60	4.80	5.02	5.43		7 8 7
											•	•	•	•	•			•	•	6.27	6.77		a u
	Rate	of Shear			120	1 0 1 0 1 0 1 0 1 0	700	516	949	775	100	1033	1162	1631	1420	1679	1808	1937	2060	2195	2453		

TABLE 21

FLOW DATA FOR METHYLCELLULOSE SOLUTIONS CORRESPONDING TO EMULSIONS OF SERIES III

		0.326	0.17	0.28	0.38	0.48	0.57	0.68	0.80	06.0	0.99	1.10	1.20	1.30	1.40	1.50	1.60	1.70	1.80	1.90	2.00		55.9
		0.134	0.18	0.30	0.42	0.54	0.05	0.75	0.88	1.00	1.10	1.21	1.32	1.42	1.53	1.64	1.73	1.85	1.95	2.05	2.17		82.5
		0.543	24.0	0.62	0.82	1.02	1.20	1.38	1.57	1.75	1.92	8.09	2.25	24.2	2.57	2.74	2.88	3.05	3.22	3.39	3.57		77.2
Shearing Stress	Lulose (% w/w)	0.65	0.43	0.79	1.14	1.48	1.80	2.10	2.40	2.72	2.98	3.24	3.52	3.81	4.05	4.30	4.52	4.79	5.02	5.25	5.46	Stress Conversion Factor Dyne - cm. 2	67.4
Shearing	Conc. Methylcellulose (% $w/w$ )	0.780	64.0	0.89	1.27	1.62	1.95	2.28	2.57	2.88	3.17	3.42	3.73	3.97	4.21	4.48	4.70	46.4	5.19	5.42	6.14	ress Conversion Fac	82.3
		1.002	0.77	1.39	1.94	2.46	2.92	3.33	3.75	4.12	64.4	4.82	5.17	5.56	5.80	6.12	6.41	6.70	7.00	7.26	7.54	Stı	104.4
		1.170	0.85	1.50	2.05	2.55	3.00	3.40	3.80	4.17	4.50	4.82	5.13	5.42	5.72	5.98	6.25	6.51	6.77	7.02	7.27		146.9
		1.337	0.83	1.45	1.95	2.37	2.76	3.12	3.43	3.72	4.01	4.27	4.52	4.75	5.00	5.20	5.42	5.63	5.83	6.01	6.22		233.6
	kate of Shear	Secil	129	258	387	516	9+9	775	504	1033	1162	1291	1420	1549	1679	1808	1937	5060	2195	2324	24:53		

TABLE 22

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.337% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.68 11.15 12.17 13.17 14.12 14.14 14.15 14.15 14.15 15.17 16.17 1	322.7
		16.2	0.1110 0.000 0.000	323.8
		27.0	0.10 0.10	277.1
Stress	Conc. Oil (% $v/v$ )	32.4	1.11 1.80 2.40 2.85 3.29 3.89 4.05 4.05 6.05 6.05 6.05 6.78 7.24 7.24 7.24 7.24	273.4
Shearing Stress	Conc. Oi	37.9	1.24 2.01 2.59 3.08 3.95 4.66 5.00 5.00 5.31 5.60 6.16 6.42 6.92 7.16 7.40 7.40 7.40 8.63 8.63 8.63 8.74 8.74 8.74 8.74 8.74 8.74 8.74 8.74	273.4
		43.3	8.7.7.7.5.66.65.92 8.7.7.4.88 8.7.7.4.88 8.7.7.4.88 8.248 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	273.4
		48.7	88887777777777777777777777777777777777	273.4
		54.2	9.15 9.15 9.15 9.15 9.15 9.15	273.4
	Rate	Shear	255 255 255 255 255 255 255 255 255 255	

TABLE 23

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.170% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.97	1.71	N. 3.	2.85	3.36	, c.	4.25	49.4	5.00	5.37	5.74	90.9	6.38	6.70	2.00	7.30	7.58	7.85	8.14		147.3
		16.2																		8.15			147.3
		21.6	1.16	1.96	2.65	3.28	3.85	4.35	4.80	5.25	5.68	6.07	6.48	6.85	7.22	7.57	7.89	8.23	8.55	8.87	9.17		6.941
	(	6.75	0.76	1.32	1.77	2.16	2.52	2.87	3.16	3.45	3.75	7.00	4.25	4.48	4.71	4.93	5.15	5.36	5.58	5.79	5.98	yne - cm. <sup>2</sup>	240.7
Shearing Stress	Conc. Oil $(\% \ \mathrm{v/v})$	32.4	0.85	1.47	1.92	2.38	2.76	3.11	3.44	3.75	4.05	4.32	4.57	4.82	5.08	5.32	5.55	5.78	0°.9	6.23	44.9	rsion Factor - Dyne	243.0
		37.9	1.00	1.63	2.13	2.60	3.00	3.37	3.74	4.07	4.37	4.65	4.93	5.20	5.47	5.73	5.97	6.20	6.45	69.9	6.92	Stress Conversion	242.4
		43.3	1.17	1.85	2.45	2.94	3.39	3.80	4.16	4.50	48.4	5.15	5.45	5.74	6.01	6.30	6.57	6.82	70.7	7.34	7.58		237.1
		48.7	1.19	1.85	2.37	2.83	3.24	3.60	3.95	4.27	4.57	÷.85	5.12	5.38	5.65	5.90	6.15	6.38	6.62	<del>1</del> 8°9	7.07		274.1
		54.2	1.50	2.20	2.75	3.24	3.68	4.07	4.45	+•77	5.08	5.38	5.68	5.37	6.25	6.51	6.79	7.05	7.31	7.55	7.80		274.9
	Rate Of Abean	11.0e0	(J)	200	387	576	979	5-5	400	1033	2522	1881	775C	1519	523	i aca	1937	2060	27.35	2324	2+53		

TABLE 24

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.002% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.77	1.36	1.89	2.40	2.80	3.25	3.65	00.4	4.38	4.71	5.02	5.34	2.67	5.97	6.25	6.55	6.82	7.10	7.38		, Q.L
		16.2	0.82	1.49	2.00	2.52	3.00	3.45	3.87	4.29	49.4	5.00	5.35	5.70	6.02	6.37	6.67	6.98	7.30	7.57	7.87		
		21.6	1.01	1.72	2.39	2.95	3.50	7.00	4.45	4.89	5.29	5.70	6.10	24.9	6.83	7.18	7.52	7.85	8.19	8.51	8.82		
	(	27.0	1.07	1.92	2.60	3.25	3.82	4.38	4.88	5.35	5.80	6.25	6.68	7.07	7.47	7.83	8.20	8.55	8.92	9.27	9.65	Dyne - cm <sup>7</sup> 2	
Shearing Stress	Conc. Oil (% v/v)	32.4	1.00	1.71	2.32	2.85	3.35	3.83	4.25	4.65	5.05	5.42	5.79	6.13	6.48	6.82	7.13	64.7	7.75	8.05	8.36	Conversion Factor Dyne	
		37.9	1.18	•	2.75	3.40	3.95	64.4	4.97	5,42	5.89	6.30	6.70	7.10	7.49	7.85	8.20	8.57	8.90	42.6	9.60	Stress Conv	
		43.3	1.18	2.35	3.10	3.75	4.38	4.92	5,42	5.92	6.38	6.85	7.27	7.70	8.10	8.50	8.87	9.25	9.62	9.97	10.34		
		7.84	1.41	2.27	26.2	3.51	4.03	4.52	2,00	5,42	5.85	tz.9	49.9	7.00	7.35	7.71	8.04	8.38	8.70	9.05	9.34		
		54.2	1.87	2.77	3.55		4.81	7.38	200.00	98.99	6.82	7.27	7.69	80.0	8.50	88.88	9.25	9.65	96.6	10.34	10.68		
	Rate of	Secil	129	1 ( 7.50)	387	5.16	0 /± 1 + 0 1	775	10°	1033	7162	1001 1001	1420	1549	1679	1808	1937	2060	2195	23.24	2453		

TABLE 25

FLOW DATA FOR EMJLSIONS OF SERIES III WITH 0.780% METHYLCELLULOSE SUSPENDING AGENT

		10.8	09.0	1.10	1.56	1.98	2.40	2.77	3.15	3.49	3.80	4.12	44.4	92.4	5.07	5.38	5.65	5.92	6.22	6.50	6.73		84.5
		16.2	0.68	1.23	1.71	2.17	2.62	3.02	3.44	3.82	4.17	4.52	4.87	5.19	5.53	5.85	6.20	64.9	6.80	7.09	78-7		83.9
		21.6	74.0	0.87	1.27	1.62	1.95	2.26	2.56	2.85	3.18	3.45	3.70	3.98	4.22	24.4	4.70	4.95	5.19	5.42	5.65		109.3
		27.0	. 63	1.17	1.62	2.01	2.40	2.76	3.12	3.49	3.82	4.15	4.45	4.75	5.07	5.33	5.62	5.89	6.17	6.43	6.70	. Dyne - cm. <sup>2</sup>	109.0
Shearing Stress	Conc. Oil (% v/v)	32.4	0.75	1.32	1.84	2.29	2.74	3.16	3.55	3.93	4.30	79.4	5.02	5.35	5.68	5.98	6.30	6.62	6.92	7.21	7.51	Conversion Factor Dyne - cm. $^2$	109.3
	D	37.9	1.07	1.82	2.50	3.10	3.62	4.15	4.65	5.10	5.57	00.9	6.42	6.83	7.18	2.60	7.98	8.35	8.70	9.07	9.40	Stress Conv	108.7
		43.3	0.82	1.34	1.82	2.27	2.67	3.05	3.43	3.77	4.10	4.42	4.72	5.00	5.31	69.9	5.87	6.14	6.41	99•9	46.9		148.7
		48.7	1.05	1.70	2.27	2.80	3.25	3.70	\$0°±	4.45	4.85	5.20	5.55	5.89	6.22	6.54	6.85	7.16	64.7	7.77	8.05		149.5
		54.2	1.24	1.90	2,46	2.93	3.38	3.83	4.23	4.57	†6.4 	5.27	5.62	5.95	6.27	9.60	9.30	7.19	7.50	7.77	8.07		163.5
	Rate of Cheer	Sec.1	129	258	387	516	949	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 26

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.651% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.54	0.99	1.40	1.81	2.19	2.54	2.92	3.27	3.62	3.94	4.25	4.57	4.87	5.16	5.47	5.75	₹0 <b>.</b> 9	6.33	<b>6.</b> 62			4.73
		16.2	0.34	19.0	0.89	1.15	1.38	1.61	1.84	2.05	2.27	2.47	2.67	2.87	3.05	3.24	3.42	3.60	3.79	3.96	4.14			119.6
		21.6	0.38	0.70	0.98	1.25	1.50	1.74	1.39	2.20	2.43	2.64	2.84	3.05	3.25	3.44	3.65	3.84	4.02	4.23	4.40			119.0
	(	27.0	0.43	0.78	1.10	1.39	1.67	1.94	2.20	2,45	5.69	2.92	3.15	3.37	3.60	3.82	4.02	4.23	4.42	4.63	4.84	- Dame - cm:2	21.5	119.7
Shearing Stress	Conc. Oil (% v/v)	32.4	0.50	06.0	1.25	1.58	1.88	2.17	2.45	2.73	3.00	3.24	3.52	3.78	7.00	45.4	4.47	7.68	4.92	5.13	5.35	Atress Conversion Hactor		121.1
		37.9	09.0	1.07	1.45	1.83	2.19	2.54	2.85	3.17	3.46	3.75	40.4	4.32	4.57	4.82	5.07	5.32	5.57	5.84	6.07	Stress Con		121.1
		43.3	0.75	1.30	1.77	2.22	2.60	3.00	3.39	3.74	4.07	4.39	4.70	2.00	5.28	5.60	5.88	6.17	44.9	6.72	7.00			121.1
		7.84		1.70	2.25	2.75	3.23	3.68	4.10	4.50	7.86	5.21	5.57	5.92	6.25	6.59	6.91	7.24	7.53	7.83	8.14			121.7
		54.2	1.35	2.10	2.77	3.18	3.87	4.35	28.4	5.23	5.67	6.07	6.47	6.88	7.23	7.59	7.95	8.32	8.65	00.6	9.35			121.7
	Rate of Sheer	Sec.1	129	258	387	516	949	775	#00°	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	4282	2453			

TABLE 27

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.543% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.23	0.53	0.76	0.98	1.20	1.42	1.63	1.83	2.04	2.23	2.43	2.63	2.82	3.00	3.18	3.37	3.56	3.74	3.94		11 94
		16.2	0.32	0.58	₹8 <b>.</b> 0	1.10	1.34	1.57	1.82	5.04	2.25	2.48	2.68	2.88	3.10	3.32	3.52	3.71	3.92	4.10	4.32		5 44
		21.6	0.39	0.70	1.00	1.30	1.57	1.85	2.12	2.38	2.62	2.87	3.12	3.35	3.60	3.82	4.05	4.28	4.50	4.73	4.95		1 22
		27.0	94.0	0.82	1.16	1.46	1.80	2.08	2.38	2.67	2.96	3.23	3.50	3.76	4.02	4.27	4.51	77.4	5.01	5.25	5.50	Dyne - cm. <sup>2</sup>	0 44
Shearing Stress	Conc. Oil (% v/v)	32.4	0.54	76.0	1.34	1.71	2.08	2,42	2.75	3.07	3.38	3.72	4.01	4.31	7,60	4.87	5.16	5.45	5.75	6.02	6.30	Stress Conversion Factor Dyne	1 72
		37.9	0.68	1.16	1.62	2.02	2.45	2.84	3.22	3.58	3.95	4.30	4.62	4.97	5.29	5.62	5.92	6.25	6.57	6.87	7.18	Stress Conve	1( 94
		43.3	0.62	1.06	1.47	1.84	2.19	2.52	2.85	3.17	3.47	3.78	4.07	4.34	4.62	4.88	5.15	5.42	5.69	5.95	6.22		103.0
		48.7	18.0	1.40	1.87	2.30	2.75	3.11	3.50	3.87	4.21	4.56	4.88	5.19	5.52	5.83	6.13	6.45	6.74	7.03	7.35		0.501
		54.2	1.23	1.90	2.48	3.02	3.50	3.96	04.4	4.82	5.20	5.62	00.9	6.38	6.75	7.10	7.45	7.80	8.13	8.47	8.82		103 5
	Rate of	Sec.1	129	258	387	516	9+9	775	400	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 28

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.434% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.22	0.37	0.52	29.0	0.82	0.95	1.10	1.24	1.37	1.51	1.65	1.77	1.92	2.03	2.17	2.30	2.43	2.57	2.68		
		16.2	0.22	0.39	0.57	0.74	0.89	1.06	1.24	1.38	1.54	1.68	1.83	1.98	2.12	2.25	2.37	2.50	29.2	2.75	2.92		
		21.6	0.25	94.0	0.65	0.84	1.04	1.22	1.40	1.57	1.75	1.92	2.08	2.25	2.40	2.55	2.73	2.91	3.10	3.24	3.42		
		27.0	0.37	0.65	06.0	1.16	1.42	1.67	1.92	2.14	2.37	2.62	2.85	3.07	3.30	3.52	3.73	3.97	4.18	04.4	4.62	Dyne - cm:2	
Shearing Stress	Conc. Oil (% $\mathrm{v/v}$ )	32.4	0.43	0.77	1.09	1.40	1.70	2.00	2.23	2.56	2.84	3.12	3.38	3.64	3.92	4.17	4.40	99*†	4.92	5.14	5.39	Conversion Factor Dyne - cm:2	
	0	37.9	74.0	0.82	1.15	7.44	1.75	2.03	25.5	2,58	2,85	3.1.8	3.36	3.62	3.87	4.13	4.36	7.60	†8 <b>*</b> †	5.07	5.30	Stress Conve	
		43.3	0.45	0.77	1.08	1.35	1.60	1.85	0.00	2.34	2,57	. 00	3.02	3.23	3.45	3.68	3.88	60•4	4.30	4.50	4.70		
		48.7		00.1	98. [	74, 1	00.	3.30		0.00	3.15	7 T-1	. 60	75°C	4.18	†\t\* \	4.67	4.92	5.17	5.40	5.63		
		54.0	0.75	, ,	j	1 C			0 1 0				\_t \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	0.4	4.32	+ 	4.77	5.01	7.24	7.0	5.70		
	Rate of	Shear ceI	-222	4 () 1 π, 7 α	ν 1 1	ر د رو	7 T C	110	7.5	1007 L	よっている	1000	1457 1400	이 () 11 년 11 년 11 년	707	να. γα. Ι ι -	1937	- 0908	7017	シスプト	24.53		

TABLE 29

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.326% METHYLCELLULOSE SUSPENDING AGENT

		10.8	0.20	0.35	64.0	0.62	0.75	0.88	1.02	1.15	1.28	1.41	1.54	1.68	1.80	1.93	5.06	2.18	2.32	7.5	2.57		55.9
		16.2	0.20	0.34	0.48	0.62	0.7 <sup>4</sup>	0.87	1.03	1.16	1.28	1.42	1.54	1.68	1.82	1.95	2.07	2.19	2.33	2.45	2.57		63.7
		21.6	0.23	0.38	0.52	0.70	0.85	1.00	1.15	1.32	1.47	1.61	1.75	1.92	2.05	2.20	2.35	2.50	2.65	2.78	2.93		2,49
		27.0		0.48	99.0	0.85	1.04	1.21	1.40	1.57	1.77	1.93	2.10	2.27	2.45	2.62	2.77	2.96	3.13	3.30	3.48	Dyne - cm <sup>2</sup>	8,49
Shearing Stress	(^/v)	32.4	0.27	0.46	0.64	0.82	0.99	1.17	1.34	1.51	1.68	1.87	2.03	2.20	2.37	2.53	2.70	2.87	3.05	3.21	3.37	Stress Conversion Factor Dyne - cm. 2	70.0
	Conc. Oil (% v/v)	37.9	0.35	0.59	0.82	1.04	1.26	1.48	1.69	1.89	2.09	2.30	2.50	2.68	2.88	3.08	3.28	3.48	3.68	3.86	4.05	Stress Conv	78.8
		43.3	0.42	0.68	0.98	†2°:	1.47	1.70	1.95	2.18	2.38	2.62	2.85	3.07	3.31	3.52	3.75	3.95	4.17	4.37	4.58		78.3
		48.7	0.63	1.05	1.42	1.80	2.15	2.47	2.80	3.12	3.42	3.73	t-03	4.33	4.61	4.89	5.17	5.46	5.75	6.00	6.30		78.0
		54.2	0.73	1.16	1.52	1.87	2.20	2.51	2.80	3.10	3.38	3.67	3.92	4.18	4.45	02.4	4.95	5.19	5,45	5,69	5.93		104.3
	Rate of	Sec.1	129	258	387	516	0+0	775	±06	1033	1162	1291	1420	1549	1679	1808	1937	5060	2195	2324	2453		

TABLE 30

FLOW DATA FOR SODIUM CARBOXYMETHYLCELLULOSE SOLUTIONS CORRESPONDING TO EMULSIONS OF SERIES III

		0.281	0.18	0.30	0.42	0.54	0.65	0.76	2.87	0.98	1.09	1.20	1.30	1.41	1.51	1.62	1.71	1.82	1.92	2.02	2.12		65.7
		0.562	0.22	0.39	0.57	0.73	0.89	1.05	1.20	1.35	1.49	1.62	1.77	1.90	2.05	2.19	2.32	2.44	2.57	2.70	2.84		88.1
	(w)	692.0	0.52	0.85	1.13	1.45	1.70	1.95	2.20	2.43	2.65	2.88	3.11	3.32	3.53	3.75	3.94	4.15	4.34	4.55	4.75	Ŋ	80.3
Stress	Conc. Sodium Carboxymethyl Cellulose (% w/w)	1.86.0	0.35	99.0	0.95	1.21	1.46	1.73	1.95	2.17	2.42	2.62	2.84	3.03	3.23	3.42	3.61	3.80	3.98	4.15	4.32	Conversion Factor Dyne - cm=2	113.9
Shearing Stress	, Sodium Carboxymet	1.153	0.52	46.0	1.32	1.65	1.98	2.27	2.56	2.83	3.12	3.37	3.62	3.87	4.10	4.37	4.52	4.75	4.95	5.17	5.38	Stress Conversion Fe	0 761
	Conc	1,265	0.47	0.84	1.17	1.46	1.76	2.04	2.28	2.50	2.75	2.97	3.19	3.40	3.60	3.77	3.99	4.18	4.36	4.53	4.72	Ω	7 91/1
		1.476	0.70	1.25	1.75	2.13	2.52	88	3.25	3.57	8.6		4.48	4.75	5.02	5.27	5.52	5.77	6.01	6.25	6,49		0 0/(1
		1.687	0.62	1.07	1.45	1.80	0	0.40	2.67	10.0	. 0	いい、	~ 64 *•64	3,85	4.05	4.25	44.4	4.63	-t-	5.00	5.17		035
	Rate of	Shear	200	1 0 0 0 0	387	516	- CT/	775	\_t - 0	1001	1001 r	1001	1 C C T C C C C C C C C C C C C C C C C	1549	1,679	1808	1937	2060	2195	4080	2453		

TABLE 31

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.687% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	0.73	1.20	1.62	1.98	2.32	2.65	2.95	3.07	3.52	3.75	4.02	4.27	4.48	4.71	4.92	5.14	5.34	5.57	5.75		232.6
		16.2	0.89	1.42	1.85	2.26	2.65	3.00	3.35	3.67	3.98	4.26	4.52	4.80	5.06	5.29	5.54	5.77	9.00	6.24	6.48		235.2
		21.6	1.00	1.57	2.08	2.52	2.95	3.35	3.72	90.4	04.4	4.70	5.00	5.28	5.57	5.84	6.11	6.37	6.62	6.88	7.12		234.2
	v)	27.0	1.13	1.75	2.27	2.75	3.21	3.65	4.03	4.47	4.75	5.10	5.45	5.75	6.05	6.35	49.9	6.92	7.20	7.47	7.74	Dyne - cm.	232.3
Shearing Stress	Conc. Oil (% v/v)	32.4	1.32	2.00	2.66	3.15	3.67	4.12	4.58	4.98	5.39	5.76	6.15	6.50	6.85	7.17	7.50	7.82	8.10	8.40	8.69	Stress Conversion Factor Dyne	230.2
		37.9		2.30	3.00	3.55	4.12	4.63	5.14	5.60	6.05	64.9	6.90	7.30	7.68	8.05	8.40	8.75	9.07	04.6	9.72	Stress Conv	227.7
		43.3	1.45	2.20	2.78	3.37	3.86	4.33	4.75	5.18	5.59	5.98	6.35	6.71	7.05	7.39	7.71	8.04	8.35	8.64	8.95		298.8
		48.7	1.23	1.82	2.33	2.80	3.23	3.60	3.98	4.32	4.65	4.97	5.28	5.53	5.89	6.15	6.42	02.9	6.97	7.21	7.47		388.9
		54.2	1.30	2.32	2.93	3.48	3.96	4.44	†8 <b>*</b> †	5.26	5.66	6.03	6.40	6.75	7.10	7.43	7.74	8.07	8.37	8.66	8.97		378.4
	Rate of Shear	Sec:1	129	258	387	516	949	775	<sub>7</sub> 06	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 32

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.476% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	%.°	1.52	2.02	2.50	2.94	3.35	3.75	4.12	4.47	4.81	5.14	5.46	5.77	90.9	6.37	99.9	†6 <b>.</b> 9	7.23	7.50			144.9
		16.2	1.04	1.67	2.20	2.69	3.15	3.60	4.01	04.4	4.78	5.14	5.49	5.84	6.16	6.47	6.79	7.10	7.41	7.70	8.00			142.7
		21.6	1.23	1.93	2.50	3.00	3.55	<sup>†,</sup> 0. <sup>†</sup>	64.4	4.93	5.33	5.75	6.13	6.50	6.87	7.21	7.55	7.89	8.23	8.55	8.88		\I	146.5
STRESS	Conc. Oil (% v/v)	27.0	0.76	1.18	1.52	1.88	2.20	2,48	2.75	3.02	3.27	3.54	3.78	4.01	45.4	*******	4.65	4.86	5.07	5.27	5.48		Stress Conversion Factor Dyne - cm. 2	262.9
SHEARING STRESS	Conc. Oi	32.4	0.98	1.49	1.87	2.26	2.65	3.00	a	3.66	3.96	- 50°-	4.53	4.87	5.07	ر س س	5.60	5.85	6.10	6.34	6.58		ress Conversion Fa	262.9
		37.9	1.27	1.88	44.8	2,93	3,40	3.85	4.23	09*1	4.98	5.32	5.69	000	48.9	99.9	6.97	7.27	7.57	7.87	8.16		St	262.1
		148.7	05.1	0 0	2.78	34.50	3,05	04.4	4.87	ייי ר	100		6.50	06.9	20.50	7.62	7.97	- w	2000	8.96	9.27			262.1
		5.4.5	1 83	72.0	, w		000	5.37	70.1	L'-	- a + 0	) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) (	7.93	, o		†a, o	09.0	\\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\	10.49	) to 0.	11,25			1 090
	Rate of	Shear Sec-1	120	4 C V α	2 c 2 c 1 c	ر ا ا	7.T.O.	775	706	400 1	1007 0711	1201	1674	1420 15/10	7477 0770	7 C C C C C C C C C C C C C C C C C C C	1037	- O	2003	7771	7,173	07.1		

TABLE 33

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.265% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	0.82	1.38	1.85	2.29	2.70	3.12	3.53	3.88	4.26	4.60	†6 <b>•</b> †	5.24	5.57	5.91	6.20	6.50	6.81	7.11	7.43		114.0
		16.2	1.00	1.61	2.13	2.62	3.15	3.57	7.00	74.42	4.78	5.17	5.55	5.95	6.26	09.9	46.9	7.27	7.60	7.92	8.23		114.0
		21.6	1.00	1.62	2.13	2.62	3.07	3.51	3.95	4.35	4.72	5.12	5.47	5.82	6.18	6.51	6.85	7.17	7.49	7.79	8.12		123.9
	(,	27.0	1.15	1.77	2.35	2.87	3.40	3.87	4.32	4.74	5.14	5.56	5.96	6.35	6.73	7.12	7.47	7.82	8.16	8.52	8.87	Dyne - cm <sup>-2</sup>	126.4
Shearing Stress	Conc. 0il (% v/v)	32.4	1.37	2.07	2.73	3.33	3.65	4.48	4.97	5.47	5.95	6.42	6.87	7.29	7.73	8.16	8.56	8.96	9.37	9.75	10.12	Stress Conversion Factor Dyne - cm. 2	125.0
		37.9	1.77	1.19	1.54	1.85	2.16	2.45	2.72	3.00	3.25	3.50	3.74	3.97	17° t	††* †	4.66	4.89	5.10	5.31	5.52	Stress Conve	7.776
		43.3	0.98	1.44	1.85	2.24	2.62	2.95	3.29	3.60	3.91	. 4.22	64.4	4.77	5.04	5.30	5.57	5.83	6.07	6.32	6.58		3,46.3
		148.7	1.20	1.75	2.24	5.69	3.12	3.53	3.00	4.27	4.63	4.95	5.29	5.62	5.92	, 5.5 . 0	6.53	6.84	7,12	7.41	7.68	,	9 1790
		54.2	1.45	2.11	2.70	3,25	3.74	4.22	4.63	5.07	5,16	7,88	6.26	6.63	6.9	7.33	7.68	8,01	8.33	8.67	8,98		0 090
	Rate of	Sec.1	129	258	387	516	9+9	775	406	1033	1162	1291	1400	1549	9291	1808	1937	2060	2195	2324	2453		

TABLE 34

FLOW DATA FOR EMULSIONS OF SERIES III WITH 1.153% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	0.63	1.07	1.48	1.81	2.13	2.46	2.77	3.07	3.35	3.65	3.89	4.17	††† †	4.70	4.95	5.18	5.43	5.68	5.90		124.9
		16.2	0.72	1.19	1.58	1.94	2.39	2.64	2.96	3.28	3.58	3.89	4.20	4.45	4.74	2.00	5.25	5.52	5.79	6.05	6.29		125.4
		21.6	0.86	1.36	1.79	2.17	2.55	2.92	3.27	3.62	3.95	4.28	4.59	4.88	5.19	5.49	5.78	6.07	6.35	6.63	6.90		124.9
	( A	27.0	1.02	1.59	2.05	2.50	2.95	3.34	3.74	4.15	4.50	4.85	5.20	5.57	5.91	6.25	6.57	6.89	7.20	7.50	7.83	Dyne - cm.2	124.5
Shearing Stress	Conc. Oil (% $v/v$ )	32.4	1.28	1.94	2.45	2.97	3.45	3.92	4.38	4.81	5.22	5.65	6.07	94.9	6.85	7.22	7.59	7.96	8.33	8.68	9.02	Stress Conversion Factor	124.8
		37.9	1.50	2.20	2.80	3.40	3.95	4.48	5.00	5.46	5.95	6.43	<b>6.</b> 88	7.34	7.77	8.20	8.62	9.05	9.43	9.85	10.25	Stress Conv	124.1
		43.3	0.88	1.28	1.62	1.93	2.25	2.54	2.82	3.10	3,36	3.62	3.87	4.12	4.35	4.59	4.82	5.05	5.27	5.50	5.72		261.2
		48.7	1.10	1.57	2.98	2.36	2.72	3.07	3.40	3.73	4.05	4.34	t9.t	4.93	5.21	5.49	5.76	6.03	6.32	6.57	6.83		259.6
		54.2	1.38	1.95	2.45	2.92	3.37	3.80	4.19	4.56	4.93	5.30	5.65	00.9	6.33	99.9	8.9	7.29	2.60	7.96	8,22		259.5
	Rate of Shear	Sec.1	129	258	387	516	949	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 35

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.984% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	0.52	0.88	1.22	1.51	1.80	2.07	2.38	<b>5.66</b>	26.2	3.18	3.42	3.68	3.92	4.13	4.38	4.57	4.81	5.04	5.24		114.3
		21.6	0.70	1.14	1.52	1.87	2.23	2.56	2.88	3.19	3.50	3.81	4.10	4.38	4.65	4.90	5.17	5.45	5.70	5.95	6.22		113 3
		27.0	0.89	1.36	1.80	2.20	2.62	2.99	3.36	3.72	70.4	04.4	η <b>.</b> 74	5.06	5.37	5.68	5.97	6.27	6.57	6.87	7.17	0.1	0 71.1
Stress	(n/n %)	32.4	1.03	1.60	2.07	2.52	2.98	3.43	3.82	42.4	4.60	4.97	5.34	5.70	90.9	6.41	6.75	7.10	7.47	47.7	8.07	Stress Conversion Factor Dyne - cm. $^2$	0 7/11
Shearing	Conc. Oil (% v/v)	37.9	1.27	1.93	2.52	3.04	3.58	4.09	4.58	5.03	5.49	5.95	6.38	6.81	7.21	7.63	8.02	8.43	8.81	9.39	9.57	ress Conversion Fa	7 1/11
		43.3	1.41	2.05	2.68	3.20	3.70	4.27	77.4	5.25	5.72	6.17	6.61	7.03	7.46	7.88	8.30	8.70	80.6	64.6	9.88	St	0 261
		7.84	1.43	2.08	2.68	3.24	3.77	4.28	77.4	5.24	5.71	6.16	9.60	7.00	7.42	7.83	8.24	8.63	9.01	9.39	9.76		1, 17.
		5,4.2	0.83	1.23	1.55	1.87	2.17	2.45	2.72	2.98	3.24	3.48	3.73	3.97	4.19	4.41	4.62	4.83	5.05	5.26	5.47		1/ 800
	Rate of Shear	Sec.1	129	258	387	516	949	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2050	2195	2324	2453		

TABLE 36

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.769% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	0.38	0.85	1.13	1.45	1.70	1.95	2.20	2.43	2.65	2.88	3.11	3.32	3.53	3.75	3.94	4.15	4.34	4.55	4.75		80.3
		16.2	0.45	0.76	1.03	1.25	1.50	1.72	1.92	2.14	2.35	2.57	2.77	2.98	3.18	3.37	3.57	3.78	3.97	4.15	4.33		106.14
		21.6	0.58	0.90	1.20	1.47	1.72	1.96	2.21	2.45	2.68	2.93	3.17	3.39	3.62	3.84	4.05	4.27	4.48	4.68	4.90		106.6
		27.0	0.68	1.04	1.35	1.64	1.92	2.20	2.46	2.74	3.00	3.25	3.52	3.77	h.02	4.27	4.48	4.73	76.4	5.18	5.43	Dyne - cm. 2	1 80 1
Shearing Stress	Conc. Oil (% v/v)	32.4	0.85	1.26	1.60	1.93	2.25	2.57	2.90	3.20	3.50	3.82	4.10	4.38	4.67	4.93	5.20	5.48	5.75	6.02	6.28	Stress Conversion Factor Dyne - cm.2	0 001
	ŭ	37.9	1.03	1.49	1.89	2.26	2.68	3.03	3.38	3.74	4.07	4.42	4.74	5.05	5.38	5.72	6.02	6.34	t9 <b>.</b> 9	6.95	7.27	Stress Conve	0.00
		43.3	1.27	1.79	2.28	2.73	3.18	3.62	4.02	4.43	4.82	5.22	5.61	6.00	6.38	6.75	7.12	7.47	7.84	8.18	8.54		2 00 1
		7.84	1.27	1.77	2.24	2.68	3.06	3.49	3.88	4.26	4.63	4.98	5.36	5.73	6.07	6.42	6.72	60.7	7.43	7.75	8.07		0 001
		54.2	1.57	2.24	2.80	3.34	3.83	4.32	4.79	5.25	5.70	6.16	6.58	7.00	7.41	7.83	8.20	8.60	9.00	9.38	9.75		0 061
	Rate of Shear	Sec.1	129	258	387	516	646	775	406	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 37

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.562% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

		10.8	0.31	0.52	0.73	06.0	1.07	1.25	7.42	1.59	1.76	1.93	2.10	2.26	2,42	2.58	2.74	2,90	3.06	3.21	3.38			88.1	
		16.2	0.39	0.64	0.86	1.06	1.27	1.48	1.68	1.88	2.08	2.27	2.48	2.67	2.86	3.04	3.22	3.40	3.57	3.76	3.94			87.6	
		21.6	0.45	0.75	66.0	1.22	1.46	1.69	1.92	2.15	2.39	2.62	2.83	3.06	3.27	3.47	3.68	3.89	4.08	4.29	4.50			88.1	
		27.0	0.58	0.89	1.15	1.43	1.70	1.97	2.22	2.50	2.75	3.00	3.25	3.48	3.72	3.97	4.20	†† <b>*</b> †	4.68	4.92	5.14	C	- Dyne - cm:	87.6	
Shearing Stress	Conc. Oil (% v/v)	32.4	0.72	1.05	1.38	1.72	2.03	2.34	2.65	2.95	3.25	3.52	3.79	4.08	4.37	†9°†	4.92	5.19	5.45	5.75	5.98	1	Stress Conversion Factor Dyne - cm.	4.78	
		37.9	0.88	1.29	1.68	2.05	2.42	2.80	3.15	3.50	3.84	4.17	4.50	4.82	5.17	5.49	5.80	6.11	6.41	6.71	7.00		Stress Con	4.78	
		43.3	02.0	1.15	1.48	1.80	2.12	2,42	2.75	3.04	3.33	3.65	3.92	4-23	8 <sup>†</sup> • †	4.77	5.03	5.30	5.58	5.84	6.12			111.6	
		48.7	0.72	1.07	1.36	1.66	1.95	2.22	2.50	2.77	3.03	3.29	3.55	3.79	†0°†	4.28	4.50	4.74	±- 86.±	5.22	5.55			155.9	
		54.2	0.95	1.39	1.75	2.12	2,48	2,82	3.16	3.48	3.82	4.12	U. + . + .	4.77	2.00	5.30	5.58		6.16	6.42	6.70			155.2	
	Rate of Shear	Sec-1	129	258	387	516	949	775	†06 †	1033	1162	1291	1420	1549	1679	1808 1808	1937	2060	2195	2324	2453				

TABLE 38

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.281% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT

Shearing Stress	Conc. Oil (% v/v)	10.8	0.26	0,40	0.55	0.68	0.80	0.95	1.07	1.20	1.34	1.48	1.60	1.72	1.85	1.98	2.10	2.24	2.35	2.47	2.57		65.7
		21.6	0.32	0.48	t-9°0	0.78	0.93	1.07	1.22	1.39	1.53	1.68	1.83	1.98	2.12	2.27	24.2	2.57	2.70	2.83	2.97		65.7
			0.33	0.52	0.68	0.83	1.00	1.16	1.33	1.50	1.65	1.82	1.97	2.12	2.29	2.43	2.60	2.75	2.90	3.03	3.19		9.69
		27.0	04.0	09.0	0.80	76.0	1.17	1.38	1.57	1.75	1.94	2.12	2.32	2.49	2.68	2.86	3.05	3.22	3.40	3.57	3.75	Dyne - cm. <sup>2</sup>	4.69
		32.4	0.42	09.0	0.78	0.98	1.17	1.36	1.56	1.74	1.92	2,10	2.27	2.47	2.65	2.82	3.00	3.18	3.36	3.52	3.69	Stress Conversion Factor Dyne - cm. 2	80.08
		37.9	0.50	0.74	96.0	1.19	1.42	1.63	1.85	2.07	2,28	2.50	2.71	2,92	3,12	3.34	3.54	3.74	36.8	4.15	4.35	Stress Conve	BO 3
		43.3	0.61	0.89	1.14	1.40	1.66	1.93	2.18	2.43	2.69	26.2	3.18	3,42	3.67	3.91	4.15	4.37	7,09	78.4	5.07		77 5
		7.84	0.57	0,82	1.07	- 25-1	1,55	1.80	2.02	2.25	2.78	2.64	2,92	۲, ۶	3.35	3.57	3.77	3.97	- 0-7	4.30	4.00		7 80 1
		54.2	0.66	0.97		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1.79	2.05	5.50	25.5	02.0		3.27	3.50	0 / C	3.06	7.7	04.4	クン. t	10.4	5.07		3 101
	Rate of chos	Sec. 1	129	1 0 0 1 0 0 1 0	307	516	0.4C 0.4C	775	106 106	1033	1760	1291	1700	J740	7679	1808	1937	0000	70.0 70.0	<b>へいさい</b> たのでの	2453	) ) )	

TABLE 39

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.187% CARBOPOL-934, SODIUM SALT SUSPENDING AGENT AND THE CORRESPONDING SUSPENDING AGENT SOLUTION

	Conc. Oil (% v/v)	0.0	0.38	0.58	0.36	0.92	1.06	1.22	1.36	1.50	1.62	1.75	1.87	2.00	2.12	2.24	2.37	2,49	2.61	2.74	2.83		79.3
		16.2	0.35	0.54	0.74	0.88	1.05	1.20	1.37	1.50	1.65	1.80	1.93	2.07	2.20	2.33	2.46	2.57	2.73	2.84	2.99		80.3
			0.33	0.52	0.72	0.87	1.05	1.22	1.38	1.52	1.67	1.83	1.97	2.12	2.25	2.39	2.53	2.67	2.80	2.93	3.07		80.5
		21.6	0.37	0.57	0.78	0.93	1.15	1.32	1.49	1.65	1.82	1.98	2.15	2.30	2.45	29.2	2.75	2.92	3.07	3.18	3.35	- cm:2	81.2
ng Stress		27.0	0.41	1.9.0	0.86	1.07	1.26	1.47	1.65	1.83	2.00	2.19	2.35	2.53	2.70	2.88	3.04	3.20	3.38	3.52	3.69	actor Dyne -	81.4
Shearing		32.4	94.0	0.76	0.99	1.26	1.47	1.70	1.90	2.13	2.33	2.54	2.75	2.95	3.15	3.34	3.52	3.71	3.92	4.08	4.27	Stress Conversion Factor	82.3
		37.9	0.57	0.93	1.23	1.51	1.80	2.05	2.30	2.56	2.82	3.03	3.26	3.49	3.73	3.93	4.16	4.37	4.57	4.80	4.98	Str	82.3
		43.3	0.86	1.29	1.68	2.02	2.37	2.70	3.00	3,32	3.60	3.88	4.17	4.43	4.70	76.4	5.24	5.48	5.75	00.9	6.25		82.3
		48.7	1.40	2.00	2.52	3.00	3.43	3.84	†√5°†	09.4	4.97	5.33	5.67	00.9	6.34	6.67	- 86.9	7.30	7.60	7.88	8.16		82.3
		64.2	11.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.									7.43		109.8									
-	kate of Shear	Sec.1	129	258	387	516	949	775	<del>1</del> 06	1033	1162	1291	1+20	1549	1679	1808	1937	2060	2195	2324	2453		

TABLE 40

FLOW DATA FOR EMULSIONS OF SERIES III WITH 0.125% CARBOPOL.-934, SODIUM SALT, SUSPENDING AGENT AND THE CORRESPONDING SUSPENDING AGENT SOLUTION

Shearing Stress		0	0.19	0.33	74.0	0.55	0.66	0.76	0.87	1.00	1.07	1.17	1.27	1.37	1.48	1.57	1.67	1.76	1.86	1.94	2.06		53.0
		10.8	0.19	0.31	0.42	0.54	0.64	0.74	0.83	46.0	1.03	1.13	1.22	1.31	1.41	1.51	1.58	1.69	1.78	1.87	1.97		4.09
		21.6 16.2	0.24	0.36	0.48	0.59	0.70	0.82	0.92	7.04	1.14	1.25	1.34	1.45	1.57	1.67	1.77	1.87	1.99	2.09	2.18		8.09
			0.22	0.33	0.45	0.57	69.0	0.78	0.90	1.01	1.10	1.21	1.31	1.42	1.53	1.63	1.75	1.84	1.94	2.04	2.14	- cm-2	70.8
	Conc. 011 (% v/v)	27.0	0.26	0.39	0.53	99.0	0.78	0.92	1.04	1.17	1.30	1.44	1.57	1.69	1.81	1.92	2.05	2.16	2,28	2.39	2.52	Stress Conversion Factor Dyne - cm. 2	4.07
		32.4	0.28	74.C	0.65	0.82	0.99	1.16	1.31	1.45	1.60	1.75	1.90	2.05	2.20	2.35	2.50	2.64	2.80	2.94	3.10	ress Conversion	72.6
		37.9	0.37	09:0	0.82	1.04	1.25	1.45	1.65	1.84	2.03	2.22	2.38	2.54	2.70	2.94	3.11	3.30	3.46	3.62	3.81	St)	72.6
		43.3	0.53	0.87	1.16	1.43	1.70	1.98	2.23	2.47	2.70	2.93	3.15	3.39	3.60	3.83	40.4	4.27	84.4	t- 68	4.89		72.2
		48.7	0.89	1.36	1.75	2.11	2,46	2.80	3.10	3.42	3.72	00.4	4.29	4.57	4.83	5.10	5.38	5.62	5.90	6.17	6.42		71.9
		54.2	1.08	1.57	1.97	2.32	2.65	2.95	3.24	3.53	3.81	70.4	4.34	4.58	4.83	5.07	5.32	5.57	5.80	6.03	6.28		4.86
	Rate of Shear	Sec.1	129	258	387	516	949	775	904	1033	1162	1291	1420	1549	1679	1808	1937	2060	2195	2324	2453		

## Treatment of the Data

## Selection of a Flow Equation

Since the Ree-Eyring equation represents a theoretical approach to non-Newtonian flow, it was decided to test it on flow data for emulsions. The equation may be written:

$$V = \frac{n}{2} \frac{x_n \beta_n}{\alpha_n} \frac{\sinh^{-1} \beta_n S}{\beta_n S}.$$

Because of the occurrence of one of the constants,  $\frac{\beta_n}{n}$ , in the inverse hyperbolic sine function this equation is difficult to apply. The methods which have been used have involved assumptions regarding the shape of flow curves, extrapolations of curves well beyond the range of measurement and insertion of approximate values for certain of the constants.

Ree and Eyring<sup>12</sup> proposed graphical methods for evaluating  $\underline{\beta}_n$  for systems requiring up to three components to describe the flow. The simplest case was that of a Newtonian system where  $\underline{\beta}_n << \underline{1}$  and  $\underline{\underline{h}}$  is equal to  $\underline{x}_1 \, \underline{\beta}_1 / \underline{\alpha}_1$ . For a system with a Newtonian and one non-Newtonian component the equation becomes:

Since the last portion of the right side of the equation approaches zero at high rates of shear, it was reasoned that only the Newtonian component, called \( \frac{1}{20} \), is measured under these conditions. Accordingly, Ree and Eyring obtained the value of \( \frac{1}{20} \) by extrapolation of the curve relating

 $\frac{1}{2}$  and  $\frac{1}{2}$  to zero value of  $\frac{1}{2}$ . The flow equation was then expressed as:

$$\frac{1}{2} - \frac{x_2 \beta_2}{x_2} = \frac{\sinh^{-1} \beta_2 s}{\beta_2 s}$$

Following this  $\frac{1}{2} - \frac{1}{2}$  was plotted  $\frac{1}{2} \cdot \frac{1}{2}$  as the intercept on the S axis, the hyperbolic function going to  $\frac{1}{2}$  as S approaches zero:

$$\lim_{s \to 0} \sqrt{-\gamma_{\infty}} = \frac{x_2 \beta_2}{\ll 2}.$$

Having thus described the evaluation of  $x_1 \not \beta_1/\chi_1$  and  $x_2 \not \beta_2/\chi_2$ , Ree and Eyring did not present a method for determining the value of  $\beta_2$ , but it is assumed that they utilized the approximation,  $\sinh^{-1}\beta_2 S \simeq \ln 2\beta_2 S$ , for high values of  $\underline{S}$ . If the parameters determined in this manner reproduced the curve satisfactorily they concluded that the system had flow units belonging to these two groups only.

For a system requiring three groups to describe its flow, one of the groups being Newtonian, the curve of  $\underline{\underline{N}}$  vs.  $\underline{\underline{S}}$  would rise sharply in the low range of  $\underline{\underline{S}}$ . The part of the experimental curve corresponding to high values of  $\underline{\underline{S}}$  was extrapolated to zero value of  $\underline{\underline{S}}$ , and the parameters for the first two components were evaluated as in the previous case. The parameters for the third component were calculated from the equation:

$$\gamma - \gamma_{\infty} - (\frac{x_2 \beta_2}{\cancel{\sim} 2} \frac{\sinh^{-1} \beta_2 S}{\cancel{\beta}_2 S}) = \frac{x_3 \beta_3}{\cancel{\sim} 3} \frac{\sinh^{-1} \beta_3 S}{\cancel{\beta}_3 S}.$$

For a system of two non-Newtonian and no Newtonian components an approximate equation was written in terms of shearing stress:

$$F = \underbrace{x_1 \beta_1}_{A \pm} S + \underbrace{x_2}_{A \pm} \ln 2S + \underbrace{x_2}_{A \pm} \ln \beta_2.$$

The first right hand term was evaluated from data representing low rates of shear, and the other two terms approximated from high shear data. From these values approximate viscosities,  $\frac{1}{2}$ , were calculated.  $\frac{9}{2}$  was then obtained from the following relationship using high values of  $\frac{5}{2}$  only:

$$\eta^{1} - \eta = x_{1}\beta_{1} \quad (1 - \frac{\sinh^{-1}\beta_{1}S}{\beta_{1}S}).$$

This method gave approximate values for the parameters which were judged by the fit of the equation to experimental data.

Other methods for evaluation of parameters of the Ree-Eyring equation were described by Maron and Pierce<sup>17</sup> and Maron and Sisko<sup>98</sup>. For a system requiring one Newtonian and one non-Newtonian component, the equation was written in the form:

$$\gamma = a + b \frac{\sinh^{-1} 2S}{2S} ,$$

where  $\underline{a}$  is  $(x_1 \beta_1/\alpha_1)$  and  $\underline{b}$  is  $(x_2 \beta_2/\alpha_2)$ . Values of  $\underline{\beta}_2$  were arbitrarily selected and plots of  $\underline{\gamma}_2$  versus  $(\sinh^{-1}\beta_2 S/\beta_2 S)$  were made. Values of  $\underline{\beta}_2$  were adjusted until a linear graph was obtained. A similar method was used for a system with one Newtonian and two non-Newtonian components.

In attempting to apply the Ree-Eyring equation to emulsions and solutions of suspending agents it was found that curves relating  $\underline{\gamma}$  and  $\underline{1/S}$  were continuously curved throughout and that extrapolation was not reasonable. A curve of this type is illustrated in Fig. 4.

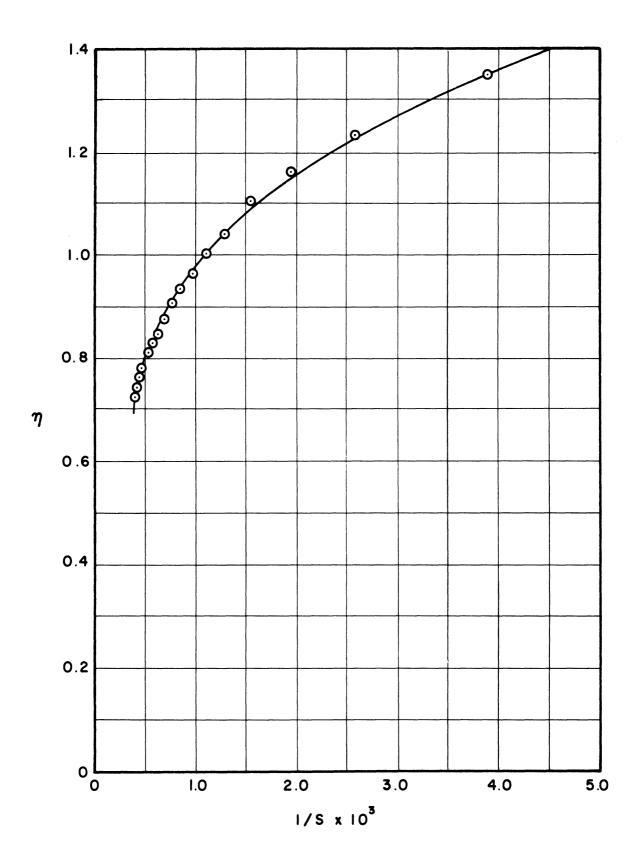


Fig. 4. Plot of  $\underline{\eta}$  Versus  $\underline{1/S}$  for the Ree-Eyring Equation; 1.17% Methylcellulose Solution of Series II

Further, when a value of  $\frac{1}{2}$  was taken from the graph and  $\frac{1}{2}$  plotted vs. S, this curve was also non-linear throughout, making extrapolation difficult. Attempting the graphical method for a three-component system showed, again, that one would need to extrapolate a curved line well beyond the range of its measurement.

When the method of Maron and co-workers was attempted it was found that little change in curves of  $\underline{\underline{\gamma}}$  vs.  $\sinh^{-1} \underline{\beta}_2 s/\underline{\beta}_2 s$  occurred with large change in arbitrarily-selected values of  $\underline{\underline{\beta}}_2$ . Thus, a wide range of  $\underline{\underline{\beta}}_2$ , as much as ten- or twenty-fold, gave essentially the same slopes, and there was little basis for acceptance of any one value.

From these results it was concluded that, however desirable it may be to utilize the equation of Ree and Eyring, there is yet no satisfactory method for determination of its parameters. A similar comment was made by Maron and Krieger who stated that although the Ree-Eyring theory looks very promising as a general flow law, the equations yielded by this theory are difficult and tedious to handle and the parameters of the equation are not always easily interpretable.

Although Williamson's equation, when applied by means of least squares, fitted flow curves for methylcellulose<sup>8</sup> and for various suspensions<sup>100</sup> quite well, certain weaknesses of this equation were noted by  $\operatorname{Grim}^{10}$ . The assumption of the simple hyperbolic form for the lower portion of the flow curve, the poor fit of the assymptote,  $\frac{1}{20}$ , to the curve and the failure of the constants to change in regular fashion with increase in concentration

were pointed out as objectionable features. Thus, the Williamson equation was not considered the best to use for flow curves of emulsions.

The Structure equation, presented by Grim<sup>100</sup>, was evaluated by converting it to linear form:

$$F = b_0 + b_1 x_1 + b_2 x_2$$

where  $b_0$ ,  $b_1$  and  $b_2$  are f,  $b_2$ , and  $b_2$ , respectively,  $b_2$  is  $b_2$  and  $b_2$  is  $b_2$ . The constant  $b_2$  was assigned a value of 0.001 by Grim who evaluated the other constants by least squares utilizing the square root method of  $b_2$ . The equation was found to fit the flow data on suspensions and the constants were found to bear a simple relationship to concentration of suspended solid.

Thus, the Structure equation appears to be the best equation available for the description of non-Newtonian flow curves, at least for aqueous solutions and dispersions. Accordingly, it was selected for use with the aim of correlating flow constants with the variables investigated.

## Computational Method

With the extensive data obtained in this study, it was desirable to evaluate the constants of the Structure equation by means of an automatic computer. The IBM 704 data processing system (International Business Machines Corp.) was used for this purpose. The program, written in Fortran language, is presented in Fig. 5.

```
Statement
                                            Statement
   No.
              DIMENSION A(3,4), X(50,5), B(4), AO(12), Y(50), C(50)
              EQUIVALENCE (A,AO)
    2
              READ INPUT TAPE 7,3, NRUN, NDATA, PT, T
              FORMAT (213, F4.1, F7.3)
              D0 5 I = 1,12
   56
              AO(I) = O
              DO 12 K = 1, NDATA
   7
              READ INPUT TAPE 7,8 (X(K,I), I = 2,4)
   8
              FORMAT (2F4.3, F4.2)
   9
              X(K,I) = 1.0
              D0 12 I = 1,3
  10
  11
              DO 12 J = 1,4
              A(I,J) = A(I,J) + X(K,I) * X(K,J)
  12
  13
              D0 19 K = 1,3
  14
              D0 19 I = 1,3
  15
              IF (I-K) 16,19,16
  16
              D = A(I,K)
  17
              DO 18 J = 1,4
              A(I,J) = A(K,K) * A(I,J) - D * A(K,J)
  18
  19
              CONTINUE
  20
              DO 21 I = 1,3
              B(I) = (A(I,4)/A(I,I)) * T
  21
  22
              B(2) = B(2) * 0.001
  23
              WRITE OUTPUT TAPE 6,24, NRUN, NDATA, (B(I), I = 1,3)
  24
              FORMAT (1HOI3, ILO, 3F15.8)
  25
              S = 0.
  26
              DO 32 K = 1, NDATA
              Y(K) = B(1) + (B(2) (X(K,2)*1000.)) + B(3)*X(K,3)
  27
 127
              X(K,5) = X(K,4) * T
  28
              C(K) = (ABSF(X(K,5)-Y(K)))/X(K,5)
  29
              S = S + C(K)
  30
              WRITE OUTPUT TAPE 6, 31, K, X(K,5), Y(K), C(K)
  31
              FORMAT (1H, I3, 3F15.8)
  32
              CONTINUE
  33
              DEV = S/PT
  34
              WRITE OUTPUT TAPE 6,35, NRUN, DEV
  35
              FORMAT (1H, I3, F15.8)
  36
              GO TO 2
```

Fig. 5. Computer Program for Evaluating Constants of the Structure Equation, Fortran Language

The symbols used in this program are explained below:

NRUN -Identifying number of the run. NDATA - Number of data points used in the calculation. NDATA written as a floating point number. T -Factor for converting stress to absolute units. X(K,2) - .001. S. $X(K,3) - e^{-aS}$ . X(K,4) - Shearing stress in arbitrary recorded units. B(1) -The constant f. B(2) -The constant  $\eta_{\infty}$  \* 1000. B(3) - The constant  $\overline{b_{v}}$ . X(K,5) - Observed value of stress, in absolute units. Y(K) - Calculated value of stress, corresponding to X(K,5). C(K) -Deviation of Y(K) from X(K,5), expressed as a fraction of X(K,5). S -Summation of C(K).

The flow diagram of the program is shown in Fig. 6.

Average deviation.

DEV -

The program writes the three simultaneous equations for the three unknowns, resulting from application of the method of least squares, in the form of matrix. Statement 5 sets all elements initially at zero. In statements 6 through 12, elements of the matrix are calculated for each set of data points, X(K,I), values of the elements being accumulated as the data are read in. Statements 13 through 19 calculate new values for the diagonal elements and those in the fourth column, while all other elements are eliminated. In Statement 21, the value of the constant is calculated from the diagonal and the corresponding element in the fourth column.

The computation of the coefficients is illustrated by a simple example in which the constants B(1), B(2) and B(3) are assigned values of 0, 1 and -1 respectively:

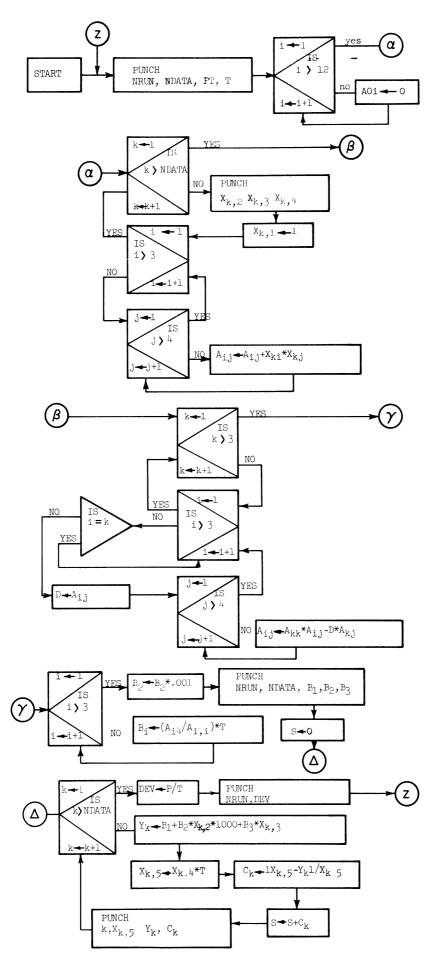


Fig. 6. Flow Diagram of Program for Calculating Structure Equation Constants

Three simultaneous equations relating these constants may now be written in the form of a matrix, to be called the  $\underline{a}$  matrix, as follows:

1	2	3	-1	
3	1	0	1	
2	3	3	0	

Following the program, elements of a new matrix, to be called the c matrix, are calculated setting  $\underline{K}$  at 1,  $\underline{I}$  at 2 and 3, and  $\underline{J}$  at 1,2,3,4. It must be noted that  $\underline{K}$  cannot have the same value as  $\underline{I}$  by the specification in Statement 15. According to Statement 18, the new values for the elements of the  $\underline{c}$  matrix are:

$$c_{21} = 1 \times 3 - 3 \times 1 = 0$$
 $c_{22} = 1 \times 1 - 3 \times 2 = -5$ 
 $c_{23} = 1 \times 0 - 3 \times 3 = -9$ 
 $c_{24} = 1 \times 1 - 3 \times -1 = 4$ 
 $c_{31} = 1 \times 2 - 2 \times 1 = 0$ 
 $c_{32} = 1 \times 3 - 2 \times 2 = -1$ 
 $c_{33} = 1 \times 3 - 2 \times 3 = 0$ 
 $c_{34} = 1 \times 0 - 2 \times -1 = 2$ 

Since  $\underline{K}$  is not equal to  $\underline{\underline{I}}$ , the elements of the first row are not changed. The  $\underline{c}$  matrix may then be written as:

Elements of another matrix, to be called the <u>d</u> matrix, are now calculated by setting <u>K</u> at 2, <u>I</u> at 1,3 and <u>J</u> at 1,2,3,4, as done previously. The elements of the <u>d</u> matrix are as follows:

$$d_{11} = -5 \times 1 - 2 \times 0 = -5$$

$$d_{12} = -5 \times 2 - 2 \times -5 = 0$$

$$d_{13} = -5 \times 3 - 2 \times -9 = 3$$

$$d_{14} = -5 \times -1 - 2 \times 4 = -3$$

$$d_{31} = -5 \times 0 - (-1) \times 0 = 0$$

$$d_{32} = -5 \times -1 - (-1) \times -5 = 0$$

$$d_{33} = -5 \times -3 - (-1) \times -9 = 6$$

$$d_{34} = -5 \times 2 - (-1) \times 4 = -6$$

The elements of the second row are not changed. The  $\underline{d}$  matrix may then be written as follows:

Finally, elements of another matrix, to be called the <u>e</u> matrix, are calculated setting <u>K</u> at 3, <u>I</u> at 1,2 and <u>J</u> at 1,2,3,4. The elements of the <u>e</u> matrix are as follows:

$$e_{11} = 6 \times -5 - 3 \times 0 = -30$$
  
 $e_{12} = 6 \times 0 - 3 \times 0 = 0$   
 $e_{13} = 6 \times 3 - 3 \times 6 = 0$   
 $e_{14} = 6 \times -3 - \times -6 = 0$   
 $e_{21} = 6 \times 0 - (-9) \times 0 = 0$   
 $e_{22} = 6 \times -5 - (-9) \times 0 = -30$   
 $e_{23} = 6 \times -9 - (-9) \times 6 = 0$   
 $e_{24} = 6 \times 4 - (-9) \times 6 = -30$ .

The e matrix may then be written as follows:

-30 0 0 0 0 -30 0 -30 0 0 6 -6

It may be seen that the  $\underline{e}$  matrix above gives the values assigned to the constants in this calculation.

Multiplication of the coefficients by the conversion factor to give the constant in absolute units is carried out in Statement 21. B(2) must be decoded by a factor of 0.001, this being done in Statement 22. Statement 27 is used to obtain calculated values of stress and Statement 127 to obtain the corresponding observed values in absolute units. In Statement 28, the deviation from observed value is calculated as a fraction of observed value. The deviation is cumulated over all the data points, and the average deviation is obtained in Statement 33. The information obtained from the three output Statements 23, 30 and 34 includes the constants of the Structure equation, observed values of stress in absolute units and the corresponding calculated values, deviation of the calculated values from the observed expressed as fraction of the observed value, and the average deviation.

## Relationships of Constants of the Structure Equation to the Variables Investigated

## Series I Emulsions

The constants of the Structure equation computed for Series I emulsions are presented in Table 41.

TABLE 41

STRUCTURE EQUATION CONSTANTS FOR SERIES I EMULSIONS: CETYL ALCOHOL WITH SODIUM LAURYL SULFATE EMULSIFIER; EQUILIBRIUM FLOW CURVES.

Conc. Cetyl Alcohol % w/w	f Dyne/cm <sup>2</sup>	η O Poise	b <sub>v</sub> Dyne/cm. <sup>2</sup>	f O Dyne/cm?
5.4	425.6	0.2803	141.9	283.7
5.0	402.9	0.2346	159.3	243.6
4.5	22.4	0.2076	142.1	82.3
4.0	257.0	0.1939	103.4	153.6
3 <b>.</b> 5	180.0	0.1622	98.3	81.3
3.0	155.2	0.1186	85.8	69.4
2.5	84.9	0.1304	33.7	51.2
2.0	106.1	0.1346	66.4	39•7
1.5	136.3	0.2560	72.6	63.7
1.0	20.9	0.1294	0	20.9

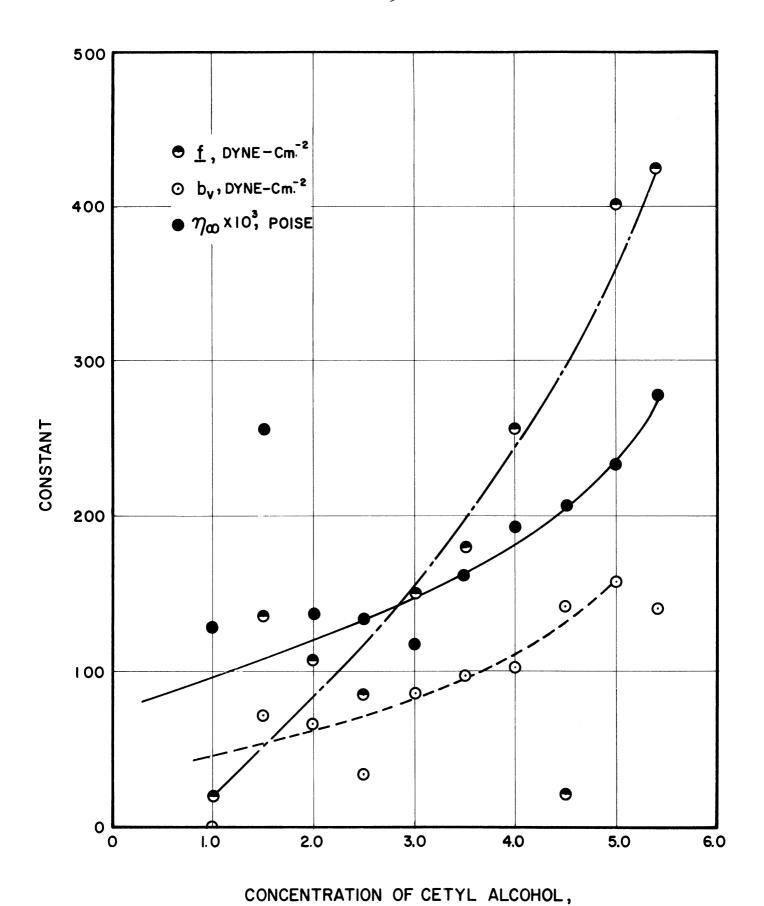
The only variable investigated in this group of emulsions was concentration of the dispersed phase, cetyl alcohol. A plot of the constants,  $\eta_{\infty}$ ,  $b_{V}$  and  $\underline{f}$  versus concentration is shown in Fig. 7. The constants did not follow concentration in as regular manner as might be desired; nevertheless, it was thought worthwhile to determine whether the reciprocal relationship to concentration, as found by Grim with suspensions, might be applicable. Reciprocal plots are shown in Figs. 8-10, where it is seen that fair agreement with the reciprocal equation was obtained. The yield values,  $\underline{f_{O}}$ , for this series die not fit in terms of concentration but did in terms of log concentration, as is shown in Fig. 11. The reciprocal equation is generally expressed as follows:  $1/\mathrm{Flow}$  Constant =  $\mathrm{k/S^{+}}$  -  $\mathrm{kC}$ ,

where  $\underline{k}$  is a constant,  $\underline{S'}$  is the reciprocal of the intercept on the abscissa and C is the concentration of dispersed phase. The values of  $\underline{k}$ ,  $\underline{k/S'}$  and  $\underline{S'}$  obtained for series I constants are shown in Table 42.

TABLE 42

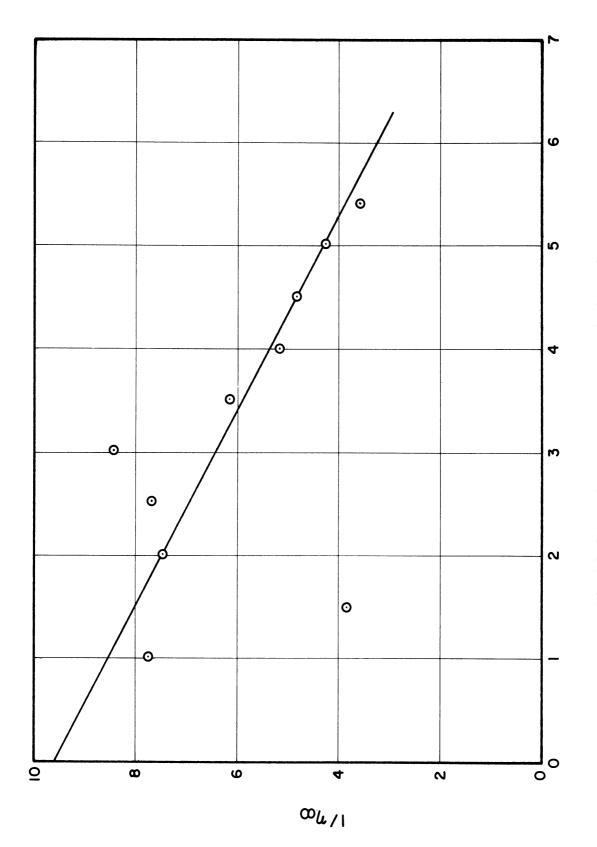
PARAMETERS OF THE RECIPROCAL EQUATION RELATING STRUCTURE EQUATION CONSTANTS TO CONCENTRATION SERIES I EMULSIONS

Flow Constant	k/S'	S'	k
η <sub>∞</sub>	9.60	11.1	1.065
b <sub>v</sub>	0.023	14.1	0.324
f	0.012	15.9	0.195



% W / W

Fig. 7. Plot of Structure Equation Constants,  $\eta_{\infty}$ ,  $b_{V}$  and f Versus Concentration of Cetyl Alcohol for Emulsions of Series I



CONCENTRATION OF CETYL ALCOHOL, % W/W

Fig. 8. Plot of  $1/\eta_{\infty}$  Versus Concentration of Cetyl Alcohol for Emulsions of Series I

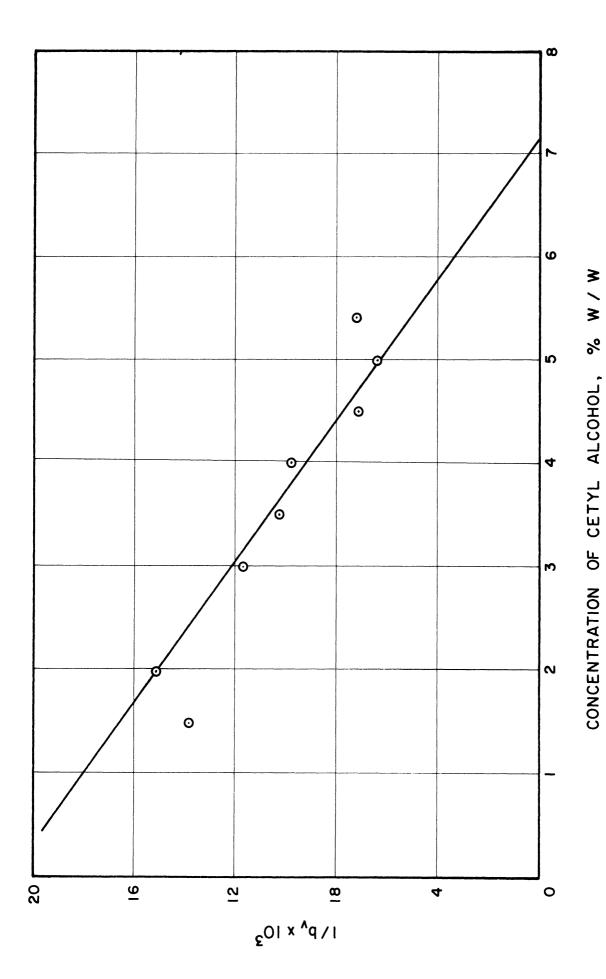


Fig. 9. Plot of  $1/b_{\rm v}$  Versus Concentration of Cetyl Alcohol for Emulsions of Series I

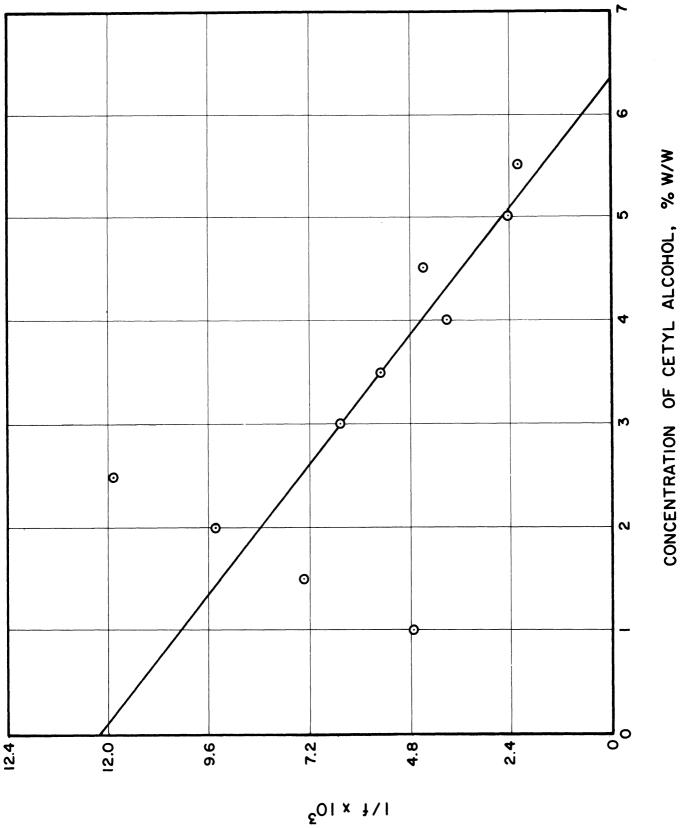


Fig. 10. Plot of 1/f Versus Concentration of Cetyl Alcohol for Emulsions of Series I

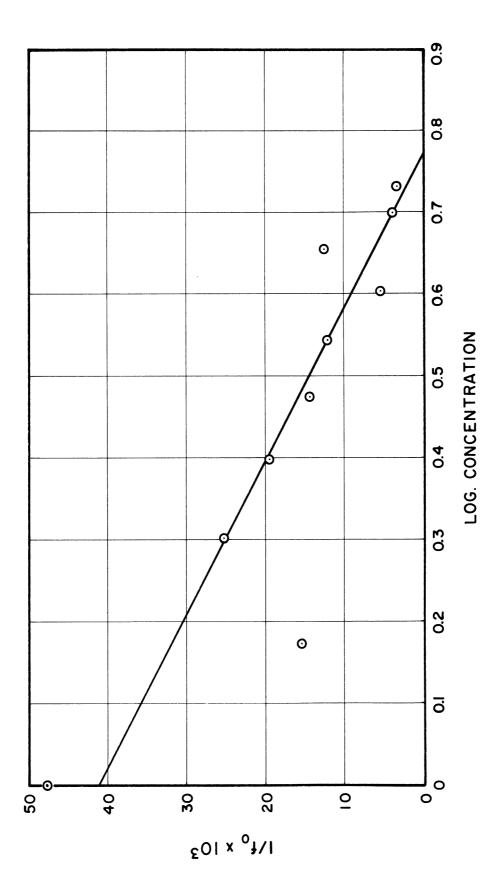


Fig. 11. Plot of  $1/f_{\rm O}$  Versus Logarithm of Concentration of Cetyl Alcohol for Emulsions of Series I

Values of k/S' obtained in this or a similar manner have been proposed as the value of the reciprocal for the dispersion medium alone, but this has been questioned 103. If these values were so-interpreted for series I emulsions the suspending medium, which is water, would be non-Newtonian. Thus, this interpretation of k/S' does not appear acceptable. Values of S' have been regarded as the reciprocal of the ultimate settling volume, although this has not been proven. The predicted value of sedimentation constant, 1/S', is different for each constant, although they may agree within error for this series. All of them indicate, as would be noted from the flow data, that the ultimate settling volume for cetyl alcohol particles is quite high, ranging from 11 to 16% by volume of cetyl alcohol. Considering that for rhombohedral packing the volume of solid in the sediment would be about 74%, this indicates that the cetyl alcohol particles might have an effective volume several times their actual volume. This is not unexpected for cetyl alcohol, since it has been noted that emulsions with concentrations of 10% are creams which do not flow when subjected to gravitational force.

The effective-volume concept can be used for further speculation. One can calculate the limiting viscosity,  $\underline{\underline{\mathsf{N}}}_{\mathtt{O}}$ , representing the viscosity as  $\underline{\mathtt{S}}$  approaches zero, from the Structure equation as follows:

$$F = f + \infty S - b_v e^{-aS},$$
 
$$dF/dS = \bigwedge_{\omega} + ab_v e^{-aS},$$
 
$$\lim_{S \to 0} dF/dS = \bigwedge_{\omega} - b_v + ab_v.$$

These can then be used to calculate specific viscosities,  $\frac{\sum p}{sp}$ , by the formula:

$$\int_{\text{sp}} = \int_{\text{o}} (\text{emul.}) / \int_{\text{o}} (\text{solv.}) -1.$$

Calculated values of  $\frac{\sqrt{}_{0}}{\sqrt{}_{0}}$  and  $\sqrt{}_{\mathrm{sp}}$  for series I emulsions are shown in Table 43. A plot of  $ln \gamma_{sp} \underline{vs}$ .  $\underline{C}$  is commonly used to obtain intrinsic viscosity, [n], as the slope of the line, and this type of graph is shown in Fig. 12. An intrinsic viscosity of 29.4 was obtained in this manner. The Einstein equation predicts an intrinsic viscosity of 2.5 and experimental determinations have produced values in the range of 2.0 to 2.8<sup>104</sup>. The high value of 29.4 can be explained on the basis of electroviscous effect or formation of liquid sheaths about the particles. It is a common concept that emulsion particles may bear surface charges such that they repel one another and thus behave as though they were of much larger volume. The presence of immobilized liquid envelopes about the particles has also been frequently proposed  $^{27,47}$ , and this, too, gives the particles a large effective volume. With series I emulsions the emulsifier, sodium lauryl sulfate, may be expected to be attached to the cetyl alcohol through the hydrocarbon chain and have the hydrophilic sulfate radicals extended outward into the aqueous phase. The sulfate groups would thus constitute charged hydrated layers on the particle surfaces causing large electroviscous effects. The ratio of effective to actual concentration might be estimated by dividing the volume corresponding to rhombohedral packing, 74%, by the volume concentration predicted by

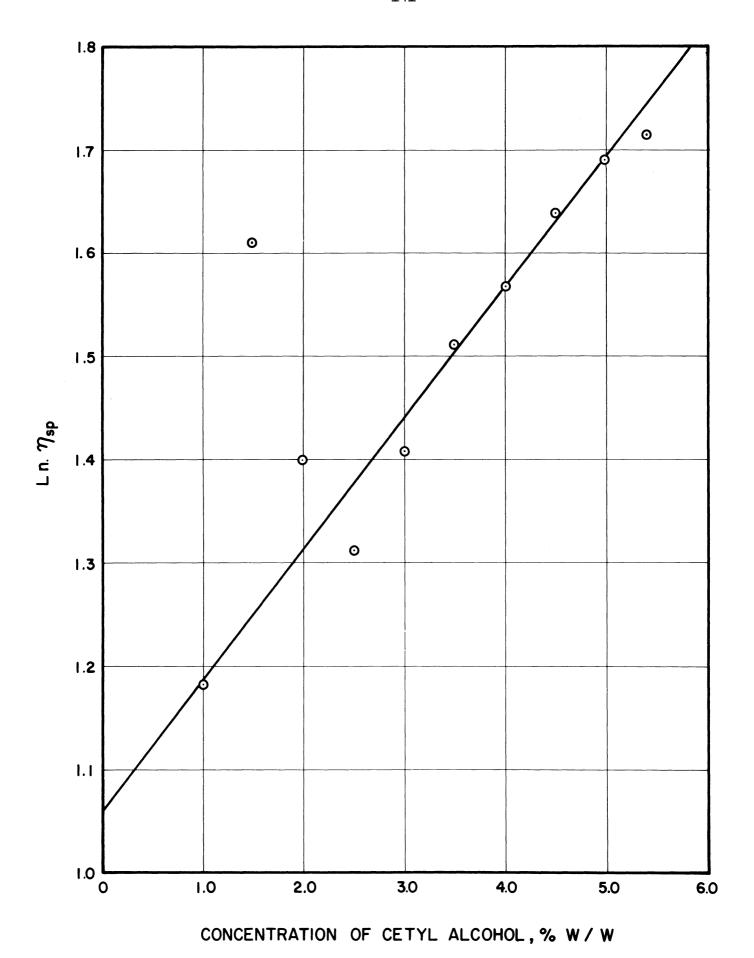


Fig. 12. Plot of Log  $\eta_{\, \mbox{\scriptsize sp}}$  Versus Concentration for Series I Emulsions

the reciprocal plots, Fig. 8-10, to be the ultimate settling volume. The ratios obtained might then be divided into the intrinsic viscosity, 29.4, to obtain values corrected for the effective volume. Results of this treatment, shown in Table 44, show these values for intrinsic viscosity to be grouped about the Einstein constant.

TABLE 43 LIMITING VISCOSITIES,  $\gamma_0$ , FOR SERIES I EMULSIONS

Conc. Cetyl Alcohol %w/w	η.	√ sp
0.0	0.008	0.0
1.0	0.129	15.2
1.5	0.329	40.0
2.0	0.201	24.1
2.5	0.164	19.5
3.0	0.204	24.5
3.5	0.261	31.5
4.0	0.297	36.1
4.5	0.350	42.7
5.0	0.394	48.2
5.4	0.422	51.7

TABLE 44
ESTIMATED INTRINSIC VISCOSITIES
BASED ON LIQUID SHEATHS

Constant	Ratio	Estimated
Used To	Effect.	Intrinsic
Estimate	:Actual	Viscosity
S'	Vol.	_
	8.2	3.6
p <sup>xx</sup>	10.4	2.8
$\mathtt{f}^{v}$	11.8	2.5

## Series II Emulsions

The constants of the Structure equation for series II emulsions are presented in Tables 45-57.

Emulsions of this series contained one concentration of corn oil, 40% w/w, as the dispersed phase. Two emulsifiers were utilized, and several suspending agents in varying concentration were investigated. Different homogenization pressures were used.

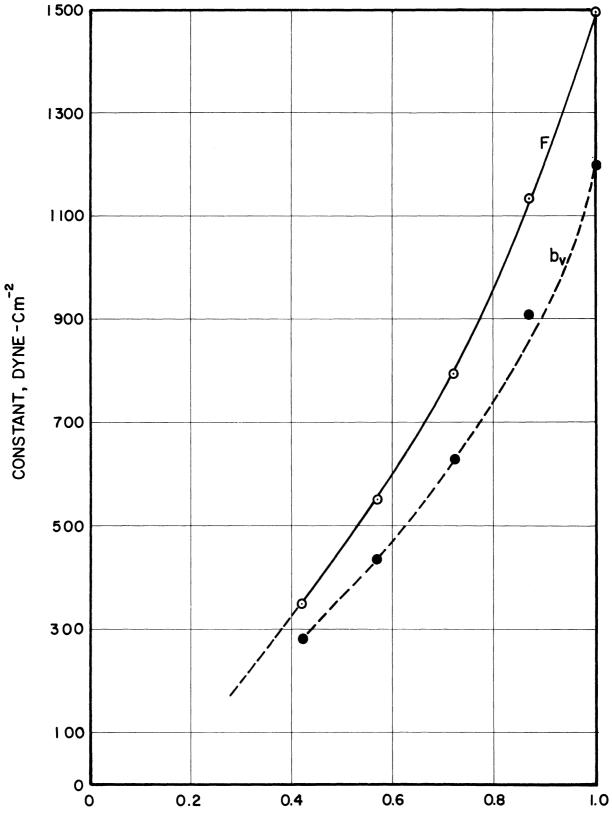
It was expected that variation in homogenization pressures would yield different particle size distributions and that this effect on flow properties of emulsions might be investigated. Size-measurements were made on the basic emulsions and data are presented in Table 58. From these measurements it may be seen that no significant differences in particle size resulted from verying homogenization pressures or the use of two different emulsifiers. Further, on inspection of the flow constants, Tables 45-57, it was concluded that no consistent changes in flow properties accompanied the change in homogenization pressure. Thus, the effect of homogenization pressure within the range of study was concluded to be negligible and subsequent treatment of flow constants utilized averages of those obtained at different homogenization pressures.

A typical set of curves showing the change in constants of the Structure equation with variation of concentration of suspending agent is shown in Figures 13 and 14.

Although the Structure equation constants of emulsions and solutions of suspending agents increased with increased concentration of suspending agent, no simple relationship of flow constants to concentration could

TABLE 45
STRUCTURE EQUATION CONSTANTS FOR SERIES II
EMULSIONS WITHOUT SUSPENDING AGENTS.

Homogenizing Pressure lb./in?	f Dyne/cm?	ზ.∞ Poise	b <sub>v</sub> Dyne/cm?	f <sub>o</sub> Dyne/cm?
	-,	Podium Tours		
2000 2500 3000 4000	39.8 95.6 50.4 42.2	0.568 0.0947 0.0391 0.0629	Sulfate Emulsifie 17.9 42.2 26.7 19.2	21.9 47.4 23.7 23.0
		Span-Tween	Emulsifier	
1000 2000 3000 4000 5000	6.0 6.2 9.9 9.5 10.0	0.0517 0.0546 0.0574 0.562 0.0565	4.9 3.0 6.2 5.3 5.4	1.1 3.1 3.7 4.2 4.6



## CONCENTRATION OF SUSPENDING AGENT IN AQUEOUS PHASE %W/W

Fig. 13. Plot of Structure Equation Constants f and b $_{\rm V}$  Versus Concentration of Suspending Agent for Series II Emulsions with Sodium Alginate Suspending Agent, Sodium Lauryl Sulfate Emulsifier

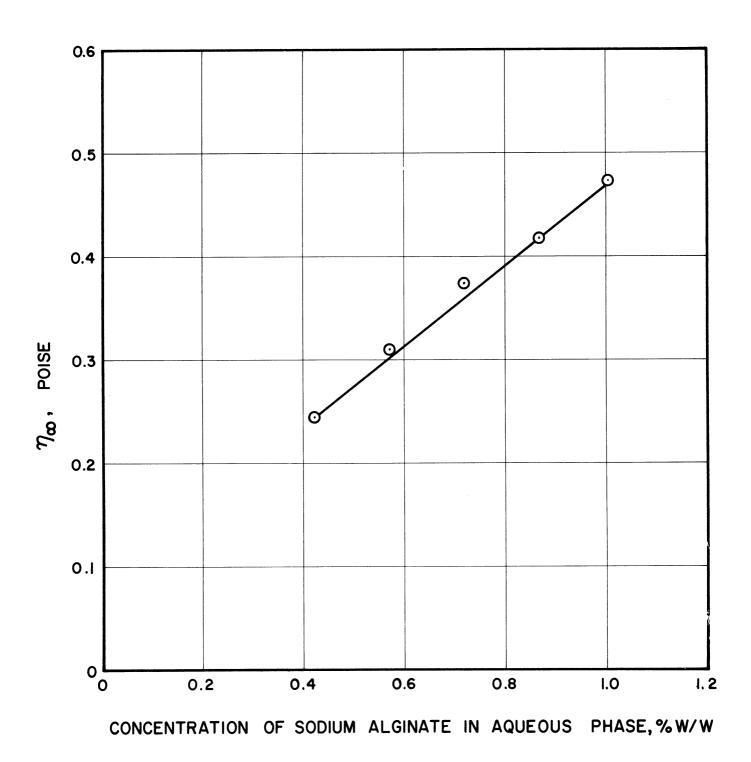


Fig. 14. Plot of Structure Equation Constant  $\eta_{\infty}$  Versus Concentration of Suspending Agent for Series II EmuIsions with Sodium Lauryl Sulfate Emulsifier, Sodium Alginate Suspending Agent

TABLE 46

STRUCTURE EQUATION CONSTANTS FOR SOLUTIONS OF SUSPENDING AGENTS CORRESPONDING TO EMULSIONS OF SERIES II WITH SODIUM LAURYL SULFATE EMULSIFIER.

Conc. Suspending Agent % w/w	f	n se	b <sub>v</sub> , o	f <sub>0</sub> / 2		
Agent % w/w	Dyne/cm2	Poise	Dyne/cm?	Dyne/cm <sup>2</sup>		
	Sodium Alginate					
1.02	853.4	0.1471	737.8	115.6		
0.87	593.3	0.1403	528.9	64.5		
0.72	425.9	0.1173	400.0	25.9		
0.57	201.6	0.1166	188.8	12.8		
0.42	80.5	0.0869	79.3	1.2		
	Tragaca	anth				
	11agac		i 2	ĺ		
1.01	402.7	0.0650	268.3	134.4		
0.85	348.9	0.0601	253.7	95•2		
0.71	249.5	.0591	183.6	65.9		
0.56	171.2	.0494	139.2	32.0		
0.41	71.0	.0450	58.9	12.2		
Sodium (	Carboxymethyl	Cellulose	Type 7MP			
<del></del>			i			
2.07	866.2	0.3935	811.2	55.1		
1.76	515.5	0.3196	489.8	25.7		
1.46	246.5	0.2304	236.0	10.5		
1.14 0.84	112.7 42.2	0.1675	107.0	5.6 2.4		
0.04	42.2	0.1144	39.8	/ Co4		
	Acacia					
19.95	71.5	0.3191	67.4	4.1		
17.02		0.3478				
14.81		0.2074	<b></b>			
11.35 8.16		0.1156				
O. TO		1 0.0030				

TABLE 47

STRUCTURE EQUATION CONSTANTS FOR SERIES II
EMULSIONS WITH SODIUM LAURYL SULFATE EMULSIFIER,
ACACIA SUSPENDING AGENT.

Conc. Suspending Agent in Aqueous Phase % w/w	f Dyne/cm <sup>2</sup>	Poise	bv Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>		
	Hom. Press. 2000 lb./in?					
19.95 17.02 14.81 11.35 8.16	1442.8 579.7 343.6 172.2 160.3	1.1205 0.7945 0.5760 0.3619 0.2041	1015.7 361.1 233.6 79.4 55.8	427.2 218.5 110.0 92.9 104.5		
	Hom. Press 25	00 lb./in?	i			
19.95 17.02 14.81 11.35 8.16	2182.1 806.3 568.1 270.4 186.3	1.2409 0.4456 0.7168 0.4359 0.1867	1479.5 410.1 369.3 141.8 69.6	702.5 396.2 198.8 128.6 116.7		
	Hom. Press. 3	000 lb./in?				
19.95 17.02 14.81 11.35 8.16	2316.5 985.8 522.0 301.3 245.6	1.2022 0.8605 0.6430 0.3773 0.2213	1599.9 661.3 349.0 151.4 109.7	716.6 324.5 173.1 149.9 135.9		
	Hom. Press. 4000 lb./in?					
19.95 17.02 14.81 11.35 8.16	2223.3 986.5 564.1 362.2 284.6	1.1805 0.8343 0.6135 0.3663 0.2427	1376.7 621.1 347.5 164.0 120.9	846.6 365.4 216.5 198.2 163.6		

TABLE 48

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS
WITH SODIUM LAURYL SULFATE EMULSIFIER, SODIUM
CARBOXYMETHYLCELLULOSE SUSPENDING AGENT.

Conc. Suspending	٩	na	1-	٩	
Agent in Aqueous Phase % w/w	f Dyne/cm <sup>2</sup>	Poise	b <sub>v</sub> /cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>	
				2,7110/01116	
	Hom. Press. 2	2000 lb./in=		1	
2.07	1306.6	0.5807	893.6	413.1	
1.76	990.0 464.1	0.4759	663.7	326.3	
1.15 0.84	292 <b>.</b> 6	0.2834 0.2231	291.5 170.8	172.6 121.8	
	Hom. Press. 2	2500 lb./in=	ŀ	1	
2.07	1395.0	0.5636	940.5	454.5	
1.76	1079.6	0.4713	721.2	358.5	
1.46 1.15	796.7 519.4	0.3961 0.3087	509.4 292.6	287.3 226.8	
0.84	353.3	0.2046	223.8	130.1	
	Hom. Press. 3	3000 lb./in <sup>2</sup>			
2.07	1455.9	0.5078	989.6	466.3	
1.76 1.46	1049.9 883.3	0.4010 0.3543	700.7 581.8	349.2 301.5	
1.15	601.8	0.2820	390.4	211.4	
0.84	391.8	0.2173	242.5	149.2	
	Hom. Press. 4000 lb./in?				
2.07	1677.1	0.5460	1116.1	561.0	
1.76	1474.7	0.4516	1064.4	410.3	
1.46	1035.0	0.3111	705.9	329.0	
1.15 0.84	658.8 434.3	0.2894 0.2120	409.7 269.8	249.1 164 <b>.</b> 5	
• • • • • • • • • • • • • • • • • • • •	<u> </u>				

TABLE 49

STRUCTURE EQUATION CONSTANTS FOR SERIES II
EMULSIONS WITH SODIUM LAURYL SULFATE EMULSIFIER,
TRAGACANTH SUSPENDING AGENT.

Conc. Suspending Agent in Aqueous Phase % w/w	f Dyne/cm <sup>2</sup>	ر Poise	b <sub>v</sub> Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>	
	Hom. Press. 2000 lb./in.				
1.01 0.85 0.71 0.56 0.41	596.1 508.8 399.7 278.4 224.6	0.2246 0.1942 0.1637 0.1491 0.1152	339·3 303·436 237·1 142·5 143·8	256.7 205.403 162.6 135.9 80.9	
	Hom. Press.	2500 lb./in?			
1.01 0.85 0.71 0.56 0.41	646.1 535.3 449.9 342.8 236.2	0.2095 0.1741 0.1425 0.1247 0.1071	390.1 319.2 284.3 218.9 157.0	256.0 216.0 165.6 123.9 79.2	
	Hom. Press.	3000 lb./in?	ı	1	
1.01 0.85 0.71 0.56 0.41	560.9 393.6 267.8 233.6 170.4	0.2270 0.1742 0.1578 0.1308 0.1045	359.5 252.2 208.7 148.9 111.8	201.3 141.1 59.1 84.7 58.7	
	Hom. Press. 4000 lb./in?				
1.01 0.85 0.71 0.56 0.41	589.8 486.9 383.5 240.1 196.9	0.2202 0.1867 0.1622 0.1596 0.1188	348.3 298.9 241.7 116.6 128.1	241.5 188.0 141.8 123.6 68.8	

TABLE 50

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS WITH SODIUM LAURYL SULFATE EMULSIFIER, SODIUM ALGINATE SUSPENDING AGENT

Conc. Suspending	2	$n_{\infty}$			
Agent in Aqueous   Phase % w/w	f Dyne/cm <sup>2</sup>		b <sub>v</sub> Dyne/cm <sup>2</sup>	fo Dyne/cm2	
I Hase /o w/ w	Dyne/cm.	Poise	Dyne/cm.	Dyne/cm-	
	Hom. Press. 2	000 lb./in <sup>2</sup>			
1.02 0.87 0.72 0.57 0.42	1188.6 901.4 740.5 329.3 265.6	0.3131 0.2780 0.2621 0.2020 0.1716	827.3 643.2 522.2 209.2 174.6	361.3 258.2 218.3 120.1 91.0	
	Hom. Press. 2	500 lb./in <sup>2</sup>			
1.02 0.87	1310.7 994.3	0.2710	939.2 706.6	371.5 287.7	
0.72	695•3	0.2316	493.0	202.3	
O•57	473•9	0.1930	334.5	139.3	
0.42	269.9	0.1769	169.1	100.8	
	Hom. Press. 3	000 lb./in <sup>2</sup>			
1 00	1)158 0	0 26/17	000 6	h58 h	
	,	0.2459	740.6	329.6	
0.72	785.6	0.2099	556.2	229.4	
0.42	320.0	0.1611	244.0	112.0	
	Hom. Press. 4000 lb./in?				
1.02	1202.8	0.4100	655.4	547.4	
0.87	1165.8	0.2367	828.5	337.3	
0.42		0.1541	273.0	116.5	
1.02 0.87 0.72 0.57 0.42 1.02 0.87 0.72 0.57	269.9  Hom. Press. 3  1458.0 1070.2 785.6 547.8 356.6  Hom. Press. 4	0.1769 0.1769 0.2647 0.2459 0.2099 0.1905 0.1611 000 lb./in? 0.4100 0.2367 0.2122 0.1875	999.6 740.6 556.2 385.4 244.6 655.4 828.5 584.2 407.1	100.8 458.4 329.6 229.4 162.3 112.0 547.4 337.3 250.4 174.6	

TABLE 51

STRUCTURE EQUATION CONSTANTS FOR SUSPENDING AGENT SOLUTIONS CORRESPONDING TO EMULSIONS OF SERIES II WITH SPAN-TWEEN EMULSIFIER.

Conc. Suspending	f	70	b <sub>v/ 2</sub>	f <sub>o</sub> , 2		
Agent % w/w	Dyne/cm?	Poise	Dyne/cm?	Dyne/cm?		
	Methylcellulose 1500 CPS					
1.661 1.415 1.168 0.922 0.676	1496.8 868.3 475.9 274.4 79.7	0.3573 0.3117 0.2342 0.1851 0.1165	1341.3 797.6 442.5 257.8 75.9	155.6 70.7 33.4 16.6 3.8		
Sodium	Sodium Carboxymethylcellulose Type 7MP					
2.259 1.924 1.589 1.254 0.919	1408.5 828.5 387.0 208.9 143.8	0.3394 0.2935 0.2267 0.1662 0.1382	1258.1 761.6 357.2 197.0 119.1	150.3 66.9 29.7 11.8 24.7		
	Carbopol-934, Sodium Salt					
0.334 0.285 0.235 0.185 0.136	488.2 351.5 200.2 77.8 21.8	0.1829 0.1197 0.0913 0.0701 0.0493	334.9 298.1 177.5 64.2 13.3	153.3 53.4 22.7 13.6 8.4		

TABLE 51-Continued

Conc. Suspending	r / 2	n =	p^A S	fo / 2			
Agent % w/w	Dyne/cm <sup>2</sup>	Poise	Dyne/cm <sup>2</sup>	Dyne/cm <sup>2</sup>			
	Acacia						
	ACA	Acacia					
19.245	42.2	0.3645	49.4				
16.391		0.2536		=			
13.537		0.1672					
10.683		0.1138					
7.828		0.0769					
	Sodium 1	Alginate					
1	0	1					
1.034	859.9	0.2499	603.1	256.8			
0.881	750.2	0.1748	625.1	125.2			
0.727	535•7	0.1435	459.8	75.9			
0.574	339.0	0.1267	297.4	41.6			
0.421	179.4	0.0959	158.2	21.1			
	Пто по	oonth					
	Traga	Samon	1				
1.163	566.8	0.1052	371.6	195.2			
0.991	462.1	0.0951	319.3	142.8			
0.818	326.9	0.0861	229.5	97.4			
0.646	229.8	0.0656	170.9	58.9			
0.473	127.7	0.0635	99.4	28.3			
	·						

TABLE 52

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS WITH SPAN-TWEEN EMULSIFIER, SODIUM ALGINATE SUSPENDING AGENT.

Conc. Suspending Agent in Aqueous Phase % w/w	f Dyne/cm?	√∞ Poise	b Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>
	Hom. Press. 1	000 lb./in		
1.034 0.881 0.727 0.574 0.421	1523.6 1155.5 773.3 553.2 371.8	0.4558 0.4004 0.3462 0.2860 0.2319	1263.7 966.9 616.8 467.4 317.0	259.9 188.6 156.4 85.8 54.9
	Hom. Press. 2	2000 lb./in4	) F	
1.034 0.881 0.727 0.574 0.421	1550.3 1123.0 855.8 590.6 362.4	0.4749 0.4448 0.3722 0.3235 0.2576	1250.8 893.8 693.8 476.8 290.7	299.5 233.1 161.9 113.8 71.7
	Hom. Press. 3000 lb./in?			
1.034 0.881 0.727 0.574 0.421	1446.7 1144.9 810.0 554.9 394.2	0.4927 0.4233 0.4035 0.3142 0.2560	1132.0 903.4 622.0 431.3 266.1	314.7 240.9 188.0 123.6 83.1
	Hom. Press.	+000 lb./in <sup>2</sup>	2	
1.034 0.881 0.727 0.574 0.421	1469.2 1080.9 759.8 539.0 325.1	0.4636 0.4260 0.3797 0.3063 0.2406	1161.5 845.2 584.8 421.0 251.8	307.7 235.7 175.1 118.0 73.3
	Hom. Press. 5000 lb./in?			
1.034 0.881 0.727 0.574 0.421	1480.5 1165.8 795.8 516.1 351.1	0.4744 0.4040 0.3757 0.3204 0.2425	1156.3 937.3 618.4 394.9 275.0	324.1 228.5 177.4 121.2 76.1

TABLE 53

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS
WITH SPAN-TWEEN EMULSIFIER, TRAGACANTH SUSPENDING AGENT.

Conc. Suspending Agent in Aqueous Phase % w/w	f	∫∞	b <sub>v</sub>	fo		
	Dyne/cm?	Poise	Dyne/cm?	Dyne/cm2		
	Hom. Press.	Hom. Press. 1000 lb./in?				
1.163	831.8	0.2688	636.8	195.0		
0.991	652.5	0.2517	513.2	139.3		
0.818	466.7	0.2304	368.4	98.2		
0.646	293.7	0.2018	338.3	54.4		
0.473	497.8	0.1719	164.4	33.5		
	Hom. Press.	2000 lb./in <sup>2</sup>	) -			
1.163	691.2	0.2810	508.442	182.8		
0.991	538.8	0.2464	407.4	131.5		
0.818	472.2	0.2367	359.2	113.0		
0.646	313.3	0.2140	242.1	71.2		
0.473	154.8	0.1630	120.4	34.4		
	Hom. Press.	Hom. Press. 3000 lb./in?				
1.163	632•2	0.2561	461.6	170.6		
0.991	457•2	0.2322	336.0	121.2		
0.818	374•6	0.2177	278.8	95.8		
0.646	224•1	0.1823	166.1	57.9		
0.473	115•5	0.1519	85.2	30.3		
	Hom. Press.	4000 lb./in?				
1.163	596.9	0.2467	440.6	156.2		
0.991	443.3	0.2331	322.9	120.3		
0.818	301.1	0.2045	229.7	71.4		
0.646	163.6	0.1793	117.7	45.9		
0.473	115.3	0.1494	85.9	29.4		
	Hom. Press. 5000 lb./in <sup>2</sup>					
1.163	562.0	0.2497	409.9	152.1		
0.991	559.9	0.2152	442.8	117.1		
0.818	326.3	0.2084	247.9	78.4		
0.646	198.0	0.1789	147.8	50.2		
0.473	94.9	0.1488	68.8	26.1		

TABLE 54 STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS WITH SPAN-TWEEN EMULSIFIER, ACACIA SUSPENDING AGENT.

Conc. Suspending		h			
Agent in Aqueous	f D2	Dod -	b <sub>v</sub>		
Phase % w/w	Dyne/cm <sup>2</sup>	Poise	Dyne/cm?		
	Hom. Press. 1000 1	b./in <sup>2</sup>	ı		
19.24	869.3	0.7854	860.8		
16.39	462.6	0.6806	462.2		
13.54	455.1	0.7149	337.3		
10.68	109.7	0.3656	107.8		
7.83	58.8	0.2488	56.3		
	Hom. Press. 2000 1	b./in <sup>2</sup>			
- 0 0	000 5	7 0/25	061. 7		
19.24	990.5	1.0475 0.8852	964.1 435.2		
16.39 13.54	457.4 232.6	0.6727	216.6		
10.68	112.0	0.4738	101.9		
7.83	72.8	0.3179	64.8		
	Hom. Press. 3000 1				
	11011. 11088. 3000 1				
19.24	1099.8	0.7844	1003.0		
16.39	609.8	0.6259	550.8		
13.54	263.3	0.5801	215.1		
10.68	104.1	0.4228	68.2 46.2		
7.83	00.9	0.2000	40.2		
	Hom. Press. 4000 1	b./in <sup>2</sup>			
19.24	843.6	0.6982	783.6		
16.39	523.8	0.7598	509.4		
13.54	316.4	0.3565	298.2		
10.68	113.2	0.3155	84.9		
7.83	60.7	0.2361	10.4		
	Hom. Press. 5000 lb./in?				
19.24	949.8	0.5933	886.8		
16.39	532.3	0.4604	502.3		
13.54	332.7	0.4172	320.2		
10.68	198.7 62.1	0.3181	184.0		
7.83	, OC+⊥	0.2384	17.9		

TABLE 55

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS WITH SPAN-TWEEN EMULSIFIER, SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT.

Conc. Suspending Agent in Aqueous Phase % w/w	f Dyne/cm?	Poise	b <sub>v</sub> Dyne/cm <sup>2</sup>	fo Dyne/cm <sup>2</sup>	
	Hom. Press.	1000 lb./i	n <sup>2</sup>	1	
2.259 1.924 1.589 1.254 0.919	2200.2 1714.0 1496.5 629.9 338.6	0.6527 0.6226 0.6189 0.4518 0.3542	1898.4 1478.1 1291.1 535.8 266.8	301.9 235.9 205.3 94.1 70.7	
	Hom. Press.	2000 lb./i	n <del>?</del>	ı	
2.259 1.924 1.589 1.254 0.919	2317.7 1793.6 998.2 594.9 315.2	0.7178 0.6742 0.5618 0.4647 0.3615	1939.9 1499.2 823.3 458.2 221.6	377.8 294.4 174.8 136.6 93.6	
	Hom. Press. 3000 lb./in?				
2.259 1.924 1.589 0.919	2289.1 1616.9 1111.6 331.2	0.7370 0.6596 0.5590 0.3352	1893.6 1312.3 890.9 231.3	395.4 304.6 220.7 99.8	
	Hom. Press.	4000 lb./i	n <del>?</del>		
2.259 1.924 1.589 1.254 0.919	2260.6 1556.9 906.0 512.5 287.9	0.7391 0.6776 0.5469 0.4232 0.3205	1846.2 1243.2 712.9 383.4 192.3	414.4 313.7 193.2 129.1 95.6	
	Hom. Press. 5000 lb./in?				
2.259 1.924 1.589 1.254 0.919	1963.4 1481.3 909.2 539.8 276.0	0.7137 0.6462 0.5357 0.4312 0.3306	1604.0 1218.2 724.4 410.7 185.2	359.4 263.0 184.9 129.1 90.8	

TABLE 56

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS WITH SPAN-TWEEN EMULSIFIER, METHYLCELLULOSE SUSPENDING AGENT

Conc. Suspending Agent in Aqueous	f	200	b <sub>v</sub>	f
Phase % w/w	Dyne/cm?	Poise	Dyne/cm?	f <sub>o</sub> Dyne/cm <sup>2</sup>
	Hom. Press.	1000 lb./ir	2	í
1.661	1646.0	0.4610	1373.7	272.3
1.415 1.168	1574.0 899.2	0.4161 0.3859	1331.0 771.4	243.0
0.922	527.5	0.3086	478.5	127.7 49.0
0.676	281.9	0,2356	258.0	23.9
	Hom. Press.	2000 lb./ir	2	
1.661	1868.4	0.4520	1519.8	348.6
1.415 1.168	1309.5 826.1	0.4021 0.3613	1120.8 686.8	188.7 139.4
0.922	488.9	0.2992	418.3	70.6
0.676	241.8	0.2241	210.4	31.4
	Hom. Press.	3000 lb./in	<u>2</u>	ı
1.661	1818.3	0.4354	1483.6	334.7
1.415 1.168	1282.0 789 <b>.</b> 5	0.4035 0.3430	1069.8 664.2	212.2 125.3
0.922	456.3	0.2980	381.2	75.031
0.676	228.7	0.2362	200.1	28.5
	Hom. Press.	4000 lb./in	2	
1.661	2050.2	0.4378	1668.3	381.9
1.415 1.168	1394 <b>.</b> 7 917.0	0.4008 0.3499	1154.8 780.6	239.9 189.4
0.922	512.6	0.2913	445.0	67.6
0.676	270.0	0.2238	234.4	35.5
	Hom. Press. 5000 lb./in2			
1.661	1887.9	0.4453	1554.2	333.7
1.415 1.168	1362.7 899.2	0.3985 0.3357	1127.0 769.2	235.7
0.922	572.8	0.3357	502.5	130.0 70.2
0.676	265.1	0.2182	230.7	38.4

TABLE 57

STRUCTURE EQUATION CONSTANTS FOR SERIES II EMULSIONS WITH SPAN-TWEEN EMULSIFIER, CARBOPOL-934, SODIUM SALT, SUSPENDING AGENT.

Conc. Suspending		ls.		
Agent in Aqueous	f , o	Poise	b <sub>v</sub>	f <sub>o</sub> ,
Phase % w/w	Dyne/cm <sup>2</sup>	Poise	Dyne/cm <sup>2</sup>	Dyne/cm <sup>2</sup>
		1000 lb./in		ı
0.334	420.8	0.2584	324.7	96.0
0.285	304.7	0.2153	247.6	57.1
0.235	236.2	0.1940	195.8	40.4
0.185	123.7	0.1461	108.3	15.4
0.136	63.1	0.1161	56.1	7.0
		2000 lb./in	2	
0. 221	1.00 5	0.0600	210 (	7.02.0
0.334	436.5	0.2620	312.6	123.9 81.7
0.285 0.235	315.0 210.4	0.2199 0.1725	233.3 167.8	42.7
0.185	142.2	0.1518	109.2	32.9
0.136	80.1	0.1167	63.2	16.9
	Hom. Press.	3000 lb./in	<u></u>	ŀ
0.33 <sup>1</sup> +	450.0	0.2467	335.6	114.4
0.285	299.8	0.2101	222.2	77.6
0.235	231.9	0.1801	181.4	50.6
0.185	1.52.0	0.1471	121.5	30,4
0.136	88.1	0.1184	70.5	17.5
	Hom. Press.	4000 lb./in	2	
0.334	470.5	0.2553	340.0	130.4
0,285	343.0	0.2188	252.7	90.3
0.235	271.3	0.1872	205.3	66.0
0.185	172.3	0.1530	135.5	36 <b>.</b> 8
0.136	102.8	0.1228	81.9	20.8
	Hom. Press.	5000 lb./in	<u>C</u>	1
O <b>_</b> 33 <sup>1</sup> 4	510.8	0.2597	356.7	154.0
0.285	371.5	0.2153	273.4	98.1
0.235	259.5	0.1834	196.9	62.6
0.185	164.0	0.1499	129.1	34.8
0.136	101.4	0.1206	81.2	20.1

TABLE 58

PARTICLE SIZE DISTRIBUTION FOR SERIES III, BASIC EMULSIONS

Particle		Counted Particle	es, Stated Size		
Diameter Microns		Homogenizing P	lb/in <del>?</del>		
u		Sodium Lauryl Sul	fate Emulsifier		
	2000	2500	3000	4000	
< 1.5	111	75	140	250	
1 <b>.</b> 5 <b>-</b> 3	179	216	192	106	
3 <b>-</b> 4.5	69	61	81	38	
7 <b>.</b> 5 <b>-</b> 6	32	19	23	28	
6-7.5	15	7	2	14	
		Span-Tween l	Emulsifier		
	1000	2000	3000	<sup>1</sup> 4000	5000
< 1.5	233	288	306	266	336
1.5-3	205	165	165	175	172
3-4.5	22	9	6	7	2
7 <b>.</b> 5 <b>-</b> 6	8	3	2	1	1
6 <b>-</b> 7 <b>.</b> 5	-	-	-	3	2

be found. Reciprocal plots, semi-logarithmic and logarithmic plots were generally non-linear. Certain qualitative comparisons can be made, however, from an examination of the tables of flow constants. The constants, by and important were larger with sodium lauryl sulfate emulsifier in all cases except when carboxymethylcellulose was the suspending agent. Acacia solution alone was Newtonian, except for the highest concentration, but emulsions containing acacia were non-linear. Those with Span-Tween emulsifier showed no yield value, but those with sodium lauryl sulfate did exhibit yield values. Emulsions without suspending agents were non-linear with rather high yield values, the yield value for the emulsion with sodium lauryl sulfate being higher than that with Span-Tween.

Since the Structure equation constants could not be directly related to concentration of suspending agent, limiting viscosities,  $\underline{\eta}_{0}$ , were calculated as for series I. These values were then examined for quantitative relationships to concentration. The equation of Robinson (104 for suspensions of spherical particles was found to fit the data for suspending agents. This equation may be expressed as:

$$C/f(\eta) = a - bC,$$

where  $\underline{f(\eta)}$  may be  $\underline{ln}$   $\underline{\eta_{rel}}$ ,  $\underline{\eta_{sp}}$  or  $\underline{\eta_{rel}}^{1/2}$ -1. An important difference was noted, however, in that the slope of the curves, when  $\underline{f(\eta)}$  was  $\underline{ln}$   $\underline{\eta_{rel}}$ , was positive instead of negative as generally is found with suspensions. A typical curve is shown in Figure 15. This is not surprising, since there is no reason to believe that suspending agents in solution would have effects equivalent to solid spheres. Thus, the constants of this equation cannot be interpreted in the manner used for dispersions of

spherical particles, and the equation must be considered as simply an empirical description of the data. As such it enables one to compare the flow properties of one suspending agent with another. The equation,  $\frac{\text{C/ln }\eta_{\text{rel}} = \text{a} + \text{bC}, \text{ was used for sodium alginate, sodium carboxymethylcellulose,}}{\text{tragacanth, and methylcellulose solutions.}}$  For acacia, the equation  $\text{C/}\eta_{\text{sp}} = \text{a} - \text{bC}, \text{ was used, and none of the three functions fitted the data for Carbopol-934.}}$  Values of the constants obtained are shown in Table 59.

Suspending Agent	Emulsifier				
0	Sodium Lauryl Sulfate		Span-Tw	<i>r</i> een	
	a	ъ	a	Ъ	
Acacia	0.72	0.07	0.59	0.05	
Sodium Alginate	0.08	0.31	0.06	0.35	
Sodium Carboxy- methylcellulose	0.20	0.24	0.20	0.24	
Tragacanth	0.06	0.48	0.06	0.48	
Methylcellulose	-	-	0.14	0.21	

The constants, <u>a</u> and <u>b</u>, determined in this manner, can be used to compare relative viscosities of solutions of suspending agents or might be used to determine the concentration required to furnish a solution with a given relative viscosity. Relative viscosity in this case refers only to limiting

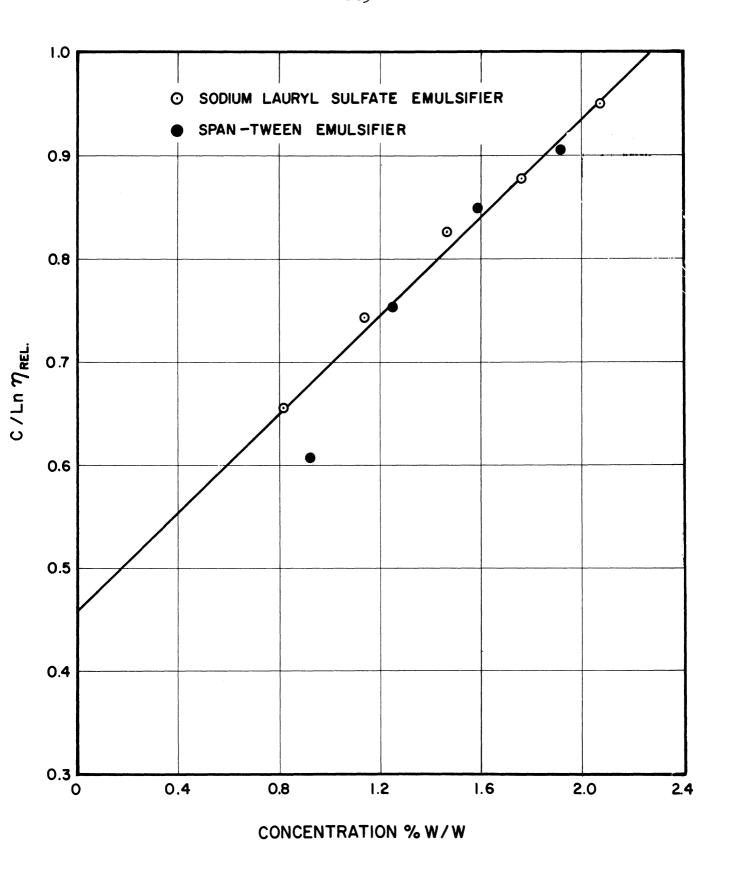


Fig. 15. Plot of C/log  $\eta_{\text{rel}}$  Versus C for Suspending Agent Solutions of Series II, Sodium Carboxymethylcellulose Suspending Agent

viscosities and not to flow properties at high rates of shear. The limiting viscosities of the emulsions of series II did not yield specific viscosities which followed the equations commonly used to calculate intrinsic viscosity. Values of  $\underline{\eta_0}$  for the emulsion were linearly related to those for the solvent (solution of suspending agent) by the equation:

$$\eta_{o(emul.)} = A + B \eta_{o(solv.)}$$
,

where  $\underline{A}$  and  $\underline{B}$  are constants. Values of these constants are shown in Table 60. From them it can be seen that the addition of oil to the emulsifier-suspending agent solution caused a greater increase in limiting viscosity in some cases than in others. The change was greatest for acacia as the suspending agent and, in most cases, for Span-Tween as the emulsifier.

TABLE 60 PARAMETERS OF THE EQUATION  $\eta_{o(emul)} = A + B\eta_{o(solv)}$ FOR SERIES II EMULSIONS

Suspending Agent	Emulsifier				
	Sodium La	uryl Sulfate	Span-Tween Mixture		
	A	В	A	В	
Tragacanth	0.13	1.12	0.25	0.96	
Acacia	0.11	3.73	0.02	4.35	
Sodium Algimate	0.19	1.23	0.15	1.45	
Sodium Carbo- methylcellulose	0.33	0.93	0.19	1.79	
Methylcellulose	<b>-</b>	· -	0.25	1.20	
Carbopol-934 Sodium Salt	-	-	0.14	0.78	

## Sedimentation of Series II Emulsions

It was decided to measure ultimate settling volumes of the emulsions of series II in order to see if flow constants might be related to degree of sedimentation. Samples of each emulsion were placed in 100-ml. graduated cylinders with glass stoppers and allowed to stand at room temperature. The volume of the sedimented disperse phase was measured at intervals of about one week until no further sedimentation was noted. These observations were continued over a period of six months, at which time all samples showing sedimentation had reached equilibrium. Some of the samples exhibited no separation during this period. Average values of relative settling volume,  $\underline{S}'$ , limiting viscosities,  $\underline{\eta}_{0}$ , and yield values,  $\underline{f}_{0}$ , are shown in Table 61.

Plots of  $\underline{S^{\dagger}}$  vs. constants of the Structure equation, vs.  $\underline{\eta}_{0}$  and vs  $\underline{f}_{0}$  were non-linear in every case, and comparisons of the curves indicated no clear relationship of sediment volume to these constants. On the other hand, sediment volume appeared to be a linear function of concentration of suspending agent. This indicates that the factors contributed by the suspending agent are not simply flow properties and that these unknown factors influencing sedimentation have a greater effect than viscosity or yield value.

By means of the linear plots of  $\underline{S'}$  vs. concentration of suspending agent it is possible to make some comparisons as to effectiveness of different suspending agents within the ranges of concentration studied. Acacia was quite inferior to the other suspending agents, regardless of which of the two emulsifiers was used, and it had the peculiar property of increasing

TABLE 61

RELATIVE SETTLING VOLUMES, LIMITING VISCOSITIES AND YIELD VALUES OF EMULSIONS AND SOLUTIONS OF SUSPENDING AGENTS, SERIES II

2.75.	Sodium Lauryl Su	lfate Emulsi:	fier				
Conc. Suspending Agent in Aqueous Phase, % w/w	Relative Settling Volume S'	η <sub>o(emul)</sub> Poise	η <sub>o(solv)</sub> Poise	formul) Dyne-cm-2	f <sub>o</sub> (solv) Dyne-cm		
	Tragacanth						
1.01 0.85 0.71 0.56 0.41	2.25 2.07 2.01 1.84	0.580 0.476 0.399 0.300 0.246	0.333 0.314 0.243 0.189 0.104	171 126 91 36 31	134 95 66 32 12		
		Acacia	a.				
19.95 17.02 14.81 11.31 8.16	1.64 1.71 1.74 1.80 1.83	2.554 1.372 0.962 0.519 0.303	0.386 0.348 0.207 0.116 0.070	673 326 175 152 130	14 O O O		
		Sodium Al	ginate	<u> </u>			
1.02 0.87 0.72 0.57 0.42	2.17 2.16 2.10 1.93 1.82	1.170 0.985 0.768 0.527 0.381	0.885 0.669 0.517 0.305 0.166	301 225 172 113 65	116 64 26 13 1		
	Sodi	um Carboxyme	thylcellulo	se			
2.07 1.76 1.46 1.15 0.84	- - 2.23 2.06	1.53 <sup>4</sup> 1.223 0.953 0.637 0.441	1.205 0.809 0.466 0.274 0.154	370 282 196 88 90	55 26 10 6 2		
		No Suspendi	ng Agent	,			
	1.76	0.090	0.008	31	0		

TABLE 61
(Cont'd)
RELATIVE SETTLING VOLUMES, LIMITING VISCOSITIES
AND YIELD VALUES OF EMULSIONS AND SOLUTIONS
OF SUSPENDING AGENTS, SERIES II

Span-Tween Emulsifier

	Span <b>-</b> Twe	en Emulsifier			
Conc. Suspending Agent in Aqueous Phase, % w/w	Relative Settlin Volume S'	€ ″o(emul)	η <sub>O</sub> (solv)	f (emul) Dyne-cm-	folion (solv) 2 Dyne-cm
		Tragaca	nth		
1.16 0.99 0.82 0.65 0.47	2.20 2.11 2.16 2.04 1.87	0.752 0.642 0.516 0.374 0.262	0. <sup>1</sup> 477 0.1 <sup>1</sup> 41 0.316 0.237 0.163	239 188 132 117 72	195 143 97 59 98
A THE COLOR OF THE		Acaci	a.		
19.24 16.39 13.54 10.68	1.3 <sup>4</sup> 1.41 1.53 1.56	1.682 1.174 0.826 0.489	0.414 0.273 0.171 0.114	0 0 0	0 0 0
		Sodium Al	ginate	All of the second secon	
1.03 0.88 0.73 0.57 0.42	2.28 2.25 2.24 2.24 2.23	1.665 1.329 1.003 0.748 0.526	0.853 0.800 0.603 0.424 0.254	434 303 225 149 105	257 125 76 42 21
	So	dium Carboxyme	thylcellulo	se	
2.26 1.92 1.59 1.25 0.92	2.20 2.16 2.06 1.87 1.85	2.549 2.006 1.453 0.890 0.560	1.598 1.055 0.584 0.363 0.257	474 339 306 215 263	150 77 30 12 25
		Methylcell	ulose		
1.66 1.41 1.17 0.92 0.68	2.18 2.19 2.20 2.12 2.11	1.966 1.565 1.090 0.741 0.454	1.699 1.109 0.676 0.443 0.192	334 224 132 67 31	156 71 33 17 4
		Carbopol-934,	Sodium Salt		
0.33 0.28 0.23 0.18 0.14	- 2.28 2.24 2.06	0.591 0.462 0.346 0.270 0.190	0.518 0.418 0.269 0.134 0.063	124 81 53 30 16	153 53 23 1 <sup>4</sup> 8
		No Suspendi	ing Agent		
	2.10	0.060	0.008	3	0
	L				

the degree of sedimentation with increasing concentration. All other suspending agents decreased the degree of sedimentation with increasing concentration.

Tragacanth and carboxymethylcellulose gave lower values of <u>S'</u> with Span-Tween than with sodium lauryl sulfate emulsifier; sodium alginate gave lower values with sodium lauryl sulfate. With Span-Tween emulsifier the suspending agents may be ranked as follows: Carbopol > Sodium alginate > tragacanth = methylcellulose > carboxymethylcellulose >> acacia. With sodium lauryl sulfate emulsifier the ranking is: tragacanth > sodium alginate > carboxymethylcellulose >> acacia. With no suspending agent Span-Tween gave higher values of <u>S'</u> than sodium lauryl sulfate.

## Series III Emulsions

Emulsions of series III were prepared and measured with the aim of obtaining more detail as to effects of concentration of suspending agent and disperse phase on flow properties of emulsions. For this purpose eight levels of sodium carboxymethylcellulose, eight of methylcellulose and two of Carbopol were used with seven to nine different concentrations of oil at each level of suspending agent. Only one emulsifier, Span-Tween, was used. Structure equation constants for series III emulsions are presented in Tables 63-71. Constants for the solutions of suspending agents are in Table 62.

Structure equation constants for suspending agents did not follow the reciprocal relationship found by  $\text{Grim}^{(10)}$  for suspensions, but the values of  $\eta_{\text{rel}}$  computed from  $b_V$  and  $\eta$  did fit the equation used for the

TABLE 62

STRUCTURE EQUATION CONSTANTS FOR SUSPENDING AGENT SOLUTIONS CORRESPONDING TO EMULSIONS OF SERIES III.

Conc. of	f	ħ. ~	b <sub>v</sub> , 2	f <sub>o</sub> ,
Suspending Agent % w/w	Dyne/cm <sup>2</sup>	Poise	Dyne/cm <sup>2</sup>	Dyne/cm?
		3.500.00	DC	
	Methylcelli	lose 1500 C	<del>75</del>	I
1.3367	918.5	0.2433	837.1	81.4
1.1696	580.4	0.2156	540.1	133.2
1.0025	361.5	0.1846	341.9	19.6
0.7797	111.7	0.1526	98.8	12.8
0.651	100.7	0.1131	99.2	1.46
0.543	36.6	0.0904	30.9	5.8
0.434	19.5	0.0652	14.9	4.5
0.326	6.6	0.0392	3.2	3.4
Sodium	Carboxymeth	ylcellulose '	Type 7MP	
60	(-0.6		-00 l	000 1
1.687	638.6	0.2559	588.4	280.4
1.476	433.2	0.2120	404.1.	29.1
1.265	282.7	0.1757	266.1	1.6.6 1.4.0
1.153	267.8	0.1752 0.1433	253.8 152.2	3.0
0.984 0.769	155.2 114.6	0.1119	97.7	16.9
0.762	47.7	0.0838	44.7	3.0
0.281	18.1	0.0500	14.6	3.6
O . COT	10.1		1100	1
	Carbopol-934, Sodium Salt			
0.181	70.0	0.0649	52.9	17.1
0.125	17.8	0.0344	13.6	4.3

TABLE 63

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 1.337% AND 1.170% METHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil % v/v	f Dyne/cm?	$egin{array}{c} egin{array}{c} egin{array}$	b <sub>V</sub> Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>	
/0 V / V	Dyne/ cm-	10150	Dylic/ ciii.	Dylle/ cliff	
1.337 %	w/w Suspending	Agent in Ac	queous Phase	1	
54.2 48.7 43.3 37.9 32.4 27.0 16.2 10.8	1602.4 1517.2 1422.2 1328.0 1255.0 1187.8 983.1 979.4	0.4056 0.3914 0.3737 0.3434 0.3269 0.3253 0.2942 0.2768	1253.8 1224.6 1182.6 1135.6 1096.8 1045.4 883.3 886.2	348.5 292.5 239.6 192.4 158.2 142.4 99.8 93.2	
1.170 %	w/w Suspending	Agent in Ac	queous Phase		
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	1257.1 1145.1 1041.3 936.1 872.2 793.3 718.9 644.6 637.691	0.3892 0.3513 0.3347 0.3266 0.3066 0.2859 0.2771 0.2629 0.2471	981.2 949.9 840.3 814.9 778.5 717.3 651.1 588.7 540.153	275.9 195.2 151.1 121.2 93.8 76.1 67.8 56.0 48.6	

TABLE 64

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 1.002% AND 0.780% METHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil % v/v	f Dyne/cm <sup>2</sup>	Poise	b <sub>v</sub> Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>		
1.002 %	w/w Suspending	Agent in A	queous Phas	e		
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	999.9 836.3 767.9 669.6 566.2 550.4 490.2 400.4 387.5	0.3539 0.3314 0.2878 0.2826 0.2721 0.2532 0.2382 0.2269 0.2097	806.7 701.5 691.2 599.9 510.3 509.3 450.4 372.4 362.9	193.2 134.8 76.6 69.6 56.0 41.1 39.8 27.9		
0.780 %	0.780 % w/w Suspending Agent in Aqueous Phase					
54.2 48.7 43.3 32.4 27.0 21.6 16.2	635.599 540.6 433.6 301.9 258.8 202.5 169.7	0.3142 0.2857 0.2561 0.2209 0.2004 0.1760 0.1940	514.040 466.2 388.1 278.8 241.1 197.0 150.1	121.559 74.4 45.5 23.0 17.7 5.4 19.6		

TABLE 65

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 0.651% AND 0.543% METHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil % v/v	f Dyne/cm <sup>2</sup>	Υ Poise	b <sub>v</sub> Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>	
0.651 % w/w Suspending Agent in Aqueous Phase					
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	513.4 431.6 326.6 262.4 206.7 178.1 149.6 137.3 119.8	0.2678 0.2398 0.2213 0.2004 0.1864 0.1690 0.1573 0.1503 0.1369	426.6 374.2 292.8 242.3 190.6 166.8 139.4 131.3 115.1	86.8 57.4 33.8 20.2 16.1 11.2 10.2 6.0 4.7	
0.543 %	w/w Suspending	; Agent in A	queous Phase		
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	363.9 264.5 195.7 148.0 112.7 98.5 80.6 56.9 45.3	0.2326 0.2072 0.1865 0.1678 0.1528 0.1361 0.1253 0.1128 0.1016	295.6 227.1 174.6 132.9 102.7 91.7 76.1 54.8 46.2	68.3 37.3 21.2 15.0 10.0 6.8 4.4 2.1	

TABLE 66

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 0.434% AND 0.326% METHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil % v/v	f Dyne/cm <sup>2</sup>	Poise	bv Dyne/cm <sup>2</sup>	f Oyne/cm <sup>2</sup>
	Dyne/ Cill.	10126	Dyne/ Cm.	Dyne/ cm.
0.434 %	w/w Suspending	Agent in A	Aqueous Phas	se <del>F</del>
54.2 48.7 43.3 37.9 32.4 27.0 21.6 10.8	295.9 182.3 132.7 100.4 73.1 46.5 37.1 27.4	0.2041 0.1866 0.1614 0.1425 0.1264 0.1133 0.1008 0.0800	251.8 158.0 115.4 89.6 67.7 40.2 32.5 22.5	44.1 24.3 17.3 10.8 5.4 6.3 4.6 4.9
0.326 %	w/w Suspending	Agent in A	lqueous Phas	<u>se</u>
54.2 48.7 43.3 37.9 27.0 21.6 16.2	198.9 119.4 59.5 44.5 21.6 14.0 12.4 10.2	0.1761 0.1546 0.1239 0.1132 0.0834 0.067 0.0586 0.0508	161.7 100.9 47.5 35.2 16.0 10.6 9.1 6.7	37.3 18.6 12.0 9.3 5.6 3.4 3.3 3.6

TABLE 67

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 1.687% AND 1.476% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil	f	Υ	b <sub>v</sub>	f <sub>o</sub>	
% v/v	Dyne/cm. <sup>2</sup>	Poise	Dyne/cm <sup>2</sup>	Dyne/cm <sup>2</sup>	
1.687 % w/w Suspending Agent in Aqueous Phase					
54.2	1863.4	0.6670	1557.2	306.2	
48.7	1445.0	0.6331	1168.5	276.5	
43.3	1350.4	0.5759	1102.1	247.7	
37.9	1119.0	0.4790	398.6	180.4	
32.4	1001.9	0.4370	849.0	152.8	
27.0	872.7	0.4016	742.5	130.1	
21.6	832.6	0.3637	724.5	108.1	
16.2	744.1	0.3380	650.1	94.0	
10.8	652.9	0.2988	585.5	67.4	
1.476 % v	y/w Suspending	Agent in A	queous Phase	T	
54.2	1431.5	0.6571	1151.1	280.4	
48.7	1149.1	0.5537	928.1	220.9	
43.3	1145.0	0.5198	940.6	204.8	
37.9	967.5	0.5027	782.3	185.3	
32.4	721.8	0.4307	583.1	138.8	
27.0	616.8	0.3527	519.7	97.1	
21.6	566.9	0.3145	479.8	87.0	
16.2	491.2	0.2791	424.2	67.0	
10.8	475.5	0.2630	422.8	52.9	

TABLE 68

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 1.265% AND 1.153% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil	f	η <sub>∞</sub>	b <sub>v</sub>	f <sub>o</sub>		
% v/v	Dyne/cm <sup>2</sup>	Poise	Dyne/cm <sup>2</sup>	Dyne/cm <sup>2</sup>		
1.265 % w	1.265 % w/w Suspending Agent in Aqueous Phase					
54.2	1045.4	0.5614	825.7	219.7		
48.7	839.5	0.5091	659.1	180.4		
43.3	691.5	0.4500	550.9	140.6		
37.9	557.0	0.3902	444.9	112.0		
32.4	483.7	0.3329	402.0	81.7		
27.0	411.2	0.3004	342.5	68.7		
21.6	378.0	0.2667	323.0	54.9		
16.2	256.0	0.2475	308.9	47.6		
10.8	293.0	0.2330	258.0	35.9		
1.153 % w	/w Suspending	Agent in	Aqueous Phase	<u> </u>		
54.2	837.3	0.5496	615.2	222.1		
48.7	640.8	0.4772	465.4	175.5		
43.3	530.6	0.4058	394.9	135.7		
37.9	432.1	0.3532	327.1	105.0		
32.4	379.5	0.3148	290.1	89.4		
27.0	322.2	0.2749	257.2	64.7		
21.6	280.0	0.2453	227.8	52.2		
16.2	261.6	0.2226	223.5	38.0		
10.8	245.3	0.2082	215.3	30.1		

TABLE 69

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 0.984% AND 0.769% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT.

Conc. Oil	f	η∞	b <sub>v</sub>	f <sub>o</sub>		
% v/v	Dyne/cm <sup>2</sup>	Poise	Dyne/cm <sup>2</sup>	Dyne/cm <sup>2</sup>		
0.984 % w/w Suspending Agent in Aqueous Phase						
54.2	680.1	0.4723	523.9	156.2		
48.7	533.6	0.4157	412.5	121.1		
43.3	434.7	0.3697	332.9	102.7		
37.9	340.7	0.3199	263.8	77.7		
32.4	291.1	0.2641	233.0	58.1		
27.0	253.5	0.2364	207.1	46.3		
21.6	216.5	0.2052	184.0	32.4		
10.8	174.1	0.1793	156.6	17.5		
0.769 % w	/w Suspending	Agent in A	Aqueous Phas	e <del>-</del>		
54.2	455.0	0.3820	316.3	138.8		
48.7	327.8	0.3347	216.3	111.5		
43.3	250.6	0.2842	166.7	83.9		
37.9	203.5	0.2448	136.7	66.8		
32.4	171.8	0.2138	119.3	52.4		
27.0	142.7	0.1846	103.2	39.4		
21.6	125.1	0.1652	93.6	31.5		
16.2	105.7	0.1478	83.2	22.5		
10.8	96.7	0.1337	82.0	14.7		

TABLE 70

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 0.562% AND 0.281% SODIUM CARBOXYMETHYLCELLULOSE SUSPENDING AGENT.

		<del> </del>		
Conc. Oil % v/v	f Dyne/cm <sup>2</sup>	کر Poise	b <sub>v</sub> Dyne/cm <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>
0.562 %	w/w Suspending	Agent in	Aqueous Phase	: <del>:</del>
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	294.5 195.8 154.9 134.6 104.6 78.9 70.3 59.5 45.9	0.3113 0.2729 0.2187 0.1988 0.1733 0.1536 0.1348 0.1182 0.1035	210.5 131.6 113.6 95.6 73.8 54.3 53.5 45.5 34.8	83.9 64.1 41.3 39.0 30.9 24.6 16.8 14.0 11.1
0.281 %	w/w Suspending	Agent in	Aqueous Phase	е Г
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	139.8 88.4 58.9 47.2 34.8 29.6 26.4 18.5 21.3	0.1975 0.1699 0.1376 0.1244 0.1085 0.0948 0.0806 0.0728 0.0612	95.5 55.3 34.2 26.2 18.4 16.5 15.6 7.9 14.0	44.3 33.1 24.7 20.9 16.4 13.1 10.8 10.6

TABLE 71

STRUCTURE EQUATION CONSTANTS FOR SERIES III EMULSIONS WITH 0.187% AND 0.125% CARBOPOL-934, SODIUM SALT, SUSPENDING AGENT.

	,		<del></del>				
Conc. Oil % v/v	f Dyne/cm <sup>2</sup>	\ \ Poise	b <sub>v</sub> Dyne/cm. <sup>2</sup>	f <sub>o</sub> Dyne/cm <sup>2</sup>			
	251107 01110	10100	2,110, 0111	DJIIC/ CIII			
0.187 <b>%</b> w/	0.187 % w/w Suspending Agent in Aqueous Phase						
54.2 48.7 43.3 37.9 32.4 27.0 21.6	363.1 284.9 168.7 120.4 85.7 68.3 62.5	0.1920 0.1651 0.1450 0.1217 0.1107 0.0964 0.0871	244.1 212.1 130.4 99.1 68.8 53.0 49.2	119.0 72.8 38.3 21.2 16.9 15.3 13.3			
16.2 10.8	59.9 62.4	0.0779 0.0736	49.1 49.6	10.9 13.5			
	0.125 % w/w Suspending Agent in Aqueous Phase						
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.2 10.8	252.3 155.4 93.2 51.9 33.2 22.6 18.6 16.9 19.4	0.1544 0.1284 0.1085 0.0930 0.0747 0.0637 0.0547 0.0477	180.1 119.1 76.8 41.3 24.8 14.9 11.4 9.4 14.4	72.1 36.3 16.4 10.6 8.4 7.6 7.1 7.5 5.0			

suspending agents of series II; i.e., C/ln  $\eta_{\text{rel}}$  = a + bC, and the constants obtained are shown below:

Suspending Agent	a	<u>b</u>
Methylcellulose	0.14	.21
Carboxymethyl- cellulose	.123	0.29

These values agree reasonably well with those from series II.

The Structure equation constants for the emulsions of series III did not follow a simple relationship to concentration of oil, but a polynomial with three terms adequately described the change in reciprocals of the flow constants with change in oil concentration for all but the emulsion containing Carbopol.

$$1/\text{Constant} = b_0 + b_1 \phi + b_2 \phi^2$$
.

Coefficients of this equation were evaluated by least squares using the IBM 704 computer and a program quite similar to the one previously described. Values obtained for the coefficients are given in Table 72.

These coefficients were found to be related logarithmically to concentration of suspending agent:

$$\log b_i = \alpha + \beta \log c$$
,

where  $\underline{i}$  is  $\underline{0}$ ,  $\underline{1}$ , or  $\underline{2}$ ,  $\underline{c}$  is the concentration by weight of suspending agent in the aqueous phase,  $\underline{\alpha}$  and  $\underline{\beta}$  are constants. Thus, with the two equations the flow constants for emulsions with any oil concentration and any suspending agent concentration can be calculated. Values of  $\underline{\alpha}$  and  $\underline{\beta}$  are in Table 73.

Emulsions with Carbopol exhibited a peculiar property; these with low concentrations of oil were less viscous than the suspending agent alone. This was though to be due to concentration of the salf at the interface,

TABLE 72 PARAMETERS OF THE EQUATION 1/Constant =  $b_o$  +  $b_1 \phi$  +  $b_2 \phi^2$  FOR EMULSIONS OF SERIES III

		onstant	b2x103	0.819 1.443 1.574 -1.100 5.890 9.010 9.29	-0.084 -0.260 -0.341 -7.400 -3.280 -15.17 60.20	Zq	3.001 6.589 1.787 2.210 2.748 7.287 14.115 29.377
	Carboxymethylcellulose	Polynomial Constant	-b <sub>1</sub> x10 <sup>3</sup>	2.716 4.385 6.450 6.186 12.54 28.88 28.88 111.4	2.262 3.555 5.634 2.444 8.400 11.75 90.27	-b1	6.239 9.767 7.358 8.555 10.26 16.159 23.722 44,110
	rboxymethy	Φ	box10 <sup>3</sup>	1.787 2.634 5.979 4.830 7.081 13.04 28.81 63.60	1.925 2.845 4.361 5.075 7.355 13.93 36.56	Oq	3.954 4.896 5.160 5.766 6.765 9.179 11.968
	Sodium Ca.	Structure Equation Constant	4-1		ρ	الم	
Agent		Conc. Suspending Agent in Aqueous Phase, % w/w		1.687 1.476 1.265 1.153 0.984 0.769 0.562	1.687 1.476 1.265 1.153 0.984 0.769 0.281		1.687 1.476 1.265 1.153 0.984 0.769 0.562 0.281
Suspending		ъ В В	50				
Susp		Const	b2x10 <sup>3</sup>	0.676 19.57 29.45 49.74 77.77 88.66 107.3	1.106 0.839 5.872 6.970 74.43 161.4 678.6	p5	0.495 2.747 0.950 2.834 2.018 10.458 17.326 47.144
		Polynomial Constant	-b <sub>1</sub> x10 <sup>3</sup>	1.415 3.320 5.588 6.700 20.26 99.59 1149.5 438.4	1.588 2.209 6.106 6.635 19.98 89.17 200.5	-b1	2.933 5.225 4.857 8.903 9.404 19.367 28.806 62.711
	lose	ture ion ant	b <sub>0</sub> x10 <sup>3</sup>	1.189 2.206 3.193 12.49 10.48 53.43 143.3	1.314 1.943 3.427 9.760 10.80 30.16 65.12	Oq	3.894 4.670 5.219 7.499 8.245 111.759 15.383 25.922
	Methylcellulose	Structure Equation Constant	Į.		,¢	٦٥	
	Methy	Conc. Suspending Agent in Aqueous Phase, % w/w		1.337 1.170 1.002 0.780 0.551 0.543	1.337 1.170 1.002 0.780 0.651 0.543 0.434		1.337 1.170 1.002 0.780 0.543 0.434 0.326

TABLE 73  $\begin{array}{ll} \text{PARAMETERS OF THE EQUATION log b}_{i} = \alpha + \beta \log C \\ \text{RELATING CONSTANTS OF THE POLYNOMIAL EQUATION} \\ \text{TO CONCENTRATION OF SUSPENDING AGENT} \\ \end{array}$ 

Suspending Agent	Structure Equation Constant	Polynomial Constant	α	β
Methyl- cellulose	f	b <sub>0</sub> -b <sub>1</sub> b <sub>2</sub>	-2.485 -2.485 -1.750	-3.877 -3.343 -2.367
	$\eta_\infty$	ьо -рЈ ро	0.743 0.724 0.095	-1.213 -2.127 -3.190
	${ t b}_{f V}$	р5 -р1 р <sup>0</sup>	-2.578 -2.278 -2.431	-3.870 -4.377 -4.592
Sodium Carboxy- methyl-	f	bo -b1 b2	-2.129 -1.847 -2.641	-0.340 -0.345 -0.119
cellulose	$\eta_\infty$	ь <sub>о</sub> -ь1	0.838 1.025 0.535	-0.101 -0.139 -0.242
	b <sub>v</sub>	b <sub>0</sub> -b1 b2	-2.112 -2.050 -2.590	-0.267 -0.225 -0.640

though other explanations might be proposed. Carbopol is more sensitive to added substances than most other suspending agents, being a linear polymer thought to be kept extended through charged groups along the chain. The flow constants for the emulsions containing Carbopol did not fit the same equations as did the constants for the other emulsions, and no satisfactory relationship of flow properties to concentration of Carbopol was found.

Limiting viscosities were calculated for this series, and the equation previously used for series II, relating  $\underline{\eta}_{\underline{0}}$  of emulsion and solvent was found to apply to most of the emulsions. The equation, which is as follows:

$$\eta_{o(emul)} = A + B \eta_{o(solv)}$$

fitted all of the carboxymethylcellulose data and the methylcellulose data where the concentration of oil was 27% or less. Constants of the equation are given in Table 74.

PARAMETERS OF THE EQUATION  $\eta_{o(emul)} = A + B \eta_{o(solv)}$ FOR SERIES III EMULSIONS

Conc. Oil		Suspending Agent			
% v/v	Sodium Carbox	ymethylcellulose	Methylcellulose		
	A	В	A	В	
54.2 48.7 43.3 37.9 32.4 27.0 21.6 16.0 10.8	0.17 0.12 0.05 0.05 0.04 0.03 0.02 0.01 0.00	3.43 2.02 1.95 1.64 1.76 1.66 1.30 1.07	- - - 0.06 0.04 0.03 0.01	1.26 1.10 1.10	

Limiting viscosities were used to calculate specific viscosities for series III emulsions, and from these values intrinsic viscosities were obtained by plotting  $\log \frac{\eta_{\rm sp/c}}{\rm vs.~c.}$  There are two theoretical equations for intrinsic viscosity, Einstein's, which predicts a value of 2.5 for rigid spheres, and Taylor's, which predicts a value less than 2.5 for liquid spheres. Taylor's equation may be expressed as follows:

where  $\eta_{\underline{i}}$  is the viscosity of the dispersed phase and  $\underline{K}$  is equal to  $(\eta_{\underline{i}} + 2/5\eta_{0}(\text{solv}))(\eta_{\underline{i}} + \eta_{0}(\text{solv})).$  Since Taylor's derivation is based on low concentrations of dispersed phase it is commonly evaluated in the form:

$$\eta_{sp} = \eta_{rel} - 1 = 2.5 \text{ KØ}$$
, 
$$[\eta] = \lim_{\phi \to 0} \eta_{sp/\phi} = 2.5 \text{ K} .$$

Values of intrinsic viscosities found and calculated by Taylor's equation are presented in Table 75.

From Table 75 it is seen that the observed intrinsic viscosities increased with decreased  $\eta_{o(solv)}$  as predicted by Taylor's equation but the observed values were, in all cases but one, smaller than predicted. Deviations from Taylor's equation have been noted before  $^{(45,105)}$  and Oldroyd developed a modified equation to account for the rigidity of the oil particle occurring due to the absorbed film of emulsifying agent. Oldroyd's equation predicts a higher value than expected from Taylor's equation. Likewise, doublet formation by the particles or other forms of agglomeration are said to increase the value of intrinsic viscosity  $^{(105)}$ . The two factors

which might explain the lowering of intrinsic viscosity are slippage at the surface of the particles and distortion of the particles

TABLE 75

INTRINSIC VISCOSITIES OF SERIES III EMULSIONS

OBSERVED VALUES AND VALUES CALCULATED WITH TAYLOR'S EQUATION

Conc. Suspending Agent in Aqueous Phase, % w/w	[η] Observed	[η] Calculated	
	Methylcellulose		
1.34 1.17 1.00 0.78 0.65 0.54 0.43 0.33	0.673 0.245 0.608 0.794 1.153 1.439 1.713 2.495	1.429 1.558 1.687 1.958 2.015 2.177 2.318 2.369	
	Sodium Carboxymethylcellulose		
1.69 1.48 1.26 1.15 0.98 0.77 0.56 0.28	0.713 0.718 0.837 0.322 0.209 0.455 1.432 1.820	1.517 1.629 1.713 1.763 1.901 2.019 2.164 2.314	
	Carbopol-934, Sodium Salt		
0.19 0.12	0.159 0.504	1.230 2.350	

Slippage at the surface of dispersed particles might occur through shear of a thick layer of absorbed emulsifier. If such shearing took place a velocity gradient would exist between the continuous medium and the dispersed particle

which would have the same effect as decreasing the viscosity of the liquid in the particle, causing the intrinsic viscosity to decrease.

Deformation of the dispersed particle may occur as the size of the particle is larger and as the rate of shear is greater. Since the lowest value of shear used for numerical evaluation of flow constants was 129 sec.—1 it seems possible that the emulsion particles might have been deformed to some extent throughout the portion of the curves used for measurement. An estimate of the distortion at 129 sec.—1 by the equation presented by Nawab and Mason (106),

$$\frac{L-B}{L B} = \frac{Ga\eta_0}{2r} (\frac{1 + 19p/16}{1 + p})$$
,

where <u>L</u> and <u>B</u> are the length and width of the prolate spheroid, <u>a</u> is the diameter of the undeformed sphere, <u>r</u> is the interfacial tension, <u>G</u> is the velocity gradient and <u>p</u> is  $\eta_{O(oil)}/\eta_{O(solv)}$ , indicated about 2% distortion. This does not make it seem that distortion is the cause for low values of intrinsic viscosity in series III emulsions.

## DISCUSSION

Perhaps the most significant result of this work is the demonstration that the Structure equation can be applied to emulsions. Previously, this equation had been found to describe accurately the flow curves of about two hundred systems representing solutions of several suspending agents and suspensions of several different solids. The fact that the equation was equally applicable to about six hundred flow curves representing solutions of suspending agents and emulsions used in this study indicates its broad usefulness.

Because of the lack of suitable equations for non-Newtonian flow, workers studying emulsions have carefully avoided non-Newtonian systems or have assumed linear flow at low rates of shear and used low-shear instruments for measurement. At the same time, the complexities of non-Newtonian flow have been avoided in theoretical developments so that the fundamental equations of Einstein, Taylor and Oldroyd assume Newtonian properties for the media and are limited to suspensions so dilute that no interaction between particles occurs.

One of the pitfalls of using low shear measurements and assuming Newtonian flow is that a material which has a yield value may not be in laminar flow at such shear rates, making the measurements erroneous. Also, it is generally found with non-Newtonian materials that no linear portion exists in the lower part of the flow curve but that instruments are frequently used which cover so narrow a range of shear that the curve appears linear in the region of measurement.

As was shown in this work, use of the Structure equation enables one to describe non-Newtonian flow over a wide range of shear and, from the flow constants, to obtain limiting viscosities which might be used to test theoretical equations and concepts. There is yet some question as to the validity of limiting viscosities obtained from flow constants, especially in view of the fact that yield values are commonly found in disperse systems but do not contribute to the limiting viscosity as calculated. To justify the soundness of this use of limiting viscosity it appears necessary that simplified systems be studied which will satisfy the assumptions of the theoretical equations. For example, the dispersed particles should be uniformly sized and not agglomerated, the emulsifying agent should either be one known to have no effect or one with known surface properties, and electroviscous effects should be eliminated. Once simplified systems of this sort are shown to be predictable by theory, the effects of added factors can be evaluated systematically.

Some evidence to support the use of limiting viscosities from the Structure equation was obtained in this work. Values for series I emulsions yielded estimates of intrinsic viscosity agreeing with the Einstein factor of 2.5 when corrected for ultimate settling volume. Similar applications of samples of Grim's data on suspensions of solids yielded intrinsic viscosities quite close to Einstein's constant except where the concentration of suspending agent was high. Test of Taylor's equation indicated agreement with the equation at low concentration of suspending agent but poor agreement at high concentration.

The reciprocal relationship of flow constants to concentration of dispersed phase was not applicable to the data on emulsions obtained

in this work. This is believed to be due to the effect of flow in the dispersed droplets, and some modification of the equation, similar to that used by Taylor, appears to be needed in order to predict ultimate settling volume. Also, the actual measurement of sedimentation is so crude as to make difficult any test of an equation. Refinement of laboratory methods for sedimentation is greatly needed for this purpose.

The status of the rheology of emulsions was aptly described by Oldroyd (106) in a recent paper: "Naturally, the cases which the mathematician finds easiest to make detailed calculations about are so idealized ... that they must always remain the most difficult on which to carry out observations. But one must admit that real emulsions and suspensions cannot be expected to have rheological properties any simpler than the idealized infinitely dilute ones amenable to theoretical analysis."

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