NOTATION

C = dimensionless moisture concentration; C/C_o
$\overline{C}$ = an average value of C over the thickness
$₵$ = free moisture concentration; weight of free moisture per unit weight of bone dry solid
$₵_{cr}$ = critical moisture concentration
$₵_s$ = free moisture concentration on the surface
F = dimensionless time as defined by Equation (14)
h = heat transfer coefficient
k_g = convective mass transfer coefficient
L = half thickness of a slab
P = a dimensionless parameter as defined by Equation (16)
P_g = vapor pressure of evaporating liquid in the gas stream
$P_g{}^o$ = vapor pressure of evaporating liquid at the dry bulb temperature
P_s = vapor pressure of evaporating liquid at the surface temperature, T_s
Q = dimensionless temperature as defined by Equation (11)
R = gas constant
S = relative humidity
T_g = dry bulb temperature of gas stream
T_s = surface temperature
t = time
X = dimensionless distance of x as defined by Equation (13)
x = distance from the center of a slab toward surface
Y = an experimental constant as defined by Equation (4)
Z = a dimensionless parameter as defined by Equation (15)
α = effective diffusivity of free moisture within the drying solid
γ = correction factor for effective mass transfer area and coefficient as defined by Equations (2) and (4)
λ = latent heat
ρ_o = density of bone dry solid

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Surface Rheological Properties of Foam Stabilizers in Nonaqueous Liquids

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The rheological properties of foam stabilizers have been measured with an improved canal viscometer that provides absolute values of surface shear viscosity and yield strength. Studies conducted in room air confirmed previous reports of complex non-Newtonian film properties for oil soluble surfactants at the air-oil interface. Both shear and time dependent behavior were observed in which the apparent surface viscosity increased with decreasing rotational speed. Surface viscosities were low at all fresh interfaces but generally increased with the age of the surface over a period of several hours to several days. Experiments conducted in a controlled humidity environment have established that the phenomenon of aging in room air is due to adsorption of moisture from the gas by the surfactant film. Preliminary results indicate that the shear dependency of films in a high humidity environment can be approximated by a Bingham Plastic model which characterize their rheological behavior in terms of a Newtonian surface viscosity and yield value.

In 1962, the U.S. Army Fuels and Lubricants Research Laboratory began a basic study of the various factors that affect the foaming of gear oils. This paper, which deals with the rheological properties of surfactant films that form at the air-oil interface, presents the results of a part of the program that have been found to be of primary importance to the foam stability of nonaqueous systems. During the course of this investigation, an improved viscometer was developed that enables one to calculate absolute values for the surface shear viscosity and yield strength of soluble films. The mathematical development of the equations, which relate these surface properties to experimental parameters, was the subject of an earlier paper by Burton and Mannheimer (*1*); however, this present paper is the first to report measured values of surface viscosity and rigidity that have been determined by this technique.

THE ROLE OF SURFACE RHEOLOGY IN FOAMING

The concept of surface viscosity was first proposed by

Plateau (*2*), who also recognized its importance as a possible mechanism of foam stability. Today, it is generally conceded that films of surface active materials possess mechanical properties which are responsible for the stability of some foaming solutions (*3*), however, there is as yet no clearcut correlation between surface rheology and foaming (*4*). This is due in part to the complex nature of foams in which several mechanisms of stability may mask the effects of surface viscosity (*6*). Also, it is known that the more effective foam stabilizers generally exhibit highly non-Newtonian behavior which has not been characterized in terms of known rheological models. The situation is further clouded by the fact that present techniques for measuring adsorbed films, such as the rotating bob or oscillating pendulum viscometer, have not been properly analyzed (*7*), consequently experimental results obtained by these methods, particularly of non-Newtonian film behavior, are difficult to interpret.

Because of the unusual properties of nonpolar solvents such as the liquid hydrocarbons, stabilizing effects from surface tension gradients and electrical double layer repulsion can be minimized thereby making it possible to isolate the effects of surface rheology on foaming. Unfortunately, few investigations of foam stabilizers at the air–oil interface have been reported. Furthermore, what information we do have indicates that the rheology of oil soluble surfactants is rather complex in that the apparent surface viscosity is generally a function of both the rate of shear and the age of the film. With these comments as a background, the purpose of this paper is twofold: first, to demonstrate a rheological technique that provides absolute values of surface viscosity and yield strength and secondly, to explain the apparently complex behavior of foam stabilizers at the air-oil interface.

DETECTION OF FILM FORMATION AT AIR-OIL INTERFACE

Due to the limited information concerning the surface rheological properties of nonaqueous solutions, initial experiments were directed toward establishing whether or not a superficial or surface viscosity was detectable with gear oils which had been found to form exceptionally persistent foams. The viscous traction canal viscometer that was used has been described in detail by Davies (*5*). The walls of the canal were formed by two concentric cylinders (r_i = 2.23 in., r_o = 2.45 in.) and a glass petri dish which contains the liquid sample (5½ × ¾ in.) serves as the canal floor. Rotation of the dish, by means of a turntable, produces a tractive force that causes the liquid to flow through the canal. One of the principal departures from the method described by Davies was that the canal walls were immersed in the oil; whereas, Davies coated the rings with paraffin wax so that essentially line contact with the water surface could be realized. A constant depth of liquid was maintained by utilizing a fixed volume of oil for each determination and by holding the bottom of the cylinders at the same relative position with respect to the dish.

Since the theoretical treatment of this viscometer had not been fully developed at the beginning of this program, these measurements do not represent absolute values of surface viscosity, and for the purpose of this early work we refer to the relative surface viscosity of the film as:

$$\mu^s_{\text{rel.}} = \frac{t_c - t_c^*}{t_c^*}$$

In this relation, t_c^* is the surface rotational time along the centerline of the canal for a pure base oil and t_c is the time for an oil which contains foam stabilizers. This relation assumes that any difference in the time of a pure oil and one on which a film has been formed would be due to the extra shear resistance of the film. Later developments showed that under reasonably restrictive conditions, this quantity is in fact proportional to the surface viscosity [see Equation (1)].

Measurements of the surface rotation time (t_c^*) were made for a reference grade base oil (4.0 poise at 75°F.), mineral white oil (1.6 poise at 75°F.) and *n*-cetane (3.6 centipoise at 75°F.). These results established that t_c^* was inversely proportional to the rotational speed of the turntable and essentially independent of the physical properties of the liquid. Identical measurements were made with several gear oils that had been found to form exceptionally stable foams. The results of duplicate experiments with a typical oil (a field sample of military gear oil which foamed in service) are presented in Figure 1, in which the relative surface viscosity is plotted as a function of the age of the surface for different rotational speeds denoted by t_c^*. In general, the relative surface viscosity was found to increase with the age of the surface and with decreasing rotational speed but, in addition, the film appeared to be rigid below some critical speed. These results are representative of most of the nonaqueous solutions that we have studied to date (including blends of calcium phenates and synthetic metal sulfonates in base oils and mineral white oils). Similar shear and time dependencies for foam stabilizers at the air-oil interface have been reported by McBain and Robinson (*8*) and also by Criddle and Meader (*9*).

Since the attainment of surface tension equilibrium may require in excess of several hours for some colloidal surfactants, it was originally suspected that the aging process, which is so common for surface rheological measurements, was due to slow adsorption of the additive. However, measurements indicated that the minimum or equilibrium surface tension of these solutions was reached within 10 to 20 min. Other evidence suggested that in addition to the adsorption of surfactant molecules at the air-oil interface, a really coherent film also required the presence of moisture. Several observations contributed to this hypothesis but most important was the fact that the moisture content of the gas used in foaming tests was found to significantly affect foam stability (Figure 2). Whereas, all previous surface rheological measurements had been made

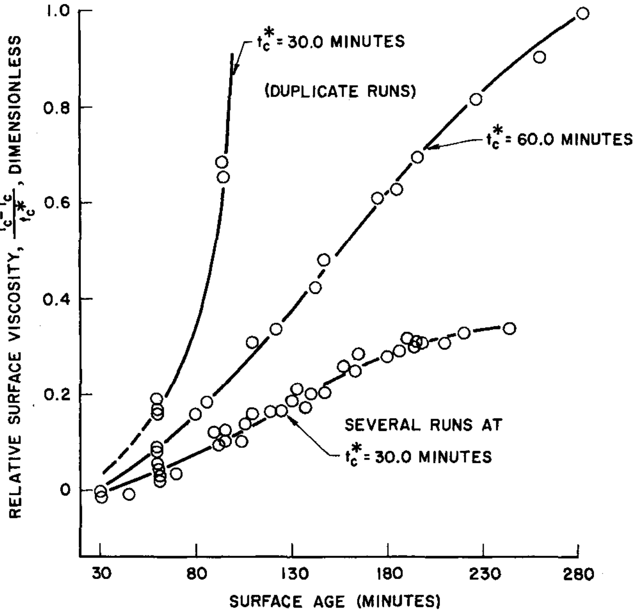

Fig. 1. Effect of aging and rotational speed on the relative surface viscosity of a gear oil in room air.

in ordinary room air, the experiments described in the experimental section were designed specifically to study surface rheological properties in a controlled humidity environment.

THEORETICAL DEVELOPMENTS

The original canal viscometer proposed by Dervician and Joly (*10*) and also by Harkins and Kirkwood (*11*) has long been recognized as the only method which provides quantitative values of surface viscosity, however, this technique is not applicable to adsorbed films due to the requirement of a surface pressure gradient to maintain flow. Davies (5) demonstrated a viscous traction technique which eliminated the troublesome surface pressure gradient but his proposed configuration is difficult to analyze. A recent paper by Burton and Mannheimer (*1*) has presented an analysis of an improved canal viscometer (Figure 3) which has resulted in the following equations for surface viscosity and yield strength:

$$\mu^s \doteq \frac{y_o\mu^b}{\pi}\left(\frac{w_c^*}{w_c}-1\right)\coth\pi D \doteq \frac{y_o\mu^b}{\pi}\left(\frac{t_c}{t_c^*}-1\right), \qquad D>\frac{2}{\pi} \qquad (1)$$

and

$$\tau_o^s \doteq w_c^*\mu^b\coth\pi D \doteq w_c^*\mu^b, \quad D>\frac{2}{\pi} \qquad (2)$$

Equation (1) expresses the surface viscosity (μ^s) of either an adsorbed or insoluble monolayer as a function of the canal width (y_o), the viscosity of the liquid substrate (μ^b) and the surface speed ratio (w_c^*/w_c) or equivalently the surface period ratio (t_c/t_c^*). The surface period (t_c) is the time for a centerline element at the gas-liquid interface to travel a specified distance in the canal. The asterisk in these equations denotes that the liquid substrate has a *negligible surface viscosity*. When the liquid depth to width ratio (D) is greater than $2/\pi$, the absolute value of the surface viscosity and yield strength is essentially independent of the exact value of the liquid depth as long as it is held constant during a given series of measurements. The yield value of a solid film (τ_o^s) is given in Equation (2) by the product of the liquid viscosity (μ^b) and the equivalent floor speed required to produce surface flow (w_c^*).

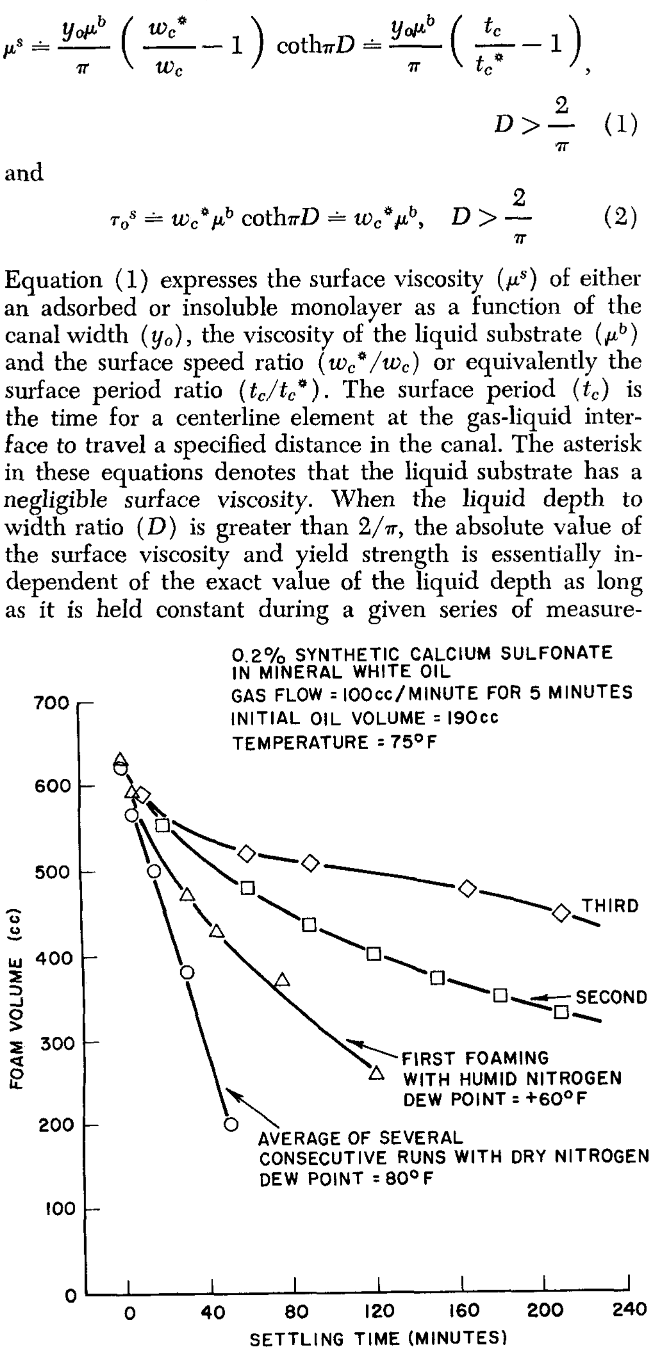

Fig. 2. Effect of humidity on foam stability.

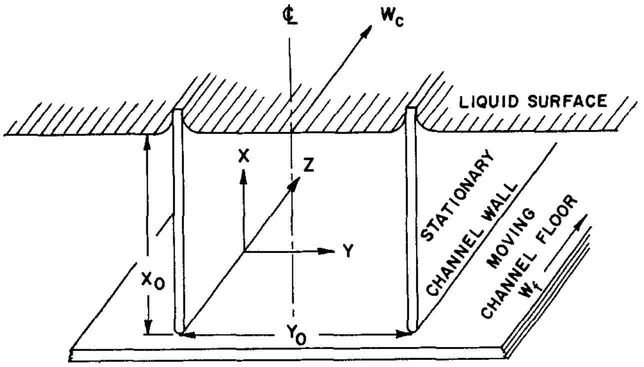

Fig. 3. Idealized canal geometry.

One of the basic assumptions of this analysis is that the curvature of the canal walls is negligible when in fact an annular canal is used in practice. Schechter and Mannheimer (*12*) have analyzed the more difficult annular geometry and have shown that the curvature is negligible whenever the ratio of the two radii which form the walls of the canal is less than 1.26. For example, the equation for the surface viscosity in a canal for which $r_o/r_i = 1.26$ was found to differ from Equation (1) by a factor of $3.148/\pi$. Under these same conditions use of the linear approximations result in an error in the value of the yield strength of less than 2%. Since the experimental measurement normally involves an error of this order of magnitude or greater, the use of the simpler equations have been used for calculating the surface viscosities and yield strengths reported in this paper.

Whereas Equation (1) is applicable strictly to films which exhibit a Newtonian surface viscosity, Schechter and Mannheimer (*13*) have recently analyzed a Bingham plastic film which can be characterized by surface yield value and Newtonian surface viscosity. To determine the surface viscosity of a Bingham plastic film, the yield value (τ_o^s) is determined first and then the surface period ratio (t_c^*/t_c) is plotted as a function of the dimensionless stress ratio ($T_x^* = \tau_o^s/\mu^b w_c^*$). The surface viscosity is then obtained either by interpolation between the theoretical curves provided in their paper or by determining the value of t_c^*/t_c which corresponds to infinite shear stress, that is, $T_x^* = 0$, and by using this quantity to calculate the surface viscosity with the aid of Equation (1).

EXPERIMENTAL

Effect of Humidity on the Surface Rheology of Foam Stabilizers

The viscous traction canal viscometer used in this investigation (Figure 4) has been described in detail earlier (*1*). Basically, the instrument consists of an annular canal with a moving floor. The dimensions of this particular configuration were chosen so that both the linear canal approximations would be valid, that is, $r_o = 2.19$ in., $r_i = 1.75$ in. and $D = 0.728$.

In order to investigate film development in a controlled gas environment, the viscometer was enclosed in a glass bell jar and provided with auxiliary components so that the entire sequence of operations (including filling the viscometer with the test fluid) could be performed in a closed system. The function of these various components is best explained by describing a typical experiment.

First, the entire system is purged with the gas that has been chosen for study. Next, the liquid is transferred to the stainless steel dish by applying a slight pressure to the externally mounted sample container. A small gap (approximately 0.005

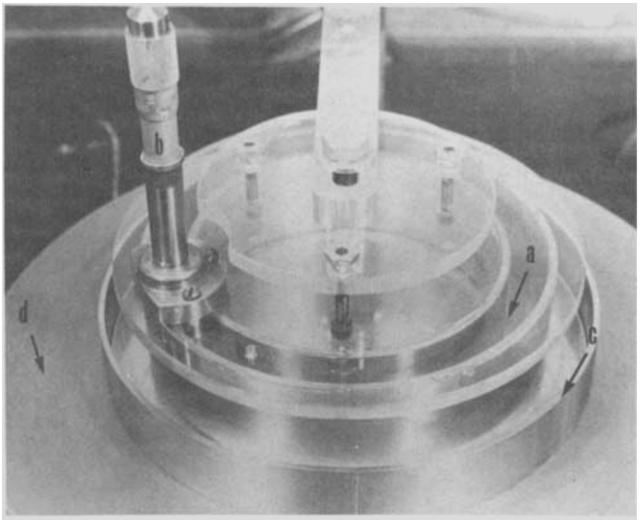

Fig. 4. Annular canal viscometer. (a) Annular canal, (b) Micrometer, (c) stainless steel dish, (d) turntable.

in.) is left between the bottom of the canal walls and floor so that the oil flows into the canal by seeking its own level. It has been found that the primary effect of the gap is to deepen the canal, and can be allowed for by calibrating the system with pure liquids such as mineral oil or cetane to determine t_c^*. Transfer of the sample is terminated when a micrometer needle, which is preset to the desired depth, just dimples the surface. The needle is then withdrawn and a few nonwetted particles are dropped onto the surface by gently tapping the lower end of the particle dispenser. After filling the viscometer, which usually took less than 30 min., the turntable motor was started and measurements made of the time for a particle to make a complete revolution while traveling along the centerline of the canal. This quantity, which is denoted as t_c, is the principle indicator of surface viscosity in that $t_c > t_c^*$ for solutions of surface active additives which form coherent films.

In situations where it was desired to study the effect of varying shear on the rheological properties of the film, several different motors were used (2, ½, 1/5, 1/10, 1/20, and 1/40 rev./min). Since even pure liquids have excessively long rotational periods at the lower speeds, it was found convenient to measure the time of travel over a small fraction of the canal length. This was accomplished by the use of a specially designed low power (16 ×) microscope and a linear 5.00 mm. scale having 50 subdivisions. Alignment of the scale with the centerline of the canal was accomplished by means of an inscribed radius on the bottom of the stainless steel dish which served as the canal floor.

Calibration of the viscometer with mineral oil and cetane reconfirmed the earlier results in which the centerline surface period for pure liquids (t_c^*) was found to be independent of bulk fluid properties (viscosity and surface tension) and to vary in direct proportion to the rotational period of the turntable (*1*). Due to the improved method for controlling the liquid depth, the precision of measurement was increased somewhat so that the experimental error in determining t_c^* was generally less than 1% of the average value. With this particular canal geometry and mineral oil ($\mu_b = 1.6$ poise at 75°F.) a 1% error in t_c^* is equivalent to a surface viscosity of 6×10^{-3} surface poise. While this may seem to be rather insensitive in view of reported surface viscosities for aqueous solutions as low as 1×10^{-4} surface poise, it must be remembered that the sensitivity of the viscous traction technique is directly proportional to the viscosity of the solution. Consequently, this same 1% error with low viscosity liquids (that is, 1×10^{-2} poise) would be equivalent to a surface viscosity of about 3×10^{-5} surface poise.

The yield strength of a film is determined by measuring the rotational speed at which surface flow is zero. Because of the difficulties involved in deciding when the surface is completely rigid, the ratio t_c^*/t_c is plotted as a function of the turntable speed (or equivalent $1/t_c^*$) and extrapolated to zero. The rotational speed corresponding to this condition is then used to calculate the yield strength from Equation (2).

RESULTS

To investigate the hypothesis that film aging was due to adsorption of moisture by the surfactant at the air-oil interface, measurements were made with a blended mineral oil which contained 2% by weight of a synthetic calcium sulfonate. While this additive is not pure in the strict sense of the word, the physical properties of synthetic sulfonates are much more consistent and better known than the natural petroleum sulfonates. The viscosity of the blend was measured by ASTM method D-445-53T, and was found to be very close to that of the pure base oil. Essentially the same value was observed in capillary tubes having different diameters, which indicates that the viscosity of the blend was Newtonian (Table 1).

TABLE 1. EFFECT OF SHEAR ON BULK VISCOSITY OF MINERAL OIL AND CALCIUM SULFONATE BLEND AT 100°F.

Material	Viscometer Tube ID (cm.)	Viscosity (cs)	Shear Stress at Wall (dynes/sq.cm.)
mineral oil	0.126	79.2	25
mineral oil	0.102	79.0	21
mineral oil	0.063	78.9	13
2% calcium sulfonate	0.126	80.1	25
2% calcium sulfonate	0.102	80.0	21
2% calcium sulfonate	0.063	80.1	13

In these initial experiments, extremes of dry and humid air environments were compared to measurements made in room air. The dry environment was achieved by passing laboratory line air through a solid dessicant (Dryrite), while humid conditions were obtained by bubbling the air through distilled water. The results of duplicate experiments at each of these conditions are presented in Figure 5 in which the relative surface viscosity is plotted as a function of the age of the surface. Measurements in room air exhibited the same characteristics that have been found to be typical of foam stabilizers in nonpolar solvents; that is, the apparent surface viscosity was initially low and increased with the age of the surface. These results were also observed when the experiments were performed in dry air; however, the apparent surface viscosity was at all times lower than in the untreated air. Altogether different results were obtained when measurements were made in the humid environment. In this case, the apparent surface viscosity was at its highest value initially and was found to decrease with time. For presently unaccountable reasons, the surface flow in both humid tests became quite erratic and the experiments were terminated after 1½ to 2 hours since the particles refused to remain in the center of the canal. Aside from this rather unusual behavior, which may have resulted from normal forces generated by the film, these other observations are easily explained in terms of the stated hypothesis. For example, at the low moisture content of the dried air (and room air), diffusion of water vapor from the gas to the adsorbed surfactant is relatively slow; therefore, the coherency of the film increased slowly. In a humid environment, the much higher partial pressure of the water vapor results in rapid transfer of moisture to the film and maximum surface viscosity is attained in a very short time; that is, less than the time required to make the first observation of t_c. The noted decrease of the surface viscosity with time is apparently due to the thixotropic character of the film which will be discussed later.

That these observations were not simply due to the interaction of moisture with a solution of calcium sulfonate is evident from the fact that the same additive

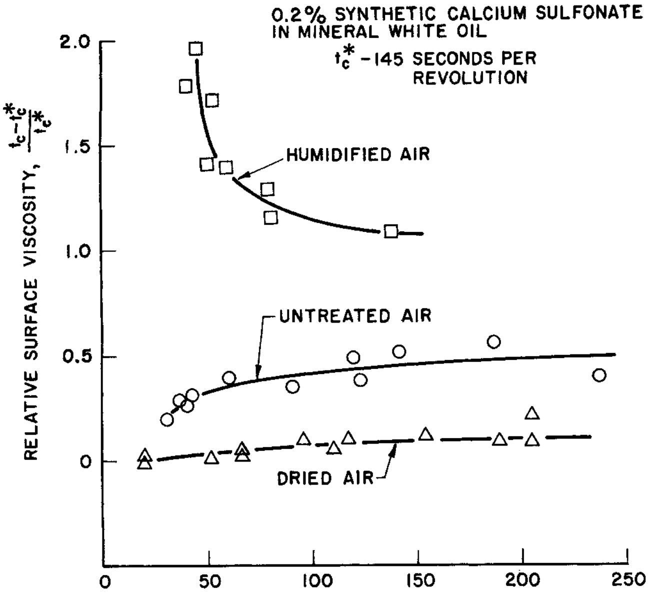

Fig. 5. Effect of humidity on the development of surface viscosity.

gave no indication of film formation (or foam stability) in humid air when cetane was substituted for the mineral oil. The reason for this is that the additive is surface active in mineral oil but not in cetane. Whereas, the calcium sulfonate produced a small, but measurable, surface tension depression in the mineral oil (0.5 dynes/cm.) no surface tension lowering was observed with cetane. These results indicate that some net adsorption of surfactant (that is, surface activity) is required for the development of a measurable surface viscosity.

Up to this point only measurements which depended strongly on the age of the film have been reported; however, by allowing the film to adsorb moisture from a humidified gas and then flushing the system with a dry gas, time independent measurements were made in which the effects of rotational speed on surface rheological properties were observed. In the following experiments high purity nitrogen which had a dew point of —80°F., was used instead of air. In order to hasten purging of the gas environment immediately above the liquid surface, a small capillary tube diverted a portion of the gas entering the bell jar directly into the canal. The absence of any detectable surface flow for mineral oil, with the turntable motor stopped, insured that the gas flow rate was sufficiently low so as not to affect the measurement. As a result of residual surface moisture, the nitrogen leaving the system had a higher humidity (dew point was —10 to 0°F. as determined by a Dew Pointer). This could be reduced somewhat by increasing the flow, but excessively high rates were required to approach the —80°F. dew point of the nitrogen entering the system.

Contrary to the previous results with dry air, it was found that t_c remained constant for an indefinite period of time in the dry nitrogen environment. For example, at a turntable speed of 2 rev./min. ($t_c^* = 145.5 \pm 0.5$ sec.) t_c was 149.5 sec. at a surface age of 30 min and 149.4 sec. 16 hr. later. It is presently felt that the aging of the film in air, after passing through a dessicant, was due to insufficient drying of the air in the earlier experiments rather than to the presence of oxygen. A series of measurements was made at different turntable speeds, then the flow of dry nitrogen was stopped and humidified nitrogen (dew point = + 60°F.) was passed into the system. Following a short induction period of 15 to 20 min., a rapid increase in t_c was noted. At this time the flow of humid nitrogen was stopped, the dry nitrogen restarted, and the system allowed to equilibrate by continuously running the turntable motor. The erratic surface flow in which particles moved out of the center of the canal and toward the inner wall was again observed when humid nitrogen was used. However, after several hours, the particles returned to the center and remained there. Generally, the viscometer was allowed to run overnight in order to assure that t_c was constant. Another series of measurements at different speeds were made after which additional moisture was added to the system (followed by dry nitrogen). After each exposure to humid nitrogen, a corresponding increase in t_c was noted. Finally, measurements were made in a high humidity environment in which the surface was allowed to equilibrate with the +60°F. dew point gas.

Some of the results of these experiments are presented in Figure 6, in which the ratio (t_c^*/t_c) has been plotted as a function of the equivalent rotational speed ($1/t_c^*$). This method of presentation is particularly useful in that it allows one to examine a wide range of rheological behavior on a single graph. For example, when t_c^*/t_c is near 1.0, the surface viscosity is negligible. Conversely, as this ratio approaches zero, the surface viscosity is equivalent to a rigid film. The numbered curves in Figure 6 represent increasing exposures to humid nitrogen with no. 1 exposed to 0°F. dew point nitrogen only and no. 5 full equilibrium with +60°F. dew point nitrogen. The constancy of t_c^*/t_c over a wide range of rotational speeds represents the first reported measurements of Newtonian surface viscosity in nonaqueous solutions (curves 1 and 2 in Figure 6). The data for the lowest values of surface viscosity (that is, $t_c^*/t_c = 0.973$) were typical of several different experiments in which the film was exposed only to a dry nitrogen environment and are equivalent to a surface viscosity of 1.6×10^{-2} surface poise. Brief exposure (15 to 20 min.) to humid nitrogen always resulted in a decrease in t_c^*/t_c (that is, an increase in surface viscosity). It was not possible to reproduce exactly the same degree of change each time the experiment was repeated with a fresh sample; nevertheless, all of the experiments which resulted in values of $t^*_c/t_c \geqq 0.888$ (that is, $\mu^s \leqq 7.3 \times 10^{-2}$ surface poise), were shear independent. Also, once equilibrium was reached at one speed, essentially no thixotropic behavior was observed when other speed changse were made.

Additional exposure of the oil to humid nitrogen resulted in a film which exhibited a marked shear dependency. The apparent surface viscosity generally increased (that is, t_c^*/t_c decreased) with decreasing rotational speed (curves no. 3 and no. 4), however, only the film which was allowed to fully equilibrate with the humid nitrogen (curve no. 5) gave evidence of a measurable yield value. The films in dry nitrogen also exhibited only slight thixotropic behavior. For example, in a particular experiment (curve no. 4), measurements of t_c were 229 sec. ($t_c^* = 145.5$ sec.) in the afternoon and 238 sec. for the first full rotation the next morning after the surface had been allowed to remain undisturbed overnight in a dry nitrogen environment. Within 30 min. after restarting the turntable, t_c was back down to 230 sec. after which time it showed only slight fluctuations of ±0.5 sec.

Measurements of the film, which was equilibrated with humid nitrogen (curve no. 5), indicated that the surface became rigid when the turntable motor was reduced from 2 to ½ rev./min. (that is, $1/t_c^*$ from 0.412 to 0.103 rev./min. Since additional motors in this speed range were not on hand, four different pulleys were made up so that we could more thoroughly investigate the shear dependency of the film. The surface yield value of

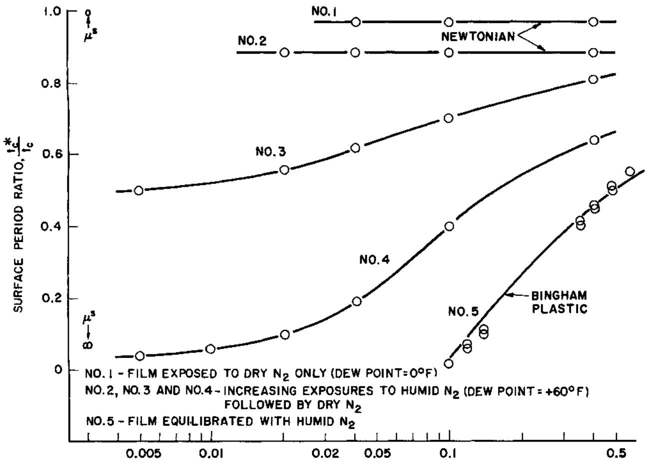

Fig. 6. Effect of rotational speed on surface rheological properties at different moisture levels.

7.5×10^{-2} dynes/cm. was determined by extrapolating t_c^*/t_c to zero at which $1/t_c^* = 0.090$ rev./min. (Figure 6). Observation of the surface with the microscope at this rotational speed showed evidence of a small, but measurable, surface flow; however, the value of $t_c^*/t_c = 0.003$, for all practical purposes is zero. The pronounced thixotropic behavior of this film at this low turntable speed (t_c^*/t_c decreased from its initial value of 0.007 to 0.003 in approximately 4 hr.) implies that even lower values of t_c^*/t_c would eventually be attained. These results illustrate the continuous transition from Newtonian to non-Newtonian surface rheological behavior due to increasing exposures of the film to moisture. Moreover, it is interesting to note that the most effective condition for foam stabilization with this system (that is, high humidity) was the only condition which resulted in a measurable yield value.

Because of the obvious non-Newtonian behavior, it is difficult to interpret the high apparent surface viscosity that was observed in humid nitrogen (curve no. 5). However, Schechter and Mannheimer (13) have recently reported an analysis for Bingham plastic surface flow in which the rheological properties of the film are characterized by a yield value and a Newtonian surface viscosity. The solid curve no. 5 drawn through the data corresponds to a Bingham Plastic film with a yield stress of 7.5×10^{-2} dynes/cm. and a surface viscosity of 2.2×10^{-1} surface poise. While the measured data do not correspond exactly to the Bingham model, the curve describes the variation of t_c^*/t_c remarkably well over a rather wide range of rotational speeds. Additional measurements are required before any definite conclusions can be drawn, but these initial results are encouraging in that they indicate that the apparently complex surface rheological behavior of these films may be approximated by relatively simple models. Since most of the really effective foam stabilizers are reportedly non-Newtonian and exhibit a yield value, future studies may explain some of the apparent anomalies which have frustrated attempts to correlate foam stability with surface viscosity.

CONCLUSIONS

This paper demonstrates a new surface rheological technique that is both simple and accurate and which provides a quantitative measure of the surface viscosity and yield strength of surfactant films at the gas/liquid.

Nonpolar solvents containing effective foam stabilizers have been found to exhibit complex rheological behavior at the air-oil interface. As with previously reported results for lubricating oils, the apparent viscosity was generally a function of both the rate of shear and the age of the surface. Strong evidence is presented that explains the prolonged aging of the air-oil interface as being due to the slow absorption of moisture by the surfactant film. Initial results also indicate that the highly non-Newtonian behavior of the calcium sulfonate-mineral oil system in a high humidity gas environment can be approximated by a Bingham plastic film.

While it has been observed that high humidity is essential for the rapid development of a coherent film at the gas oil interface and also produces the most stable foam, many questions regarding surface rheology and foam stability of even the simpler nonaqueous systems remain unanswered. For example, it has been observed that antifoamants may increase, decrease, or have no effect on film development, even though the same material effectively eliminates all foaming (8). Consequently, it must not be construed that surface rheology measurements tell the whole story; however, the mechanical properties of films at the gas liquid have been found to be the most distinguishing property of oils which foam and therefore are the most likely candidates for future study.

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NOTATION

D = channel depth/width ratio
w_c = midchannel velocity in free surface of liquid
w_c^* = midchannel velocity in free surface of liquid with negligible surface viscosity
t_c = midchannel period in free surface of liquid
t_c^* = midchannel period in free surface of liquid with negligible surface viscosity
y_o = channel width
r_o = radius of outer wall
r_i = radius of inner wall
μ^b = bulk viscosity of liquid, dynes sec./sq.cm.
μ^s = surface viscosity, dynes sec./cm.
τ_o^s = yield value for rigid films, dynes/cm.
T_x^* = $\tau_o^s/\mu^b w_c^*$ surface stress ratio, dimensionless

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