

Design and Evaluation of a Pressure Attachment for a Rotational Rheometer

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Abstract □ The problems associated with the measurement of the rheological properties of pressurized aerosol concentrates consisting of emulsions and/or micellar solutions are discussed. A pressure attachment for a commercially available rheometer is described, and data are presented for simple soap formulations. Pressurized concentrates exhibited pseudoplastic properties which could not always be correlated with the flow properties of resultant foams.

Keyphrases □ Rheometer, rotational—*aerosol rheological properties* □ Pressure attachment, rheometer—*design, evaluation* □ Diagram—*pressure attachment, rheometer* □ Viscosity-increasing additives—*aerosol foam effect*

A major problem, which has plagued the formulators of "aerosol" foams and other products utilizing high-consistency concentrates, has been the lack of a suitable and convenient means to evaluate their rheological properties. Most pharmaceutical and cosmetic foams utilize a pressurized concentrate in which the insoluble propellant is emulsified or micellized into the internal phase of an oil-in-water system by means of a suitable surfactant. Evaluation of the flow properties of the concentrate prior to the addition of propellant is of limited usefulness, because it does not reflect the influence of the internal phase. The fact that the concentrate systems are almost always non-Newtonian complicates the situation even further. The rheology of these pressurized concentrates plays an important role in the flow of material in the dip tube and valve assembly and influences drainage from the inside of the can during product use.

Although the importance of determining rheological characteristics of the non-Newtonian concentrates under pressure has been well recognized, very few reports are available in the literature. A preliminary report on the pressure-viscosity-time factors in dispensing of liquid aerosols was published by Mina in 1959 (1). The author measured the delivery rate of dimethyl silicone oils using a Precision Valve ($3 \times 0.040/0.080$) (Precision Valve Corp., Yonkers, N. Y.) at different pressures. By the use of suitable blending of different hydrocarbons and halocarbon propellants, the author was able to achieve a range of pressure from 10 to 100 psig. inside the sealed container. Viscosity determinations were made with an Ultra-Viscoson viscometer (Bendix Research Corp., Towson, Md.), utilizing a special twin-top adapter on the container to accommodate the ultrasonic probe as well as a normal valve. The author concluded that viscosity is significantly lowered under pressure as the pressure is increased, and

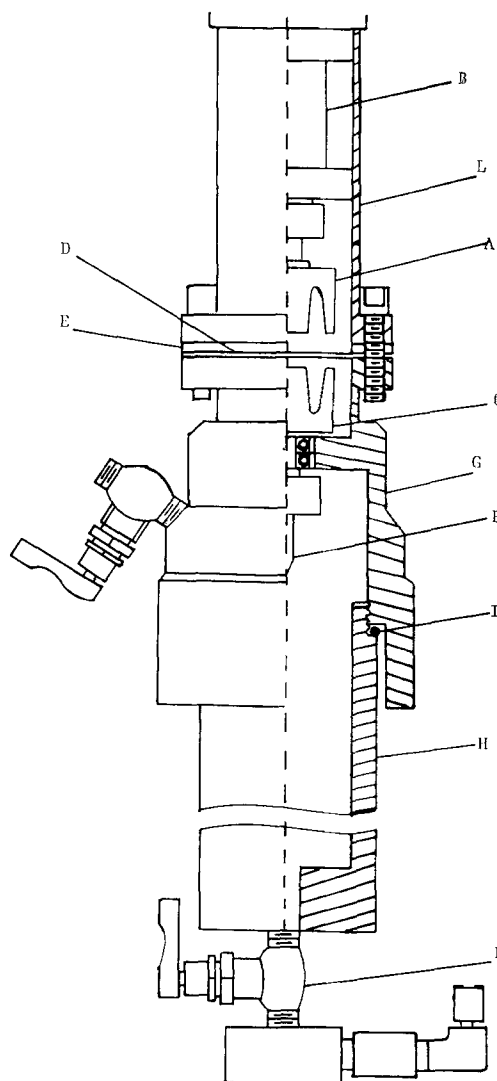


Figure 1—A schematic diagram of the pressure assembly for the Rotovisco viscometer.

this phenomenon is reversible upon removal of the added pressure.

Cohen *et al.* have described the use of the Brookfield viscometer (Brookfield Engineering Laboratory, Stoughton, Mass.) for measuring viscosity at low rates of shear, supplemented by use of the Severs extrusion rheometer model A-100 (Castor Laboratory Equipment Co., Pittsburgh, Pa.) for high shear measure-

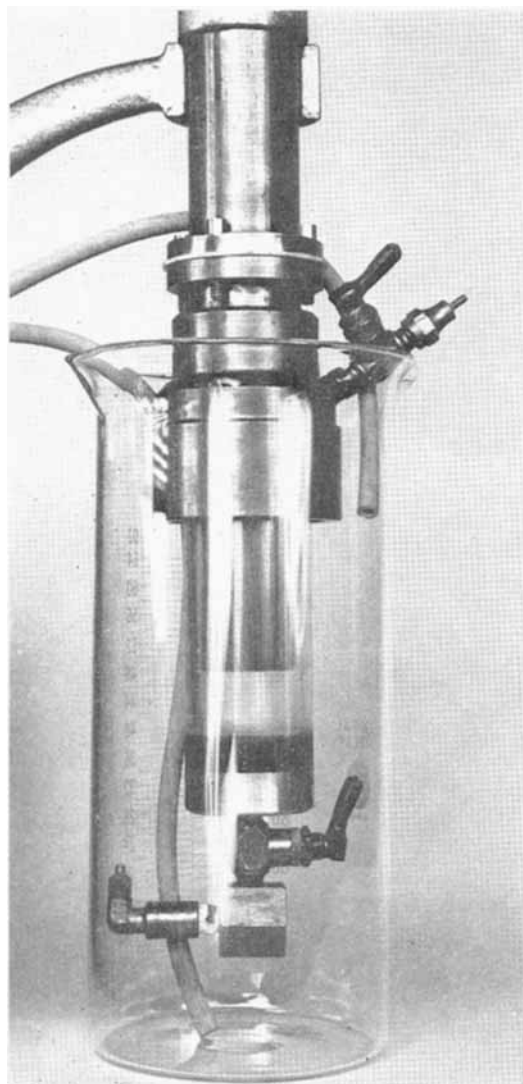


Figure 2—Assembled pressure attachment.

ments (2, 3). A series of aerosol valves were calibrated in the Severs extrusion rheometer for pressures varying from 10 to 100 psig., and the rheological characterization method was demonstrated by the use of polymer "solutions" as well as a group of four commercial pressure-packaged toothpastes.

A qualitative method of evaluating pressurized emulsion systems was reported by Strickland (4). He compared different emulsions under pressure by measuring the time required for a 5-mm. diameter glass bead to fall through the emulsion when the transparent bottle was inverted. Sanders reported a method for evaluating the approximate viscosity of pressurized emulsions by inverting bottles slowly and noting the flow characteristics (5).

Augsburger made use of the Rotovisco viscometer with a modified pressure chamber assembly to accommodate the emulsion concentrate under pressure (6). Although Augsburger concluded that further modifications were necessary in the design of the pressure assembly, he was able to carry out rheological measurements of soap concentrates under pressure. He found that at a 5% (w/w) concentration of soap, propellant was solubilized in the soap solution, giving lower

viscosity values; at higher concentrations of soap the propellant was emulsified, giving higher viscosity values (6).

DESIGN AND CONSTRUCTION OF PRESSURIZED RHEOMETER

Rotational viscometers offer a means of transferring the standard model of Newtonian flow in a plane to a closed continuous system in which the liquid is trapped between the surfaces of a cup and a bob. By rotating either surface at a fixed rate and measuring the viscous drag transferred through the liquid (or on the rotating member itself), the two necessary parameters of viscosity—rate of shear, which is proportional to r.p.m., and shear stress, which is proportional to viscous drag—can be measured. Rotational viscometers are particularly useful in measuring non-Newtonian systems, because rates of shear can be varied and relationships between rate of shear and shear stress within a particular system can be established. These are most often described as flow curves.

The Haake Rotovisco rotational viscometer (Polyscience Corp., Evanston, Ill.), was employed in this study to determine the viscosity of the liquid concentrates as well as the rheological properties of the foams produced by the pressurized emulsion systems. The measuring head of the Rotovisco viscometer contains two readily interchangeable torsion springs, one of 50-g. cm. capacity for low-viscosity fluids and the other of 500-g. cm. capacity for medium-viscosity fluids. The use of the 50 head allows for expansion of lower stress readings over the entire dial range, giving greater accuracy to low-viscosity readings.

The pressure assembly previously utilized by Augsburger in his preliminary work on pressure rheometry was used in the current study, with some modifications. This assembly involves the use of a "driving" magnet, which is attached to the spindle of the viscometer in the same fashion that a bob is normally attached. On rotation of the spindle, this magnet drives a second magnet situated across a seal within a pressure chamber. A bob attached to the driven magnet inside the sealed chamber is held concentrically in the cup by means of a pair of ball bearings.

A schematic diagram of the pressure assembly is presented in Fig. 1. A magnet (A), attached to the spindle of the Rotovisco measuring head (B), drives a magnet (C) across the pressure seal plate (D). A spacer (E) assures that the driving magnet will not contact the pressure plate. Previous experience had shown that, under pressure, the pressure plate tends to become convex in the direction of the driving magnet, and that the clearance originally allowed for this magnet was insufficient. The driven magnet, tapped onto a standard Rotovisco spindle (F), rides on two Fafnir No. F4DD bearings (The Fafnir Bearing Co., New Britain, Conn.). The pressure chamber housing (G) is threaded to accommodate the sample cup (H). The dimensions of the cup and its relationship to the spindle are identical to that of the standard Rotovisco assembly. Consequently, all instrument constants remain the same for this attachment. An O-ring (I), at the base of the threads of the cup, seats itself against a ledge cut into the inner surface of the housing. By virtue of this O-ring, only minimal hand-tightening of the cup is required to make a pressure-tight seal. Hoke No. 450 toggle valves (Hoke, Inc., Cresskill, N. J.) are tapped into both the cup and the housing. The valve (K) in the cup was used to fill the chamber with the pressurized emulsions using a transfer actuator. The sample was removed from the same valve, because this minimizes internal foaming into the bearings when the pressure is released. The sleeve (L) is designed to fit over the lower portion of the Rotovisco measuring head where it is fastened with two thumb screws. While the housing was machined from brass, the cup was machined from plastic. A photograph of the pressure assembly is shown in Fig. 2.

Before proceeding further, it might be appropriate to summarize the difficulties encountered in the construction and operation of the pressure rheometer as follows:

(1) *Sealing of pressure chamber:* difficulty was solved by means of a Teflon spacer seal next to the brass plate and an O-ring at the base of the threads of the cup.

(2) *Concentricity of bob in the cup:* two bearings instead of one bearing were used to support the drive spindle more rigidly.

(3) *Introduction of samples into the cup:* as pressurized soap concentrates were transferred, they would foam into the cup. The foam

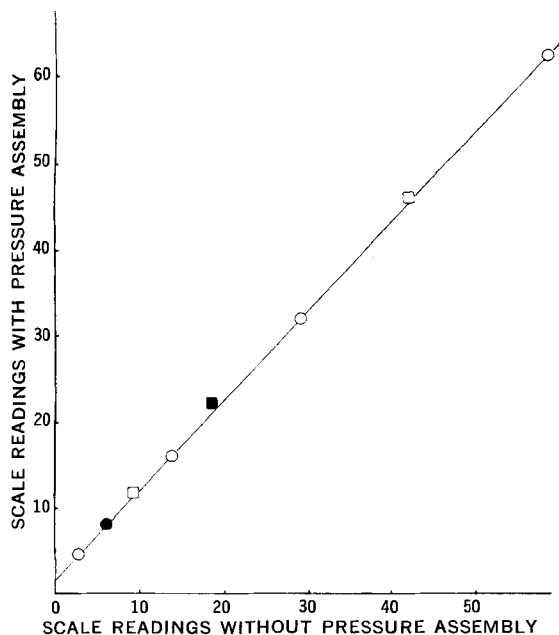


Figure 3—Relationship of shearing stress with and without pressure assembly, obtained with various standard viscosity liquids. Key: \circ , 9.2; \bullet , 18.4; \square , 27.6; and \blacksquare , 55.2.

would occupy the gap between the cup and the bob, giving abnormally high readings. This difficulty was solved as follows: (a) prepressurizing the cup before loading the sample; and (b) machining the cup out of clear plastic so that the sample could be observed and determinations disregarded if foaming occurred.

(4) *Slippage on the surface of the bob*: the use of the MVII-P profiled bob (with serrated surface) minimized the slippage encountered with high-viscosity systems.

A major problem was associated with the small but ever present additional frictional drag on the measuring head produced by the

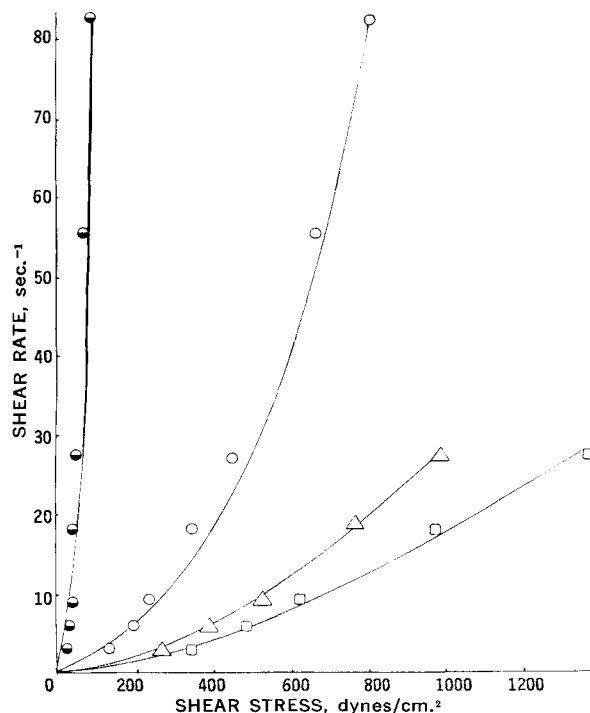


Figure 4—Pressurized emulsion flow curves—the effect of methylcellulose on the rheology of formulations containing 10% (w/w) soap. Key: \bullet , control soap formulation; \circ , 1.0% methylcellulose; \triangle , 1.5% methylcellulose; and \square , 2.0% methylcellulose.

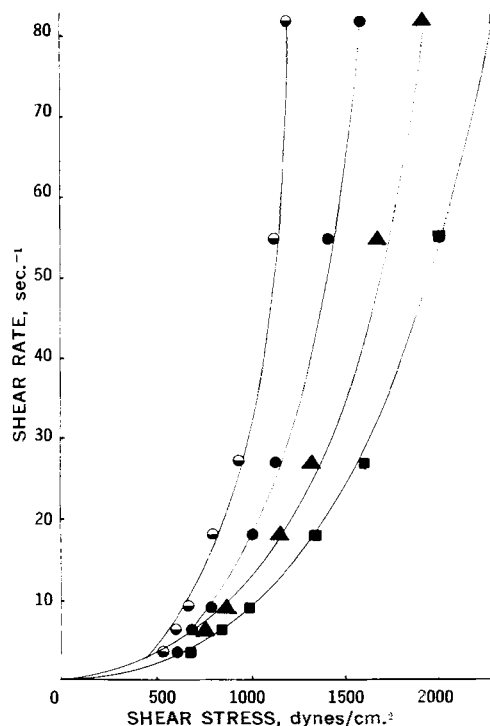


Figure 5—Pressurized foam flow curves—the effect of methylcellulose on the rheology of high consistency soap foams extruded from formulations containing 10% (w/w) soap. Key: \circ , control soap foam; \bullet , 1.0% methylcellulose; \blacktriangle , 1.5% methylcellulose; and \blacksquare , 2.0% methylcellulose.

magnetic clutch and bearings. Standard viscosity liquids were measured and shear stress values at various rates of shear were determined, both with and without the pressure assembly. A relationship was found to exist between the stress values with and without the pressure assembly. As can be seen from Fig. 3, this relationship proved to be linear. The slope of the straight line is 0.95, which means that actual stress values were 95% of those observed with the pressure assembly.

EXPERIMENTAL

Pressurized Packaging—Soap concentrates were weighed into “6-ounce” standard coated cans¹ which had been previously purged with a few drops of propellant, and Precision 0.020/0.080 valves (Precision Valve Corp., Yonkers, N. Y.) were crimped into place. Dip tubes were omitted to facilitate the filling of test vessels. The propellant was filled into the test containers by weight. The finished products were shaken vigorously and placed in a 50° water bath for 20 min. to test for leakage and can distortion. After removal from the water bath, the cans were allowed to remain at room temperature for 3 days prior to testing; all tests were completed within 2 weeks of preparation to minimize any possible aging effects.

Foam Rheology—Foam rheology was carried out after the manner of Richman (7) using the Haake Rotovisco viscometer and the MVII-P profiled bob and cup system. After shaking the pressurized containers for 15 sec., the foam was introduced directly into the cup through a 12.7-cm. (5-in.) extension of 0.64-cm. (0.25-in.) polyethylene tubing attached to Precision foam actuator SP-115. The cup was filled slowly from the bottom up, and shearing was begun 1 min. after the cup was filled. Since dip tubes were not employed, pressurized containers were inverted during actuation. All measurements were made at $28 \pm 0.5^\circ$.

Basic Soap Formulation—Richman reported rheological measurements of soap solutions at atmospheric pressure and observed the dilatant nature of the flow curves at high-shear rates in the region of about 500 sec.⁻¹ (7). An experiment was designed to measure the

¹ Spratiner, Crown Can Co., Philadelphia, Pa.

Table I—Relationship of Shear Rate to Shear Stress in a Basic Soap Formulation Consisting of 10% (w/w) Soap and 10% (w/w) Propellant Blend 12/114 (57:43)

Shear Rate, sec. ⁻¹	Fine Scale Value (Viscometer Reading)			Normal Scale Value ^a	Scale Value × Pressure Factor ^b	Stress Value, dynes/cm. ² × 10 ⁻³	Foam Stress Value, ^c dynes/cm. ² × 10 ⁻³
	Sample 1	Sample 2	Mean				
3.0	1.2	1.1	1.15	0.29	0.28	0.011	0.57
6.1	1.6	1.7	1.65	0.41	0.39	0.015	0.61
9.2	1.9	1.9	1.90	0.48	0.46	0.018	0.68
18.4	2.5	2.6	2.55	0.65	0.61	0.024	0.79
27.6	3.9	4.0	3.95	0.99	0.94	0.037	0.92
55.2	5.4	5.6	5.50	1.37	1.30	0.051	1.08
82.8	8.2	8.4	8.30	2.07	1.97	0.077	1.17

^a Normal scale value is one-fourth of fine scale reading. ^b Pressure factor = 0.95, from Fig. 3 (a factor to convert scale values with pressure assembly into equivalent values without pressure assembly). ^c Values for the foam extruded from the same basic formulation presented in this table for comparison and reference in the following sections.

shear stress values under pressure of the following basic soap formulation:

Soap concentrate	10%	} 90%
Stearic acid	5 parts	
Coconut oil fatty acids	3 parts	
Triethanolamine	5 parts	
Additive	(-%)	} 10%
Distilled water <i>q.s. ad.</i>	100%	
Propellant blend 12/114 (57:43)		

No additives were employed in the control formulation. Samples were prepared in duplicate, and the rheological measurements were carried out at 28 ± 0.5°. Shear stress values obtained at varying rates of shear are presented in Table I. The flow curve appears in Fig. 4 as the control soap formulation.

Effect of Additives—Once the basic rheology of a simple pressurized concentrate was determined, the effects of viscosity-increasing additives were studied. Methylcellulose (4000 cps.) was selected for its known property of increasing the viscosity of aqueous soap solutions; three different concentrations (1.0, 1.5, and 2.0% w/w) were employed. The flow curves obtained from these systems are

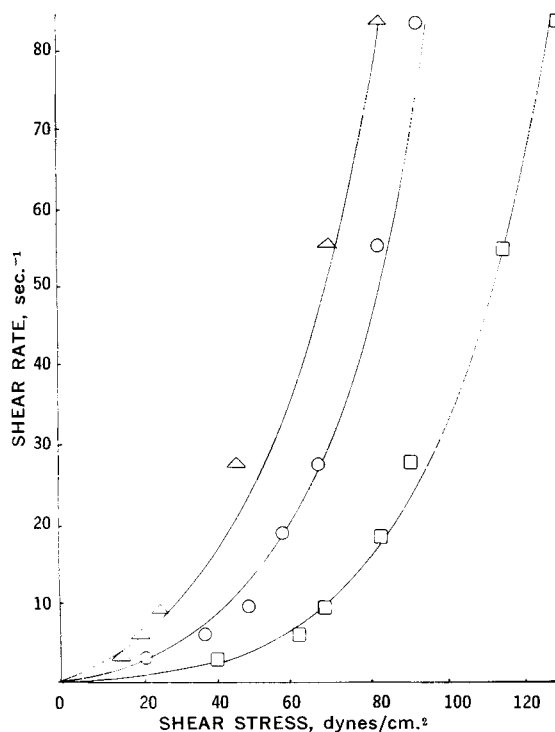


Figure 6—Pressurized emulsion flow curves—the effect of additives on formulations containing 10% (w/w) soap. Key: Δ , 0.125% hydroxyethylcellulose; \circ , 0.125% commercial hydrocolloid; and \square , 40% glycerin.

presented in Fig. 4. To compare the effect of this additive on the rheology of foams produced from these same formulations, rheological measurements were carried out on the corresponding foams and the results are shown in Fig. 5. It becomes obvious upon examination of these data that the sequence of flow curves remains the same in both the concentrate and foam. In a subsequent experiment, soap solutions were prepared containing different additives known to increase the consistency of aerosol foams. While glycerin was selected for its Newtonian property, hydroxyethylcellulose and a commercial hydrocolloid² were selected for their non-Newtonian and pseudoplastic properties in aqueous solutions. Flow curves of the emulsion concentrates with various additives are presented in Fig. 6, and flow curves of the corresponding resultant foams are shown in Fig. 7. The sequence of flow curves is not the same in both figures. The pressurized emulsion containing the hydrocolloid gave higher shear stress values than the one containing hydroxyethylcellulose, whereas this order was reversed in the case of pressurized foams. Thus, it can be noted that the agents that affect bulk viscosity

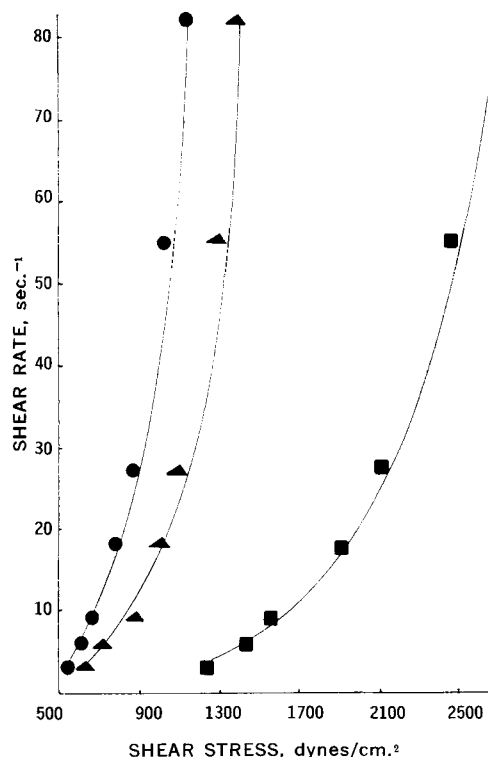


Figure 7—Pressurized foam flow curves—the effect of additives on formulations containing 10% (w/w) soap. Key: \bullet , 0.125% commercial hydrocolloid; \blacktriangle , 0.125% hydroxyethylcellulose; and \blacksquare , 40% glycerin.

² Polyhall-295R₁, a water-soluble nonionic polyacrylamide hydrocolloid of high molecular weight, Stein, Hall and Co., Inc., New York, N. Y.

of a concentrate may not affect the viscosity of the resulting foam in exactly the same manner. Surface viscosity and surface area are dominant factors in the viscosity of the pressurized foam.

The pressure rheometer can be a useful tool for studying aerosol concentrates containing propellants. Since foam-producing systems are generally emulsions or micellized solutions, determining the rheological properties of concentrates before pressurization is of limited value. Commercial pressure rheometers have become available since this research was begun. However, the magnetic clutch unit (introduced by the Polyscience Corp., Evanston, Ill.) for use with the Rotovisco viscometer requires a sample size of approximately 1 l., which makes it unattractive for product-development work. The Viscoclav MA attachment to the Contraves rheometer (Oikon Corp., Stanford, Conn.), which also utilizes a magnetically driven bob, employs a much smaller (10 ml.) sample.

It is important that cosmetic and pharmaceutical aerosol chemists investigate their pressurized systems using techniques such as those described in this paper if meaningful rheological data are to be generated.

SUMMARY AND CONCLUSIONS

The design of a device for modifying a commercially available rotational viscometer to measure the rheological properties of fluids under pressure is described.

Data presented for simple aerosol concentrate soap formulations revealed pseudoplastic properties which could not always be correlated with the flow properties of the resultant foams. This lack of

correlation may be attributable to the role that surface viscosity (rather than bulk viscosity) plays in determining foam consistency.

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Titanium Dioxide Lakes I: Prepared from Certified Water-Soluble Dyes and Employed in Color-Coating Tablets

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Abstract □ Titanium dioxide, ranging in particle size from 0.005 to 0.040 μ , has been investigated as an adsorbate in the manufacture of lake dyes from certified water-soluble dyes. The manufacturing technique for the titanium dioxide lakes and the pharmaceutical application in color-coating tablets have been demonstrated and discussed in conjunction with automatic spray coating.

Keyphrases □ Titanium dioxide lakes—preparation □ Lakes, water-soluble dyes—titanium dioxide adsorbate □ Spray drying—titanium dioxide lake preparation □ Color coating, tablets—titanium dioxide lakes

Color lakes, prepared in liquid suspension, have been extensively employed pharmaceutically for coloring sugar-coated tablets. There are advantages for using the color lakes rather than the water-soluble dyes, which are well known to the coating expert. These advantages consist of: significant time reduction for the color-coating operation, greater color stability, and greater color uniformity for consecutive batches (1). The majority of color lakes are manufactured by employing alumina as the adsorbate material interacted with various dyes. Commercial lakes are available

as micronized powders that render better color dispersion in liquid suspensions than if not so treated.

Color-concentrate suspensions prepared from color lakes are commercially available and are extensively used by the pharmaceutical industry for coloring sugar-coated tablets.

The purpose of this study was to determine the acceptability of titanium dioxide as an adsorbate material for color lake manufacture from water-soluble dyes. The titanium dioxide selected is referred to as "fumed" and possesses a submicron particle size. The ultimate goal of this project was to prepare extemporaneously color lakes for tablet coating.

EXPERIMENTAL

Materials—Fumed titanium dioxide¹ was selected for study as an adsorbate in the manufacture of color lakes because it possesses a suitable particle-size range from 0.005 to 0.040 μ . Titanium dioxide USP differs significantly from the fumed material with

¹ Titanium Dioxide P-25, DeGussa, Inc., Kearny, N. J.; Cab-O-Ti, Cabot Corp., Boston, Mass.