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Aerosol Report

STIFFNESS MEASUREMENT OF AEROSOL FOAMS

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AEROSOL AGE
Volume 8, No. 7, July 1963, page 33

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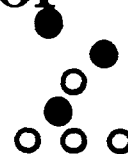
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EID11633

Stiffness Measurement of Aerosol Foams

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AEROSOL foams have a number of qualities which make them desirable for many uses. They may be applied to any given place and they are attractive in appearance. Foam formulations are economical since they usually employ only a small quantity of propellant. Their physical properties, such as stability, stiffness, and wettability may be varied to meet the needs of different applications.

A foam property such as density, can be measured accurately and easily if the foam has sufficient stability to permit a given volume of foam to be weighed. Other properties, such as the resistance of foam to deformations have also been used to characterize qualities of foams, but often the deformations were of a rather indefinite kind.¹ One method, for example, was to determine the rate of descent of objects such as glass tubes into the foam. Another method of demonstrating the stiffness or strength of foam has involved the ability of the foam to maintain an object like a pencil in a vertical position without allowing it to tilt to the side.

In 1952, R. A. Foresman, Jr. reported that the three most important characteristics for aerosol shave creams were strength (or foam stiffness), stability, and wettability.² In discussing the foam strength of the products, he disclosed a procedure for measuring the comparative strength or stiffness of aerosol foams which involved determining the grams of force necessary to insert a standard knife through the foam at a uniform rate of speed. The instrument used by Foresman was an American Standard Dairy Curd-O-Meter, manufactured by the Submarine Signal Co. in Salt Lake City.

Following Mr. Foresman's original work, a similar procedure for measuring foam stiffness was adopted at the "Freon" Products Laboratory. Since the American Standard Dairy Curd-O-Meter was no longer available commercially, a Cherry-Burrell curd tension meter was used. Although these curd tension meters are admirably

suited for making comparative stiffness measurements on aerosol foams, they apparently have not yet been widely used in the aerosol industry. It is the purpose of this paper to illustrate the use of the Cherry-Burrell curd tension meter for making comparative stiffness measurements on aerosol foams and to investigate any possible relationship between the stiffness values and other properties of aerosol foams.

Apparatus and Procedure

The Cherry-Burrell Curd Tension Meter³ is illustrated in Figure 1. It is automatic and gives direct readings.

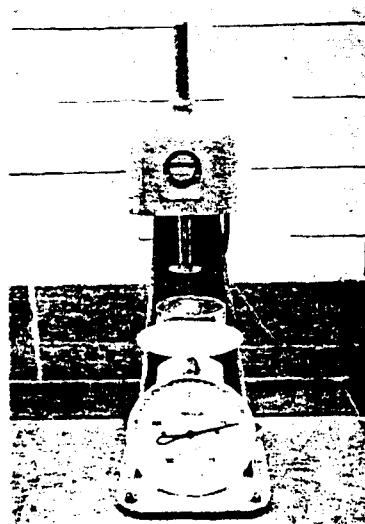


Figure No. 1

In carrying out the test, the operator fills a suitable vessel with the aerosol foam and any excess foam is removed with a scraper. A crystallizing dish, 9.7 cm in diameter and 4.7 cm deep, has been found to be a satisfactory container for the foam. Since the volume and weight of the dish can be determined, it was comparatively easy to determine the foam density immediately

* Freon is Du Pont's registered trademark for its fluorocarbon propellants.

before the stiffness measurements were carried out. Foam densities are usually given in the tables along with stiffness results.

The dish with the foam is placed on a scale platform which is directly underneath a specially designed curd knife and the rotating dial on the scales is adjusted so that the pointer is set at zero. The scale has a capacity of 500 grams and is graduated in 2 gram divisions so that measurements may be recorded to the nearest gram. After the starting button has been depressed, the curd knife is driven downwards at a constant, controlled rate of speed of 1 inch per 7.5 seconds by a synchronous motor. After the knife has contacted the foam, the resistance of the foam to penetration by the knife causes the scale platform to depress. The extent of the foam resistance (and therefore the degree of depression of the scale platform) is measured by the number of grams recorded on the dial. The instrument is adjusted so that the knife will automatically reverse before it touches the bottom of the vessel containing the foam.

The readings are obtained in grams and provide a valuable means for comparing the stiffness of different foams. They also may be used to detect changes in foams occurring during aging or variations that occur as the container is discharged. Stiffness measurements are also suitable for detecting changes in foam structure that occur with modifications in the aerosol formulation. The application of the instrument for some of these uses is illustrated by the data in the following sections.

Experimental Results

I. Effect of Time

There are certain limitations that must be recognized in attempting to characterize foam properties by numerical values. Foams may change rapidly after discharge and in many cases if a numerical value that describes a physical property is to have any significance, the time interval between discharge and the measurement must be specified.

If a foam is comparatively stable and expands very little after discharge, then measurements of stiffness and density may be made within a reasonable time after discharge and the results will be reproducible. Some foams, however, expand immediately after discharge and continue to expand for a considerable length of time. This is particularly characteristic of foams formulated with "Freon-114" propellant. In reporting the density of foams of this type it is necessary to specify the time after discharge that the determination was made since the density changes rapidly with time. It was rather surprising that although the density changes rapidly, the stiffness remains relatively constant for the periods up to 20 minutes after discharge.

On the other hand, foams prepared with "Freon-12" "Freon-114" (40/60) propellant expand very little after discharge so that both the density and the stiffness remain relatively constant for some time. These effects

were illustrated by measuring the stiffness and density of foams prepared with 10% of either "Freon-114" or "Freon-12"/"Freon-114" (40/60) propellant and 90% of the following aqueous concentrate A:

AQUEOUS CONCENTRATE A	
Stearic Acid	6.31%
Coconut Fatty Acid	1.58%
Triethanolamine	5.16%
Polyethylene Glycol 400	1.05%
Mineral Oil	0.11%
Water	85.79%

The variation of the stiffness and density of the foams as a function of time after discharge is illustrated by the data in Table I.

TABLE I
Effect of Time

Propellant	Time After Discharge	Stiffness (grams)	Density (g/cc)
"Freon-114"	2 Minutes	48	0.142
"Freon-114"	6 Minutes	48	0.086
"Freon-114"	10 Minutes	46	0.081
"Freon-114"	20 Minutes	51	0.073
"Freon-12"/ "Freon-114" (40/60)	2 Minutes	58	0.063
"Freon-12"/ "Freon-114" (40/60)	10 Minutes	62	0.061

Thus, with "Freon-114" foams, the stiffness remained essentially constant while the density decreased rapidly during the first 20 minutes after discharge. The stiffness and density of foams prepared with "Freon-12"/"Freon-114" (40/60) propellant changed very little during the first 10 minutes after discharge.

In order to obtain reproducible stiffness measurements it, therefore, is not as important to adhere to a rigid time interval after discharge as it is for reproducible density values. However, in order to standardize the procedure as much as possible, both density and stiffness measurements were carried out immediately after discharge. Both measurements were completed within two minutes.

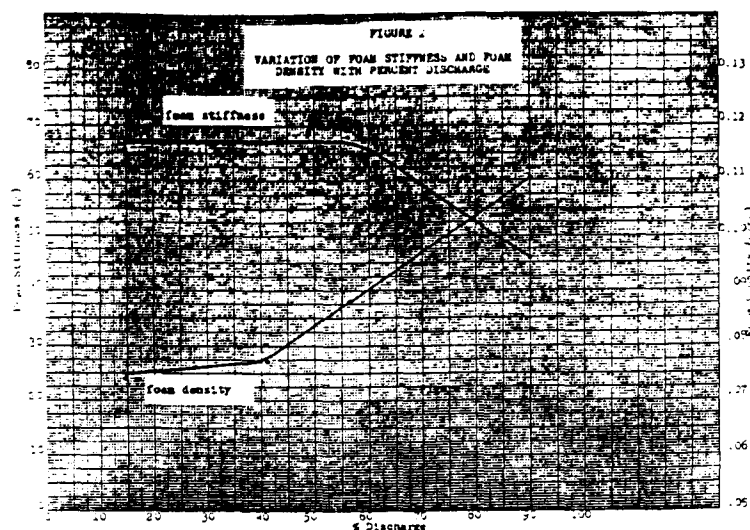
II. Sample Variation

In order to obtain some idea of the variation in readings that might be expected from different samples of the same formulation, five samples of an aqueous foam product were prepared using 10% "Freon-12" "Freon-114" (40/60) propellant and 90% of aqueous concentrate A. The samples were packaged in six-ounce lacquer-lined tinplated containers and allowed to age for 24 hours before testing. The samples were shaken by hand immediately before discharge. The readings obtained with the five samples are listed in Table II.

The average for the five samples is a stiffness of 72

TABLE II
Effect of Sample Variation

Sample Number	Stiffness (grams)
1	74
2	69
3	77
4	71
5	68



grams and the difference between the low and high readings is 9 grams. The major reason for the variation is probably differences in the sampling technique in layering the foam into the crystallizing dish.

III. Effect of Variation in Propellant Concentration

The fact that increasing the propellant concentration in an aqueous foam product increases the stiffness was first reported by Reed⁴. Reed observed that with a shampoo concentrate higher propellant loadings resulted in stiff, dry elastic foams and lower propellant concentrations gave soft and less resilient foams.

This characteristic can be demonstrated very effectively by measuring the foam stiffness at various propellant concentrations. Thus, a series of samples was prepared using from 5% to 50% "Freon-12"/"Freon-114" (40/60) propellant with the remainder consisting of aqueous concentrate A. Foam stiffness and densities of the various formulations are listed in Table III. These data show very conclusively how increasing the propellant concentration increases foam stiffness and decreases foam density.

Propellant Concentration (Wt. %)	Stiffness (grams)	Density (g/cc)
5	43	0.138
10	65	0.078
15	94	0.053
25	114	0.045
50	126	0.036

IV. Effect of Aging the Emulsion

The effect of aging the aerosol formulation in the container for periods up to one month was found to be almost negligible upon foam stiffness and density. Thus, at least with the present formulation, it is not necessary to define foam stiffness in terms of some specific time

after the formulation has been prepared. This, of course, may not be true of other formulations.

The present study was carried out by preparing a series of samples formulated with 10% "Freon-12"/"Freon-114" (40/60) propellant and 90% aqueous concentrate A. The samples were packaged in lacquer-lined tinplate containers, shaken vigorously, and then allowed to stand at room temperature for various periods up to one month. After each aging period, the samples were shaken again and stiffness and density determined. Individual samples were used for each measurement so that no sample was discharged twice.

The results of the measurements are given in Table IV. These data indicate that aging periods up to one month have little effect upon foam stiffness. There appears to be a slight tendency for the density to increase, but the densities differ so little that the significance of the trend is questionable.

Aging Period	Foam Stiffness (grams)	Foam Density (g/cc)
0	68.5	0.066
24 hours	71.5	0.069
48 hours	68.0	0.070
1 week	67.0	0.072
1 month	66.0	

V. Effect of Extent or Discharge

Mr. Foresman pointed out in his discussion of foam properties² that there is a drop in foam strength as increasing amounts of material are dispensed. The reason for this is as follows: as an aerosol product is discharged from the container, the volume of the liquid phase decreases and the volume of the vapor phase increases correspondingly. In order to maintain a constant pressure in the aerosol container during discharge, it is necessary for some of the propellant in the liquid phase to vaporize and migrate to the vapor phase.

In spray products containing a relatively high pro-

TABLE VI
Effect of Variation in Propellants

Propellant	Foam Stiffness (grams)		Density (g/cc)		% Drainage
	Initial	Retention of Stiffness After Aging 2 Hours	Initial	After Aging 2 Hours	
"Freon-12"	56	80%	0.053	0.049	0
"Freon-12"/"Freon-114" (40/60)	72	76%	0.069	0.058	1.5
"Freon-12"/"Freon-114" (15/85)	48	83%	0.090	0.061	7.0
"Freon-114"	46	70%			15.0
"Freon-12"/"Freon-11" (50/50)	42	64%	0.057	0.056	21.0
"Freon-12"/"Freon-11" (30/70)	36	50%	0.061	0.058	33.0
Propellant 142b	37	78%	0.039	0.037	0
Propellant 152a	42	74%	0.042	0.039	22.5

portion of propellant, the loss of propellant from the liquid phase to the vapor phase has little noticeable effect upon the spray characteristics as the product is discharged, since the percentage loss of propellant is small. However, in foam products, which are usually formulated with a minor proportion of propellant, the change in concentration of propellant in the liquid phase as the product is discharged is significant and will cause a noticeable change in foam properties.

The data in Table III, which illustrate the change in foam stiffness and density as the propellant concentration changes, predict that as the concentration of propellant in the liquid phase decreases during use the foam stiffness also will decrease and the density will increase. This effect of discharge upon foam properties was shown experimentally as follows: a 12-ounce container of the aerosol emulsion was prepared with 10% "Freon-12"/"Freon-114" (40/60) propellant and 90% of the aqueous concentrate A. After the container had been rolled for 10 minutes, it was discharged into the crystallizing dish for stiffness and density determinations. The container was then reweighed to obtain the quantity of product that had been discharged. After rolling for an additional 10 minutes, stiffness and density were again determined. This procedure was repeated until the amount of product remaining in the container was insufficient for a stiffness measurement.

The relationship between the extent of discharge of the can contents and the foam stiffness and foam density is illustrated in Figure 2. Foam stiffness remains relatively constant until almost 60% of the can contents have been discharged. Foam density, however, appears to increase almost from the start. The extent to which these changes take place during discharge will vary, of course, with both the quantity of propellant initially present and the type of propellant that is used.

VI. Effect of Variation in Propellant

The type of propellant used in formulating aqueous aerosol foams may have a considerable effect upon foam properties, such as stiffness. This is illustrated by the data in the following sections:

A. Effect Upon Stiffness

The effect of varying the propellant upon stiffness was checked with 10% propellant and 90% of two different concentrates. One was concentrate A, which has a slight molar excess of triethanolamine relative to the fatty acids, and the other was concentrate B, which has a slight molar excess of fatty acids. Concentrate B is similar to many of the products now marketed as aqueous shaving-lathers⁵ and has the following composition:

AQUEOUS CONCENTRATE B	
Stearic Acid	7.06%
Coconut Fatty Acid	1.72%
Triethanolamine	4.40%
Glycerine	2.00%
Water	84.82%

The stiffness results obtained with a variety of propellants and the two concentrates are listed in Table V.

TABLE V
Effect of Variation in Propellant

Propellant	Foam Stiffness (grams)	
	Concentrate A	Concentrate B
"Freon-12"	56	53
"Freon-12"/"Freon-114" (40/60)	72	67
"Freon-12"/"Freon-114" (15/85)	48	48
"Freon-114"	46	41
"Freon-12"/"Freon-11" (50/50)	42	35
"Freon-12"/"Freon-11" (30/70)	36	43
Propellant 142b	37	43
Propellant 152a	42	45

Maximum stiffness is achieved with "Freon-12"/"Freon-114" (40/60) propellant. It is possible that some other ratio of "Freon-12" to "Freon-114" would produce stiffer foams, but this has not been checked.

B. Effect Upon Stability

In an attempt to determine if there were any correlation between stiffness values and foam stability, the samples listed in Table V that were prepared with concentrate A were treated for foam stability as follows:

1. Foams were discharged onto paper towels and

checked for foam collapse at intervals.

2. Foams were discharged into crystallizing dishes and the densities and stiffness values determined before and after aging for two hours.
3. Foams were also discharged into glass funnels inserted in graduates and the percent drainage determined after aging 18 hours. Drainage rates are considered as one of the methods for indicating the stability of foams.⁶

No conclusions regarding relative foam stability could be obtained from discharging the foams onto paper towels. The foams were all too much alike in their stability by this test to distinguish any real differences. The difficulty in judging foam stability by this test has been mentioned by Mr. Foresman.²

The results of the aging tests upon foam stiffness and foam density and the results of the drainage tests are given in Table VI. There appears to be little correlation between the initial foam stiffness and either the percent retention of stiffness during aging or the percent drainage. Foams with the highest stiffness values were *not* necessarily the most stable.

There appeared to be a trend for the foams which showed the *highest retention of stiffness during aging* to also exhibit the *least* drainage. There very well may be a correlation between the two, but certainly the correlation was not as pronounced as could be desired.

The change in density during aging of most of the

foams was very slight. Since most of the foams decreased slightly in density, this indicated that the foams expanded very slightly.

VIII. Properties of Commercial Aerosol Shaving-Lathers

Nine different commercial aerosol shaving-lathers were evaluated in duplicate for foam stiffness, foam density, and drainage. The results were averaged and are listed in Table VII.

The data show that foams may have the same stiffness with different densities and, conversely, foams may have the same densities with different stiffness values.

The data in Table VII confirm the previous conclusion that the foams with the highest stiffness values were not necessarily the most stable, as shown by the comparison of the foam stiffness results with the percent drainage figures. Thus, two products both having an intermediate foam stiffness value of 87, had the highest and lowest drainage rates, respectively, of the entire series.

IX. Summary

The use of a Cherry-Burrell curd tension meter as an instrument for determining the comparative foam stiffness of a variety of aerosol foams has been illustrated. The effects of varying such factors as the type of propellant, the proportion of the propellant, and the age of the samples, upon foam stiffness have been presented. A comparison of other foam properties, such as stability and density, with foam stiffness, indicates that there is no apparent correlation. ★

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TABLE VII
Properties of Commercial Shaving-Lathers

Product No.	Foam Stiffness (grams)	Foam Density (g/cc)	% Drainage (24 Hrs.)
1	111	0.067	6.5
2	106	0.084	16.0
3	98	0.093	22.0
4	89	0.093	9.5
5	87	0.116	44.0
6	87	0.092	2.5
7	82	0.097	32.0
8	76	0.091	18.0
9	75	0.107	16.0

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