make varifiable or refutable predictions. The techniques discussed assist in predicting short-term emulsion stability, but the practical cosmetic chemist is vitally interested in long-term stability, not minutes or hours, but weeks or months. At present he cannot find out empirically; if prophetic judgment can be made this would be most valuable. It is appreciated, of course, that such long-term stability may be affected in complex systems by migration of trace impurities to the interface, but could these techniques be of assistance?

THE LECTURER: The techniques I have described could give you the information you require provided the change taking place occurs at the interface. It is my experience that there is no substitute for time and one must therefore be prepared to set up the experiment to last for the required period. It may be that surface chemical techniques will detect changes much earlier than those detected by storage tests on the product. For instance, migration of divalent ions to a surface stabilised by a sodium soap will be manifest as a change in rigidity of the interface.

TECHNIQUES OF FOAM MEASUREMENT

G. E. NEU, B.Sc.*

Delivered at the Summer Conference of the Society on 25th August 1960.

The physical properties of shampoo and toothpaste foams are characterised using seven different measurements. These measurements are easy to perform and yield reproducible results. A subjective assessment of the foam is correlated with the measurements described.

INTRODUCTION

FOAMING IS of major importance in shampoos and toothpastes, and the nature of the foam may be critical in determining the acceptability of these products. With toothpaste, the volume must be sufficient but controlled, and one of the chief qualities required is easy rinsing away; the foam is also important to the flavour which it disperses throughout the mouth to allow maximum contact with the taste buds.

The actual requirements of these two products are very different. A shampoo is normally expected to give a thick, creamy, voluminous foam, which is associated by the user with cleansing power and emolliency. Even if a shampoo has excellent cleansing properties and leaves the hair in very good condition afterwards but only provides a small amount of a thick,

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weak foam, it is unlikely to be accepted as a good shampoo. Rinsing is expected to be easy. The domestic user assesses the foam removed by what is seen in the wash basin, so that it is important that the collapse should be rapid and complete on dilution, and the foam should not simply wash off the hair. The detergent concentration in the solution applied to the soiled head, even allowing for the amount of water in the wetted hair, is high (1·5%–2·0%), which is well above the critical micelle concentration for the detergents studied. The amount of soil removed from the hair exhausts only about 5% of the detergency of the shampoo.

Toothpaste foams are generated under more diverse conditions than shampoos. The volume and composition of the saliva, the amount and type of debris in the mouth, the vigour and time of brushing the teeth, vary considerably. Thus a toothpaste has to be more versatile in producing foam under these differing conditions. The volume must be sufficient to fill, but not overfill, the mouth ; it must feel solid, creamy and viscous and not elastic, thin or light. Finally, it must rinse out easily, but it is not important if it does not collapse. The concentration of detergent in toothpaste/saliva mixture from the mouth is about 0·25–0·40% which in some cases is very near the critical micelle concentration level.

What are the important factors controlling the properties of foams ? We would like to be able to express the subjective properties in objective parameters, and a better understanding achieved by empirical methods will point to further research work in this field. Our aim has been to generate a foam under conditions which simulate actual usage, and to develop techniques for measuring all of the properties of the bulk foams which are possibly important in the subjective assessment. Previous work in this field has been almost exclusively devoted to a consideration of foam volume and drainage. These are relatively simple parameters which can easily be assessed, but we have extended the work to cover other, more nebulous, factors.

These factors are, beside the foam volume and drainage, the viscosity, the change in viscosity with age of the foam (here called viscosity differential), light transmission, bubble size and distribution, and breakdown during rinsing. Results on the last technique are not yet sufficiently complete for presentation. When these properties are known it may be possible to forecast the characteristics and expected behaviour of the foam. The methods described are applicable to both toothpastes and shampoos and to other products.

Experimental

Generation of Foam

Our aim was to make large amounts of foam under strictly controlled conditions. This foam should be similar to the foam produced under usage conditions.

The simplest foam generation experiments were carried out by shaking the detergent solution in a cylinder a number of times. Some authors[1, 2] evolved shampoo foams by bubbling a known volume of air through a detergent solution, or by using an oscillating perforated disc in a cylinder of detergent. The first technique is not reproducible. The second is not realistic as there is no work simultaneously "making and breaking" the foam. The third technique is too restricted in the amount of air which can be incorporated. The generation of foam by beating with food mixers is widespread and was used as far back as 1933 by Henry and Barbour[3] in their studies on egg white. Besides food mixers, adapted food mixers and various other stirrers are also used.

We chose a Sunbeam Mixmaster to generate the foams. Our choice was governed by the following factors:

1. The foam generated in the Mixmaster at the faster speeds is comparable to the actual shampoo and toothpaste foams.
2. Air is freely incorporated.
3. Excellent reproducibility because of easy and accurate controls.
4. Speed of beaters is practically independent of the load on them.

We measured the properties and specific (bulk) volume of foam produced on a head of hair when shampooed with a mild anionic detergent shampoo. When beating a similar solution on the Mixmaster the foam after 4 minutes' beating at 720 r.p.m. was found to be similar to the foam after 30 seconds' shampooing on the second application. The testing of toothpaste foams in a similar manner is technically impossible as saliva rapidly ages and the amount of foam produced when cleaning teeth is insufficient for experiments on the foam properties. Subjective tests, however, indicated that toothpaste foam whipped between 720 and 820 r.p.m. for 1–4 minutes is similar in feel to the foam produced during the tooth brushing.

Materials Tested

We tested four shampoo detergent solutions and four toothpastes. The shampoo detergent solutions were typical detergents of the following types:—

A "mild" anionic detergent	ref. M
A "harsh" anionic detergent	ref. H
A non-ionic detergent	ref. N
A cationic detergent	ref. C

The anionic detergents are referred to as good foamers. When used as a shampoo the mild anionic produces a rich, creamy, voluminous foam.

The harsh anionic detergent is not as satisfactory in this respect as the mild anionic. The non-ionic detergent produces a small volume of foam which feels dry. The cationic detergent produces only a poor foam, which feels soft and elastic, and is hard to rinse out.

The following types of toothpaste were tested :—

2 phosphate-based toothpastes + synthetic detergent	Ref. PD/1, PD/2
Chalk-based toothpaste + synthetic detergent	Ref. CD
Chalk-based toothpaste + soap	Ref. CS

In use, the two phosphate-based toothpastes are classed as high foamers. PD/2 is the more acceptable of the two because of its rinsing out properties. CS is a very poor foamer and CD is intermediate between phosphate-based toothpaste and CS.

Experimental Techniques

a. *Specific Foam Volume*

The foam is withdrawn from the mixing bowl at the required time with a glass tube and a container of known volume is filled with it. The amount of foam in this container is weighed, and the density and thence the specific volume calculated in ml/g.

b. *Measurement of Viscosity*

A modified Techne viscometer is used for all viscosity measurements. The principle of this viscometer is a weighted piston producing a constant air pressure which forces the foam under test through a capillary tube into the viscometer tube. The viscometer tubes are calibrated with standard mineral oils at 25°C.

50 ml aliquots are whipped in the small bowl of a Mixmaster. The samples are withdrawn with a wide bore glass tube at 1, 2, 4, 6 and 8 minutes after beating commences. During withdrawal the Mixmaster is momentarily stopped. Care is taken to avoid the formation of air pockets when withdrawing the foam from the mixing bowl and transferring it to the viscometer cup. The viscometer head is placed over the cup (*Figure 1*), some foam having first been smeared around the edge of the cup. It is then connected to the pressure unit, the plunger released and the time taken by the foam to travel between two marks on the tube is noted. The viscosity, in centistokes, is the time in seconds multiplied by a factor, if any, for the viscometer tube.

In order to study the variation of viscosity with the age of a foam, numerous viscosity measurements are carried out on one foam at quick time intervals.

MODIFIED TECHNE VISCOMETER

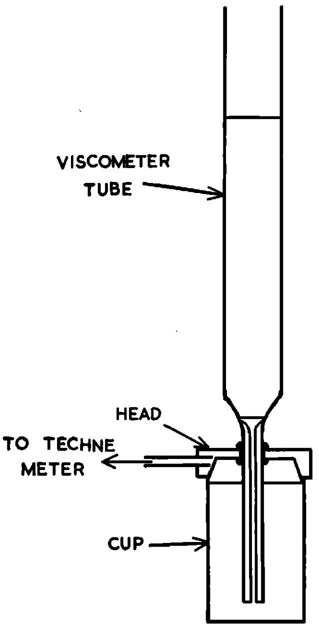


Figure 1

APPARATUS TO MEASURE LIGHT TRANSMISSION OF FOAMS

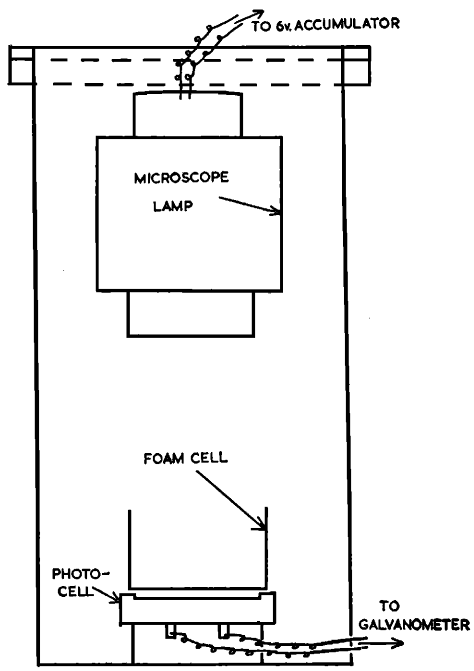


Figure 2

Foam is generated in the usual way. The t = o for the age of foam is taken as soon as the mixer is stopped. Six to seven samples are withdrawn at this stage, and placed in viscometer cups. Viscosity is then determined at regular intervals. The first determination is carried out about 15–17 seconds after zero time.

c. Light Transmission

The transmission of light through foams was investigated by Clark and Blackman[4]. They postulated that the loss of light transmission through a layer of foam is a function of the degree of dispersion of air. They expressed the loss of light in terms of loss factor which is defined as the ratio of the incident to the emergent light. This method was successfully adopted by Ross and his co-workers[5,6] in their work with transmission of light by unstable and stable foams. The method we use is similar in many respects to the above.

Our apparatus consisted of a selenium photo-cell (Barrier Layer type) of 12 sq. cm. The incident light is provided by a 6-volt 36 watt bulb in a parabolic reflector, with current supplied by a 6-volt car battery. The foam cell differed from the cells previously used. It is an open cell 50 mm in diameter and 30 mm deep. We used the open cell to simulate usage conditions. Experiments showed that an airtight cell retards the collapse of the foam. As we do not shampoo our hair or brush our teeth in airtight conditions, results from closed cells will be unreal from our point of view. The foam is generated in the Mixmaster in the usual way and transferred to the cell by means of a glass tube (*Figure 2*).

The first light transmission readings are taken as soon as possible after beating (about 20 seconds) and further readings are taken at regular intervals up to 10 minutes. With the absorbing solutions (toothpastes) the light absorbed by the cell containing the weight of toothpaste solution equivalent to the weight of foam in the cell is noted each time.

DRAINAGE APPARATUS

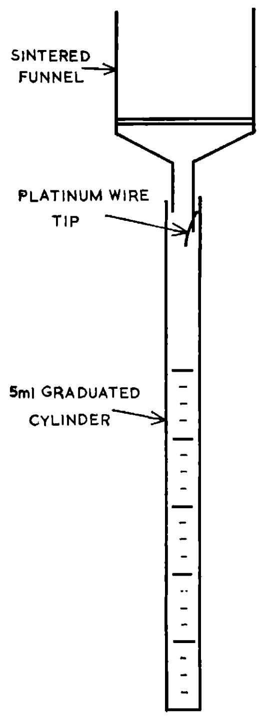


Figure 3

d. *Photomicrography*

A Zeiss Demoscope microscope with Zeiss photomicrographic attachments is used for taking the photographs.

Foam is generated in the Mixmaster in the usual manner and is transferred into an open cell, 3·5 cm diameter and 1 cm deep. The cell was illuminated with transmitted light from an electronic flash. Exposure time was $^{1}/_{25}$ of a second. HP3 plates were used in the camera. The photographs were enlarged so the final magnification is × 45.

The particle size counts were made on a 100 sq. cm area of the photograph, and the specific surface of the foam calculated. The specific surface as defined by Clark and Blackman[4] is the total surface area in sq. cm of the gas liquid interface in 1 cc of foam. It is calculated using the formula :—

$$\text{Specific surface} = \pi\Sigma\,(x_1d_1 + x_2d_2 \ldots\ldots)$$

where d_1, d_2 etc. represent the mean diameters of the various size groups of the bubbles, and x_1, x_2 etc. the number of bubbles assigned to each 1 sq. cm of the observed area.

e. Foam Drainage

The apparatus (*Figure 3*) consists of a 30 mm sintered glass (Grade 3) mercury filter sealed in a glass funnel. Two minutes before foam is introduced 1 ml of the mother liquor is allowed to drain through the filter, then a 20 ml aliquot of the foam is transferred from the mixing bowl into the funnel with a syringe, and the amount of liquid drained is measured at intervals.

With toothpaste solutions the sinters are cleaned in chromic acid after each application.

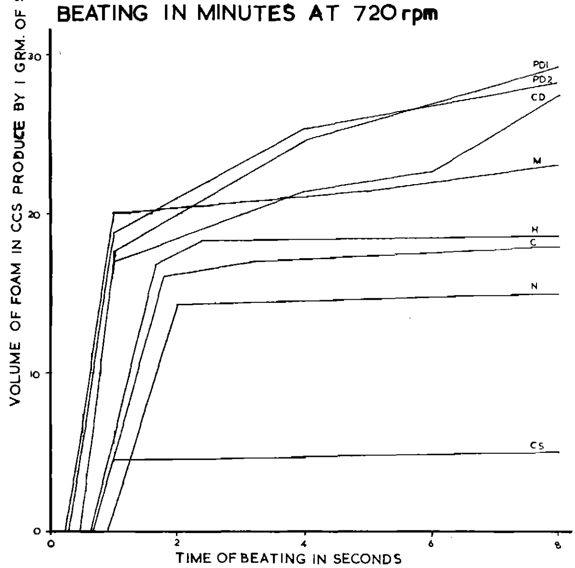
RESULTS AND DISCUSSION

1. *Shampoo Detergent Solutions*

A most important criterion for a foam both from the user's and manufacturer's point of view is the volume of foam generated by the shampoo. It is for this reason that we include the specific volume measurement as one of the standard characteristics of a foam.

GRAPH I

PLOT OF VOLUME OF FOAM PRODUCED BY ONE GRAM OF SOLUTION V/S TIME OF BEATING IN MINUTES AT 720 rpm



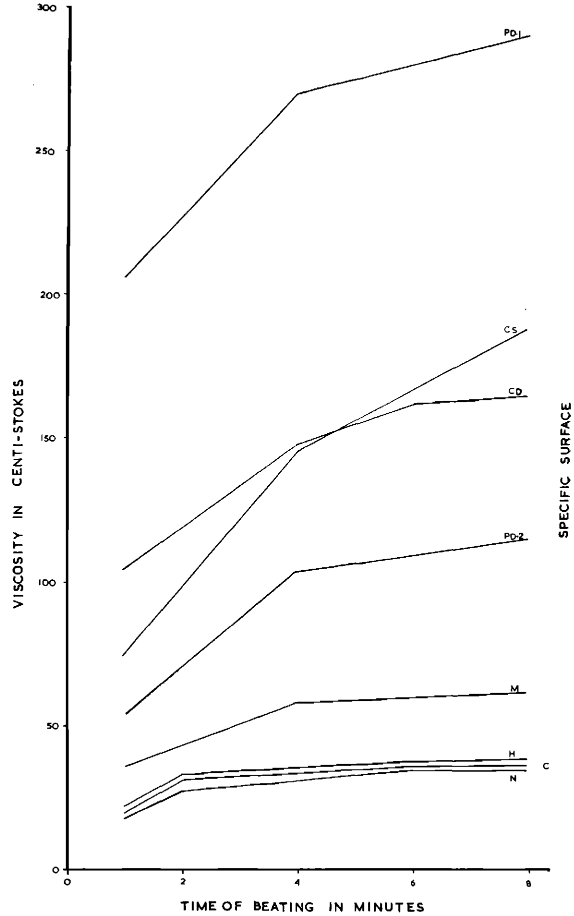
The shampoo detergent solutions begin foaming very rapidly so that after 15–30 seconds there is no liquid layer at the bottom of the bowl. *Graph 1* shows characteristic curves for the generation of foam volume.

The rate of building up of the volume of the foam is at a maximum between 30 and 90 seconds. M is the quickest to build up a foam, then H, C and N.

GRAPH 2

PLOT OF FOAM VISCOSITY IN CENTI-STOKES

V/S TIME OF BEATING IN MINUTES



The variation of the specific volume with various factors which are encountered under usage conditions were also investigated. Only variations of the speed of the Mixmaster, which is equivalent to the briskness of rubbing of the hair, has a significant effect on the maximum volume of foam produced by a given aliquot of a shampoo detergent solution. At any given speed the rate of building up of the foam volume reaches a maximum, then drops to zero. During this equilibrium, state, the building up and breaking down forces are obviously equal. An increase of speed shifts the equilibrium state in favour of the building up forces, until an equilibrium is again attained at a higher specific volume. For example, the specific volume of foam for M at which this equilibrium is attained is 7·9, 11·5, 16·6 and 21·4 ml/g of solution for speeds of 520, 620, 720 and 820 r.p.m. respectively.

The subjective feel of a shampoo foam is also influenced by other characteristics not studied in this programme. For instance, the adsorption of detergent on the hands is important, so two foams of similar physical characteristics may still feel different.

We studied the viscosity of the foam during building up and during its breaking down. The viscosity build up is similar to the foam volume generation, except that peak viscosity is reached after only 4–6 minutes' beating (*Graph 2*). M produces the most viscous foam, reaching a peak after 4 minutes' beating. H, C and N reach their peaks after 6 minutes' beating.

The speed of beating has a great influence on the viscosity of the foam produced (*Table 1*). This is true with both toothpastes and with shampoos.

Table 1

Effect of speed of Mixmaster on the foam viscosity of M and CD

Speed in r.p.m.	Viscosity in centistokes	
	Shampoo detergent M	Toothpaste CD
520	16·8	66·6
620	30·6	88·0
720	48·6	148·4
820	57·0	195·0

In practice, therefore, the manner in which the shampoo is used is a critical factor in the production of a foam. From the user's point of view, a shampoo which foams when very little work is done on it would be popular. Detergents H, N and C are not suitable for such a shampoo as no foam is produced below 400 r.p.m. M, however, produces foam at 250–300 r.p.m. and this possibly provides further justification of its use.

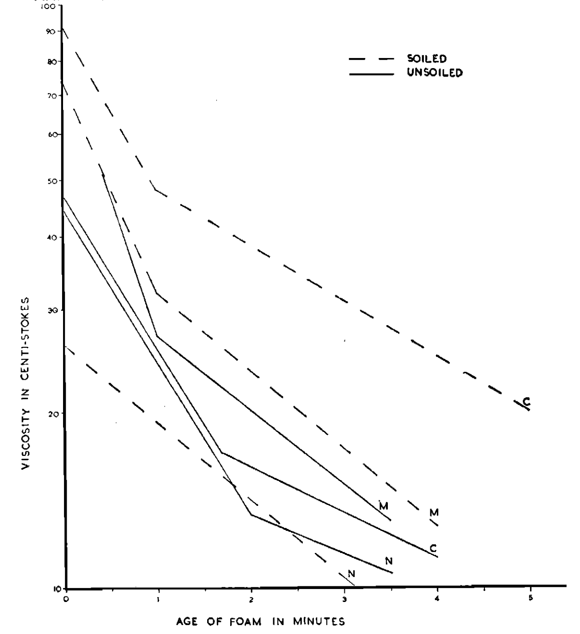
The concentration of the shampoo detergent under usage conditions is about 5–10 times the critical micelle concentration. This means that the detergent concentration should not be very critical. In fact, the variations in foam viscosity are negligible between 1% and 2% active detergent concentration so that differences which are likely to be encountered in practice are unimportant.

The effect of temperature on the viscosity of the foam was also investigated. The air was kept at constant temperature, but the detergent solution and the mixing bowl and beaters were heated or cooled to the required temperature, between 10 and 40°C. The 10°C solution of M produced a more viscous foam (19·2 centistokes at 1 minute beating at 720 r.p.m.) than the samples at 20°C, 30°C and 40°C. The foam viscosities of these samples were almost the same (13·0, 12·6 and 12·4 centistokes for the 20, 30 and 40°C samples respectively), which is surprising.

The size of the aliquot in the mixing bowl does not influence the foam viscosity. A 25 cc aliquot is insufficient to produce any foam. 50 and 75 cc aliquots generate foams which have similar viscosity characteristics.

GRAPH 3

PLOT OF VISCOSITY DIFFERENTIAL FOR SOILED AND UNSOILED SHAMPOO DETERGENT SOLUTIONS



Some detergents produce initially viscous foams which after a few minutes lose most of their viscous nature, whilst other detergents produce less viscous foams which are stable for 3–5 minutes. The viscosity differential measures this rate of degradation of the foam. We have found the viscosity differential to be a distinct characteristic of each foam.

The viscosity differential results of the shampoo detergent solutions are shown in *Graph 3*. The curves show two distinct sections, a steep initial line, followed by a second, less steep, section. We decided to call the steep section of the curve the "super foam state". This super foam state is an "over energised" form of the foam. The length and slope of the super foam curve of a detergent depends upon the amount of work put into the foam. It follows that if equal amounts of work are put into various detergent solutions, the longer the life of the super foam and the steeper the gradient of its slope, the easier it is to generate that particular foam. The super foam does not contribute to the cleansing or other useful properties of the foam, but the ability to produce a super foam may be essential to achieve the desired rapid collapse and easy rinsing out characteristics, which are expected from shampoo and toothpaste foams. The duration of the super foam state will be discussed further in our light transmission results.

The change in loss factor with time of the four shampoo detergent solutions investigated are similar in character. The slopes of the light transmission curves vary in the same way as those of the viscosity differential and show the super foam state. The significance of these results is discussed in connection with the toothpaste results. The highest loss factor for a foam is obtained after 4 minutes' beating, the 2 and 6 minute foams having about the same loss factor. Temperature of detergent solution has only a slight influence on the loss factor of the foam, the 40°C sample is the only one with a significantly lower loss factor.

The loss factor results are used to obtain the specific surface of the foam in question by adapting Clark and Blackman's methods. We also measured the specific surface of the foam using photomicrography. The plot of specific surface with loss factor at a given time yielded straight lines (*Graph 7*) so for a shampoo foam the loss factor expresses the specific surface.

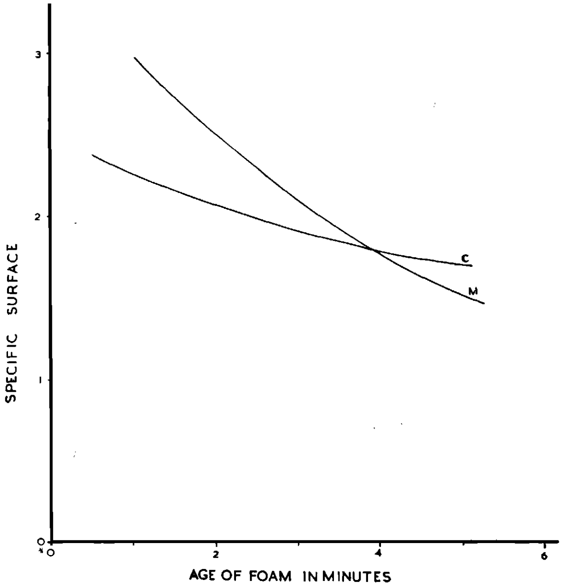
Although the character of the four shampoo detergent foams vary considerably, the specific surfaces are similar. M has the highest specific surface, N a poor foamer, also has a surprisingly high specific surface. The variation of specific surface with the age of the foam is shown on *Graph 4*. The curve is similar to the loss factor curves and is relatively the same for all the four shampoo detergent foams. D and H have similar specific surfaces and C has the lowest, but the rate of the breakdown of the foam is slow.

The growth and collapse of the individual bubbles have also been followed. The larger bubbles increase in size and the smaller ones decrease until they disappear altogether. Examples of these are given in the toothpaste section.

The variation in the loss factor and in the specific surface of the foams is surprisingly small, but these differences are very significant. To achieve more diverse results, we would require either liquid with very little air present, which is not really a foam, or foams with very large bubbles, which are not encountered in shampoo practice.

GRAPH 4

PLOT OF SPECIFIC SURFACE V/S AGE OF FOAM IN MINUTES



The rate of draining of the four shampoo detergent solutions was studied after 1, 4 and 8 minutes. All the 1 minute samples drained after 6 minutes, as is shown in *Table 2*.

Table 2

Draining of Mother Liquor from Shampoo Foam.

Time minutes	M			H			N			C		
	1	4	8	1	4	8	1	4	8	1	4	8
½	0·40	—	—	0·85	—	—	1·12	—	—	1·15	—	—
1	1·05	0·30	0·27	1·77	0·52	0·37	1·88	1·18	0·40	1·95	0·42	0·40
1½	1·36	—	—	2·08	—	—	2·10	—	—	2·25	—	—
2	1·51	0·68	0·60	2·28	1·00	0·87	2·17	1·62	0·88	2·40	0·95	0·85
2½	—	—	—	2·37	—	—	2·25	—	—	2·42	—	—
3	1·70	0·86	0·88	2·42	1·27	1·20	2·30	1·78	1·10	2·50	1·20	1·02
4	1·76	1·04	1·05	2·48	1·48	1·37	2·38	1·88	1·35	2·55	1·35	1·18
5	1·81	1·12	1·22	2·55	1·58	1·50	2·40	1·98	1·45	2·60	1·48	1·30
6	1·86	1·22	1·30	2·58	1·68	1·60	2·43	2·05	1·55	2·65	1·52	1·38
8	—	1·31	1·38	—	1·78	1·72	—	2·15	1·68	—	1·68	1·48
10	—	1·39	1·48	—	1·85	1·78	—	2·20	1·75	—	1·75	1·62

M drains more slowly than the other three. This is to be expected if we consider the ease of foaming and the larger volumes of foam produced per cc of detergent solution. The draining rate of the other three shampoo detergent solutions is similar, although N is quicker draining foam than H or C.

An experiment was carried out to investigate the foam volume and viscosity of soiled shampoo detergent solutions. Carefully blended salon sweepings were washed in the shampoo detergent solution, the soiled detergent solution was squeezed out and foams generated from these detergent solutions. The foam volume and the viscosity differential of the foam was measured.

The viscosity of the soiled detergent solution is given in *Graph 3*. The characteristic of the N foam altered, the super foam curve disappearing altogether, and the detergent appeared exhausted. M and H altered their characteristics very little. There is a slight increase in viscosity with both, but the detergent solution is not exhausted, and the presence of dirt did not seem to make too much difference to the foam. There is a very great increase in viscosity with C. The specific volume of the soiled shampoo detergent solution with M, H and N are the same as with the unsoiled samples. There is a small increase in specific volume with C, the soiled solution generation 16·3 ml of foam/g of solution, and the unsoiled sample generating 19·3 ml of foam/g of solution, after 4 minutes' beating at 720 r.p.m.

It is clear that the soil has a profound effect on the foam viscosity, and this must be important in the differences in the first and second applications of a shampoo.

2. *Toothpaste*

There is very little difference between the specific volume obtained from the shampoo detergent and toothpaste solutions studied. This is surprising as the concentration of active detergent in the toothpaste solutions we have used is only 0·3%, compared with 1·5% with the shampoo detergents. Both the concentrations are similar to those used in practice. Thus the volume of foam obtained from shampoos is very much less per unit weight of detergent than from toothpastes. Other components of the toothpaste must be responsible for this increase of foam volume.

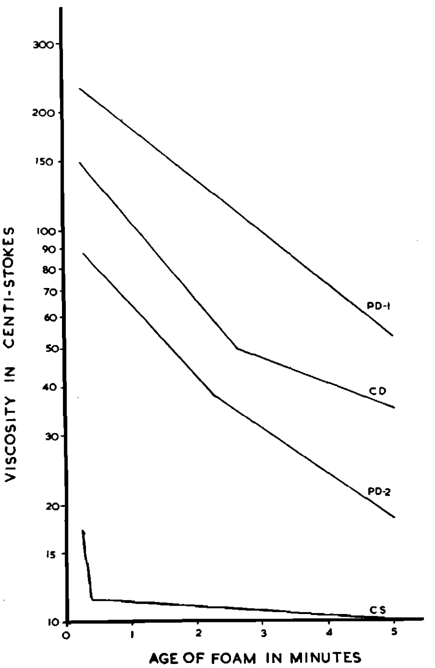
PD/1 and PD/2 produce the same volume of foam and are in practice the highest foamers among the toothpastes studied (25 cc of foam/g of slurry beaten at 720 r.p.m.). CD is slightly lower at 22 cc of foam/g of slurry. CS does not produce foam at the 15% w/w ; 25% is the lowest concentration at which a stable foam is produced. This foam is a creamy foam and yields 5 cc of foam/g of slurry after 4 minutes' beating at

720 r.p.m. CS under normal user conditions would not produce any foam, only an unstable mixture of air/saliva/toothpaste, which is generated by the brushing and breaks down instantaneously (*Graph 1*).

Toothpaste slurries produce viscous foams at a very much faster rate than shampoo detergent solutions (*Graph 2*). The relative differences of the 1–8 minute beating are considerably smaller than with shampoo. There is a wide viscosity difference between the two phosphate-based toothpastes tested. PD/1 produces the most viscous foam of the four toothpastes, while PD/2 produces the least viscous foam. CD and CS (at 30% w/w) are between the two phosphate-based toothpastes.

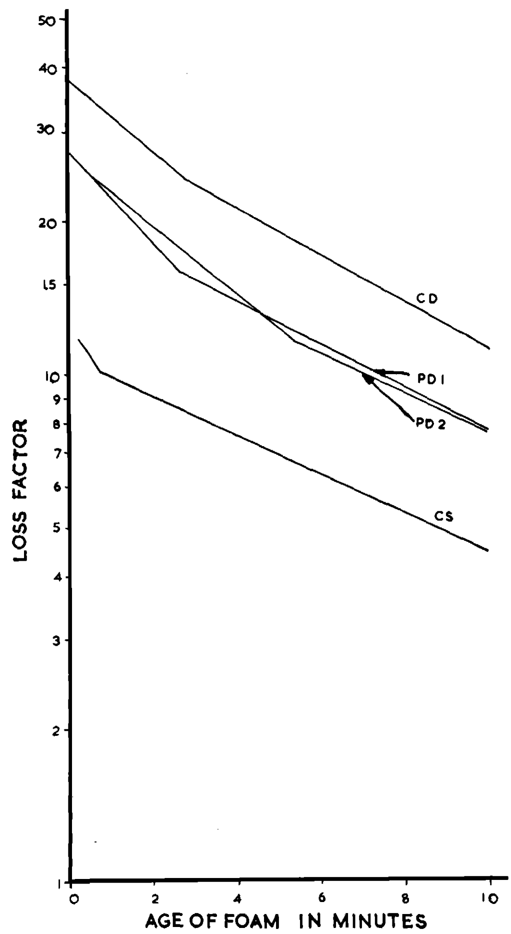
GRAPH 5

PLOT OF VISCOSITY DIFFERENTIAL OF TOOTHPASTE FOAMS



The toothpaste foams are similar to the shampoo foams in their variation with the speed of the mixer, size of aliquot and the temperatures of the slurry. The effect of the concentration of the toothpaste slurry on the foam viscosity is more noticeable than with the shampoo solutions. This is likely to be because the variations in the concentrations of detergent near the Critical Micelle Concentration level influence the properties of the foam to a greater extent than at much higher levels of concentration.

GRAPH 6
PLOT OF LOSS FACTOR V/S AGE OF FOAM IN MINUTES



Toothpaste foams, with the exception of 30% CS foam, degenerate much more quickly than shampoo foams. PD/1, whose initial viscosity (at 20 seconds) is 228 centistokes, degrades to 50 centistokes after 5 minutes. The super foam state of CS is very short. This is observed easily as the foam is seen to start degrading very quickly as soon as the mixing stops until the resulting creamy foam appears stable. PD/1, the high foamer which gives a very viscous foam, is in a super foam state for 5¼ minutes—more than twice as long as for the other foams. This indicates that PD/1 foams very easily as, although the same amount of work has been put into the four toothpastes, PD/1's foam has enough energy stored to be a super foam for 5¼ minutes. PD/2 is a super foam for 140 seconds, CD for 100 seconds, and CS for 40 seconds (*Graph 5*).

The only difference between the shapes of the light transmission curves of the toothpaste and shampoos is that the rate of the increase in light transmission with the age of foam is slightly higher with the toothpastes (*Graph 6*). The super foam state is clearly seen in these graphs.

The time of existence of the super foam state can be deduced from both light transmission and viscosity differential results. This is shown in *Table 3*.

Table 3

Toothpaste	Duration of super foam state in seconds	
	Light transmission	Viscosity differential
PD/1	315	300
PD/2	150	155
CD	140	125
CS	40	30

The agreement between the two sets of results is excellent, and proves beyond doubt the presence of the super foam state with the shampoo and toothpaste foams.

The degradation of the specific surface with the age of foam is shown in *Table 4*.

Table 4

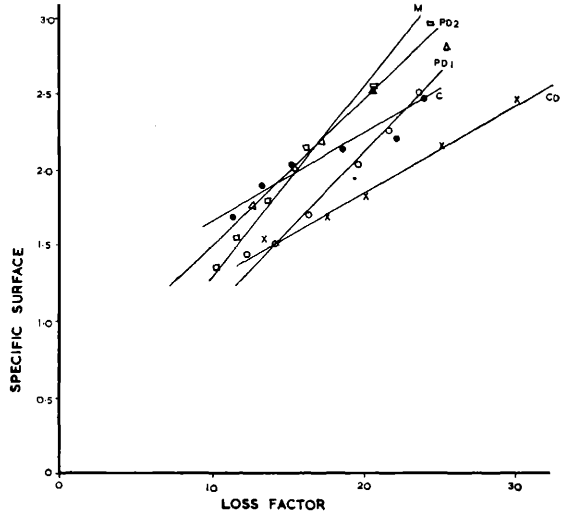
Time	PD/1	PD/2	CD
30 seconds	2·79	2·80	2·88
1 minute	2·53	—	2·43
2 minutes	2·15	2·33	2·40
3 minutes	1·67	2·06	2·08
4 minutes	—	1·98	1·83
5 minutes	1·42	1·76	1·72

Although the specific surface is very similar initially, it is seen that PD/1 degrades much more rapidly. The plot of the specific surface vs. light transmission at given times is a straight line (*Graph 7*). Thus the light transmission results can again be expressed in terms of specific surface.

There is great variation in the size of the bubbles in the foam. The distribution curve of a PD/1 foam is shown in *Graph 8*.

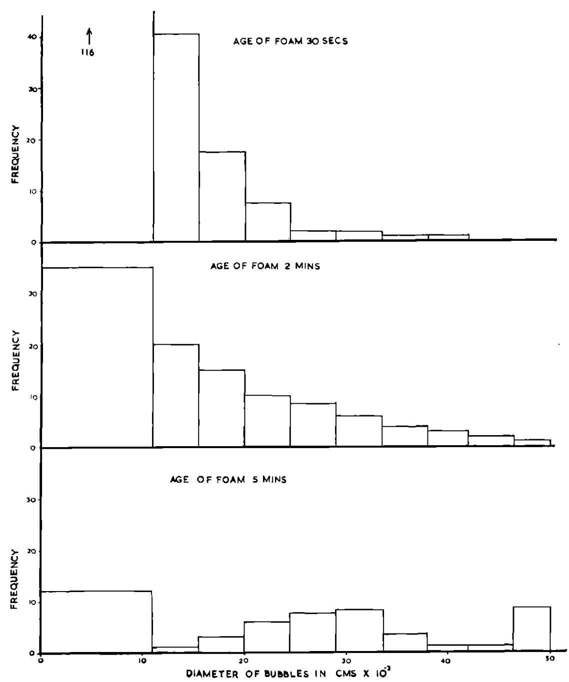
GRAPH 7

PLOT OF SPECIFIC SURFACE V/S LOSS FACTOR



GRAPH 8

BUBBLE SIZE DISTRIBUTION FOR A TOOTHPASTE FOAM (PD-1)



The very fast rate of degradation of the foam is clearly illustrated by the number of bubbles present at 30 seconds (186 bubbles) and at 5 minutes (43 bubbles).

The variation of the area of three individual bubbles with time is shown in *Table 5*.

Table 5

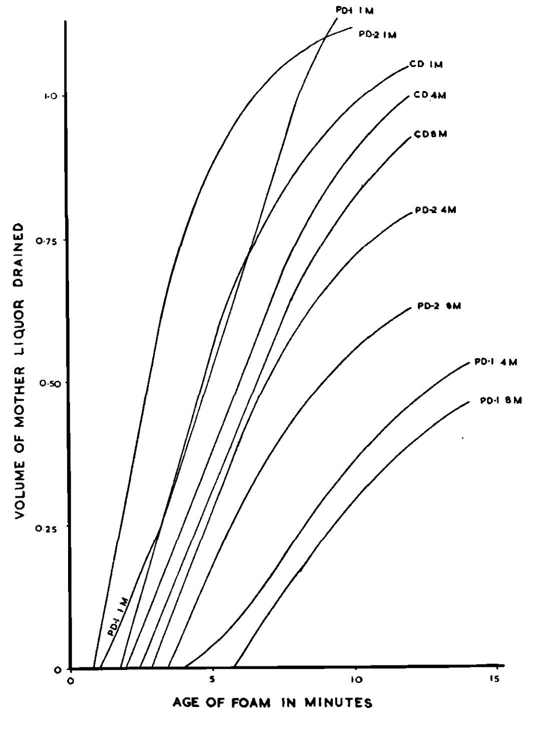
CD Bubbles—area of individual bubbles in sq. cms.

	1 min.	3 mins.	5 mins.	8 mins.
A.	0·0566	0·113	0·150	0·169
B.	0·0267	0·0780	0·113	0·156
C.	0·0011	0·0004	0·0002	—

Some diffusion is taking place since the small bubble shrinks before disappearing. We would have expected that the diffusion would have been a slower process, and we believe that some bursting must be occurring.

GRAPH 9.

RATE OF DRAINING OF MOTHER LIQUORS



The volume of liquid drained by the toothpastes is very much lower than with the shampoos. This is due to the viscous nature of the toothpaste foams.

PD/1 and PD/2 after 1 minute's beating have similar drainage rates. However, after 4 and 8 minutes the drainage rate of PD/1 is much slower.

The wide gap observed between the 4–8 minute PD/1 and PD/2 results is not present with CD, where the 1, 4 and 8 minute drainage rates are much more similar. The drainage rate of CS cannot be measured in this way as it blocks the sinter (*Graph 9*).

Conclusion

The various measurements outlined in the paper have been useful in characterising a foam. Some measurements, such as the viscosity differential, are characteristic for individual foams, whilst others like foam volume, do not in themselves characterise the foam.

When all the tests discussed are applied to one particular foam its characteristics are readily interpreted.

Acknowledgment

I wish to thank Unilever Limited for permission to publish this work, and Mr. J. Ravenhill for valuable technical assistance in developing the methods reported.

(*Received : 23rd June 1960*)

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Introduction by the Lecturer

The aim of our experiment was to have a set of physical properties with regard to foam which are similar to a liquid's boiling point, refractive index, or solubility. In other words, we wanted to get a set of practical as well as useful results. And I hope we have achieved this to some degree. These techniques which you have in front of you are, we hope, useful techniques and they give useful properties of the foam we are concerned with. To date we only had time to work with shampoo solutions and toothpaste solutions. It is easy to get a soiled shampoo solution simply by collecting the soiled water in hairdressing salons or, as we do quite often, by washing some salon

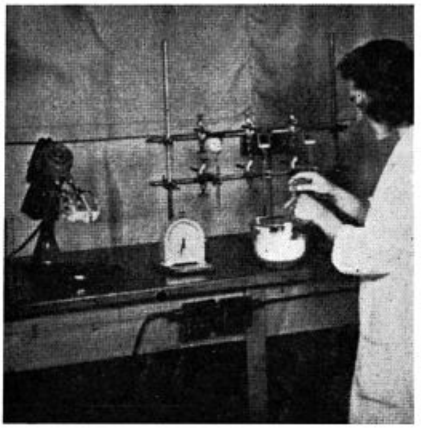

Figure 1

Transferring foam from Mixmaster dish into drainage apparatus.

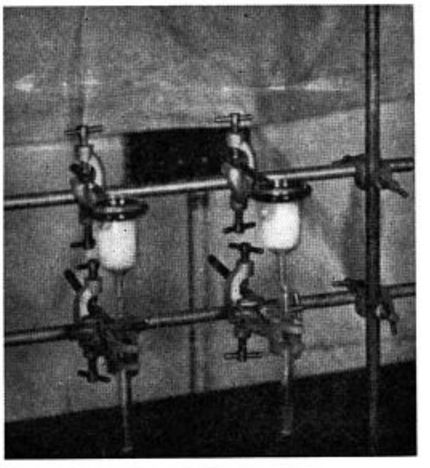

Figure 2

Drainage apparatus.

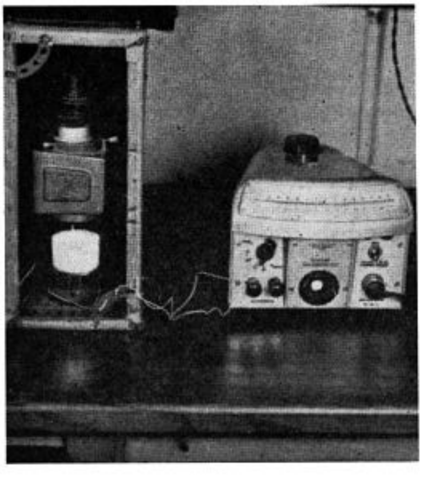

Figure 3

Light transmission apparatus-foamcell sitting directly above photoelectric cell. The black curtain, covering the front, has been removed for this photo.

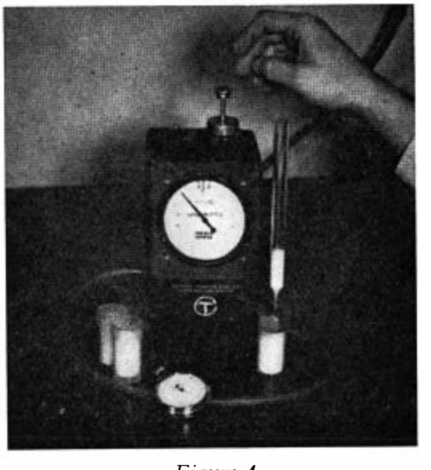

Figure 4

Viscosity apparatus—few seconds after the completion of a reading. Note viscometer cups with collapsed foam, which will be weighed for specific volume determination.

sweepings in the laboratory. I am afraid we have, as yet, not made foams from saliva because we do not have a sufficiently good synthetic saliva mixture. We hope to have one because we feel that by keeping our experiments as near as possible to user conditions and user requirements, we shall obtain very valuable results.

The generation of the foam is the crux of the whole technique. If the generation is no good, then all these results and all the test results can be scrapped. If you care to think that when you shampoo your hair, you have your hand, which is a large area, and the hair, which is an even larger surface area. They rub past each other incorporating air. I feel that the beating of the Mixmaster is similar in character to that. And we have proved this, by taking foam from hair which was being shampooed and determining its viscosity, volume, and other properties. We found that our Mixmaster at 700 revs. per min. and after three minutes of beating, gives a foam with a similar viscosity to that obtained when hair is shampooed for 90 seconds. Having established beyond doubt that our Mixmaster produces a similar type and a similar class of foam although it is about half as slow as in practice, we have gone ahead.

The techniques are extremely simple, and easy to use, and they give useful and accurate results. One point about the viscosity results, they are expressed in absolute units. At first we did not expect that we would be able to achieve this but numerous standardisations and cross-standardisations with known oils and other materials, supported it and we can assume that we are in fact getting absolute results.

Since the paper was prepared, we have done a lot on shampoo soils, and we are doing two-stage shampooing in our laboratory by using salon sweepings. Our techniques are as follows : We are wetting the hair first with water, just as if you were washing your hair and we carry out a two-stage shampoo, and a rinse after each shampooing. We collect water from it, and check the amount of dirt and soil which we get out and it is very much the same or very nearly the same as for an average head. This emphasises that our work is always parallel with practical usage conditions. We found from our experiments that petrol-ether soluble soils, which includes the greases, do not affect the foam properties very much. This is rather surprising, and perhaps many people might disbelieve it. The material which affects the foaming power and the power to produce foam at all are the water solubles. We also have the insoluble grit and dirt which simply increases the time for the shampoo to reach its optimum state. In my paper there are these optimum states in viscosity and foam volume after four minutes or six minutes. The presence of grit makes this eight to ten minutes, depending on the amount present.

In the paper I say that we do not possess a technique for foam breaking.

In the meantime, we found a machine called Struers automatic dispenser. Its main use is for biological and biochemical work to dispense a known volume of liquid at a fairly strong pressure and we have put it to use in foam breaking. We generate our foam in the way described, and put a known volume into a glass cylinder which has drainage at the bottom. This is sprayed with water in units of 5 ml at about 3 seconds' intervals to allow the water to drain away. We count the number of sprays to break the foam and we find it gives very satisfactory results.

Table 6

Number of injections to break foam

Detergent	Unsoiled	Detergent applied to hair	
		1st Application	2nd Application
M	19	16	20
H	22	18	17
N	23	8	20
C	27	25	23

I feel certain that you realise how important it is to know whether a shampoo will wash away quickly or whether it will take half an hour to wash it out. To achieve a figure of (1) no foam would be present at all even a figure of 8 is an extremely weak foam. With the unsoiled detergent we find that M is easiest to rinse and then H, N and C. If we used C as a shampoo we would be having quite a time to rinse it away. After we used a shampoo and wash in the laboratory we checked our foam again and there was quite a difference from N. The foam produced practically collapsed on the spot. This tells us that it is very easy to wash out, in fact it is dangerously easy and therefore not very good. The foam from C is no good either because it takes many injections and hence a lot of washing out but H and M are the best.

The second shampooing in most cases is very nearly the same as the unsoiled, excepting M which shows that the second shampooing is in effect more difficult to wash out than the first one or the unsoiled shampoo.

This technique is still in its infancy and we do not have very definite results, except these few on the effect of soil.

We have made a film of foam breaking-down, and although this is not terribly exciting as far as movies go, we do learn a lot from it. Besides the obvious ones such as the particle size and the film thickness we also see the mechanism of the breakdown, the formation of the large bubbles, the bursting and in fact one can see the whole structure altering in front of one's eyes. The sequence of the events is illustrated by *Figures 5-10.*

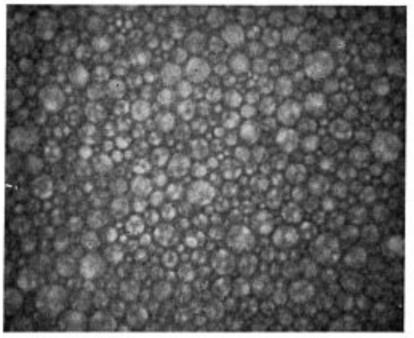

Figure 5
Toothpaste C.D.1 age 60 sec. x 15.

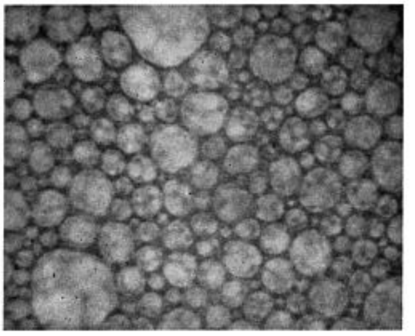

Figure 6
C.D.1 age 240 sec. x 15.

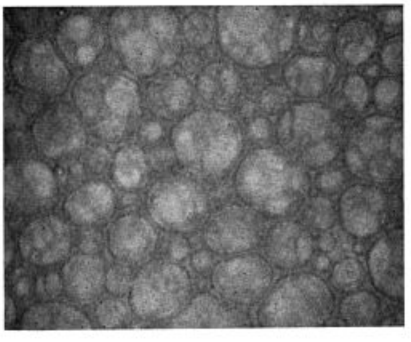

Figure 7
Shampoo M. age 60 sec. x 45.

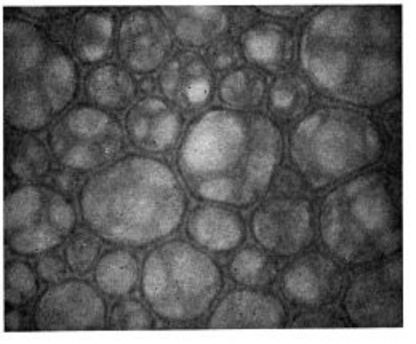

Figure 8
M. age 140 sec. x 45.

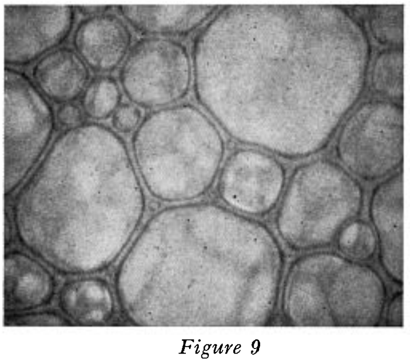

Figure 9
M. age 280 sec. x 45.

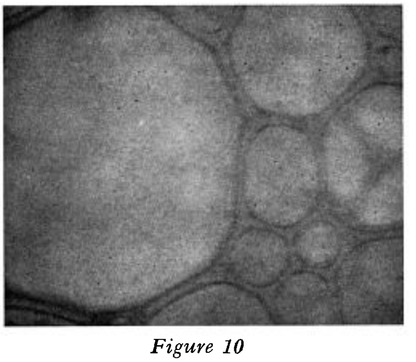

Figure 10
M. age 720 sec. x 45.

Discussion

Mr. A. Herzka : Do you have any special techniques for determining the foam density, and other characteristics of pressurized (aerosol) foams ?

The Lecturer : As I had notice of this question we did some work last week and found that these techniques stand up quite well for the pressurized pack. We have tried some shaving soap. The density was quite easy to determine, the viscosity measurement took a little longer than I would like, but by having another tube for it one can do it quite easily, and we have subjected the foam to the breakdown technique where it took approximately 34 injections. I think it is quite in order to use these measurements for pressurized packs or practically any other foam. The idea behind these techniques is not to limit these tests just to shampoo and toothpaste, but to have as wide a field as possible. At Mr. Holmes's suggestion these methods were tried for detergents and satisfactory results were obtained.

Dr. A. M. Posner : 1. What sort of correlations has Mr. Neu obtained between his experiments carried out in the laboratory and those carried out in the salon ? It is a very praiseworthy effort to try to place the subjective properties of the product on an objective basis using controlled measurements. My colleagues and I have, for many years, been trying to do a similar thing. It does seem to me, however, in the case of the present paper, that there is a convenient get-out mentioned in the case of, say, feel of the foam where part of the tactile impression would be governed by adsorption on the skin.

2. I am not very happy about the use of C.G.S. units in expressing the results on viscosity of foam, because it seems to me that a foam would be non-Newtonian in character and the use of C.G.S. units implies that it is in fact Newtonian.

   What experiments has Mr. Neu carried out to vary the shear rate applied to the foam in order to determine its thixotropic or other deviations from Newtonian behaviour ?

3. I am not clear from the text what exactly Mr. Neu means by the term "viscosity differential". Is it a differential coefficient ? If so, then the units employed on the Y axis of his figures seem to me to be wrong.

4. Can Mr. Neu explain the physical meaning of the term "superfoam" ? Does it correspond to the region of very rapid drainage ?

The Lecturer : 1. As far as feel is concerned, we cannot tell, but the viscosity we can tell very easily because a viscosity of 20 or more will mean a very creamy foam, and a viscosity of 15 or less will be practically lost on the hair. I think the correlation is extremely good, as far as these methods are concerned. We developed the methods, then we went to the salon and correlated theoretical and practical results until we knew that we were running parallel. But as far as the feel is concerned, we have no method for it and I believe, though I may be quite wrong, that I can make up two shampoos with the same viscosity, the same particle distribution volume, in fact with identical properties, but they will feel different. To the touch this is something which has nothing to do with physical property but with the adsorption on to the skin. I do not think that this is so very important in our foam work, because you know immediately without any measurements, that some types of foam will feel unpleasant. You have to assess it yourself, we cannot help. It is just the same if you put an acid on your skin, well you know how that burns. I do not think that these things can be done by physical methods ; they are not physical techniques. I wish they could be.

2. Our instrument does not allow us to vary the air pressure but what we have done is that we have various viscosity tubes which we have standardised with known oils. Measurement of foam viscosity is independent of tube diameter. This particular viscometer is claimed by its maker to give C.G.S. results although we had to modify it.

3. The viscosity differential is just a means of not having very cumbersome titles and names, and actually I do say here that the change in viscosity with the age of the foam is what I mean by viscosity differential. It is not a true calculus differential and is actually a plot of the viscosity against time, and it has exactly the same units as these which I use for viscosity.

4. A superfoam is quite a different type of foam to the more aged foam. It not only has rapid drainage, but it also has very rapid decrease of viscosity, and changing light transmission. It seems to be having a lot of excess energy in it and that excess energy dissipates by draining quickly, collapsing fast, bursting, and then it comes to the region of relative stability. You can see that in *Figures 5-10*.

MR. D. BASS : Amphoteric detergents are increasingly used in both shampoos and toothpaste. Have you conducted any of your experiments on foaming and rinsing on any amphoteric surface active agent, and if so, how did results compare with anionics, nonionics, and cationics ?

THE LECTURER : We have done no work with this class of detergent.