TABLE III

Anionic Titration Versus Acidimetric Method for Analysis of Amine Oxides (DMAO) and Amines (DMA)

	Acidimetric method			Anionic titration, meq (DMAO + DMA)/g	% Difference
	% DMAO	% DMA	meq (DMAO + DMA)/g		
Amine oxides[a]					
"C_{12}" DMAO	87.5	3.2	3.97	3.93	−1.0
"C_{14}" DMAO	83.0	7.1	3.53	3.63	+2.8
"C_{16}" DMAO	82.7	7.0	3.14	3.24	+3.2
"C_{18}" DMAO	82.9	7.4	2.90	2.99	+3.1
Amines[b]					
"C_{12}" DMA		100	4.67	4.41	−5.6
"C_{14}" DMA		100	4.15	4.06	−2.2
"C_{16}" DMA		100	3.73	3.59	−3.8
"C_{18}" DMA		100	3.37	3.30	−2.1

[a] Amine oxides prepared by H_2O_2 oxidation of the amines and analyzed by acidimetric method described in (3).

[b] Redistilled (under vacuum) commercial amines used in preparation of amine oxides. According to gas chromatographic analysis, average mol wt and per cent of principal dimethylamines (DMA) are as follows: for "C_{12}" DMA, 214, 1% C_{10}, 91% C_{12}, and 6% C_{14}; for "C_{14}" DMA, 241, 96% C_{14} and 2% C_{16}; for "C_{16}" DMA, 268, 2% C_{14} and 96% C_{18}; for "C_{18}" DMA, 296, 4% C_{16} and 96% C_{18}. Chromatographic conditions are: Aerograph gas chromatograph A-350-B; dual 10-ft x ¼-in. stainless steel columns, each packed with 20 g 20% "Apiezon" L on 60/80 Chromosorb W (HMDS); column temp 280C; injector temp, 240C; detector temp, 330C; and helium rate, 50 ml/min.

TABLE IV

Determination of Molecular Weight and Distribution of Alkyldimethylamine Oxides (DMAO) in Detergent Formulations by GLC

Amine oxide determination	Formulation E		Formulation F	
	Actual	Found	Actual	Found
Distribution				
C_{12} DMAO, wt %	62	64	51	49
C_{14} DMAO, wt %	38	36	37	40
C_{16} DMAO, wt %	....	....	12	11
Avg mol wt	239	238	245	245

well with actual values and are close to the generally expected accuracy of gas chromatographic methods (Table IV). These results indicate that pyrolysis is essentially complete or that the rate is fairly constant over the range of C_{12} to C_{16} alkyl chain.

Prior to analysis, samples are treated with anionic exchange resins to remove any alkyl sulfates which will partially decompose to olefins. Straight chain alcohols, on the other hand, do not decompose under these conditions. Treated samples are dried by refluxing with benzene before chromatographic analysis to minimize tailing. Prolonged heating with benzene should be avoided since amine oxides will decompose to olefins even under these mild conditions.

In chromatographic analysis of amine oxides, alkyldimethylamines do not decompose; and their peaks are well separated from olefin peaks as shown in Figure 2-A. Therefore, quantitative determination of the amines should be possible by the use of a suitable internal standard.

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Dynamic Foam Test[1]

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Abstract

A test has been developed for measuring the amount of foam generated by a detergent composition under dynamic conditions and in the presence of sebaceous soil. Good correlation with actual practice results because the conditions of the test closely parallel practical laundry conditions.

Introduction

FOAM IS AN IMPORTANT criterion in the evaluation of detergent compositions. Since the design of a product is often centered upon foaming characteristics, it is important to be able to measure this interesting phenomenon under many conditions. Too much foam can be troublesome and not enough may also prove to be a disadvantage. The majority of housewives still relate cleaning ability to the presence of foam and this is not without some foundation. One cannot deny the aesthetic value of observing a washing machine smoothly cushioned under a "sea of foam" as compared to a sloshing interface that resembles a myriad of miniature tidal waves.

Many companies are now engaged in making detergents that are biodegradable. This whole problem has been highlighted because of the presence of foam in sewage. Part of the characterization of these new products must be a foam profile that relates them to existing products and to molecular configurations. Individual measurements such as film drainage, viscosity, density, spreading coefficients, etc., are helpful but somewhat meaningless in portraying the gross effects. The need arose, therefore, for a simple procedure for screening new alkylates and detergent compositions in general.

A review of the literature shows the Ross-Miles (10) test to be mentioned most frequently. This has been adopted by the ASTM. Another widely used procedure is the dishwashing test (12), used most frequently for screening light duty liquids. Weeks et al. (13) developed a test for hand-dishwashing compositions. Heinz and Machemer (5) used a mechanized disc and added emulsified fat together with street dust for correlating with the "washing tub." Barnett and Powers (1) mechanized a plunger and used sebum and sweat to test the performance of shampoos. Leenerts et al. (4) developed a technique utilizing a household washer for evaluation of foaming properties of hand-dishwashing detergents. More recently, Reich et al. (9) published a test designed for low foaming surfactants.

The writer wished to incorporate the following features into any screening procedure that might be workable:

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[1] Presented at the AOCS Meeting in Minneapolis, 1963.

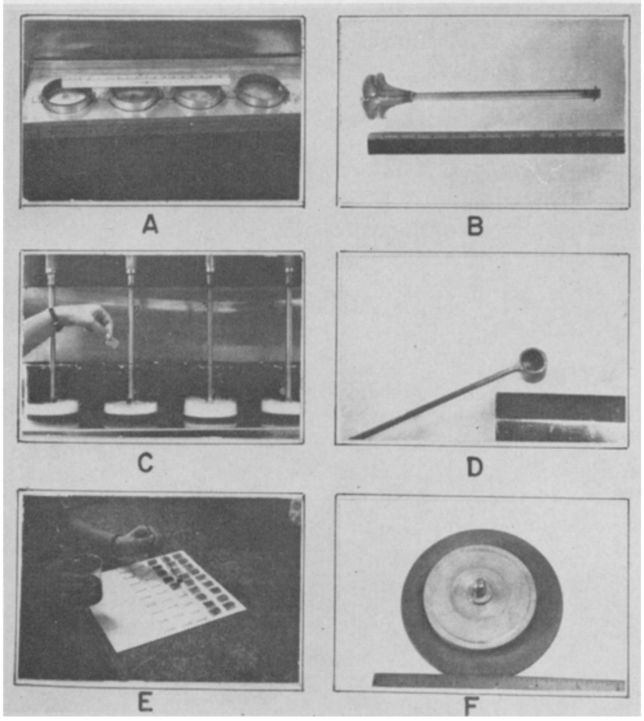


FIG. 1. Tergotometer modifications.

a) Mechanization similar to present day washers
b) Realistic soil
c) Dynamic foam generation
d) Rapid and precise measurements

Parts "a" and "c" are achieved by modifying the Tergotometer as in Figure 1. A good deal of our detergency work is done by applying sebaceous soil to fabric and it was easy to expand the scope of this work to include foam measurements to comply with part "b." The final point was accomplished by making use of the versatile Polaroid camera for making measurements, eliminating the need for wordy descriptions and providing a permanent record.

Experimental

Tergotometer. A stainless steel cover was placed over the table supporting the stainless steel beakers. Clamps were spot welded to the cover to position 1500 ml beakers immediately above the wells for the steel beakers. Brass bearings, attached to a rubber disc, were placed inside the beakers to receive the agitators which were shortened for the new set up. (A scribed plexiglas shield can be used so that measurements can be made from photos.)

Soil-Synthetic Sebum. (Modified from Barnett and Powers. See procedure No. 1.)

Palmitic acid	10.0%	Squalene	5.0%
Stearic acid	5.0%	Paraffin	10.0%
Oleic acid	15.0%	Cholestrol	5.0%
Coconut oil	15.0%	Spermaceti	15.0%
Olive oil	20.0%		

Terry Cloth.

Solvents. Isopropanol and benzene.

Procedure:

1) Dissolve 50 g sebum mixture in 1:1 isopropanol-benzene and make up to 250 ml in a volumetric flask.
2) Using 2-in. x 2-in. terry swatches, add 200 mg sebum to each of 4 swatches. Then add 100 mg to each of 16 additional. (For low foamers, make up 24 swatches, each containing 40 mg of sebum.)
3) Set Tergotometer for 100 rpm.
4) Add ca. 0.5 g representative sample to respective beakers.
5) Fill a 2000-ml flask with water at 125F. Adjust for hardness and measure 300 ml of this water into each beaker.
6) Run the Tergotometer for 3 min. Photograph foam as soon as machine stops, using 10-sec film.
7) Add one 200-mg swatch to each beaker and repeat step No. 6.
8) Continue adding 10 mg swatches at three-min intervals until foam collapses. (It is usually unwise to add more than a total of 600–700 mg sebum.)
9) Mount trimmed photos in sequence. (Note: pertinent data can be printed on contact tape and fastened to the Terge, so that it is included on prints, thus eliminating separate records.)

Note: If desired, a total soil load can be added immediately and then foam generated in its presence.

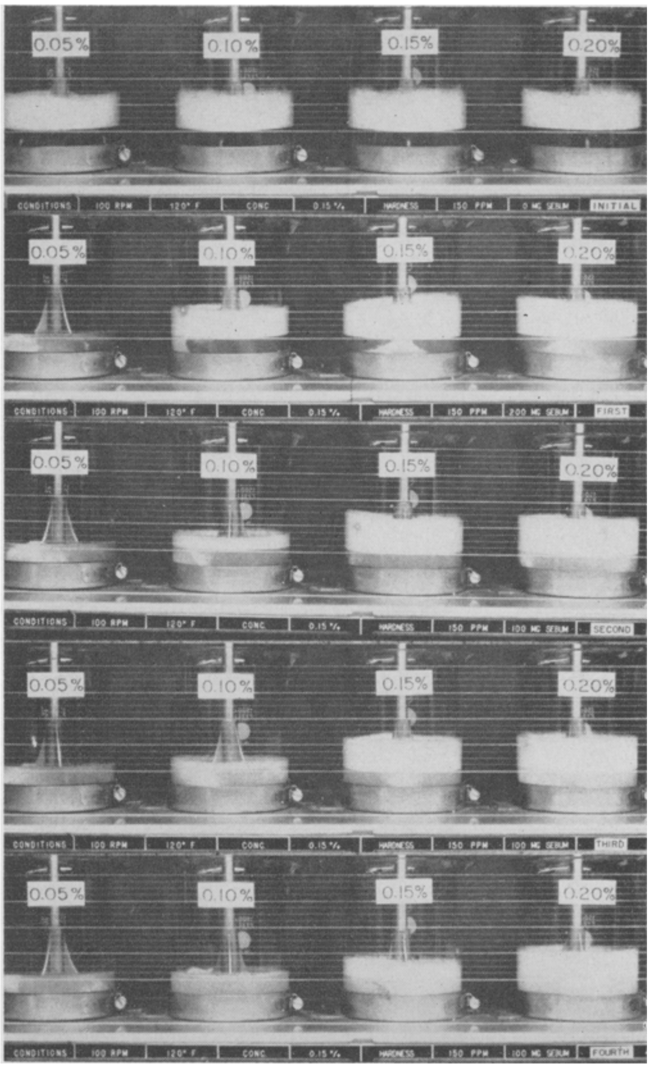


FIG. 2. Foam height vs. concn.

Results and Discussion

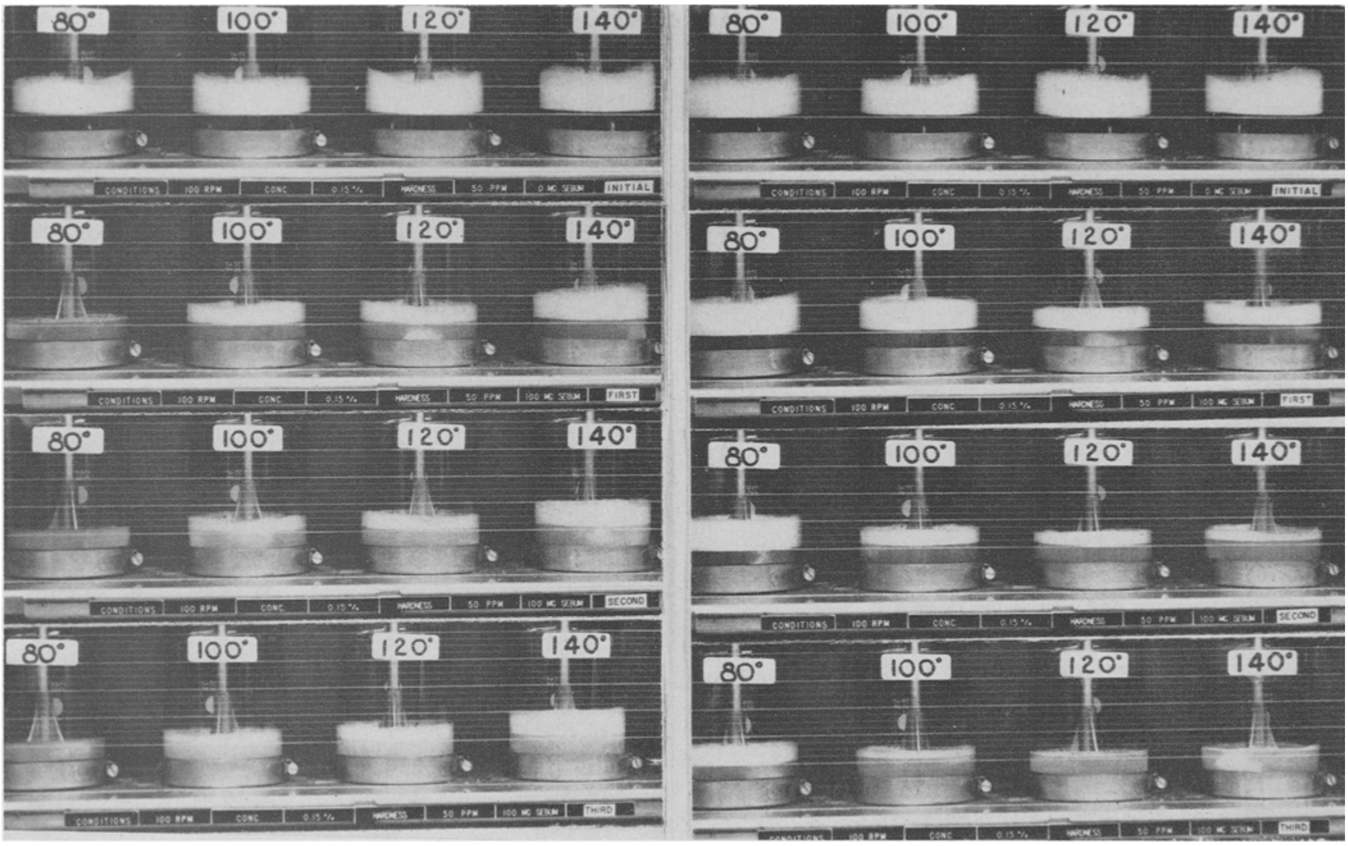
The effect of detergent concn on foam heights was determined using a high foaming heavy duty formulation (Fig. 2). Solutions ranging from 0.05–0.20% concn were prepared and initial foams generated.

These initial foams show very little difference in volume in spite of the concn variations. A 200-mg soil load of synthetic sebum was then added. The 0.05% soln collapsed completely, the 0.10% soln went down ¼ in. and the remaining solutions were the same as originally. After a total of 500 mg soil had been added, the 0.10% soln collapsed, the 0.15% had been reduced to 40% of its original volume and the 0.20% soln to 70% of its original volume. Since this particular composition contains 25% Active Ingredient, it figures that the max tolerance for 10 mg of detergent is 50 mg of soil in this particular system. A study of this kind is usually used when a new batch of sebum is made. By profiling a high foamer and a low foamer at different levels of concn, the soil can be standardized in terms of previous work.

Does the amount of foam increase or decrease with temp during a cleaning operation? To answer this question the same product as above was used and its degradation profiled at four different initial temp, with 20F intervals (Fig 3). (As in actual practice, a temp gradient is used instead of a constant temp.) The first series of prints (left) were run with sebum and the others (right) were degraded with hydrogenated vegetable oil. For brevity, hydrogenated vegetable oil will be referred to, hereafter, as fat. After generation of initial foam, 100-mg increments of soil were added. After the third increment had been added, the sebum contaminated soln at 80F had collapsed and one at the high temp had been reduced to 55% of its original volume. In contrast, the fat contaminated soln at 80F had been reduced to 50% of its original volume and the 140F soln was collapsed. Hence, one would expect the foaming action of sebum-soiled clothes to be inverse with relation to temp to those soiled with fat. It must be remembered that sebum is easily emulsified and has a lower mp than most cooking fats and at higher temp the fatty acids may be solubilized.

One of the most important considerations in aqueous cleaning is the amount of calcium and magnesium ions present. This is mainly because of the formation of insoluble soaps which interfere with detergency and foam. For an attempted explanation of this type of foam degradation, reference is made to a paper by Peper (7) on the defoaming of synthetic detergent solutions by soaps and fatty acids, and to Miles and Ross (14) on the deleterious effect of calcuim soaps of fatty acids on solutions of sodium soap.

To explore this situation, a comparison was made between foam breakdown in hard water and in soft water in the presence of fat and sebum. (Figs.4,5). Products A, B and D were built detergent compositions with alkylbenzenesulfonates of different chain lengths and branching and product C was a fatty alcohol sulfate. Soft water contained 50 ppm Ca as calcium carbonate and hard water contained 300 ppm. A total of 600 mg soil were added in 5 increments. Product B collapsed completely after the final addition in each instance. Product C has little reduction with either soil in soft water, but collapsed readily in hard water, particularly with sebum. Product D was unaffected by 600 mg fat in either hard or soft water, but collapsed to within a ¼ in. with sebum in both hardnesses. Product A was better in soft water with sebum than hard water but just the opposite in the presence of fat. Unfortunately, in dealing with foam, it is hard to correlate it with other properties of the composition. Quoting from Bikerman (11), the process of introducing air bubbles into a liquid by whipping, beating, etc., undoubtedly is very complicated and, apparently has not yet tempted any physi-



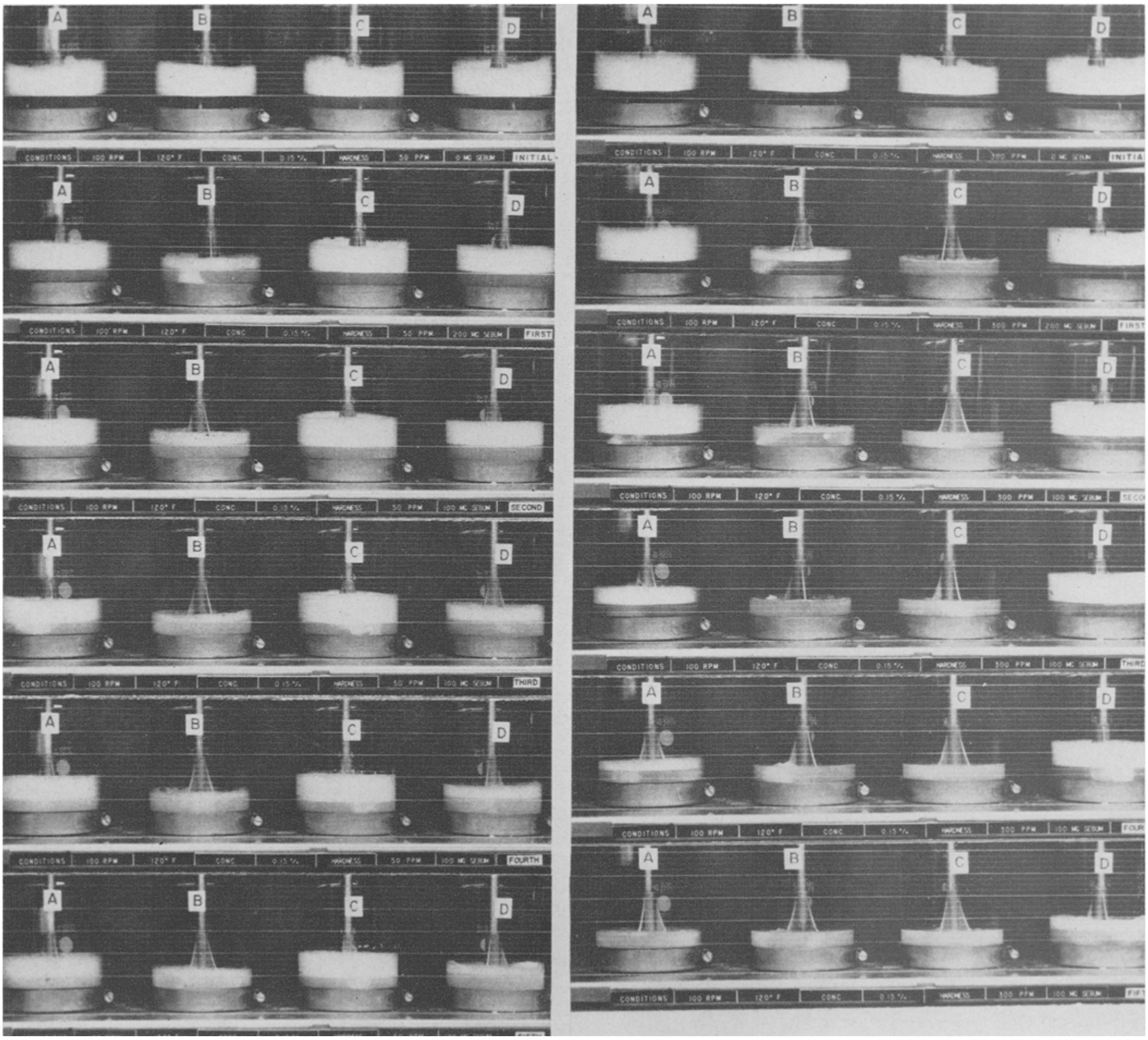
SEBUM FAT

FIG. 3. Effect of temperature on foam.

cist. In the procedure presented, we are stressing a practical application of foam stability of various detergent substances in similar formulae to destructive agents. By combining these data with mass spec and VPC data, it is hoped that relationships can be established between foaming effects and molecular structure. In addition, the effect of stabilizers and other adjuvants can be studied.

The above work shows the effects of two different soils in breaking foam. In laundry operations, the presence of "fatty and greasy soils" are not as important as the sebaceous and epidermal secretions. Therefore, most of the screening work aimed at laundry work is done using only synthetic sebum. Kind and Oldenroth (3) state that soil of the average wash load is made up of 5–10% sebaceous material, (excluding skin scales). It is estimated that a minimum secretion of sebum for the whole body in a day is about 0.3 g. The accumulation of this type of soil can amount to as high as 8% of the weight of the fabric (9). It is not too difficult to relate the results of a clean wash load and photographs of this degradation of screening with synthetic sebum to a particular washing machine with a given type of detergent. In general, the synthetic sebum is padded onto fragments tion are compared to the general screening photos. Finally, numerous loads of naturally soiled goods are photographed for comparison. Once these conditions are established, the general screening data can be extrapolated to specific laundry situations. For example, an experimental low-foaming detergent composition, when used in a particular make of front-loading machine with an average wash load of 8 lb gave the same breakdown as 80 mg sebum in the screening test. The statistical analyses of all phases of the work have not been completed but it is estimated that in the screening test, the final foam volumes have a precision of ±¼ in. at 95% confidence.

The final evaluation of many detergent compositions is the "wash tub"; others, especially light duty, must relate foam volume to a practical dishwashing procedure (12). The following dishwashing procedure has been used extensively at Colgates for many years with good results.



50 ppm SEBUM 300 ppm

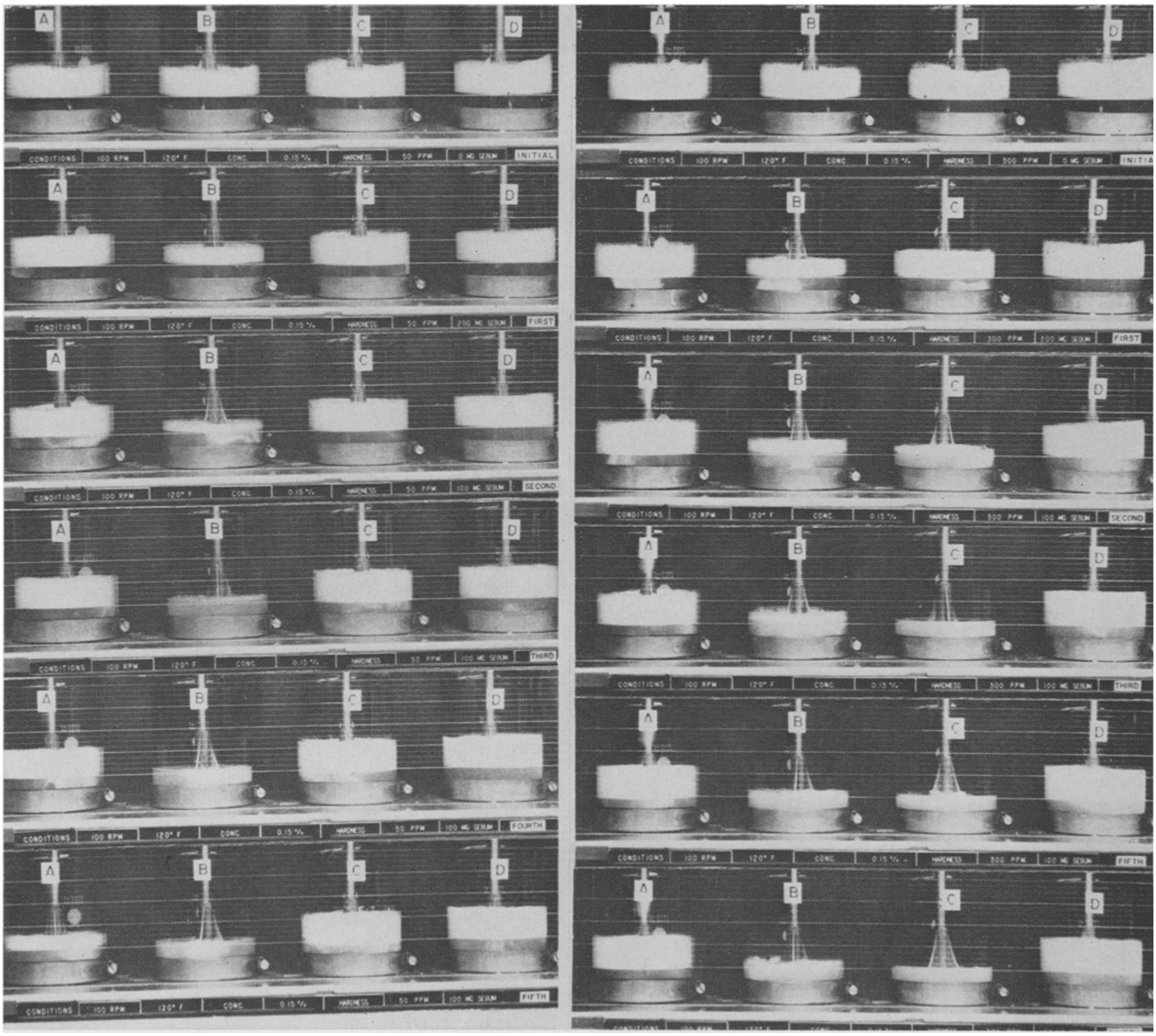
Fig. 4. Effect of composition and hardness on foam.

1) Add small amount of Sudan Red dye to hydrogenated vegetable oil and heat to ca. 130F.
2) Place ½ teaspoon soil in the center of each plate and spread over the center area.
3) Stack plates; age for not less than 30 min or longer than 4 hr.
4) Fill percolators with 6 liters water at desired hardness and 115F ±1F.
5) Place required amount of detergent in the dishpan.
6) Open faucet and allow the water to completely empty from the percolators (45–50 sec).
7) Place 5 soiled plates in each pan. Using a timer as a guide, wash dishes one at a time, using five circular strokes on the front and four on the back, each stroke consuming ca. one sec. During the washing procedure, hold plate at an angle so that about one half of plate is kept under the surface.
8) Operators should finish washing all five plates in ca. 50 sec; then rotate within the next 10 sec so they always have a common starting time as noted on the timer.
9) Continue washing procedure, rotating operators after each five-plate set until the foam disappears. This is the foam "end-point" and visually the surface will be nearly devoid of foam.

Since the Tergotometer foam test screened effectively for laundry operations, it was hoped that it may be of value in relating to the aforementioned dishwashing tests (13). The same four products chosen for hard water studied (Figs. 4,5) were again used in making the comparison. The actual dishwashing on these products gave the following results:

	No. of plates			
	A	B	C	D
50 ppm	13	11	13	18
300 ppm	21	20	12	16

The concentration of the soil per plate was then reduced one third in weight/plate and the washing time was increased one third to see if the results remained constant.



50 ppm FAT 300 ppm

FIG. 5. Effect of composition and hardness on foam.

	No. of plates			
	A	B	C	D
50 ppm	10	7	10	28
300 ppm	22	22	9	28

Product D changed ca. 10 plates in both hardnesses but the other products had little change. Hand dishwashing is cited as an excellent example of solubilization of oils, fats, and fatty acids by the detergent solution (6). Once this solubility point has been exceeded, emulsification occurs and foam beings to fall because the surfactant is adsorbed in the process. The above results seem to indicate that solubilization is dependent somewhat on manner of soil introduction and applied energy to the system. In fact, a statistical study (11) showed that a soil/detergent relationship in dishwashing was not fundamental . . . it does not hold with certain types of detergents and only with certain types of soil. Their data shows that a simple fat gives results nearly independent of the amount of fat on each plate. Hence, it must be remembered that the dishwashing procedure is an empirical situation which supposedly imitates actual home dishwashing, and strict conditions must be adhered to for good precision. The Terge procedure was modified with the hope of duplicating actual dishwashing numbers so that screening could eliminate some of the work load.

A comparison was first made between a hard substrate and a fabric substrate (Fig. 6). Foam was generated with the same high foam detergent composition used in the concentration study. A 300-mg load of fat was added to four different substrates: nylon, aluminum, terry cloth and glass fabric; and these were introduced into the respective buckets. After 5 min the foam volume was photographed. It clearly indicates that fat is most easily removed from glass.

A simulated run was then performed on the Terg by adding 0.13 g fat to glass swatches and adding them to the solutions every 10 sec until the foam collapsed. Results:

	No. of swatches (plates)			
	A	B	C	D
50 ppm	13	6	29	21
300 ppm	30	20	27	32

The same test was repeated using Terry cloth with 0.26 g fat. This was tried because terry is easier to handle and much more economical.

	No. of swatches (plates)			
	A	B	C	D
50 ppm	25	9	38	25
300 ppm	28	17	23	30

It can be observed that substrate did not change the relationship to any degree but the simulated results in general did not agree across the board with actual results, particularly product C. A change in the design of the agitator may improve the agreement, in the meantime this method is not used too frequently for screening new formulations for dishwashing but has served as an excellent control procedure. By varying swatch time, soil load, time of addition, etc., almost any formulation can be matched, number for number, with actual dishwashing and with the same precision. Some typical results are presented.

	Concentration					
	0.20%		0.25%		0.30%	
Hardness	Act	Sim	Act	Sim	Act	Sim
0 ppm	17	20	24	25	28	28
50 ppm	17	19	24	25	28	28
150 ppm	17	18	25	24	28	26
300 ppm	21	23	27	27	33	31

The following procedure is most commonly used:

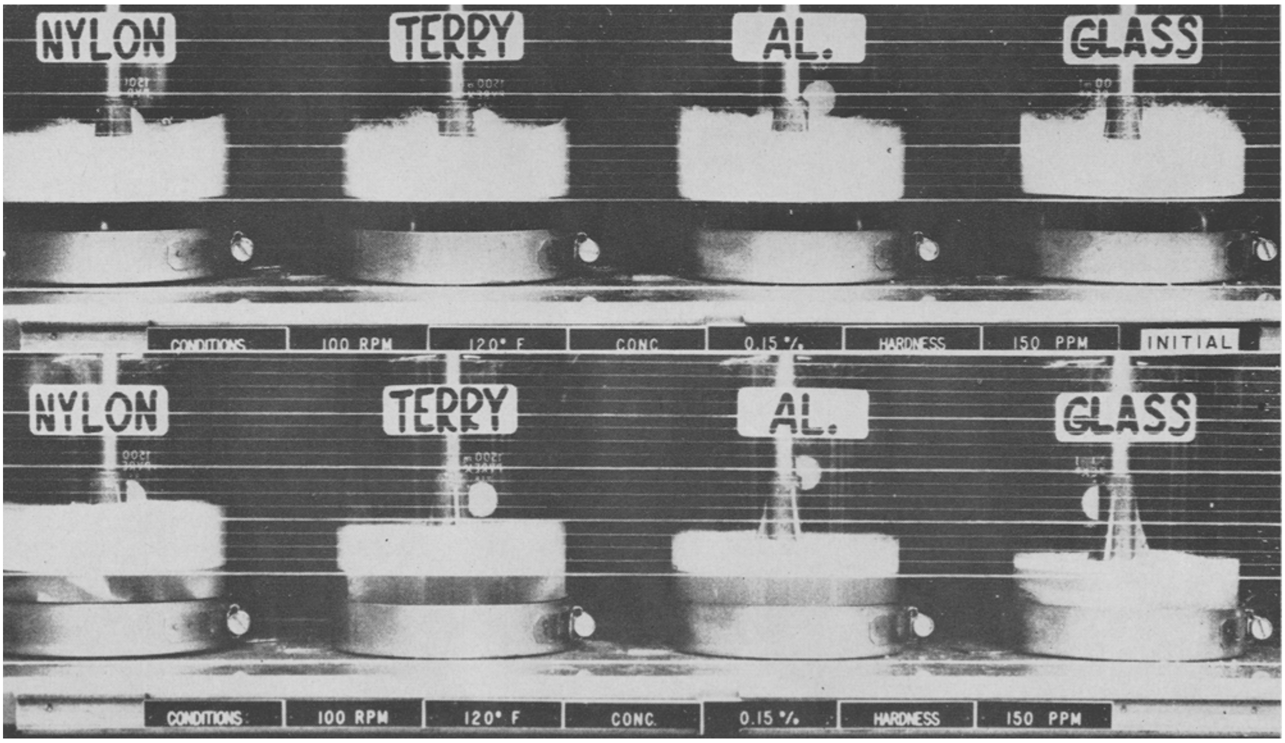


FIG. 6. Effect of substrate.

1) By means of a dipper or heated buret add .26 g fat to 1½ in. x ½ in. Terry cloth swatches (1½ in. x 1 in. for most liquids).
2) Age swatches one half hr before using.
3) Set Tergotometer at 75 rpm.
4) Add sample to respective beakers.
5) Fill a 2000-ml flask with water at 120F and adjust hardness.
6) Measure 400 ml water from the flask into each beaker.
7) After two min mixing time, add 1 swatch every 15 sec.
8) Continue adding swatches until foam disappears.
9) Number of swatches added equal number of dishes.

Summary

A Tergotometer has been modified so that foam studied can be made on laundry products. Using sebaceous soil and a Polaroid camera, a photographic record of foam breakdown can be made which fortells performance in practical laundry situations.

A simulated dishwashing procedure has been used with the same set-up as a control method once it has been correlated with a given product. It is hoped that eventually changes can be made so that there will be complete correlation with any dishwashing test and then it can double as a screening procedure for dishwashing operations.

ACKNOWLEDGMENTS

Assistance in doing much of the experimental work by R. Roga and P. Leisentritt. Help in redesigning the Tregotometer by the mechanical engineering department.

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Use of Rubber Columns for the Chromatographic Separation of Triglycerides and Other Non-Polar Compounds

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Abstract

Some applications of rubber powder as a stationary phase in the chromatographic separation of relatively nonpolar compounds are described. Evidence of a substantial degree of separation of triglyceride components in coconut oil and linseed oil is obtained using a mixture of methanol and acetone as the mobile phase. Separations of trilaurin from mono and dilaurin, of methyl esters of coconut oil fatty acids and of components in Oil of Petitgrain are also accomplished.

Introduction

A FEW YEARS AGO Boldingh (1) described a technique for the separation of saturated normal fatty acids. He prepared a column with rubber powder as the immobile phase and used benzene-saturated mixtures of 3 parts methanol, 1 part acetone, and decreasing amounts of water as successive developing solvents. By this reversed-phase procedure, the components were eluted from the column in order of decreasing polarity or increasing chain length of the acids. The process may be more comparable to liquid-liquid partition than to liquid-solid adsorption as the rubber was reported to be an excellent solvent for fatty materials and considerable swelling of the rubber was observed.

We investigated rubber in a search for a suitable method of separating hydrocarbons and other relatively non-polar compounds. Since we did not have on hand the "Mealorub" (vulcanized rubber powder) used by Boldingh, we prepared our powder from laboratory gum rubber tubing. Other laboratories may find useful applications for these conveniently prepared columns in addition to those which are described here.

A continuously recording differential refractometer (Phoenix Model R-1000-T), sensitive to a change of 4×10^{-6} refractive index units, was used to follow changes in the composition of the eluent stream and greatly aided in the search for suitable column phases by providing an immediate record of the degree of separation achieved.

Experimental Procedure

Preparation of Rubber Columns. The rubber powder was prepared from amber "pure gum" surgical tubing manufactured by the Davol Rubber Co., Providence, R. I. With the exception of a yellow latex tubing of another manufacturer, we have not investigated the suitability of other sources of rubber. The latter tubing was inferior for our purpose as it yielded a somewhat sticky powder which produced a column of low resolving power.

The end of a length of tubing (½ in. diam and ⅛ in. wall thickness) was frozen in a bath of methanol and dry ice. One or two inches was then ground off on a 6 in. diam motor-driven grindstone and the tubing was refrozen in the bath. By using several lengths of tubing in rotation, over 500 g powder

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[1] Present address: Grocery Products Div., Armour & Co., Chicago, Ill.