

(probably  $C_{26}$ ), and "the ester anhydride of an hydroxy acid" ( $C_{21}$ ) have allegedly been isolated. Arachidic acid ( $C_{20}$ ) has been isolated in a purity of 97 mol. per cent.

4. In the light of present knowledge, only two compounds have been isolated in any reasonable degree of purity from carnauba wax. These compounds are heptacosane and arachidic acid.

#### LITERATURE CITED

1. Bérard, M. P., *Bull. soc. chim.* 9, 41 (1868).
2. Bowers, R. H., and Uhl, A. H., *J. Am. Pharm. Assoc.* 30, 10 (1941).
3. Brande, W. T., *Trans. Roy. Soc. (London) B, Part 1*, 261 (1811).
4. Chibnall, A. C., Piper, S. H., Pollard, H., Williams, E. F., and Sakai, P. H., *Biochem. J.* 28, 2189 (1934).

5. Francis, F., Piper, S. H., and Malkin, T., *Proc. Roy. Soc. A* 128, 214 (1930).
6. Francis, F., and Piper, S. H., *J. Am. Chem. Soc.* 61, 577 (1939).
7. Gottfried, S., and Ulzer, F., *Chem. Umschau* 33, 141 (1926).
8. Heiduschka, A., and Garies, M., *J. prakt. Chem. N. S.* 99, 293 (1919).
9. Koonce, S. D., and Brown, J. B., soon to be published in *Oil & Soap*.
10. Krafft, F., *Ber.* 17, 1628 (1884).
11. Maskelyne, N. S., *J. Soc. Chem.* 7, 192 (1855).
12. Idem, *ibid.*, 22, 87 (1869).
13. von Pieverling, *Ann.* 183, 344 (1876).
14. Piper, S. H., Chibnall, A. C., and Williams, E. F., *Biochem. J.* 28, 2175 (1934).
15. Piper, S. H., Chibnall, A. C., Hopkins, S. J., Pollard, A., Smith, J. A. B., and Williams, E. F., *Biochem. J.* 25, 2072 (1931).
16. Pollard, A., Chibnall, A. C., and Piper, S. H., *Biochem. J.* 25, 2111 (1931).
17. Pollard, A., Chibnall, A. C., and Piper, S. H., *Biochem. J.* 27, 1889 (1933).
18. Schuette, H., and Vogel, H., *Oil and Soap* 16, 209 (1939).
19. Small, W. N., *Foreign Commerce Weekly (Dept. of Commerce, U. S. A.)* VIII, No. 10, 8 (1942).
20. Stürcke, H., *Ann.* 223, 283 (1884).

## Foaming Properties of Soap Solutions

R. C. MERRILL, JR., and FRANCES T. MOFFETT

Western Regional Research Laboratory, Albany, California  
Bureau of Agricultural and Industrial Chemistry  
Agricultural Research Administration  
U. S. Department of Agriculture

Although a number of investigations on the foaming properties of soap solutions have been made (7), the results are difficult to produce and as Lascaray (6) points out are, in many cases, apparently contradictory. Few quantitative data on the stability of foams from soap and detergent solutions are available in the literature. This paper reports reproducible quantitative data obtained by two methods on the stability of foams from solutions of various soaps and detergents and on the effects of added substances, pH, and soap or detergent concentration on foam stability. Soaps and detergents are often appraised by the volume and stability of the suds produced, and the data may prove valuable in the development of new detergents and in the understanding of mechanisms of foam formation and decay.

The first of the two methods used involves measuring the rate of drainage of liquid from a foam produced in an arbitrary manner. This simple, rapid method, requiring little special apparatus, has been frequently used as a measure of foam stability (1,3,4, 13). The second method involves measuring the lifetime of a definite area of foam monolayer (single layer of bubbles). The latter is "foam time" method developed by Schutz (16) and McBain and Ross (reported by Ross, 14) and modified by ourselves for use with soap foams.

#### Experimental Methods

*Foam drainage method.* The foam drainage apparatus (Fig. 1) is made of Pyrex glass from a 2-liter flask, a 100-ml. graduated cylinder, and a 30-mm. sintered-glass Büchner funnel (Corning medium pore size). Preliminary experiments showed that the rate of drainage of solution from a soap foam varies with the method of producing the foam. For example, foams formed rapidly are drier and lose solution more rapidly than those formed more slowly. In order to obtain comparative results on different solutions, it is therefore necessary to adopt a standard procedure of producing the foam and measuring its rate of drain-

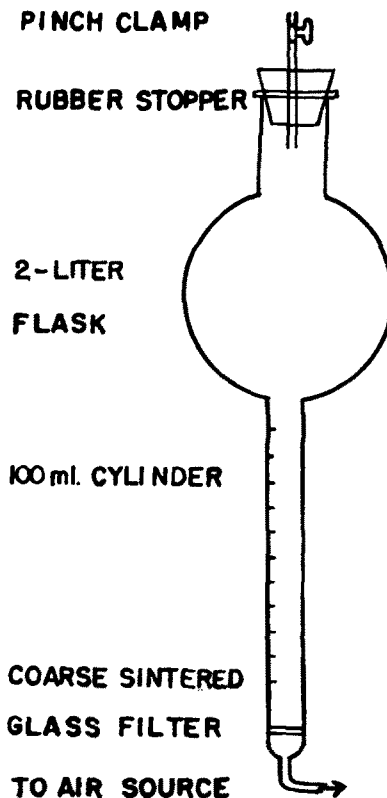


Fig. 1. Foam drainage apparatus.

age. The following method was adopted for this investigation:

All experiments were performed with the apparatus immersed in a water bath at a constant temperature of 25° C. The apparatus was filled with solution to the 70-ml. mark. Foam was produced by blowing air through the solution for exactly two minutes under a constant pressure of 6.0 cm. of mercury. This air had been passed through glass wool, soda lime,

and calcium chloride, and brought to 25°C. by passage through a 10-foot copper coil in the water bath before being introduced into the foam flask. After the air was shut off, readings were taken of the seconds required for the drainage liquid to reach the 10, 20, 30, 40, 50 and 60 ml. graduations. Zero time was taken as the time when 70 ml. of liquid remained in the foam. Back pressure to prevent liquid from draining through the filter was maintained by closing a pinch clamp on the inlet tube while air was still being forced through the system.

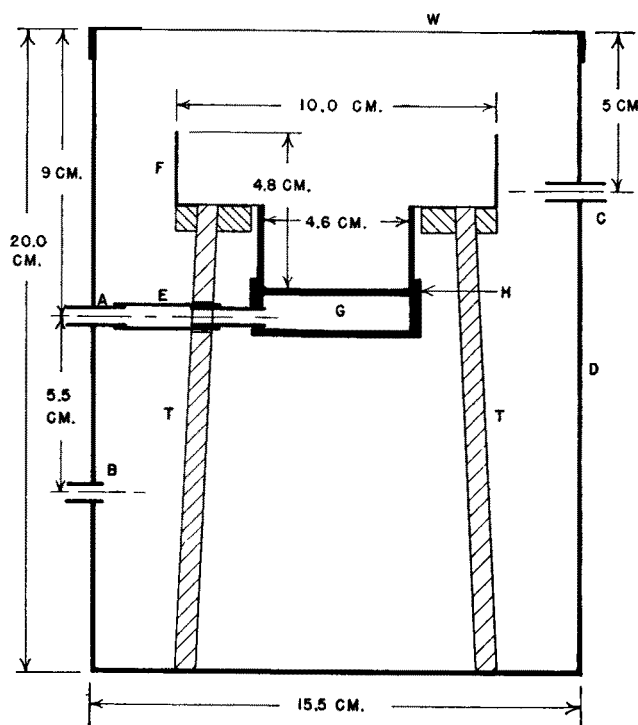


Fig. 2. Foam time apparatus.

**Foam time method.** The apparatus used (Fig. 2) was adapted from that developed by J. W. McBain and Sydney Ross at Stanford University from the Schutz apparatus. We further modified it by providing a means for passing dry air through the air thermostat in order to decrease the lifetime of the foam and make it possible to compare highly stable foams. Our apparatus consists of a brass cup *F* containing the solution to be tested; this cup is closed by a brass plate *H* at the bottom. The cup is supported by a tripod *T*. The brass plate *H*, which contains three equally spaced holes made with a No. 80 drill, is held in place by a screw cup *G*. To produce the foam, dry carbon-dioxide-free air is forced through the small holes in the plate under a pressure of 60 cm. of water. A small piece of rubber tubing *E* connects inlet *A* to cup *G*.

The entire apparatus is kept in an air thermostat *D* surrounded by a 25°C. constant-temperature bath. The top of the air thermostat contains a clear cellulose acetate window surrounded by a rubber gasket held in place by a circular metal piece attached to the lower portion by metal clamps. Since soap foams kept at a constant temperature in an enclosed atmosphere do not break for hours or even days, it is necessary to provide some means of evaporation in order to obtain measurements within a reasonable time. This is done by passing dry carbon-dioxide-free

air at 25° C. through the 4-mm. inlet *B* and out through exit *C* under a constant pressure of 1.0 cm. of mercury during the experiment. This provides a constant, reproducible atmosphere of lowered humidity.

The following procedure was used in making a run: Cup *F* was filled with solution until it overflowed. Air from *G* was bubbled through the solution until a complete monolayer of foam bubbles was present on the surface of the solution. The time required (after stopping the flow of air from *G*) for the foam monolayer to decrease from 10 cm. to 4½ cm. in diameter was measured and is designated in this paper as the "foam time," *T<sub>f</sub>*. Usually the foam monolayer broke uniformly from the edges, but occasionally it broke unevenly and the monolayer area had to be estimated. Circles of 4½ cm. diameter on the bottom of the cup and on the transparent window were used to eliminate errors due to parallax in observing the diameter of the monolayer. Foam time as defined above is more reproducible than the time required for complete disappearance of the monolayer.

The cup must be filled to overflowing if breaking of the foam is to proceed from the rim inwards; otherwise the foam breaks from the center outwards. The foam time decreases if the rate of flow of dry air through the thermostat is increased or if the temperature is raised.

**Materials.** The sodium soaps of lauric, myristic, palmitic, aleuritic (9, 10, 16-trihydroxypalmitic), erucic, cholic, capric, caprylic, caproic, and undecylenic acids were made by neutralizing acetone solutions of the pure Eastman acids with sodium ethylate. Potassium, ammonium, ethanolanmonium, and hydroxytertiary-butyl ammonium soaps were made by neutralizing acetone solutions of the Eastman acids with aqueous solutions of the corresponding bases. The soaps were made by neutralizing with phenolphthalein as an indicator, adding a slight excess of acid to remove the indicator color, and removing the excess acid by washing the dry soap with acetone. Sodium oleate *A* was prepared from a technical oleic acid by neutralizing with sodium hydroxide; sodium oleate *B* was made from sample *A* by extracting the former with boiling acetone and alcohol and drying in a vacuum desiccator. Sodium linoleate was prepared from Kahlbaum acid. Sodium ricinoleate *A* was made from Eimer and Amend ricinoleic acid of iodine number 86; sodium ricinoleate *B* was the Eastman "practical" grade soap.

The soaps of the chlorinated palmitic acids were made from acids supplied by D. F. Houston and G. R. Van Atta of this Laboratory. They were the mixtures formed by direct chlorination of the acid. The palmitic acid derivative was made by removing hydrogen chloride from these chlorinated acids and had an iodine value of approximately 145. Soaps made directly from commercial coconut, babassu, Ecuadorian palm, and soybean (soap *B*) oils were supplied by E. B. Kester of this Laboratory. The fatty acids from these soaps had equivalent weights of 206, 214, 242, and 276, respectively. The palm, soybean (soap *A*), corn, linseed, and cottonseed oil soaps, as well as the tallow soap, were from Armour and Co., double-distilled fatty acids of equivalent weights 272, 275, 289, 289, 278, and 280, respectively. Their Wijs iodine numbers were 22.8, 138, 107, 157, 97, and 60, re-

spectively. Peanut oil soap was made by direct saponification of an oil with an iodine number of 96, obtained from the Southern Regional Research Laboratory and the castor oil soap by saponification of a commercial oil. Nacconol NRSF (mainly sodium dodecyl and tetradecyl benzene sulfonate), Gardinol LS (technical sodium oleyl sulfate), Emulsol No. 607 (essentially the N-lauryl ester of colamino-formylmethyl pyridinium chloride), and Aerosol OT (sodium salt of the dioctyl ester of sulfosuccinic acid) are commercial detergents supplied by the Allied Chemical and Dye Corp., the du Pont Company, the Emulsol Corporation, and the American Cyanamid and Chemical Corporation, respectively. Nacconol NR contains 40 percent sodium alkyl aryl sulfonate and 60 percent sodium sulfate.

The vegetable gums and pectins used were commercial products. The sodium pectate was of the fibrous type obtained from the California Citrus Growers Exchange. All inorganic salts were of C. P. grade with the exception of the potassium and sodium pyrophosphates, which were technical products.

The peanut protein was obtained from the Southern Regional Research Laboratory. The peanut protein sulfate and casein sulfate were prepared by H. C. Reitz of this Laboratory by a method to be described by him in a separate publication. The recrystallized egg albumin was supplied by H. S. Olcott, also of this Laboratory.

*Preparation of solutions.* In order to obtain reproducible results with soap solutions, it is essential to prepare all solutions with carbon-dioxide-free distilled water immediately before using. Accurately weighed amounts of solid were dissolved in sufficient water to give the desired volume. The stability of foams from soap solutions allowed to stand exposed to the air is usually less than that of foams from fresh solutions, indicating that the acid soaps formed by hydrolysis are poorer foaming agents than the original neutral soaps. Soap solutions after exposure to air are also poorer emulsifying agents than the freshly prepared ones (9).

**Results and Discussion**

*Drainage method.* Experimental data on the rate of drainage of solution from foam produced by various 0.1 percent soap and detergent solutions are given in Table I. The soaps and detergents are listed in order of increasing foam time. Aerosol OT and sodium oleate formed the least stable foams, whereas soaps from the coconut, babassu, and its chlorinated palmitic acids formed the most stable. The values listed are averages of from three to six independent

runs, which usually varied from the mean by less than 4 percent. Occasionally the values obtained with slightly aged soap solutions differed as much as 8 percent as a result of hydrolysis.

Previous investigators have found empirically that the rate of drainage of liquid from foams of beer (13), wine (1), saponin solution (2), and solutions of lauryl sulfonic acid and Aerosol OT (15) during most of the drainage period obeys the equation

$$V = V_0 e^{-kt} \tag{1}$$

where  $V$  = volume of liquid in the foam at time  $t$ ,  $V_0$  = volume of liquid in the foam when  $t = 0$ , and  $k$  is a constant characteristic for each liquid from which the foam is formed.

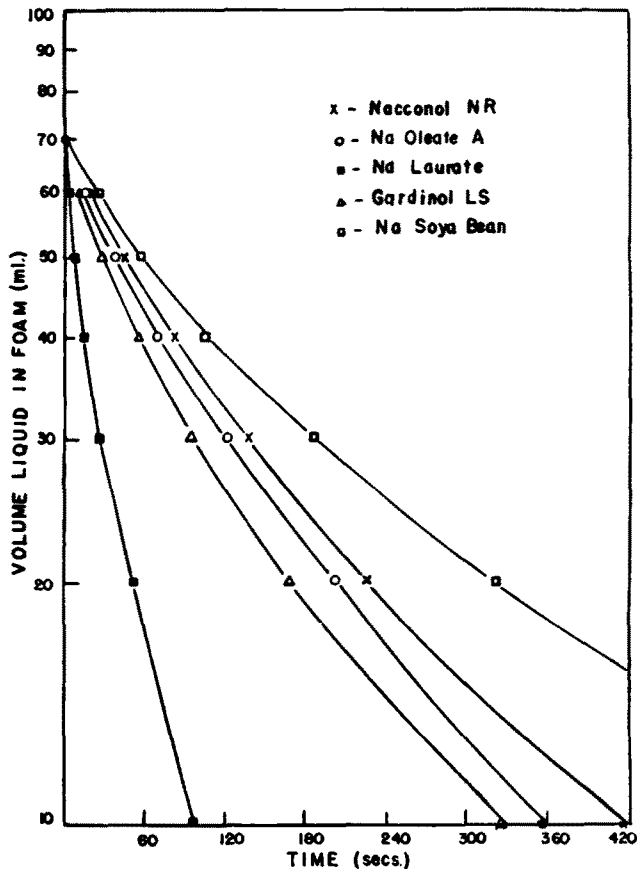


FIG. 3. Drainage of solution from soap foams.

If Equation 1 represents the drainage behavior of soap and detergent foams, the logarithm of the volume of liquid remaining in the foam should be a linear function of the time. The data in Table I do

TABLE I.  
Rate of Drainage of Solution and Foam Times From Foams Produced From 0.1 Percent Soap and Detergent Solutions.

Soap or Detergent	pH	Drainage time in seconds (Volume of liquid in foam) (70 when $t = 0$ )						Foam time $T_f$ seconds
		60 ml.	50 ml.	40 ml.	30 ml.	20 ml.	10 ml.	
		seconds	seconds	seconds	seconds	seconds	seconds	
Aerosol OT.....	6.7	23	50	85	131	200	315	39
Sodium oleate A.....	7.5	16	39	70	122	202	359	49
Sodium laurate.....	7.6	4.9	9.9	16	27	52	100	61
Gardinol LS.....	7.9	12	29	55	96	168	347	96
Nacconol NR.....	6.4	20	45	84	138	225	416	120
Sodium Ecuadorian palm oil.....	9.7	20	46	85	148	256	503	125
Sodium soybean oil A.....	9.1	24	56	106	185	337	758*	335
Sodium coconut oil.....	9.0	17	46	93	184	374	845	> 1,000
Sodium babassu oil.....	9.1	25	66	137	263	500	1,080	> 1,000
Sodium soaps of chlorinated palmitic acid (25% Cl acid).....	7.7	14	32	60	103	176	356†	> 1,000

\* Foam time at pH 9.9.

† Foam time at pH 8.0.

not confirm to this equation, as the typical examples plotted in Figure 3 show; neither do the data of Padgett and Degering (10) on solutions of alkyl sulfates and long-chain amine salts. Evidently Equation 1 is not a general law for all foams.

In this investigation, however, approximately the first 50 percent of the liquid drainage from the foams of both Aerosol OT and sodium laurate was in accordance with Equation 1. Ross (15) found for Aerosol OT foams that the position and also the extent of the portion of the drainage period which is logarithmic depended upon the experimental procedure employed. It is thus clear that Equation 1 cannot be safely applied without establishing specialized conditions for producing a foam which drains logarithmically. In addition the data show that volume and time are not related by functions of the type  $V = at^n$ ,  $V = a + bt^2$ , or  $t = a + bV^2$ , where  $a$ ,  $b$ , and  $n$  are constants.

For practical purposes, the volumes of solution drained during standardized periods can be compared. As shown by the data of Table I, however, the stability of foams from various soap and detergent solutions, as measured by the volume of liquid drained, varied slightly for different drainage times.

**Foam time method.** Foam times for foams from 0.05 and 0.1 percent solutions of single pure soaps, detergents, soaps from natural oils, and proteins are given in Tables I, II, and III. These values are averages from three to six determinations which varied from the mean by less than 3 percent. Several conclusions are obtainable from the data. First, the foam time of a mixture of equal volumes of two 0.1 percent

solutions was not in general equal to the average of the foam times of the separate solutions (Table III). The foam times of mixtures of sodium laurate or sodium oleate with other soaps, with the exception of the ricinoleate, were two to ten times those expected on this simple additive basis. Neither was the foam time of an equal-volume mixture of two 0.1 percent solutions equal to the sum of that of the 0.05 percent solutions alone, since many of the 0.05 percent solutions of the single soaps tested did not foam appreciably.

TABLE III.

"Foam Time" of 0.1 Percent Synthetic Sodium Soap Mixtures.  
(These contain equal parts by weight.)

Soaps	pH	Foam time	
		Observed	Calculated*
Laurate + linoleate.....	7.2	100	46
Oleate A + laurate.....	7.6	690	55
Oleate A + linoleate.....	9.6	65	40
Oleate A + ricinoleate B.....	....	44	57
Oleate A + aleuritate.....	9.3	61	25
Oleate A + chlorinated palmitic acid soap (12% Cl acid).....	8.9	>1,000	482
Oleate A + chlorinated palmitic acid soap (21.5% Cl acid).....	8.6	>1,000	.....
Oleate A + chlorinated palmitic acid soap (25% Cl acid).....	....	>1,000	.....
Laurate + palmitate + palmitic acid soap (12% Cl acid).....	....	>1,000	.....
Laurate + palmitate + oleate A.....	....	245	.....

\* Calculated foam times are averages of the foam time of each 0.1 percent solution.

TABLE II.

"Foam Times." Tr, of Foams From Soap, Detergent and Protein Solutions.\* (Solutions are 0.1 percent except where otherwise noted.)

Foaming Agent	pH	Tr
Sodium laurate (+ NaOH).....	8.6	seconds 150
Sodium myristate (a).....	9.8	150
Sodium palmitate (a).....	....	150
Sodium oleate B.....	....	97
Sodium linoleate.....	10.1	32
Sodium ricinoleate A.....	....	0
Sodium ricinoleate B.....	8.4	66
Sodium aleuritate.....	10.8	2
Sodium soaps of chlorinated palmitic acids (12% Cl acid).....	9.9	915
Sodium soaps of chlorinated palmitic acids (21.5% Cl acid).....	9.7	>1,000
Sodium soaps of palmitic acid derivative (b).....	....	>1,000
Hydroxy-tertiary-butyl-2-ammonium palmitate.....	....	>1,000
Hydroxy-tertiary-butyl-2-ammonium palmitate (0.05%).....	9.7	660
Ethanolammonium palmitate (0.05%).....	9.5	185
Emulsol No. 607.....	6.4	>1,000
Emulsol No. 607 (0.05%).....	6.2	47
Sodium coconut oil (0.05%).....	8.5	445
Sodium palm oil.....	10.2	>1,000
Sodium palm oil (0.05%).....	9.9	540
Sodium soybean A (0.05%).....	8.6	115
Sodium corn oil.....	9.9	390
Sodium corn oil (0.05%).....	9.2	275
Sodium linseed oil.....	9.7	>1,000
Sodium linseed oil (0.05%).....	8.8	97
Sodium cottonseed oil.....	9.8	>1,000
Sodium cottonseed oil (0.05%).....	8.4	185
Sodium tallow (a).....	9.6	>1,000
Sodium tallow (0.05%).....	9.6	>1,000
Sodium peanut oil.....	....	>1,000
Recrystallized egg albumin.....	7.6	320
Peanut protein (+ NaOH).....	10.6	220
Peanut protein sulfate.....	6.5	40
Casein sulfate.....	....	250

\*0.1 percent solutions of sodium soaps of erucic, cholic, undecylenic, capric, caproic, pelargonic, castor oil, and soybean oil B acids do not foam sufficiently under these experimental conditions to be tested. 0.05 percent solutions of the sodium soaps of lauric, myristic, linoleic, ricinoleic, and aleuritic acids do not foam under these conditions. 0.05 percent sodium oleate B foams only slightly.

(a) These solutions were warmed to dissolve the soap and on cooling to 25°C., excess soap precipitated out in finely divided particles which appeared to stabilize the foam.

(b) The preparation of the palmitic acid derivative is described in the section on materials.

Second, with a few exceptions, 0.05 or 0.1 percent solutions of soaps from naturally occurring oils and fats had far greater foam times than solutions of the single soaps that were sufficiently soluble to give 0.1 percent solutions. Soaps having a chain length of 14 or more carbon atoms are present in natural oils and fats. These probably form more stable foams, but are too insoluble in water at room temperature to exhibit any foaming. When these longer chain soaps are solubilized by mixture with soluble short-chain soaps, as is the case in soaps from most natural fats and oils, they can exhibit their excellent foaming power.

Their possible use as substitutes for coconut and palm oil soaps adds interest to the foam times of soaps from babassu, cottonseed, peanut, soybean, corn, and linseed oils. Soaps from the first three of these oils foamed very well, whereas soybean and corn oil soaps were not as good. However, the latter two may be suitable when mixed with tallow.

Certain investigators have suggested that foam stability increases with the chain length of the stabilizing agent in a homologous series, and others have suggested that stability decreases with increasing unsaturation or iodine numbers (6,7). The data of this investigation appear to be in agreement with the former hypothesis but not with the latter. In addition, our data (Table II) suggest that substitution of chlorine groups in the hydrocarbon chain of the stabilizer tends to increase foam stability, whereas substitution of hydroxyl groups tends to decrease it. Mixture, pH, solubility, and other effects make it impossible, however, to test any of these four hypotheses with the available data. Measurements at higher temperatures where the longer-chain soaps are sufficiently soluble or at room temperature on more soluble soap-like materials are desirable. The large difference in the foam times of the two substituted ammonium palmitates (Table II) is probably due to a specific cation effect.

The foam times of four protein solutions given in Table II compare favorably with those from solutions of single pure soaps and detergents.

*Effect of added substances.* That many electrolytes, nonelectrolytes, alcohols (except ethyl alcohol), vegetable gums, and pectic materials greatly increase the foam time of foams from soap and detergent solutions is shown in Tables IV, V, and VI. None of these added substances alone showed appreciable foaming

TABLE IV.

Effect of Added Substances on the "Foam Time" of Foam From 0.1 Percent Solution of Sodium Ecuadorian-Palm Oil Soap

Added Substance	pH	T <sub>f</sub>
None.....	9.7	125
0.01 M K <sub>2</sub> SO <sub>4</sub> .....	9.5	750
0.005 M Na <sub>2</sub> CO <sub>3</sub> .....	10.4	> 1,000
0.01 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	10.0	> 1,000
0.001 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	9.6	125
0.01% (0.0033 M) K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	.....	200
0.01% sodium pectate.....	9.6	370
0.05% sodium pectate.....	8.9	> 1,000
0.01% gum acacia.....	9.5	155
0.01% gum tragacanth (a).....	9.5	285

(a) solution opalescent.

TABLE V.

Effect of Added Substances on the "Foam Time" of Foam From 0.1 Percent Naconcol NRSF Solutions.

Added Substance	T <sub>f</sub>
None.....	120
0.01% Lecithin.....	360
0.01% gum acacia.....	> 1,000
0.005% gum acacia.....	190
0.01% 185 grade citrus pectin.....	315
0.01% 208 grade citrus pectin.....	425
0.01% apple pectin, 300 grade.....	> 1,000

TABLE VI.

Effect of Added Substances on the "Foam Time" of Foam From 0.1 Percent Sodium Oleate "B" Solutions\*

Added Substance	pH	T <sub>f</sub>
None.....	9.5	97
0.01 M NaCl.....	.....	540
0.01 M K <sub>2</sub> SO <sub>4</sub> .....	.....	490
0.01 M Na <sub>2</sub> CO <sub>3</sub> .....	10.6	~500
0.01 M NaHCO <sub>3</sub> .....	8.5	145
0.01 M K <sub>3</sub> PO <sub>4</sub> .....	11.3	> 1,000
0.005 M K <sub>3</sub> PO <sub>4</sub> .....	.....	950
0.005 M Na <sub>3</sub> PO <sub>4</sub> .....	11.2	555
0.001 M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	.....	> 1,000
0.01 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	10.2	> 1,000
0.001 M K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .....	.....	130
0.1% 40° Bé - Na silicate.....	9.5	> 1,000
0.01 M Na <sub>2</sub> HPO <sub>4</sub> .....	9.3	610
0.005 M (NaPO <sub>3</sub> ) <sub>n</sub> .....	8.6	> 1,000
0.005 M Na caproate.....	7.8	425
0.005 M Na caprylate.....	9.5	> 1,000
0.005 M Na di- $\alpha$ -amino caprylate.....	10.0	> 1,000
0.005 M Na pelargonate.....	8.6	120
0.005 M Na caprate.....	8.6	200
0.005 M Na laurate.....	9.4	> 1,000
0.01 M sucrose.....	9.6	255
0.01 M ethyl ether.....	8.9	160
0.01 M cyclohexanol.....	9.5	155
0.01 M ethyl alcohol.....	9.1	90
0.01 M butyl alcohol.....	9.6	185
0.1% gum acacia.....	9.0	850
0.1% gum karaya.....	8.5	> 1,000
0.1% gum tragacanth.....	9.3	> 1,000
0.1% citrus pectin, 170 grade.....	9.2	140
0.1% sodium pectate.....	.....	> 1,000
0.1% apple pectin, 300 grade.....	.....	> 1,000
0.1% apple pectin, 275 grade.....	.....	320

\* A description of the preparation of sodium oleate B is given in the section on materials.

under the experimental conditions used in this investigation. The effect of added short-chain fatty acid salts indicated no relationship of chain length, but the differences observed may be due, in part at least, to variations in pH. Ethyl ether and butyl alcohol added in bulk to the original solutions in-

creased the foam time. Ethyl alcohol, however, appeared to decrease the foam time. Pectic materials and vegetable gums were all very effective foam stabilizers, even at relatively low concentrations.

*Influence of pH.* The effects of pH upon the foam time of foams from 0.03-percent sodium tallow and sodium palm oil soaps and 0.1-percent Aerosol OT solutions are shown in Table VII. The pH was

TABLE VII.

Influence of pH on "Foam Time" of Foams From Soap and Detergent Solutions.

0.03% Sodium Tallow Soap	
pH	T <sub>f</sub>
9.35 (a)	> 1,000
9.85	400
10.07	610
10.12	670
10.53	> 1,000
10.64	> 1,000
10.73	> 1,000
11.10	> 1,000
11.15	485
11.58	115
11.76	110

0.03% Sodium Palm Oil Soap	
pH	T <sub>f</sub>
9.70	195
9.81	220
10.61	595
11.67	75

0.1% Aerosol OT	
pH	T <sub>f</sub>
6.32	40
10.31	40
10.48	40
11.36	85
11.62	65
11.63	60
11.82	115

adjusted by adding small amounts of concentrated NaOH or the corresponding free fatty acid, and was measured with a Beckman pH meter. Fatty acid in excess of that which would dissolve in the tallow soap solution remained suspended and the solid particles appeared to stabilize the foam. Both soaps showed a maximum in foam time at about pH 10.6. This is about the same pH at which a maximum occurs in the removal of dirt from cloth in the presence of alkaline electrolytes (11), although soap concentration and the specific nature of the added electrolyte have some influence (12). A sharp maximum in the effect of alkali on the ability of 3.22-percent potassium myristate solutions to carry carbon black through filter paper has also been noted (8). The effect of dilute alkali on the foams from Aerosol OT solutions was not so pronounced, although added NaOH did increase the foam time. In alkaline solutions hydrolysis of the ester portion of the Aerosol molecule became appreciable and the foam times obtained depended on the extent of hydrolysis.

*Effect of concentration.* The foam time of a dilute soap or detergent solution increased with concentration in the cases we have observed thus far. Typical data obtained for a sodium coconut oil soap are given in Table VIII. Further data are given for 0.05 percent and 0.1 percent soaps in Table II. It is evident that foam time is very sensitive to the soap concentration.

*Comparison of methods.* Comparison of the data of Table I on the rate of drainage of liquid from the

TABLE VIII.  
Influence of Concentration of "Foam Time" of Foams From  
Coconut Oil Soap Solutions

Concentration	T <sub>r</sub>	Concentration	T <sub>r</sub>
percent		percent	
0.04	0.0	0.08	655
0.05	75	0.09	855
0.06	185	0.10	>1,000
0.07	250		

foam with the foam times of the same foams shows that in all but a few cases the methods gave approximately equivalent results for the stabilities of soap and detergent foams. The differences in pH probably account for these deviations. Thus, foams from the sodium soaps of coconut and babassu oils drained the most slowly and had the longest foam times, while sodium laurate and Aerosol OT foams drained rapidly and had short foam times. The relative order of effectiveness for the soaps and detergents tested was somewhat different for the two methods, depending partly on the drainage time chosen for comparison. In general, foam time is probably the more valid measure of foam stability, since, for foams in which the drainage liquid does not arise from the collapse of bubbles, drainage is a purely hydrodynamic phenomenon which may or may not have any relation to the stability of the dry foam.

#### Acknowledgment

We express our gratitude to Drs. J. W. McBain and Sydney Ross of Stanford University for describing their apparatus to us in advance of publication.

#### Summary

This paper reports results, obtained by the "liquid drainage" method and a modified "foam time" method, on the stability of foams from solutions of soaps and detergents. The two methods gave quali-

tatively equivalent results. Rates of drainage of liquid from soap and detergent foams were not proportional to the volumes of liquid in the foam.

The stabilities of foams from 0.1 percent solutions of soaps of most of the natural fats and oils tested were much greater than those of foams from single soaps that were sufficiently soluble to form solutions of this concentration. The foam time of a mixture of equal volumes of two 0.1 percent solutions was not equal to the average of the foam times of the separate solutions.

A number of electrolytes, organic liquids, pectic materials, and vegetable gums greatly increased foam stability.

Data on 0.03 percent sodium tallow and palm oil soap solutions indicated a maximum foam time at a pH of about 10.6. Increasing the concentrations of ten soaps from 0.05 to 0.1 percent more than doubled the foam time.

#### LITERATURE CITED

- (1) Amerine, M. A., Martini, L. P., and De Mattei, W., *Ind. Eng. Chem.*, **34**, 152 (1942).
- (2) Arbuzov, K. N., and Grebenshikov, B. N., *J. Phys. Chem. (U. S. S. R.)*, **10**, 32 (1937).
- (3) Clark, G. L., and Ross, S., *Ind. Eng. Chem.*, **32**, 1594 (1940).
- (4) Gray, P. P., and Stone, J., *Wallerstein Labs. Commun. Sci. Practice Brewing*, **3**, 159 (1940).
- (5) Hilditch, T. P., "The Chemical Constitution of Natural Fats," New York, J. Wiley and Sons, Inc., 1941.
- (6) Lascaray, L., in *Hefter-schonfeld, "Chemie und Technologie der Fette und Fettprodukte,"* Vol. IV, p. 136, Vienna, Julius Springer, 1939.
- (7) Lederer, E. L., "Kolloidchemie der Seifen," Dresden and Leipzig, Theodor Steinkopff, 1932.
- (8) McBain, J. W., Harbourne, R. S., and King, A. M., *J. Soc. Chem. Ind.*, **42**, 373T (1923).
- (9) Merrill, R. C., Jr., *Ind. Eng. Chem., Anal. Ed.*, **15**, 743, 1943.
- (10) Padgett, A. R., and Degering, E. F., *Ind. Eng. Chem.*, **32**, 204, 486 (1940).
- (11) Rhodes, F. H., and Bascom, C. H., *Ind. Eng. Chem.*, **23**, 773 (1931).
- (12) Rhodes, F. H., and Wynn, C. F., *Ibid.*, **29**, 56 (1937).
- (13) Ross, S., and Clark, G. L., *Wallerstein Labs. Commun. Sci. Practice Brewing*, No. 6, 46 (1939).
- (14) Ross, S., *Ind. Eng. Chem., Anal. Ed.*, **15**, 329 (1943).
- (15) Ross, S., *J. Phys. Chem.*, **47**, 266 (1943).
- (16) Schutz, F., *Trans. Faraday Soc.*, **38**, 85 (1942).

## Analysis of Commercial Anhydrous Tetrasodium Pyrophosphate

W. H. KOCH<sup>1</sup>

Chairman, Subcommittee I, Section D, A. S. T. M. Committee D-12

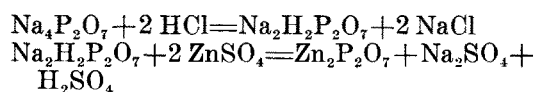
#### Abstract

A titration method of analysis is given for Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> in commercial anhydrous tetrasodium pyrophosphate using a modification of the Britske and Dragunov titration method. In the absence of other polyphosphates, a degree of precision is obtained satisfactory for the type of product supplied by the manufacturers. Time required for analysis is much less than for methods relying upon precipitation with subsequent gravimetric treatment. Results of cooperative work are given.

During 1939 Committee D-12 on Soaps and Other Detergents of A. S. T. M. formulated specifications for tetrasodium pyrophosphate (anhydrous) which now appear as their specification D 595-42 T. The subcommittee on Analysis of Special Detergents was asked to provide a method of analysis of reasonable accuracy for use on commercial material containing about 95

to 100% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. A search of the literature suggested several possible methods (1,2,3) and various modifications supplied by interested laboratories were considered. Cooperative work was carried out by ten laboratories with the result that the following modification of the Britske and Dragunov method (2) was adopted as a Tentative Standard of the A. S. T. M. (4) in 1941 and has just recently been advanced to Standard.

The procedure describes an indirect determination of tetrasodium pyrophosphate by titration of the sulfuric acid liberated by the action of zinc sulfate on an acid pyrophosphate in accordance with the following reactions:



The titration provides a measure of the pyrophosphate content and is carried out using a conventional

<sup>1</sup> Present address—The Mathieson Alkali Works, (Inc.), Niagara Falls, N. Y.