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

Concentration	Tt	Concentration	Tr
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		2 .,

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.

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Summary

This paper reports results, obtained by the "liguid 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.

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Analysis of Commercial Anhydrous Tetrasodium Pyrophosphate

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Abstract

A titration method of analysis is given for $Na_4P_2O_7$ 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% $Na_4P_2O_7$. 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:

$$\begin{array}{l} \operatorname{Na_4P_2O_7+2 HCl=Na_2H_2P_2O_7+2 NaCl} \\ \operatorname{Na_2H_2P_2O_7+2 ZnSO_4=:} Zn_2P_2O_7+\operatorname{Na_2SO_4+H_3SO_4} \end{array}$$

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

¹ Present address-The Mathieson Alkali Works, (Inc.), Niagara Falls, N. Y.

type pH meter. The method is inaccurate in the presence of other polyphosphates.

Reagents

Hydrochloric acid-0.2 N.

Sodium hydroxide solution-0.2 N. Standardize with "C. P." tetrasodium pyrophosphate which has been recrystallized three times from distilled water and dried at 400° C. to constant weight.

Zinc sulfate solution-Dissolve 125 grams of reagent-grade ZnSO₄·7H,O in distilled water and dilute to 1 liter. Filter and adjust the pH to 3.8.

Procedure

Weigh accurately approximately 1 gram of the sample and dissolve in sufficient distilled water in a 250-ml. beaker so that the resulting solution will just cover the electrodes of the titration assembly. Adjust the pH of the solution to exactly 3.8 with 0.2 N hydrochloric acid. Add 50 ml. of the zinc sulfate solution and allow five minutes for the reaction to become complete as shown by the pH becoming constant. Titrate the liberated acid with 0.2 N NaOH until a pH of 3.8 is again reached. Calculate the percentage of tetrasodium pyrophosphate as follows:

 $Na_{1}P_{2}O_{7}$, per cent = $(A \times F \times 100)/W$ where-

A=ml. of sodium hydroxide required.

- F=Grams tetrasodium pyrophosphate equivalent to 1 ml. of 0.2 N sodium hydroxide as calculated by standardization against C. P. tetrasodium pyrophosphate.
- W=weight of sample in grams.

A modification of this method was recommended as tentative by the Soap Analysis Committee of the American Oil Chemists' Society and published (5)in their 1941 report. One year later this method was adopted as official (7) by the A. O. C. S.

This modification was restricted to the determination of tetrasodium pyrophosphate in soap products. but is an indication of the versatility of the method when applied to mixtures of tetrasodium pyrophosphate with other materials.

Since the reactions shown in the above method do not occur in strictly stoichiometric proportions, the first question arising was concerned with the preparation of C. P. Na, P, O, for standardization purposes. Two methods were suggested. First, several recrystallizations of the commercial product from water with subsequent drying to constant weight at 400° C. and second, the ignition at 400° C. to constant weight of reagent grade crystalline disodium

TA	BL	Æ	I

Laboratory	Sample by recrystal- lization	Sample from disodium hydrogen phosphate	
	per cent	per cent	
P1	99.98	99 64	
P2	99.79	99.73	
P3	100.02	99.78	
P4	100.14	99.61	
P5	100.01	99.88	
C1	99.69	99.50	
C2	99.50	99.49	
C3	100.38	100.16	
C4	100.37	100.27	
C5	100.18	100.20	
Average	100.01	99.83	
Producers' Average	99.99	99.73	
Consumers' Average	100.02	99.92	

hydrogen phosphate. Samples prepared in each way were submitted to ten laboratories for the determination of $Na_4P_2O_7$ content by analysis for total P_2O_5 according to the method given in A. S. T. M. designation D 501-41 T (6). This analysis must be preceded by the addition of nitric acid with fifteen minutes boiling to convert the pyrophosphate to orthophosphate. The results of this work are shown in Table I. "P" indicates the laboratory of a producer, and "C". a consumer.

Considering the results and bearing in mind that the producer laboratories carry out these types of analyses as a matter of daily routine and are, on that account, more likely to be familiar with the technique and operation of the methods, it appeared obvious to the committee that the method of preparation of standardization material by recrystallization provided the better product.

A sample of a commercial tetrasodium pyrophosphate was then submitted to the same laboratories for analysis by this method with the results shown in Table II.

TABLE II

Laboratory	N84P2O7	Titration assembly
	per cent	
21	98.94	Beckman Research
2	98.48	(1)
>3	99.23	L & N Quinhydrone
4	98.49	Beckman Industrial
25	98.98	Coleman
1	98.93	Beckman Research
12	99.60	Beckman Research
18	98.99	Coleman
4	97.70	Beckman Research
5	98.92	Beckman Research
Verage	98.83	
roducers' Average	98.82	
onsumers' Average	98.83	

Although a casual glance at the average results in Table II appears to leave nothing to be desired, a further examination of the results again indicates the relatively higher quality of work emanating from the producer laboratories and provides an indication of the precision and reliability of the method as applied to a commercial product. Table III contains a summary of these calculations.

TABLE III

	All results	Producers'	Consumers'
Mean error of a single result Mean error of the mean result Probable error of a single result. Probable error of the mean result Average error of a single result	$\begin{array}{r} \pm 0.51 \\ 98.83 \pm 0.16 \\ \pm 0.34 \\ 98.83 \pm 0.11 \\ \pm 0.36 \\ \pm 0.11 \end{array}$	$\begin{array}{r} \pm 0.33\\ 98.82 \pm 0.15\\ \pm 0.22\\ 98.82 \pm 0.10\\ \pm 0.27\\ \pm 0.14\end{array}$	$\begin{array}{r} \pm 0.69\\98.83 \pm 0.31\\\pm 0.47\\98.83 \pm 0.21\\\pm 0.45\\\pm 0.23\end{array}$

Within the limits of precision shown in Table III the Committee on Analysis of Special Detergents believes this method to be the simplest and most expeditions available for the determination of $Na_4P_2O_7$ in commercial tetrasodium pyrophosphate. Information recorded in Table II indicates that any of several varieties of pH instruments can be used with equal success.

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