Surfactant Mixtures. The decomposition product is normally the same in mixtures of surfactants as that obtained separately. However, as might be expected, the presence of a relatively stable, strong acid, causes dehydration of alcohols to give olefins. For example, decomposing a mixture of alkylbenzenesulfonate and lauryl sulfate in phosphoric acid gives alkylbenzenes plus dodecenes. As can be seen from their relative retention times (Table I), these olefins are readily analyzed by GALIPA.

Depending on the complexity of the mixture, it may not be possible to separate all major species in the decomposition oil by GALIPA. In these cases, several other conventional analytical techniques may be useful individually or in combination. Some examples of useful techniques are urea clathration, solvent partition or crystallization and liquid-phase chromatography. It appears possible to decompose most other surfactant types selectively in the presence of detergent-range alkylbenzenesulfonates at 185°C. Excessive foaming is the chief problem in this technique but can be minimized by lowering the amount of alkylarylsulfonate charged to one gram and employing conventional defoaming procedures.

For example, a mixture of lauryl sulfate (2 g.) and commercial tetrapropylenebenzenesulfonate (1 g.) was heated for 60 min. in 185°C. (BP) phosphoric acid. Water was then removed from the trap, and the reaction mixture was heated for another 60 min. at 215°C. A normal yield of 0.90 g. of dodecenes was obtained at 185°C. and a normal 65-min. yield of 0.45 g. of alkylbenzene was recovered at 215°C. In another experiment a mixture of straight-chain olefins and polypropylenebenzene was obtained by decomposing a mixture of tallow alcohol sulfate and alkylbenzenesulfonate. Because GALIPA will not resolve these products, the olefins were separated from the alkylbenzene by forming and recrystallizing the urea adduct. Although the olefins were recovered in a pure state, the alkylbenzene recovered from the filtrate was contaminated with some olefin. However this separation was sufficient to identify the olefins as probably derived from tallow.

Phosphoric acid decomposition does not furnish a single analytical scheme for all conceivable mixtures of surfactants. The products however are more amenable to classical analytical tools than are the starting surfactants. Further work on the conditions of the decomposition reaction or subsequent analytical procedures may increase the general applicability of this method to complex surfactant mixtures.

Summary

Some data on the use of 93% phosphoric acid as a reagent for recovering the hydrophobic portion of surfactants are presented, and their application to the analysis of surfactant mixtures is discussed. Aromatic sulfonates, straight-chain alkyl sulfates, fatty acid amides, and fatty acid esters decomposed to give good yields of the starting hydrophobic materials. Dioctylsulfosuccinate gave a mixture of octyl alcohols and olefins while the ethylene oxide condensates of lauryl alcohol, tridecyl alcohol, and tertiary dodecyl mercaptan gave olefins derived from the starting hydrophobic materials. Diisobutylene phenol-ethylene oxide condensate decomposed to olefins, conjugated olefins, and alcohols formed by rupture of the aromatic ring. The products are characteristic of the hydrophobic oils, and in most cases products from mixtures of surfactants can be separated by known analytical methods. *Alpha*-sulfo fatty acids or alkane sulfonates do not give recoverable oils by this treatment.

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Distribution of Water in the United States as a Function of Hardness

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It is a well known fact, especially by the American housewife, that synthetic detergents will perform better than soap in hard water since they do not form the insoluble soaps which lead to poor detergency. The syndets do not have the inherent undesirable characteristic of leaving a ring in bath tubs and sinks or producing "tattle-tale gray" on fabrics as do soaps. A fact that is not generally known by the public, but well known by the detergent industry, is that synthetic detergents themselves have different performance characteristics in soft and hard water.

Many of the synthetic detergents used in washing dishes and doing light hand-laundry are prepared from surface-active agents derived from petroleum

TABLE I

	Urban				Rural		Total	
	Population (×1,000)	Hardness[a]			Population (×1,000)	Hardness average	Population (×1,000)	Hardness wt. av.
		Average range	Average	Wt. average				
Alabama	1,211	14–115	56	55	1,915	72	3,126	65
Arizona	799	12–500	208	216	312	215	1,111	216
Arkansas	378	11–250	61	42	1,366	80	1,744	72
California	12,923	18–561	160	118	677	189	13,600	122
Colorado	1,061	11–317	106	107	571	(107)	1,632	107
Connecticut	1,736	11–46	21	29	504	42	2,240	32
Delaware	283	24–144	75	60	147	72	430	64
District of Columbia	809	....	96	96	....	......	809	96
Florida	2,709	20–274	91	123	1,292	252	4,001	165
Georgia	1,790	18–360	76	41	1,909	126	3,699	85
Idaho	275	8–354	136	119	361	172	636	149
Illinois	6,329	80–565	215	156	3,256	358	9,585	225
Indiana	2,471	76–640	272	237	2,054	352	4,525	289
Iowa	1,192	83–632	235	212	1,604	355	2,796	294
Kansas	995	75–548	185	176	1,100	307	2,095	174
Kentucky	1,017	12–198	101	102	1,982	206	2,999	171
Louisiana	1,545	2–151	64	68	1,482	112	3,027	90
Maine	423	8–82	23	20	504	22	927	21
Maryland	2,194	3–85	40	48	633	30	2,827	44
Massachusetts	3,764	8–80	36	23	1,046	58	4,810	31
Michigan	5,283	43–405	160	115	2,505	298	7,788	174
Minnesota	1,627	46–464	224	114	1,688	280	3,315	199
Mississippi	515	2–150	35	39	1,653	34	2,168	35
Missouri	2,522	55–294	141	106	1,702	247	4,224	162
Montana	315	16–404	137	120	345	193	660	158
Nebraska	626	112–370	254	247	813	267	1,439	258
Nevada	193	33–320	154	135	64	168	257	143
New Hampshire	308	10–121	30	28	257	55	565	40
New Jersey	4,618	10–251	86	75	962	110	5,580	81
New Mexico	397	30–626	271	237	408	337	805	288
New York	12,776	7–292	74	52	3,057	106	15,833	62
North Carolina	1,606	6–113	38	34	2,811	126	4,417	93
North Dakota	178	81–406	192	170	466	300	644	265
Ohio	6,079	46–427	155	150	3,101	361	9,180	221
Oklahoma	905	8–675	169	125	1,338	246	2,243	197
Oregon	1,000	9–95	37	17	764	50	1,764	31
Pennsylvania	7,231	5–256	81	86	3,789	172	11,020	116
Rhode Island	752	17–83	34	32	78	26	830	31
South Carolina	934	3–107	22	18	1,374	19	2,308	19
South Dakota	223	70–672	292	299	472	452	695	403
Tennessee	1,486	19–177	86	70	1,957	84	3,443	78
Texas	5,108	4–700	144	132	3,845	126	8,953	129
Utah	531	152–349	217	191	316	222	847	203
Vermont	120	16–121	64	53	254	79	374	71
Virginia	1,880	8–295	70	65	1,758	141	3,638	102
Washington	1,611	12–155	52	44	1,042	83	2,653	59
West Virginia	621	28–264	94	88	1,354	202	1,975	166
Wisconsin	2,037	50–500	195	167	1,820	239	3,857	201
Wyoming	154	12–575	211	171	155	247	309	209
Total	105,540				62,863		168,403	

[a] Hardness expressed as p.p.m. $CaCO_3$.

bases. These surface-active agents have the unique characteristic of producing more voluminous and more stable foam in hard water than in soft water. This makes it desirable to add a stabilizer, such as an amide, to the product in order to produce a stable foam in soft water. The addition of a stabilizer naturally increases the cost of the detergent. It is therefore a matter of considerable economic importance to the manufacturer to be sure that this expensive formula be distributed only in the areas where it is actually needed.

From the foregoing it is obvious that many problems can arise in the distribution and manufacture of a light-duty synthetic detergent for use throughout the United States. From the manufacturing point of view a considerable savings could be effected if an economically priced, universal product capable of performance in hard and soft water could be prepared since handling and storage problems would be minimized. Similarly distribution problems would be simplified with a universal product. A study of the distribution of water throughout the United States as a function of hardness can be useful in both of the above approaches to the manufacture and distribution of soaps and synthetic detergents. In the approach toward a universal product it is necessary to formulate in such a manner that the majority of the population (an arbitrary range selected by management) will be satisfied with the performance since it is conceivable that no one product can meet the requirement of being satisfactory under all conditions. In the approach to supplying two formulas, one for soft-water areas and one for hard-water areas, it is necessary to determine which states, or areas, should be supplied with each type of detergent. In a product of the latter type, consumer preference and satisfaction depend entirely upon the proper distribution of the correct product for any particular area.

Source of Data

In order to study the distribution of water, the basic source of information was the United States Department of the Interior, Geological Survey Water Supply Paper No. 1299, entitled "The Industrial Utility of Public Water Supply in the United States, 1952." The United States Department of Commerce, Bureau of the Census, pamphlet entitled "Provisional Estimates of the Population of States and Selected Outlying Areas of the United States, July 1, 1957," was used to revise the population distribution. The distribution of home water-softeners in the United States was determined from information supplied by the Water Conditioning Research Council.

Discussion of Data

The data obtained from these sources have been arranged in tabular and graphic form.

Table I shows the distribution of water by states. This information was obtained by detailed analyses of the water supplies, both finished and raw, of 1,315 cities with more than 15,000 population. (Several small cities were tallied in order to provide adequate coverage for all states.) The population figures used were those for the civilian population of the United States. The military was excluded since it is a justifiable assumption that military personnel will not be affected by the distribution of synthetic detergents. The increase in population from 1952 to 1957 was assumed to have been in the urban areas entirely since no more recent accurate tabulation than the 1952 one was available for this study.

The average hardnesses in the urban areas are simply arithmetic means of all the water samples in any particular state. The average range is merely the listing of the lowest and highest hardness found in any state.

The weighted averages of hardness are more meaningful than the arithmetic averages since they take into consideration the number of people using water of varying degrees of hardness. Observation of the figures in Table I indicate that the weighted averages and arithmetic averages are quite similar in the many cases.

In determining the water hardness for the rural areas, another assumption had to be made. In the original compilation of data for the urban area, ground-water supplies were averaged for each state. It would be logical to assume that the water obtained for cities from this source would also be indicative of the water obtained in rural areas from similar strata. No ground-water supply information was available for Colorado; consequently the surface water supply was used for the rural hardness value.

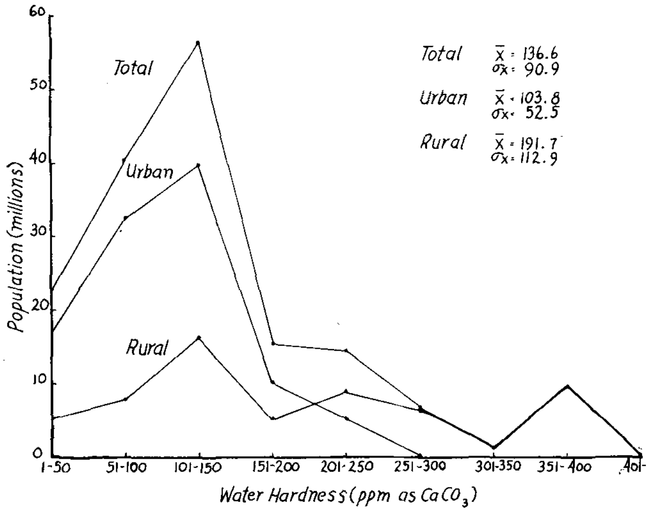

FIG. 1. Distribution of water by population.

In Figure 1 the distribution of water by population has been plotted in a frequency polygon form indicating the number of people in each range of water hardness for urban, rural, and total population. It will be observed that the range for the urban population is not as great as for the rural population. This is as would be expected, since municipalities with extremely hard water will, to some degree, soften the water before distributing it. Both the urban and total population distribution indicate a peak for the range of 101–150 p.p.m. Mathematical estimation of the mean-hardness and standard deviation for each breakdown are also shown on the graph. In making these calculations, it was necessary to assign a mean value for the open-end range over 400 p.p.m. This was taken to be 450 p.p.m. (the value obtained from the distribution by states in Table I). Examination of these calculations reveals that, on the average, the water is quite soft and that the greatest variation is found in the rural areas.

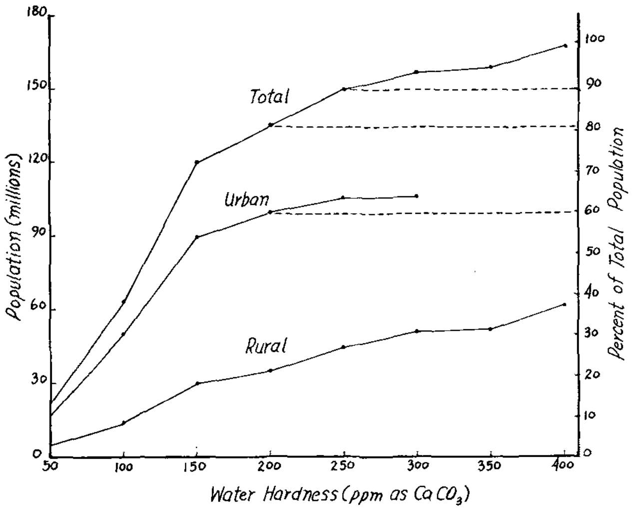

FIG. 2. Cumulative population *vs.* water hardness.

Figure 2 is an ogive, showing the accumulated totals of population plotted against hardness. The population is expressed in millions of people on the left ordinate and as percentage of the total population on the right ordinate. A few observations can be made from this plot which will be helpful in determining the performance limits for a universal product. If a product can be produced which would have satisfactory performance in all water up to 200-p.p.m. hardness, 80% of the total population would be able to use it. This percentage could be raised to approximately 90 by increasing the performance to 250-p.p.m. hardness. Urban areas would be nearly 95% (100 million out of a total of 105 million) satisfied with a product capable of good performance in 200-p.p.m. water; however this is only approximately 60% of the total population.

Estimates by the water-conditioning industry have indicated that approximately 3½ million home water-softener units are in use in the United States. This includes soft-water service, home-owned softeners, and rental units. The large majority of these units are

TABLE II

States with Weighted Average Water-Hardness Under 100 p.p.m.

State	p.p.m.	State	p.p.m.
Alabama	65	New Hampshire	40
Arkansas	72	New Jersey	81
Connecticut	32	New York	62
Delaware	64	North Carolina	93
District of Columbia	96	Oregon	31
Georgia	85	Rhode Island	31
Louisiana	90	South Carolina	19
Maine	21	Tennessee	78
Maryland	44	Vermont	71
Massachusetts	31	Washington	59
Mississippi	35		

located in the urban areas (more than 15,000 population) although, no doubt, some will be found in smaller communities. Using an average family size of 3½ members, the home softeners will affect approximately 12 million people or, in other words, 7% of the total population. Assuming that the softeners are installed whenever the water is 200-p.p.m. hardness and over, this will enable us to raise the accumulated total below this hardness by 7%. Therefore, going back to the original distribution in Figure 2, we can conclude that 87% of the total population will use water of less than 200 p.p.m. hardness and that 97% of the population, on the average, will use water under 250-p.p.m. hardness in their homes. This makes the approach toward a universal product very promising.

In the event that it would be desirable to use the two-product approach, the states listed in Table II would be singled out for distribution of a soft-water product which would be necessary in water under 100-p.p.m. hardness. The balance of the states would find the hard-water product satisfactory.

Conclusion

A study has been made of the hardness of the water throughout the United States in regard to its distribution by states and by total population. The purpose was twofold: a) to determine the range of performance necessary for a soap or synthetic detergent product in order to be satisfactory to the majority of the population and b) to determine the areas of distribution for products of varying performance characteristics in respect to water hardness. The study has taken into consideration municipal water-treatment for the urban population, the distribution of rural population, and the distribution of home water-softeners. The mean water-hardness found in the United States, ignoring the home softening-units, was estimated to be 136.6 p.p.m. with a standard deviation of 90.9 p.p.m. Twenty-one states, including the District of Columbia, were found to have a weighted average hardness under 100 p.p.m. In general, the hardest natural water is found in a narrow belt covering the states of South Dakota, Iowa, Illinois, Indiana, and Ohio.

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Bulk Sampling of Soybean Oil Meal

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DRAWING A SAMPLE from a carload of meal which will reflect the true composition of the car is a problem with which every processor is faced daily. Further it is a problem of wide applicability to industries dealing in bulk materials such as feeds, fertilizers, and chemicals.

This study was made to determine whether a continuous flow sample taken during the loading of the car is as representative of the contents as the official loading sample, which is taken by probing after loading. This study was conducted as a preliminary to a more detailed study which should be made to assess the variability of sampling and the degree of stratification, if any, which exists in a bulk car. From such a study minimum sample sizes and the most economic sampling method could be determined.

Sampling Methods. The official method of sampling soybean meal has been designated by the National Soybean Processors Association (1).

> The main features of Chapter I of the Grain Inspector's Manual (revised, effective July 1, 1942) provide that for sampling bulk shipments the sample shall be taken with a standard double tube, 11-compartment bulk grain probe. At least five probes must be taken in different sections of the car as follows:
>
> (1) probe in center of the car;
> (2) probe from 2 to 4 ft. back from the doorpost toward the end of car and approximately 2 ft. out from one side of the car;
> (3) probe from 2 to 4 ft. from same end of the car and approximately 2 ft. from the opposite side of the car as in (2);
> (4) and (5) probe same as in (2) and (3) in opposite ends and sides of the car.
>
> The probe shall be inserted at an angle of about 10 degrees from the vertical, with the slots closed. The slots shall be faced up when the probe is opened. While the slots remain open, give the probe about two slight up-and-down motions so that all the openings may be filled, close slots, and withdraw the probe, placing the contents of the probe full length on a sampling cloth.
>
> Individual probe samples shall be inspected to check on uniformity. The individual probe samples are then composited into one sample, representing the entire lot.

The official method has particular advantage in that it allows the purchaser to sample the car before unloading. Presumably the method should be used by the vendor to draw his sample before shipment. Unfortunately the method is liable to misuse by both vendor and vendee unless the sampler is carefully supervised; the practical difficulties in the use of probes are well known to those with experience in sampling meal cars. A method which is not subject to variation from a human source is desirable. Fortunately the vendor can take a continuous flow sample during the loading of the car which is not subject to the vagaries of human nature.

After some trial and error a system was designed for sampling from the loading spout.

Continuous Flow Method (dock). The sampler is a 1-in. standard pipe centered in the stream of meal as it discharges from the overhead conveyer into the vertical section of the loading spout. The upper end

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