Detergent Developments to Protect Water Quality[1]

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OVER THE NEXT TWELVE to eighteen months,[2] a major industrial product change will be made by all major detervent manufacturers. It will involve replacement of some 450,000,000 pounds of surfactant used in about four billion pounds/year of finished product. As noted in a recent address by G. E. McCallum, Assistant Surgeon General, and Chief, Division of Water Supply & Pollution Control, U.S.P.H.S., "This is the first time that a product changeover of this magnitude has been made—solely to resolve a water pollution problem." (1) In other words, here we have a multi-million dollar industry-wide research and development program—not to increase performance *in* use, but to decrease persistence *after* use. Furthermore, it has been a voluntary change: the basic studies and decisions to make a change preceded and anticipated the proposals for regulation that have recently been advanced in Congress and a number of States. In fact, they are the outgrowth of fact-finding and research that began just as soon as the problem of foaming detergent residues in water first became apparent.

As you probably know, the target date for the completion of this changeover at the retail level has been set for December 31, 1965.[2] Many *other* aspects of the pollution-abatement problem are being worked out in terms of decades, rather than years. Yet it is alleged that the detergent producers and their suppliers must be stalling, if they cannot shift to biodegradable surfactants within a few weeks or months. The complexity of an industrial change of this magnitude is not well understood.

Many of these pressures are political rather than technical. In fact, the whole course of events: the *need* for a changeover, the *decisions* to do so and the *timing* of the program—even the expectations of a successful outcome—cannot be evaluated altogether within a technical frame of reference. Problems of waste disposal and water supply are issues in which the attitudes of the non-technical public, right or wrong, help determine the most expedient course of action. The detergent industry cannot afford a bad public image. Technical evidence still supports the position that detergent residues in water in the United States are not and have not created a public health emergency. Sewage disposal improvement, as a factor more fundamental than detergent improvement, has strong advocates among health officials (2). But the esthetic effects of visible foam . . . as a sign and reminder of the whole gamut of pollution . . . are easily exploitable, even though technically it is a minor element in America's whole water resources problem. A defensive position that our product residue is less a culprit than a concurrent gross pollution is untenable for an industry which has made product improvement its major public appeal.

Strangely enough, now that the industry has launched its voluntary program of conversion, the millions of dollars of expense we cite sometimes draw a negative reaction. The industry-wide effort to convert is taken as evidence that we do have a nation-wide flood of foam menacing America's potable water supply. Otherwise, why would our concern for conversion be so great?

It is important to set the record straight on some of the technical points which were established in the industry's past ten years of fact-finding and research. This is not to defend the hard "ABS", on which most of this work was concentrated, but *to avoid unrealizable expectations* from the conversion just ahead.

For example, it is now often assumed that all foams observed on rivers are caused by detergent content. Yet here, for example (Fig. 1) is a foaming incident which took place in the Blue River, near Crete, Neb., and was photographed in the 1920's before detergents were ever invented.

At one sewage treatment plant, operators complained of unmanageable accumulations of foam on aeration tanks. Yet at another similar plant, with the same ABS content, the problem was easily kept under control (3). In one of the largest water courses in the country—receiving sewage effluent from town after town—the surfactant content, as monitored by methylene blue tests, remained well below foaming levels year after year (4). In an Association survey of 32 cities, municipal water supplies receiving no special treatment to remove surfactants, were found to be virtually free of ABS (5). (Later, an independent survey of water supplies of 165 cities confirmed these insignificant levels) (6). Nonetheless, isolated, but spectacular, foaming incidents on certain surface waters receiving sewage-plant effluent do keep coming to our attention. Usually, these result from a special combination of circumstances, such as a drought-caused drop in dilution of the effluent in the receiving stream (7).

There was well-documented scientific support for position that no emergency existed. For example, a limit of 0.5 mg/liter of ABS was defined as acceptable in water quality standards issued by the U.S. Public Health Service, and even this limit was ascribed to esthetic factors (8). It had been shown that activated sludge procedures could be operated so as to achieve 80% ABS removal (9). Advance waste treatment research—aimed at removing all types of refractory organic residues—even opened up the possibility of using the hard ABS content constructively in foam fractionation (10). Currently, a foam concentration plant for ABS removal, following standard activated sludge treatment, continues to show good results in a 10 mgd

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FIG. 1. Foaming incident on the Blue River, Neb. in early 1920's.

[1] Presented at the AOCS Meeting New Orleans, 1964, as part of the Biodegradable Detergents Symposium, page 732 of this issue.

[2] Completion date of changeover in production now scheduled for June 30, 1965.

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ABS

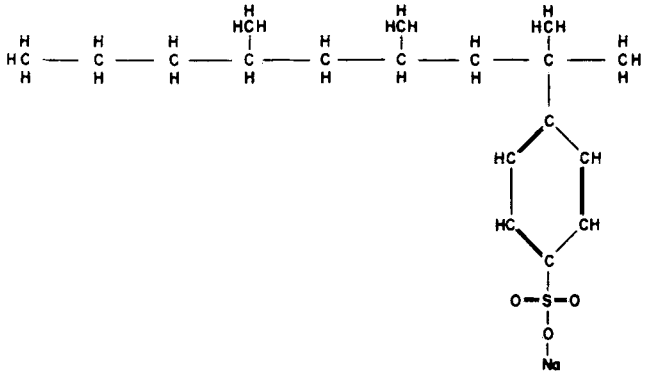

FIG. 2.

installation (11). At Santee, Calif., the recreational values of ponded effluent are being realized despite ABS contents of 5.0 mg/liter (12).

Meanwhile, misconceptions as to the taste and odor of water resulting from its ABS content, have been disproved (13), along with the allegation that it stimulated the movement of bacteria underground (14). In polluted well water, the indicator function of detergent foam, or appreciable ABS content, was cited by some authorities as a "blessing in disguise" (15).

Our current position comes down to this: We are prepared to assume responsibility for a product that will break down in a normal sewage disposal unit—but not to have responsibility thrust upon us for breakdown in an ordinary cesspool, without tile fields, or in soil that may channel the effluent directly into nearby wells.

American producers are already on record as having said that their products will equal or exceed in biodegradability the requirements of the German regulations (16). Our aim is to assure *acceptable field performance under U.S. conditions,* and seems likely to result in products containing only surfactants meeting standards considerably *higher* in biodegradability than the present German minimum.

Various test methods have been proposed or applied to measure biodegradability of surfactants, and to provide the basis for a scientific definition for what is to be considered adequate biodegradability (17). This is a far more complicated issue than it first appears because a test must correlate with breakdown as it actually proceeds in sewage plants and streams. Also, while analytical methods for minute quantities of anionic surfactants in water or sewage effluent are available, they are not equally applicable to nonionics.

Our industry has had a technical committee working for many months to come up with a procedure for evaluating biodegradability of anionic surfactants. This procedure, which requires a presumtive shake-flask culture test followed by a confirmatory activated sludge test, is now being checked for reproducibility in different laboratories. It is hoped that within a few months, this procedure will be generally adopted. Once a measure of biodegradability has received broad industry acceptance, then some value determined by this test can be publicly cited as the degree of biodegradability which the industry's voluntary changeover will assure. But, of course, practical field results, not just tests, are our real concern.

This goal is an outgrowth of the announcement by suppliers of the availability in late 1964 and early 1965 of full-scale commercial supply of newly-structured surfactants, with the right performance at the right price. Because of the articles (18) that have appeared in the technical press regarding the supplier organizations, the capacities and the processes involved, I shall not go into the commercial story here. But our confidence that these products will do the job, as evaluated from the standpoint of technical field studies as well as tests, deserves to be emphasized.

LINEAR ALKYLATE SULFONATE

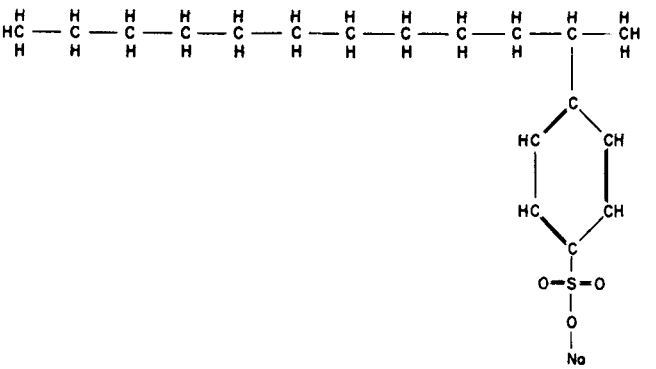

FIG. 3.

For those who are less familiar with what has been going on, the following two slides may be of interest. Figure 2 shows a typical representation of one isomer of polypropylene ABS—the so-called branched chain or hard-to-degrade material. Figure 3 shows a typical representation of straight-chain material, a type on which the major volume of five or six suppliers will be concentrated. This is being identified as linear alkylate sulfonate, or LAS. The announced capacity (19) for these plants is in excess of current industry needs on the basis of 100% conversion of ABS to LAS.

It should be emphasized here that a great many more changes in detergent composition are to be expected than that from ABS to LAS. Dozens of other surfactants, anionic and nonionic, are being re-evaluated and may be expected to be replaced to eliminate the persistence of residues in water after use. No one is holding out for the continued use of *any* hard surfactant, even in specialty uses, if it eventually is to go down the drain. But on the scale of *volume* being converted, the movement away from hard ABS will be the *key move* in the decline of the foaming sewage plant effluents, and in the drop-off of detergent residue levels in surface waters. How do we know this? Small but well-controlled field tests are showing this decline. For example: One major producer has just completed a six-month field study at a mobile home park in Virginia (20). This site was ideally suited for a study of this nature since it was equipped with a complete sewage treatment plant which served the 96 families living in the park and was sufficiently isolated so that effective control was possible over the detergent products used.

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BIODEGRADATION IN SEWAGE PILOT PLANT

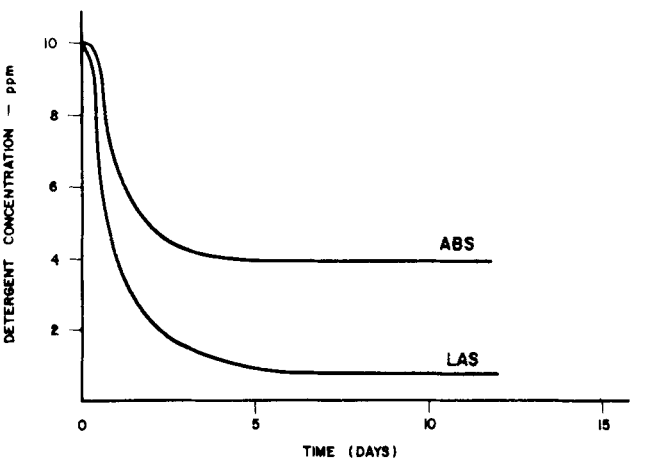

FIG. 4. Relative biodegradation of ABS and LAS in field test.

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The plant, typical of the completely mixed, total-oxidation design, was well operated and provided BOD removals in the order of 85–91%. During a preliminary survey, ABS levels ranging from 4.4–9.9 ppm were found in the effluent of the sewage treatment plant. Influent ABS levels ranged between 11.4 and 23.5 ppm. Some rather significant foam levels were observed in the plant when standard detergent products containing ABS were used.

When LAS-containing products were substituted throughout the trailer park, a marked reduction in the surfactant content was observed, LAS levels in the effluent being in the range of 0.3–0.9 ppm with an average of 0.4 ppm (Fig. 4). The results of this study were most encouraging as foam almost entirely disappeared in the treatment plant itself as well. Release of information on the other field tests is expected very soon.

After review of some of the test data, the Assistant Secretary of Health, Education & Welfare, J. M. Quigley, made this comment: "These tests, carried out on a full plant scale, afford proof that the new detergents, when subjected to efficient sewage treatment practices currently in use, can be degraded to a level which eliminates foam. When these and similar new detergents come into general use within the next year, a solution to one of America's most annoying pollution problems will have been effected."

Other field tests, here and abroad (21), including two sponsored by the Association, on which results will soon be published, confirm the adequacy of LAS breakdown in sewage treatment plants.

The issue of ground-water pollution—and particularly foaming well-water—has also drawn much attention. First, it should be understood that this situation is not general, in the sense of millions of homes, or even hundreds of thousands of homes, anywhere here. Those actually drawing foamy water from their wells on Long Island, for example, are limited to a few hundred homes . . . though there are undoubtedly increasing amounts of ABS at sub-foaming levels in thousands of other wells located close to cesspools, septic tanks, or the discharge pits of unsewered laundries, car washes and the like (22).

The requirement that tomorrow's biodegradable detergent be such as to avoid a permanent build-up in ground water is a legitimate one. Well water supplies should not be assaulted by persistent pollutants. This cannot be regarded simply as a detergent problem, however, if the conditions are such that the assault would be continued in the complete absence of detergent residues. We have taken the position that while we can provide biodegradability, we cannot, in a formula, incorporate the *conditions required for biodegradation.*

By this I do not mean to imply that LAS or other surfactants of the type our industry intends to use are impervious to breakdown in the ground. Nor should it be assumed that all discharges into septic tanks or other on-lot waste disposal units result in rising ground-water contamination. Recent work by P. H. McGauhey of the University of California has been encouraging in this respect (23). These studies, designed primarily to evaluate the improved removal achieved through the use of LAS in Septic Tank-Drain Field systems, have pointed the way to the improved design of these systems as well.

McGauhey's studies have indicated that where a 78% removal in ABS was achieved, almost 97% of LAS was removed under comparable conditions. These results were obtained under conditions in which the percolation field was operated in a non-flooded and essentially aerobic state. This principle has been found to enhance overall dissolved organic removal, and offers considerable promise in optimizing the design of septic tank-drainage field systems. Another increasing aspect of this work involved the fate of ABS and LAS when subjected to treatment in oxidation ponds. In standard rate ponds, where less than 40% of the ABS was removed, removals of over 93% of the LAS were achieved.

For the past several years, we have also been cooperating with the New York State Temporary Commission on Water Resources Planning in a study of contamination of on-lot wells from adjacent cesspools on Long Island. In this series of tests, specially formulated detergents based on LAS and other soft surfactants were used as replacements for ABS-containing products on several test sites. Frankly, the Long Island results have neither proved nor disproved whether the new linear materials will end the effects of surfactants on well-water quality where simple cesspools (without tile fields) are widely used. What these results do suggest is that concurrent contamination, including high bacteria counts, free ammonia and other pollutional danger signs, make a *general* improvement in such waste-disposal systems necessary (24). Certainly, our planned change in formulation will not be a substitute for the continuation of a program for the extension of sewers in built-up areas. The direct discharge of automatic laundry wastes into the ground water, without surfactant removal, cannot be made acceptable simply by a change in surfactant composition.

Finally, let me deal briefly with the factor of possible future non-compliance, to which those favoring regulation have given emphasis. There are in the United States, no more than six suppliers of the branched chain alkylates and, in each case, the scale of production which provided manufacturing economy arises from their volume sales to several of the large finished product producers. Statements made by these suppliers (25) suggest either the abandonment of tetrapropylene ABS alkylate production for domestic sale for detergents, or a change of cost relationships that would make ABS less available for detergent use than the improved more biodegradable material. Thus, we feel there will be no economic reason for continuing its introduction into household detergents. We believe that other slowly degradable surfactants having any appreciable mass use will also be made obsolete by competition. A statement to the U.S. Senate Public Works Committee disposed of the economic advantage of "hard" imports (26). Should there be industrial use of hard

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surfactants, the responsibility for their removal, in any case, would rest on proper treatment of waste water before discharge under present State or local industrial water pollution regulations.

Interestingly enough, the fear that small or fringe companies would be the laggards in the changeover is actually working in reverse. Smaller companies, able to purchase limited development quantities or batch lots of "soft" surfactants, are in some cases acting to publicize their ability to be the first with biodegradable formulations. Thus, in the short interim period before facilities permit complete conversion, they hope to build status and support from health authorities and conservationists. Measurable accomplishment must wait until next year when the big plants are providing steady carload quantities of surfactant, and the popular brands are all converted. But, within their own capacity limits, small companies seem more likely to be ahead, rather than behind, the parade, and this is all to the good.

As this is written, the American detergent industry is hopeful that regulatory Federal legislation can be avoided. But you may be wondering: Why are our producers so strongly motivated toward a voluntary solution, rather than to a legally instituted one if the latter is post-dated to December 1965? Having come as far as we have toward conversion, this is not a question of good faith alone. No company can gain by delay in making the change once the new surfactant, already contracted for, starts moving in. Our main concern is that regulation—once imposed—tends to grow in complexity and expense, regardless of the need.

Regulation of the *discharge* of wastes—particularly industrial wastes— has precedent and accomplishment behind it. But the banning of the sale of a specific product *prior to use* as a method of pollution control (for its possible effects *after* it has been used and discarded) would be a precedent-breaking extension of governmental power. If we succeed in meeting our commitments for improvement *voluntarily,* and on time, we may have pointed the way for dealing jointly with many of the other, more threatening aspects of pollution, entirely apart from detergents, that rising population and industrialization are sure to bring.

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[Received June 17, 1964—Accepted October 6, 1964]

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Variety was Keynote of NRA 1964 Convention in New Orleans

Keynote of the program of the National Renderers Association's 1964 Convention, Nov. 18–21, New Orleans, was variety in the various aspects of their industry.

Samuel Golden, Amburgo Co., spoke on the use of animal fats as protein supplements in high energy livestock feeds, offering constructive criticism of the use of fats in formula feed manufacture. Bartley Cardon, Erly Fat Livestock Feed Co., complemented this address by speaking from the customer's point of view. His firm has long employed animal fat in this manner and has been instrumental in helping the rendering industry develop this market.

Development of another market for the industry was presented by J. H. Chaloud, Soap Products Development Div. of Procter & Gamble. He discussed the importance of fat specifications to the soap industry and their relation to the quality of finished products. H. de Kroes, The Netherlands, presented some of the problems faced by renderers abroad. Nearly all tallow produced in Holland is consumed by the feed industry, and the Dutch renderers have developed a well-organized research program with feeding trials. NRA President J. H. Haugh, Exec. Dir. D. A. Specht and Dir. of Technical Services O. H. M. Wilder reported on the Association's 1964 activities in the U.S., Europe and Japan.

Glycerine Production Up

According to the U.S. Department of Commerce, production of crude glycerine (including synthetic) for the month of August was 29.0 million lb, up 4.8 million lb from July, and up 3.9 million lb from August last year.

At the end of August, producers' stocks of crude and refined glycerine totalled 59.4 million lb, up 2.3 million lb from the end of July, and up 19.6 million lb from August, 1963.

AUGUST
(Million Pounds)
PRELIMINARY

Glycerine 100% basis	Factory production		Producers' stocks	
	August 1964	% Change from July 1964	End of August 1964	% Change from July 1964
Crude	29.0*	+19.8	27.1	+8.0
Refined, all grades	26.5	+15.7	32.3	+0.9
			59.4	+4.0

* Includes synthetic glycerine.

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