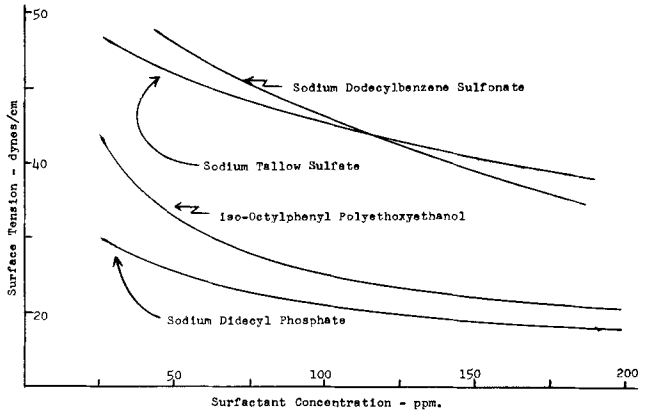

FIG. 5. Comparison of the surface tension of solutions.

Figure 5 compares the surface tension of solutions of sodium didecyl phosphate with three surfactants used in or recommended for use in built detergents. The surface tension of sodium didecyl phosphate solutions, up to a concentration of 200 ppm is far below that of either sodium dodecylbenzene sulfonate or sodium tallow sulfate and significantly lower than that of the nonionic surfactant, iso-octylphenyl polyethoxyethanol, particularly at very low concentrations.

Performance of built detergents containing these surfactants is compared in Table II. The test methods were the same as were used in comparing the alkyl phosphates. Our data indicate that sodium didecyl phosphate is about 20% more effective than sodium tallow sulfate, nearly twice as effective as sodium lauryl sulfate and three times as effective as sodium dodecyl benzene sulfonate when used in a built detergent.

TABLE II
Comparative Performance of Commercial Surfactants in Cotton Detergency

Surfactant	Performance index	% Surfactant required for maximum performance
Sodium didecyl phosphate	195	8%
Sodium tallow sulfate	155	10%
Soduim lauryl sulfate	118	14%
Sodium dodecyl benzene sulfonate	76	25%

Conclusions

A study of the sodium monoalkyl phosphates and sodium dialkyl phosphates has shown that the dialkyl esters, in general, possess markedly superior surfactant and detergent properties compared to the monoalkyl esters. This is true whether we are comparing equivalent mol wt mono- and diesters or when comparing those made from the same alcohols.

The branched chain didecyl ester, in addition to giving aqueous solutions of exceptionally low surface tensions and possessing a very low critical micelle concentration, also performs exceptionally well in built detergents. In fact, our data indicate that its performance characteristics are considerably better than commercial surfactants used today in these types of products.

The Nation's Water Pollution Problem — Detergent's Role in It

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THE petroleum industry, like others, has been importuned to conduct its industrial operations in a manner that will prevent processing wastes from polluting our water resources—from the well, to the refinery, to the petrochemical production phases of industrial operation. It is the sanitary engineering profession which has been pleading the cause for steam pollution control. I hope in the course of my presentation today to plead for your Society's active interest in this worthwhile national endeavor.

Your industry has done as well as any in pollution control. In fact, you have done more than many other basic industries to clean up pollution from your complex operations. But, there are things which you have done which should not have been done, in terms of pollution, and things you have left undone which your industry should have done, in the interests of water pollution control.

I make this point, lest it be assumed that I am placing sole responsibility for the nation's pollution problem on the doorstep of the oil chemists' profession. This I am not doing because other industries have been equally remiss; in fact, we all have! It is my earnest plea, however, that we can do better than we have done in preventing the despoliation of the nation's rivers, lakes and coastal waters and that, together, we can clean up the pollution problem which threatens the ultimate value and usefulness of the nation's greatest asset—its water resources.

I have been tempted to retitle my address, "Between the Devil and the Deep Blue Sea," because that is the dilemma your industry faces in attacking your part of the nation's water pollution control problem. On one hand, you are being pressed to prevent pollution from your various operations—which I term "back door" pollution conditions. I refer to the discharge of industrial by-products or waste materials which are the result of internal operations of product manufacture in your industry. This industrial wastes problem is so much a part of the overall threat to our water resources that the oil industry must maintain vigilant control of everything that goes out its "back door." On the other hand, you are, indeed, in the position of being between the devil and the deep blue sea, because in addition to being concerned about your "back door" wastes, you are being urged to do something about your "front door" products. I refer, of course, to detergent products.

The "Front Door" Problem . . . and the "Back Door" Problem

What makes the "front door" problem more vexing than your "back door" control problem is a two-fold situation that can be equally frustrating to scientists and industrialists:

1) You are dealing with lawmakers, not scientists, and they are being whipped into a "frenzy over foam" by well-meaning protectors of water quality—people who advocate laws which would be the first prohibition imposed on the manufacture and sale of a product with a "head" since the Volstead Act!
2) You make cleansing products to keep America clean—only to find that they are accused of making America dirty!

A month ago, I addressed the Wisconsin Medical Society's Symposium on "Foods—Fad and Fallacies." My assignment was to set the records straight on the fallacies of detergent fears in a state where legislative prohibition was being considered for detergent sale and production, and in the home area of a Congressman who is an ardent advocate of anti-ABS legislation.

I find my rationale for today's discussion in what I said in Wisconsin because my symposium presentation proved my "devil and deep blue sea" characterization of your "front door" and "back door" problems. Furthermore, the Wisconsin presentation tried to explode two fallacies:

a) That detergents in water are a health menace—by showing that we have no proof of such hazard;

b) That the presence of detergent foam is proof that it alone despoils our water resources—by showing that "ABS never walks alone."

ABS never does walk alone, except in the limited cases where detergents from industries and certain commercial operations are not admixed with other organic wastes which may be of greater importance than detergents themselves.

The simple—and often forgotten—point is: Where there is foam, there is sewage, because they "go together," like "love and marriage," to steal a phrase from a popular song!

ABS: Alkyl Benzene Sulfonate and America's Befouling Sewage

That is why I told the Wisconsin Symposium that ABS may mean *Alkyl Benzene Sulfonate* but that it also means *America's Befouling Sewage.* My plea was: Before we get too exorcised over the former, we should do something about the latter!

These are generalizations that you might like to hear after being belabored by the sanitary engineering profession about your lack of biodegradability. But, neither you, nor anyone else, have the right to feel righteous about the overall problem of pollution because you contribute to it just as surely as a little ABS makes a lot of foam!

This brings me back to my specific subject, "The Nation's Water Pollution Problem—and Detergent's Role in It." The pollution problem is accentuated by detergent foam which cannot be "swept under the rug," or eliminated by mere wishing. Or, to be even more exact, it cannot be licked by licking foam! It will take more to solve the national pollution problem than solving the detergent problem because, we must always remember, "ABS never walks alone."

We cannot put America's pollution problem into focus without putting America into focus. "Focus" means "future," because what we are doing to our water resources today will dictate whether we will have enough water for a dynamic tomorrow of urban, industrial, economic and social growth.

Predicting the future, from the period of 1975 to the year 2000, is today's favorite indoor sport. The Senate Select Committee on National Water Resources, a short time ago, predicted a potential water shortage in 1980 and placed a $54-billion price ticket on water resources' development and water pollution control between now and 1975. The House Science and Astronautics Committee went a step further, in predicting that 1970 may be the year of critical water shortage unless we learn to desalt the sea.

The head of Resources for the Future, a nonprofit organization, has added some startling predictions of his own: That a water consumption of 48 billion gallons a day would exist in the United States by the year 2000; that a population level of 330 million will be reached in this country by then; that auto production would rise to 27 million per year, as against today's modest 7 million cars per year; that housing starts in the year 2000 would reach 4,200,000 per year, as compared with the 1.4-million today.

You can pick your own predictions. Predict as you will, they all spell: More people . . . more production . . . more water . . . more sewage . . . more industrial wastes . . . and more of your cleansing materials that will go down the drain!

Our magical ability to synthesize products cannot be used to make one drop of water in our present complex world which I have described as plasticized . . . immunized . . . digitalized . . . nuclearized . . . televised . . . deep-freezed . . . videod . . . vitamined . . . hormoned . . . filtered . . . dehydrated . . . air-conditioned . . . caloried . . . and detergented.

Formula for Pollution Control: "Stir What You Got!"

Since we cannot *produce* water, we must *preserve* it. We must "stir what we got!" The story is told of a man who ordered a cup of coffee in a restaurant during the war when sugar was short and it was being dispensed from behind the counter rather than freely offered on the counter. The waitress asked: "Sugar?" The man replied: "Yes." Then the waitress added one spoonful of sugar to the man's cup. The man pushed back the cup and said: "I take two spoonfuls." The waitress then delivered one of the greatest sermons of all time: "Mister, stir what you got!"

How do we "stir what we got?" We do so by advocating adequate treatment of all sewage and industrial wastes to protect water resources against befouling and ruination. This would prevent us from practicing "brinkmanship" with our rivers, lakes, and coastal waters. "Brinkmanship" would be loading them with wastes to the point of incipient destruction. To do so would not be adequate pollution control, but to try to "polish" all of our waters, regardless of their best social usages, would be equally wasteful. The so-called Blatnik Bill, now before Congress, talks hopefully about "positive" action in preventing stream degradation rather than "negative" loading of our waters with polluting wastes. If this sounds Utopian, it is well to recognize that our whole concept of what we mean by pollution is now suspect because of new factors of pollution in a changing world. I offer four points which are indicative of this new concept of pollution and pollution control:

1) We know we must reuse our waters if we are to have enough to meet all of our present and future needs.

2) We know we must provide higher degrees of sewage and wastes treatment to make such reuse possible.

3) We know we must worry about "Rachel Carson" pollutants—and detergents.

4) We know we may have to worry about virus infections which sewage treatment and water purification processes may not correct with full degree of certainty.

The upshot is that there will be a trend toward advanced degrees of wastes treatment, to get out and to modify all pollutants—the so-called "standard" pollutants and the "exotic" contaminants which include detergents.

We are no longer faced with the simple job of considering sewage as having only three categories of objectionable contaminants: Coarse debris which can be removed by screening and grit facilities; finer solids which can be removed by settling and by bio-oxidation processes; and bacteria which can be finally destroyed by adequate disinfection by means of chlorination. We must now characterize sewage in a different vein and look upon sewage treatment as a more advanced challenge than it has been in the past. I refer, of course, to our present interest in what is being classified as "sewage treatment—plus," or the use of additional processes or refinements to take out or modify wastes constituents which are not removable with any degree of certainty in present sewage treatment plants of either the primary type or the secondary type. Various "plus" processes have been suggested, including special filtration, adsorption, ion exchange, distillation, and even nuclear reaction.

Four Billion Pounds Down the Drain!

This brings me to the point of translating ABS from Alkyl Benzene Sulfonate to America's Befouling Sewage. Detergents are in the pollution picture, not as the sole villain of the piece, but as a part of the overall problem. It must be so, because of the following points which I present to clarify the role of detergents in the nation's water pollution control problem:

. . . 4 billion pounds of detergents, which may contain from one-half to a billion pounds of surfactants, are used yearly and go down the drain.

. . . The old formula for cleanliness—soap and elbow grease—has been reformulated into a bald giant who rolls up his synthetic sleeves and uses physical chemistry instead of physique to produce the home cleanliness the American people so desire.

. . . The magic in the box and the bottle is used by people who do not know about the carbon-hydrogen ring, and who could not care less, but who do know that the new carbon-hydrogen ring leaves no ring in the bath tub.

. . . The detergents in the drain enter the sewer system and become a portion of the sewage problem of America. Parenthetically, let me describe a sewer, as one wit defined it, as a long tube at one end of which people are putting everything imaginable in, and at the other end of which people are using every imaginable means to get them out.

. . . ABS does not walk alone—it is part and parcel of sewage but not the only villain of the situation.

. . . We are not doing an adequate job of "taking things out," and detergents are only some 10 to 20% of the organics contained in the average sewage treatment plant effluent.

. . . And, finally, we must do better than we are doing to lick pollution—and ABS manufacturers must do better if we are to lick pollution because it is the part we see which has attracted more attention than the part of pollution we do not see.

Admittedly, better sewage treatment will mean better attack on the detergent problem by biodegradation in more advanced aeration processes. But in the meantime hundreds of treatment plants depend on primary processes which provide little degradation opportunities. We cannot wait for the era of higher degree of sewage treatment to solve the "back door" problem of your industry. It must be done by the prompt and effective attack on the "front door" problem of the petroleum industry and the soap and detergent industry.

The Septic Tank Problem

The challenge is the greater because of the hundreds of thousands of homes which use septic tank or cesspools for disposal of their wastes and take their waters from wells which have an "infallible" source in the unbroken chain which exists between water, to sewage, to water on these home sites. The challenge is to ascertain how much dependence we can place on the ability of soil and ground water to degrade detergents discharged into such sites.

The New York Temporary State Commission on Water Resources Planning is studying this problem on Long Island in a novel team effort with local scientists, state departments, the U.S. Public Health Service, the U.S. Geological Survey, and the Soap and Detergent Association. We find nothing incongruous in this partnership between a legislative investigative agency and the industry involved in this problem. In our opinion this partnership is in true keeping with the American way of industry and progress!

It is interesting to point out that in the studies in Long Island the scientists involved have been utilizing three types of detergents formulated by the Soap and Detergent Association. It is their task to ascertain whether these products degrade effectively in various types of soil conditions, various conditions of ground water flow, and under various circumstances of location of the source of pollution and the source of water supply drawn from the same home property site.

Behind this New York State Commission approach to the ABS problem lies our conviction that we must find an answer for the detergent problem—and that we will find it if a true spirit of team play exists. The detergent problem, in our opinion, is not the only pollution problem which New York State faces. However, it is *one* of the problems and it must be solved if we are to avoid further injury to the valuable water resources upon which the State's growth and future progress depend.

This Commission of Water Resources Planning is equally interested in all other pollution problems, including the task of shaking the complacency of cities and industries which persist in discharging untreated or inadequately treated wastes into the watercourses of the Empire State. It recognizes that we must fight the unseen pollution as well as the pollution which we can see, and that the unseen is, in many instances, more serious than the foam which becomes so apparent to the public. It is important to alert the public to the fact foam does not walk alone; that it is merely indicative of the presence of pollutional wastes containing other dangerous contaminating substances.

This is the adult way to look at the ABS problem, not through the astigmatism of the foam we can see, but through the clarity of recognizing that the unseen sewage which the foam covers may be more important than the foam itself!

We Owe ABS a Vote of Thanks—but Don't Expect It

In a sense, we owe ABS a vote of thanks. It has made people pollution conscious. But, do not expect

any applause from those who object to foam in their water supply! Rather than applause, you are being challenged to lick your problem because *you walk with sewage,* just as *sewage walks with your industry.*

You have the misfortune in your "between the devil and the deep blue sea" situation of reminding a cleanliness-loving people that we are caught in the web of our own weaving—that the foam we produce is symbolic of the wastes we produce, and that to admit it is to admit that we are guilty of fouling our own nest!

It is common for industrialized America to wave its banners and plead for free enterprise. Your industry, I am sure, pleads for the right to operate its practices in the best way it can do so, without interference in the normal operations of your business procedures. You must practice what you preach. If you plead for free enterprise, you should demonstrate your enterprise by producing formulations of detergent products which can eliminate your part of the nation's pollution problem.

I plead today for a further role for the American Oil Chemists' Society. In addition to cleaning up your "front door" problem, and in addition to carrying out the internal industrial operations of your profession in a way that will eliminate the "back door" industrial wastes pollution problem, I urge you to play a third important role in the problem of solving the nation's pollution problem.

It would be true justice if your Society would resolve to do even more. Since your foam has aroused all of the frenzy on the part of people who think *emotion* takes the place of *motion* . . . who are attacking the foam problem with more *heat* than *light* . . . you can do something about the pollution which walks with ABS. You could render a great national service by becoming a part of the great drive for licking the nation's pollution problem.

The sanitary engineering profession which I represent challenges your profession to help correct the conditions which caused the congregation to plead for forgiveness for the things we have done which we should not have done and the things we have not done which we should have done.

What is detergent's role in the nation's pollution problem? The story is told of a traveller who first saw the ocean from the rail of his steamer. He marveled over the vast expanse of water until a ship's officer said: "Yes, but that is only the top of it!" The detergent problem is only the "top" of the nation's water pollution problem, but it is the part the public can see. It is our task to clean up the "top," and, in so doing, to make certain that we lick the other wastes which "walk with ABS."

With your help, we can do both.

The Chemistry of Surfactant Biodegradation

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THE PRIMARY incentives prompting study of the biodegradation of surfactants arise from the waste detergent situation, a situation which has by now been covered so thoroughly in the technical literature and the public press as to require no further elaboration here. A comprehensive review has recently been published by the Detergent Subcommittee of the Ohio River Valley Water Sanitation Commission (1). It provides a very useful entry to the literature on all aspects of the problem.

Biodegradation of surfactants in wastewaters, in treatment plants, and in the ultimate receiving bodies is primarily the result of bacterial action, just as is the case with the other organic components of the waste. The biochemical metabolic reactions involved appear to be much the same whether surfactant or not, although there are certain characteristic features exhibited in surfactant biodegradation which arise from the characteristic structure of surfactants themselves—strongly hydrophilic and strongly hydrophobic groups joined together in the same molecule.

Accordingly, as a preliminary to the discussion of surfactant biodegradation, the more common test methods and the more likely metabolic pathways will be reviewed.

To serve as a convenient point of reference, Figure 1 shows a typical biodegradation experiment applying the river water technique devised by Hammerton (2). Here a seven-milligram sample of surfactant was dissolved in a liter of river water and the solution was anaylzed every few days by the methylene blue method. Three different surfactants are shown, one which was readily attacked by the microorganisms present in the river water, one which was quite resistant, and one of intermediate character, the present day commercial product.

Test Methods

Basically, biodegradation is measured by exposing the test compound to microorganisms and analyzing the system at intervals to determine such things as the disappearance of the test compound, the formation of degradation products or the uptake of oxygen. As will be evident, many combinations of microbiological environments with analytical methods have been used depending on the exact objectives of the work.

1. Microorganisms

The microorganisms chosen may be a pure strain or a mixture. Mixtures are ordinarily used, derived from such sources as river water (2), activated sludge (3), sewage (4), soil (5), or air (6). The general microbiological makeup of mixed cultures from these sources seems to be fairly constant, deriving from the characteristic species of common soil bacteria (4), and they should give a fairly realistic basis for extrapolation of performance from the laboratory to the field.

Pure cultures, on the other hand, should be of value in the detailed study of specific metabolic reactions, but are less suited for general screening of surfactants for biodegradability. It often happens that a specific strain of microorganism is unable to carry out some specific reaction in a metabolic sequence which a related strain can do quite readily. In a mixed culture, the species present can make up for each others' deficiencies. There is another reason