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Effects of Detergents on Surface and Ground Water Problems

W. A. KLINE, Colgate-Palmolive Co., New Brunswick, New Jersey

THE PURPOSE of this paper is to provide a brief picture of how synthetic detergents affect surface water and ground water on the basis of what is known today and what might be expected tomorrow. This subject is so complex that it is not easily or completely covered in a single paper. For those that are concerned with water quality at national, state, municipal or local levels, the Soap and Detergent Association has published a booklet, "Synthetic Detergents in Perspective" (1) that is very helpful. In addition, a report, "Components of Synthetic Detergents in Water and Sewage," prepared by ORSANCO detergent subcommittee and approved by the ORSANCO commission, is published in the March 1963 Journal of the AWWA (2). Because of the availability of the above, the effect of detergents as they are known today will be only briefly summarized here.

Present Status

The most widely used surface active agent or surfactant in household detergents today is propylene tetramer alkyl benzene sulfonate, commonly known as ABS. Since World War II the usage of ABS in the U.S. has grown to approximately 560 million lb per year. Concurrent with increased use of ABS detergents, we have had a remarkable growth in automatic washers and concomitant frequency of washing. Therefore, more water and more surfactant are now being used than was ever used in the days of laundry soap. What has been the effect of this material on the quality of surface water and ground water?

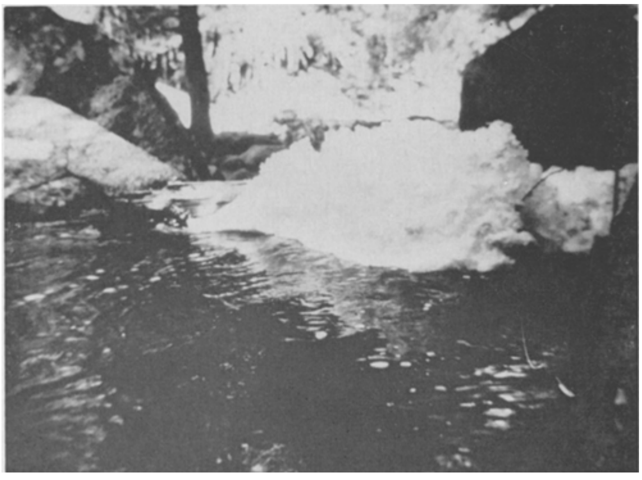

FIG. 1. Natural foam in the pristine waters below Vernal Falls in Yosemite National Park in spring of 1962.

By *surface water* we refer to streams and rivers that receive the discharge of sewage treatment plants. The first evidence of ABS is the appearance of froth or foam in waste treatment plants in the aeration stage and/or in the effluent. Prior to widespread use of ABS, sewage treatment plants often experienced frothing and foaming. This was due to other organic and protein compounds which exhibit a lowering of the surface tension much like any detergent. Thus ABS is not the only foamer in the waste, but can be a significant contributor.

Contrary to the opinion held by some, ABS is attacked by bacteria, as evidenced by the fact that approximately 60% of the material is degraded by primary and secondary treatment processes. Nevertheless, this degradation is slow to occur and consequently, measurable amounts, that is, parts per million, are present in treatment plant effluents and will enter surface waters. Appearance of foam on some surface waters that receive untreated sewage or the effluent of sewage treatment plants is usually ascribed to detergents, though other foamers may be present.

Monitoring of the ABS content of the Mississippi River at New Orleans and the Ohio River at Cincinnati, however, has not shown any build up of ABS over a two-year period, indicating that perhaps insofar as these rivers are concerned the concentration of ABS has reached an average level of about 0.05 ppm in the Mississippi and 0.16 ppm in the Ohio and is not increasing.

By *ground water* we mean deposits of water in sand and/or gravel strata at varying depths beneath the surface of the ground. In certain areas of the country, contamination of ground water by ABS and other pollutants has occurred to the extent that in a few cases the water from individual shallow wells will tend to froth when drawn from the household tap.

This tendency to froth is aesthetically objectionable, and its absence would be desirable. However, this froth basically is pointing up the fact that sewage effluent is entering the water supply and that gross contamination is occurring.

Septic tanks and cesspools are very inefficient treatment units, and may remove only a relatively small amount of all the contamination present. Experience has shown that when the effluent is discharged into a sandy soil which has little additional removal capacity, ABS and other pollutants may filter through into ground water supplies. As to the operation of septic tanks, all information available confirms the fact that no interference with the usual septic tank decomposition or flow results from the normal use of any regular household detergent product for washing clothes, dishes, and other household tasks.

Work by Government Agencies (6) and by the Soap and Detergent Association member laboratories has indicated that the threshold taste for ABS is on the order of 16 ppm for individuals having sensitive taste with the odor level considerably higher. This, of course, is well in excess of any concentrations which might be found in water normally used for human consumption and certainly well above the level of 0.5 ppm ABS suggested by the U.S. Public Health Service as the upper limit for potable water. Data from another USPHS study (7) clearly indicated that ABS alone at the concentrations usually found in finished water cannot be the cause of either taste or odor. ABS is always accompanied by other contaminants from domestic or industrial sources, however, and the reported taste and odor must be attributed to these contaminants.

So far as can be determined, there are no cases on record of fish kills in streams or lakes directly attributable to ABS even though extensive records of fish kills are compiled by the U.S. Public Health Service. Numerous studies have been reported on the effects of detergents on fish and a few studies on the effects of detergent residues on fish. Reports by Henderson, et al. of USPHS (3) and by Herbert, et al. of the British Water Pollution Laboratories (4), showed 3.5 ppm ABS as the dosage lethal to half of the fish tested in 48 hr. Herbert pointed out that "the residues of these detergents which remain in the effluent after biological sewage treatment are very much less toxic than the original materials." Niemitz and Pestlin (5) in Germany recently reported fish toxicity of fresh (undegraded) ABS as compared to residues of ABS. At concentrations of 21.3 ppm MBAS (Methylene Blue Active Substance) they obtained 100 % reaction in less than 21 hr with fresh ABS. However, on residues of ABS, no effect was produced on fish at the same concentration.

We referred earlier to the 1962 Drinking Water Standards of the U.S. Public Health Service. I would like to quote from the background used in developing the 1962 standards:

> "In a study (8) made for the purpose, 10% of those using water containing less than 1 mg/l anionic sulfonated detergents complained of an off-taste, whereas all those using water containing 1.5 ml/l complained of an off-taste. Frothing was also a common complaint occurring most frequently at concentrations of 1 mg/l and above. The off-taste has been described as oily, fishy, or perfume-like (8). ABS itself is essentially odorless. The odor and taste characteristics are likely to rise from degradation of products of other wastes, rather than from ABS. The concentration of ABS in municipal sewage is of the order of 10 mg/l. Thus waters containing ABS are likely to be at least 10% of sewage origin for each mg ABS/l present. It is recommended that alkyl benzene sulfonate (ABS) in drinking water be limited to 0.5 ml/l, inasmuch as higher concentrations may cause the water to exhibit undesirable taste and foaming. Concentrations of ABS above 0.5 mg/l are also indicative of questionably undesirable levels of other sewage pollution.
>
> "An ABS concentration of 0.5 mg/l in drinking water, in terms of a daily adult human intake of 2 liters, would give a safety factor of the order of 15,000, calculated on the results of subacute and 2-year tests on rats fed diets containing ABS. In these rat studies, it was found that levels of ABS in the diet, of 0.5 per cent and below, produced no discernible physiological, biochemical, or pathological deviations from the normal (9).
>
> "Human experience (6 subjects) with oral doses of purified ABS of 100 mg (equivalent to 2 liters of water containing 50 mg ABS/liter) daily for 4 months led to no significant evidence of intolerance (10)."

Thus, we see that ABS does not interfere with the proper functioning of sewage treatment plants and it is degraded to a significant extent in sewage treatment—it has no adverse effect on bacteria in aerobic treatment plants nor in septic tanks—does not cause taste or odor problems—is not toxic to humans—and it has not been found responsible for any adverse effects on fish. Its foam is a nuisance in sewage treatment plants and occasionally in streams and drinking water from individual wells. Many persons consider ABS is serving a valuable function as an indicator of general contamination of a water supply by sewage which might otherwise be undetected until made obvious by other, very undesirable, indications.

The detergent industry has recognized that foaming in surface water and ground water is not desirable. We are determined to eliminate ABS detergent from our products as soon as it is feasible to do so, and thus eliminate any foaming to which ABS is a contributing factor.

Present Developments for ABS Replacement

The development of a new surfactant to replace ABS is not a simple task. There are three major

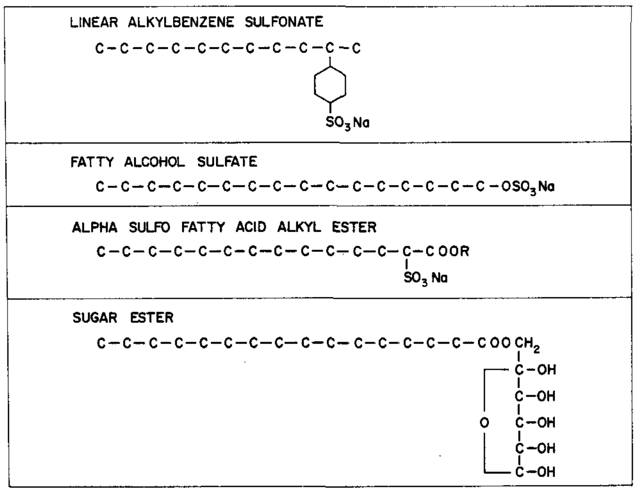

FIG. 2.

requirements that must be met. Initially, performance must at least equal that of propylene tetramer ABS. Secondly the economics must be in the same range. Third, the new surfactant must be biodegradable.

Many published articles have discussed possible new biodegradable materials and their sources. A recent article (13) reviewed the possibilities of straight chain alkylbenzene, fatty alcohols, alpha sulfo fatty acid esters and sugar esters.

Other surfactants from alpha-olefins were presented by T. M. Liddicoet of California Research Corp. Because of industry's requirements for performance, price, and biodegradability much of the research effort has been to develop a straight chain hydrocarbon to make linear alkylbenzene. From information available, linear alkylbenzenes may be obtained from alpha-olefins or from a kerosene fraction.

Alpha-olefins may be made by the Ziegler polymerization from ethylene or from paraffin wax cracking. The choice of the Ziegler chemistry route may depend to a great degree on the ethylene supply of the manufacturer. The important factors in the wax cracking route may be the utilization of by-product olefins and the purification step to remove branched and alicyclic impurities before alkylation. When starting with a kerosene fraction linear paraffins may be obtained from molecular sieve or urea adduction purification followed by chlorination and dechlorination to the olefin, before alkylation to the linear alkylbenzene. Or, the purified linear kerosene fraction may be chlorinated and alkylated directly to obtain linear alkylbenzene.

Assuming we understand the requirements of performance and economics, biodegradability becomes the keynote. How can biodegradability be measured in the laboratory? How can laboratory data be correlated with practice in a municipal waste treatment plant, a septic tank, or a flowing stream? British (11) and German (12) scientists have put a lot of effort on this problem, and we feel we have benefited by their work. Individual company laboratories have utilized several different types of tests such as: River water die-away tests, shake flask cultures, Warburg respirometers, activated sludge, trickling filter, and septic tank tests. The Soap and Detergent Association's member laboratories are cooperating on the development of simplified, reliable laboratory procedures which will more nearly suit our requirements for correlating between laboratory tests and actual waste disposal practice in the U.S. The Association is sponsoring field studies to shed more light on the problems of biodegradability. The Association is cooperating with Senator Van Lare's Temporary New York State Commission on Water Resources Planning in a Suffolk County, Long Island test, to provide data on the fate of several kinds of detergents as they pass through a septic tank system into a sandy soil structure and ground water.

New Processes for Removing ABS

There is so much work in progress that I can only refer to process studies in general terms. The Advanced Waste Treatment Research Program of the U.S. Public Health Service has two ultimate goals: One is to help abate our Nation's growing water pollution problems and the other, more startling in concept, is to renovate waste water for direct and deliberate reuse. This program was initiated about 2½ years ago. Many of the research projects used ABS as the material to remove from waste water initially because there are analytical means available to identify ABS and measure it. A few of these projects are:

> Use of Activated Carbon for Adsorption from Waste Water and Reactivation by Thermal or Chemical Means.
>
> Separation by foaming, Partial Freezing and Eutectic Hydrating or Freezing, Electrodialysis and Associated means, Evaporation, Extraction, Emulsion Separation, Oxidation, and Ion exchange.

At the December 1962 meeting of American Association for the Advancement of Science, J. M. Cohen of Taft Sanitary Engineering Center presented a two year study on "Degradation of ABS in Unsaturated Soils." The study utilized sand beds fed intermittently with effluent from a community septic tank. The retention time of various sands and soils was checked, with the basic conclusion that they showed little adsorption and/or breakdown of ABS until they were coated with organic matter. With a "mature" sand bed, up to 90% degradation of ABS could be accomplished in unsaturated soil conditions.

In another approach, success in improving the efficiency of activated sludge treatment in degrading ABS has been reported by Sharman, Kyriscou, and Searle (14). By deliberately frothing the effluent of settled activated sludge and recycling the wet froth to the activated sludge unit, total ABS removals above 90% have been obtained in laboratory units. Pilot scale studies, in cooperation with the Sanitary Engineering Research Laboratory of the University of California, are being set up.

Dr. Samples, of California Institute of Technology, has reported removal of ABS from secondary sewage treatment effluent by use of a cationic surfactant, such as quaternary ammonium chloride to "neutralize" the anionic ABS. Addition of alum would precipitate the surfactants in sand filters. Tests under actual plant conditions are in progress.

There are many other methods being studied. The more successful, if applied on a large scale, would remove not only detergent contaminants but also most of the other pollutants from sewage effluents.

Future

From this brief review you can visualize that a great deal of work has been done and is continuing on detergent product development and waste water treatment by the detergent manufacturers, raw material suppliers, universities, Public Health Service and others interested in waste treatment and water quality.

Representing a detergent manufacturer, I can only speak for my own Company. We have tested over 100 different samples of raw materials in the past year. We have made products in pilot plant and plant equipment and are continuing extensive testing that is required before a new product is put on the market shelves. Since our keyword is biodegradability, we feel that the materials we are testing look promising for aerobic type of treatment that is attainable in activated sludge systems, trickling filters, or in river water. When we refer to biodegradability under treatment conditions found with septic tanks and cesspools, the same materials do not look as promising. The rate of biological breakdown appears to be much slower in anaerobic systems as compared to aerobic systems. Therefore, it is quite possible that the detergent industry will be able to materially help the situation for municipal waste treatment, but the prospect of helping where individual septic tanks and cesspools are involved is not so bright for the near future.

The new processing technology that is evolving through the Advanced Waste Treatment Research, combined with improved biodegradable detergents will surely permit early economical re-use of waste treatment effluent for industrial and ground water recharge purposes.

The ideal solution for protection of surface waters is more biodegradable detergent products combined with improved waste treatment for all effluents. The ideal solution for protection of ground water supplies from pollution coming from septic tanks and cesspools is the installation of community sewers and treatment plants to eliminate pollution from many other materials as well as detergents.

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Foreign Requirements and Developments in Biodegradability

C. A. HOUSTON, Industrial Chemicals Division, Shell Chemical Co., New York, New York

THERE ARE TWO countries outside the U.S. where virtually all the activity in the area of development of detergents exhibiting good biodegradability properties has been centered, namely the U.K. where effective action is already well under way and West Germany where a law has recently been passed. Although this law does not take effect until October 1964, to be sure of compliance by that date, the major soap companies will switch over at least three months in advance. This is because of the necessity to clear all the distribution pipelines of obsolete product.

Historically, the first published notice of the possibility of synthetic detergents interfering with sewage purification appeared in an American magazine in 1947 and told about the problem in a small town (Mt. Penn) in Pennsylvania (1). This article was called to the attention of the Shell Dutch Laboratories. The Dutch authorities were already questioning Shell concerning the degradability of TEEPOL®, a Shell product then based on secondary alkyl sulfate. The laboratories in Amsterdam commenced work on the problem in 1948 and were publishing papers on this subject 13 years ago (2,3).

An important point here is that early recognition was given to this potential problem area by the Dutch scientific people. This recognition made available tried and rapid biodegradation test methods when they were needed in England. At about this same time, that is in the early 1950's, in England the appearance of large quantities of foam at sewage works and on the rivers taking the effluent from such works drew public attention to the existence of synthetic detergents and led to the setting up by the British government of a special committee on synthetic detergents in 1953, the Jephcott Committee. An interim report was published by the Jephcott Committee in 1954 (4). At this time there were four major worries about synthetic detergents: first, dermatitis; second, corrosion of plumbing; third, excessive foaming causing difficulty at sewage treatment plants; and fourth, excessive foaming of rivers causing concern for the purity of the rivers. The Jephcott Interim Committee Report gave synthetic detergents a rating of no worse than soap as regards dermatitis and put to rest the fears of excessive corrosion being attributable to synthetic detergents. However, it pointed out that the problem of foam in sewage works was serious, as was the situation of foaming on rivers.

In England as elsewhere a common practice is for raw sewage to be pumped to settling tanks where insoluble inorganics are removed and also some of the organics. From the settling tank the organic matter, depending on the type of plant, is sent either through percolating filters, that is a gravel bed, or an activated sludge unit, a unit which provides aeration by compressed air and/or mechanical agitation. In other words, the organic matter is given exposure to air and bacterial cultures by one of these two methods which result in the breakdown of the organic material and hence, the purification of the sewage. In the early 50's about 22 million people in England were served by percolating filter type plants and 12 million by activated sludge plants (5). The activated sludge plants are more efficient and all of the large scale modern plants are, and will be built, of the activated sludge type. Percolating filters are still used for the smaller type of purification plants. What made this situation so important in England specifically, was that after treatment in the sewage plant the effluent is pumped into various rivers and one-quarter of the population of England derive their water supply from rivers that receive effluent from sewage treatment works up-stream of the water supply intakes. Such important cities as London, Coventry, and Southampton for example, utilize such water.

Now the purification of river water to make it potable involves the removal of contaminants by methods such as flocculation and precipitation. It was conceivable, of course, that synthetic detergents