

SYNTHETIC DETERGENTS IN PERSPECTIVE

their relationship to sewage disposal and safe water supplies

TECHNICAL ADVISORY COUNCIL
THE SOAP AND DETERGENT ASSOCIATION

295 Madison Avenue / New York 17, N. Y.

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Printed in U.S.A.

FOREWORD

Without ample supplies of good water, the soap and detergent industry can neither serve the public nor prosper. It is part of our job to protect healthful living—not only by aiding the quest for cleanliness—but by concern for the after-effects of product use.

All wastes conveyed away in sewer systems must sooner or later be looked upon as possible water pollutants. Most such pollutants conceal their hazard in an invisible cloak. Detergent residues in water — though harmless to health — reveal their excess by visible foam. Indeed the mental link between detergents and foam is so close that all the other sources of foam that have historically cropped up in waste water are now often attributed to detergents alone.

Thus, a public responsibility has been thrust on makers of soaps and detergents that goes well beyond the fate of the products we make. Detergent research alone cannot answer it. It calls for a public understanding of the “big picture” of overcoming gross pollution, as well as factual evaluation of that segment of the problem attributed to our product residues.

“Synthetic Detergents in Perspective” is concerned with our industry’s efforts to meet this responsibility with more facts, more research, and broader understanding.

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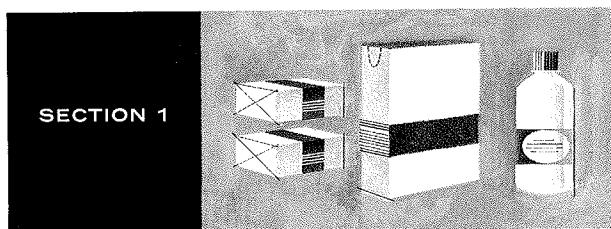
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SECTION 1

INTRODUCTION

The ability of soap and water to work together helps support America's high standards of cleanliness and public health. Soap, in this general sense, includes all the products which impart surface activity to water and make it an efficient soil remover, including the products which have come to be known as synthetic detergents, or simply detergents.

In the history of soap products over the past 100 years, there has been a tradition of constant improvement—from bulk soap to soap bars, from bars to chips and flakes, to powdered and liquid forms suited to specific cleaning tasks. Shortly before World War II, a major breakthrough toward greater efficiency and economy took place. It occurred with the development of new surface-active ingredients which made it possible for cleaning products to maintain their efficiency in hard water—something that “soap” in its chemical sense cannot do. Thus was born the *synthetic detergent*, which was able to overcome an obstacle present to some degree in virtually all water supplies—the hard water salts—and to provide the homemaker with unexcelled cleaning performance in spite of the hardness of her water supply.

Because of their improved cleaning efficiency, the synthetic detergents achieved rapid public acceptance and today constitute about 75% of the volume of the entire soap and detergent industry in the U. S. If industrial products are eliminated and only household products are considered, synthetic detergents constitute about 90% of the annual volume.

The synthetic detergent volume amounts to about 3.5 billion pounds of ingredients, of which some 900 million pounds consist of the organic surface-active (surfactant) ingredients, upon which depends the ability of the various products to remove grease and soil. About 800 million pounds of this volume represents surfactant consumption in household products. The remaining materials used in synthetic detergents also perform specific and essential tasks.

Balanced Characteristics Sought

As in all product improvement, certain difficulties may come hand-in-hand with the gains. More powerful automobile engines, for example, open up the possibility of more high-speed accidents on old-fashioned roads. In the case of the new synthetic detergents, the same in-

gredients which make them so efficient in the washing machine may have created a challenge to some traditional waste disposal methods—as have many other newly developed chemical products, apart from detergents, which end up in waste water. Manufacturers of soap and detergent products are keenly aware that they have a complex responsibility here. The homemaker wants the most efficient product at a price she can afford. Those concerned with waste water after it leaves the sink or washer want to see the excess cleaning product and its surface-active and soil-suspending properties most quickly dissipated and destroyed. Existing methods of sewage disposal and treatment are not always geared to thorough removal of the improved product, any more than narrow roads are right for today's cars. When newspapers report layers of foam on a local stream, something is amiss. But many questions still exist as to the complete cause and the most practical solution in the public interest.

Some have suggested that “he who empties the waste basket may not specify its contents,” putting the primary responsibility for disposal of all household wastes on those who operate and manage sewerage systems. The soap-products industry has not held to this point of view. We recognize that synthetic detergents should be “good citizens,” as well as good cleaners. At the same time, the homemaker has every reason to expect the most efficient products—unhampered by correctable weaknesses and lags in the handling of household wastes. This applies particularly to sewage disposal methods that would be incomplete under today's conditions, even if synthetic detergents had never been developed, or to the discharge of untreated sewage.

As a consequence, the soap and detergent industry, ten years ago, began to establish scientific facts about detergents and detergent-containing wastes as related to the broader problem of effective sewage treatment to protect streams and water supplies from pollution.

A real spirit of cooperation has grown out of the dual pathways of research initiated, on one hand, by the soap and detergent industry, and on the other, by those directly responsible for sewage treatment, water supply, and public health. Many instances of this cooperation will be found in this booklet—all pointing to improved protection for water supplies.

From its ten years of study and sponsored research on the problem of synthetic detergents in relation to water and sewage treatment, The Soap and Detergent Association has accumulated an extensive knowledge of the problems that have arisen from time to time which have been linked or attributed to its products. The Association believes the time has come when this knowledge should be made available to those interested in the subject.

This document summarizes pertinent research work by our members, by Federal and State agencies and

groups, universities, and others—some industry-sponsored and more carried on independently. Requests for additional information can be directed to The Soap and Detergent Association, 295 Madison Avenue, New York 17, New York.

Perspective on Pollution

At a recent national conference on water pollution, the Surgeon General of the United States Public Health Service, Dr. Leroy E. Burney, pointed out that the volume of fresh water used daily in the United States has increased seven-fold since 1900, and doubled since 1945.¹ The needs for 1980 are estimated at 800 billion gallons a day. A week's ration of water, at this rate, would submerge Manhattan Island to a depth of 1,000 feet.

As a consequence of this ever-increasing demand for water, reflecting both population growth and per capita increase, more and more attention is being given to the question of water re-use. For example, it is estimated that the Ohio River may be re-used four times as it flows from Pennsylvania to the Mississippi. Water supply intakes and sewage outfalls in the same stream are wedged closer together, as one city draws its water chiefly from another's wastes, wastes which in some cases are discharged with no treatment at all. The rural householder whose septic tank was once isolated in a multi-acre plot now finds his suburban neighbors constructing wells 100 feet or less away. The shopping center with its "coin-op" laundry goes up along a highway not yet served by public sewers. The falling water-table in dry areas may require the "artificial recharge" of ground water by injecting effluent from sewage treatment plants into abandoned wells.

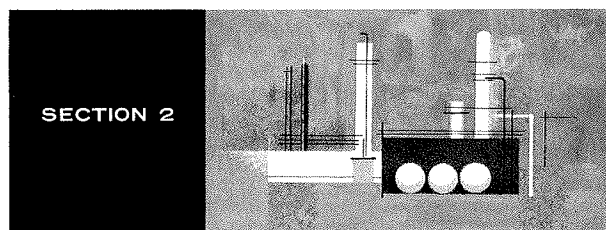
This rapid extension of water use and re-use has coincided closely in time with the increased consumption of synthetic detergents. As a result, there has been a natural tendency to equate the broad problems of water pollution with occurrences such as the appearance of foam on a local stream, ascribing the role of chief culprit to detergents. As a visual sign of increased pollution, foam has obvious photogenic appeal, and is associated by the observer with the suds he sees at home.

Yet we know that frothing problems at sewage plants existed before synthetic detergents were developed,^{2, 3} and that many substances other than detergents do cause or augment foam formation. Also, we know that on-lot wells with septic tanks in close proximity have been regarded as a health hazard for over half a century. It is essential, then, to distinguish between the overall problem of pollution, and possible specific effects for which some component of synthetic detergents can be held responsible. As the scientific reports in this booklet will show, these effects—considered apart from concurrent gross pollution—are usually correctable. They are occasionally troublesome, but offer no general threat to

public health or safety.

If a growing community is discharging its raw sewage into a local stream, for example, foaming at the outfall may simply be the outward, visible sign of a situation that would be equally menacing if the detergent content of the water were zero. Even waste water which has undergone the best of conventional sewage treatment processes has been shown to contain many "refractory" substances—entirely apart from detergent residues. Speaking of the persisting organic matter present, F. M. Middleton of the U. S. Public Health Service⁴ points out that "we do not know the composition of 65% of these components." In some such waters ABS (for definition, see page 9) may be only 10% of such total dissolved organics. Some of them (organic acids) can cause taste and odor in water at concentrations well below 1 part per million.

If the full needs for sewage treatment are to be met in an adequate way, the "detergent problem" falls into perspective as a factor of secondary importance to overall clean-up requirements. The water you drink can continue to meet high standards of safety and quality, in spite of the growing necessity for its re-use, only when all the persistent pollution, rather than a single non-toxic constituent, is the focus of advanced treatment.



SYNTHETIC DETERGENTS/WHAT THEY ARE/HOW THEY ACT

Detergents Defined

By definition, a *detergent* is anything that cleanses, including ordinary soap, the new "synthetic" powders and liquids, many alkaline materials, solvents, or even sand when used for scrubbing, whether used in the home or in industry. In popular speech, however, the term "detergent" is generally applied to packaged cleaning products used with water in the household laundry—products which exhibit "soapiness" without the disadvantages of ordinary soap when used in hard water. They were originally called "synthetic" detergents because they were first produced by a chemical synthesis more complex than the simple reaction which produces soap from fats.

Surfactant Defined

Most water-soluble cleaners (including soap) are effec-

tive removers of grease and other soil because one or more of their ingredients has the property of being "surface active." These ingredients (called *surfactants*) have a peculiar type of molecular structure (see Fig. 1.) which acts as a link between the water and the particles of dirt, loosening the dirt particles from the underlying fibers or other surfaces to be cleaned. At washing concentrations, the wash water generally contains 200-600 parts per million of surfactant. At these concentrations, the surfactants act to lower surface tension at any inter-

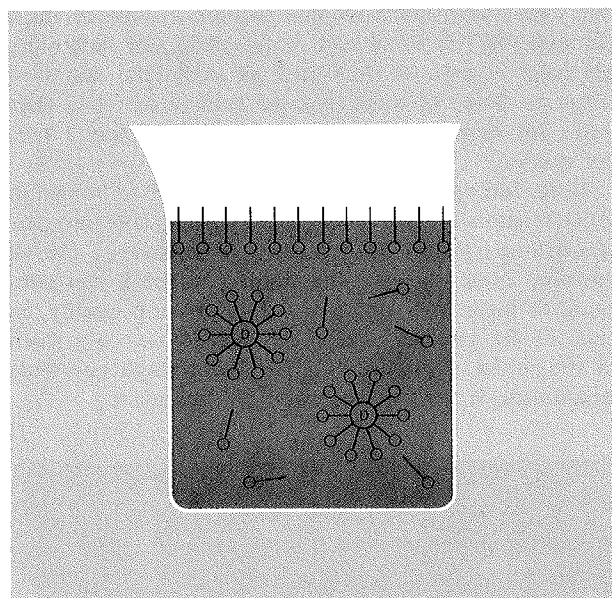


FIGURE 1 / Detergent molecules orient themselves around dirt particles (D) and at the air-water interface, according to their hydrophilic (o) and hydrophobic (l) structural groups.

face, including the air-water interface at the surface of the wash water, and they are also a cause of sudsing. However, the soil or solids in the water will preferentially attract the surfactant molecules, so that sudsing decreases as the surfactant does its work.

In ordinary soap, some 90% of the total composition of the product may be the surfactant (the sodium or potassium salts of fatty acids). Calling the entire product "soap" does not lead to confusion.

In synthetic detergent products, however, the surfactant is a much smaller percentage of the entire product—in household types less than half. This is desirable because the efficiency of surfactants for specific cleaning tasks is upgraded by the presence of "builders" which adjust the alkalinity and add to their soil-suspending power. The most common of these materials in household detergents are mildly alkaline phosphates such as pentasodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) or tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$). (See Fig. 2.)

Consequently, in referring to detergent products or their residues in waste water, it is important to distinguish between the entire synthetic *detergent*, and the *surfactant* portion which is generally measured in research studies. It is best to use the term synthetic detergent, or detergent, or syndet, for the complete product, and to use the term surfactant when only the component responsible for surface activity is being measured or discussed.

It is also important to keep in mind that the surface-active or "sudsing" properties of a surfactant at washing

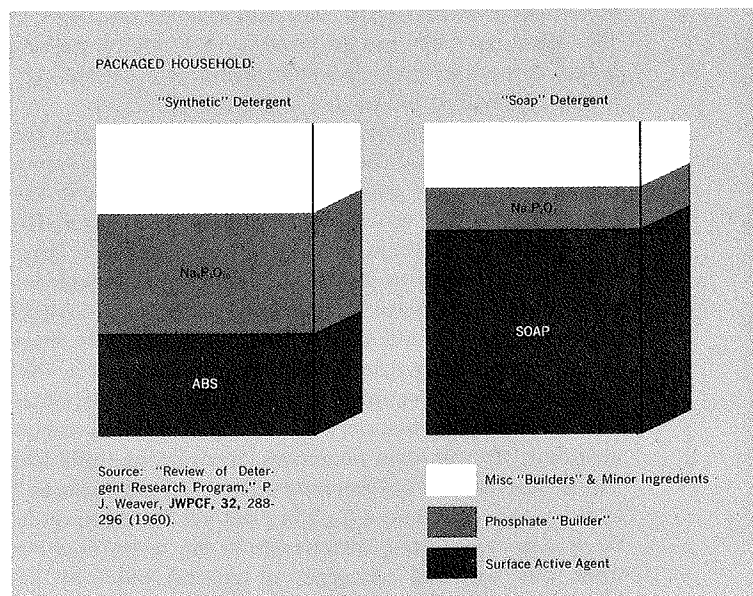


FIGURE 2 / Representation of two major types of packaged household washing products.

concentrations (200-600 ppm) has no direct relationship to its effects at a more dilute concentration of, say 10 ppm in raw sewage or 1 ppm after the effluent is discharged. Here, it has no penetrating power or effective surface-active action on soil. Its tendency to produce foam at these low levels has no relation to its sudsing power ("high-sudsing" vs. "low-sudsing") at levels of laundry use.

Identity Lost in Waste Water

After a synthetic detergent is used for a washing job, and the waste water is released down the drain, it loses its identity as formulated. Also, there are differences in the products themselves, as between one manufacturer and another, and between products for different types of duty, all of which become a "blend of residues" in waste water.

Here, then, it is not scientifically correct to talk about a detergent as such, but only about the components

which are not used up or decomposed during use. These components fall into several groups, identifiable in the waste water by their type of chemical structure—regardless of the particular detergent product from which they originated, and are discussed in these general terms below.

Surfactant Portion

Surfactants are present both in household and industrial cleaning products. While the range and variety of types having industrial use is very great, the total quantities so used are only 10 to 15% of the total volume. Furthermore, the particular function and composition of the industrial detergent may not be typical of synthetic detergents as a whole. Or surfactants may be used for functions other than cleaning. The waste disposal problems of these or any industrial processing agent can best be approached with the cooperation of the industrial plant employing them, on the basis of their composition and the volume likely to be discharged.

On the other hand, the surfactants which are employed in household synthetic detergents, or in laundries or institutions performing similar cleaning jobs, are largely of the same general type—at least on the basis of the volume significant to waste disposal. Today, the surfactant material most widely used is *alkyl benzene sulfonate* derived from polypropylene (propylene tetramer) which in turn is synthesized from petroleum or natural gas. Alkyl benzene sulfonate probably accounts for some 70% of the surfactant volume likely to be disposed of in waste water of one kind or another.

There is also a substantial amount of a somewhat similar surfactant called alkyl sulfate. As shown in Fig. 3, these two molecules, along with soap, fall into a common class called “anionics,” because once in solution, the active portions of the molecule carries a negative electrical charge identifying it as an anion. Another type of structure (Fig. 4) is typical of a “nonionic” detergent as employed in certain low-sudsing formulations. “Cationics,” used for sanitizing and softening, fall outside the field of household synthetic detergents with which we are concerned. The total volume is relatively small. Also, since their structure is such that they react with anionics, their surfactant properties will be short-lived in mixed sewage.

Alkyl Benzene Sulfonate

Alkyl benzene sulfonate (Fig. 3a) is the most important of a family of petrochemical compounds more broadly referred to as alkyl aryl sulfonates, because they combine in one molecule both an “alkyl” (non-cyclic) side chain and an “aryl” (cyclic or ring) grouping of carbon and hydrogen atoms. It has become common practice to refer to alkyl benzene sulfonate and its sodium salt as ABS, as is done frequently in this booklet. Every molecule of ABS does not have exactly the same structural

FIGURE 3 / Structure of Some Typical Anionic Detergents.

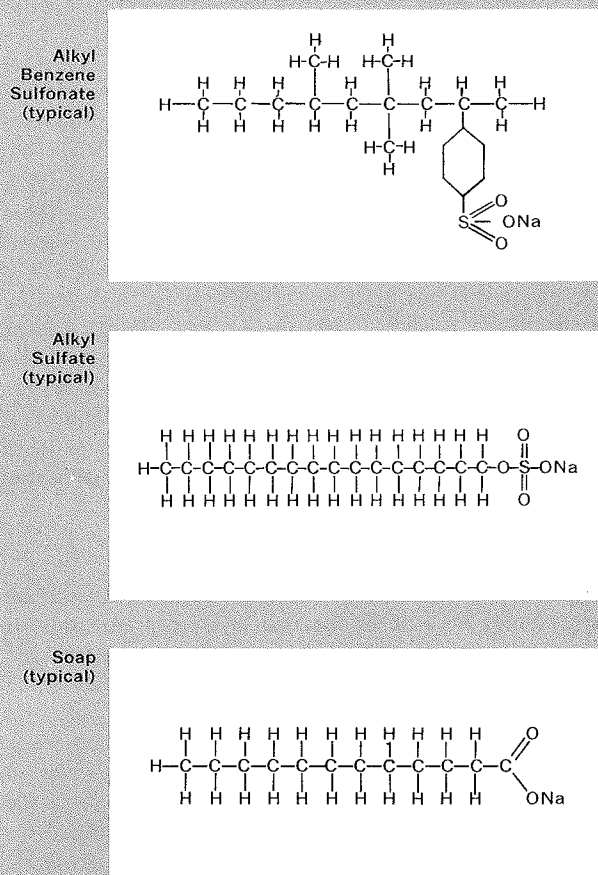
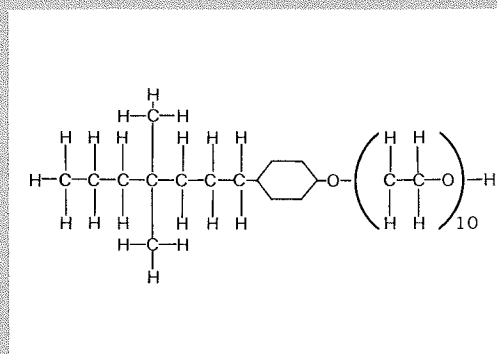


FIGURE 4 / Structure of a typical nonionic detergent.



arrangement or molecular weight, but it consists of closely related isomers or variants having the same properties. Sometimes, in the literature, the term "dodecyl benzene sulfonate" is used for this general type of surfactant, but this term is better reserved for the compound which has a C_{12} side-chain.

ABS is made by polymerizing, or linking together, molecules of propylene gas to form a chain of about 12 carbon atoms (and associated hydrogen atoms)—known as propylene tetramer. This chain is branched, rather than straight. After this tetramer is formed, a molecule of benzene is attached to the chain, probably not on the terminal atom. Next, the alkyl benzene, or alkylate, thus formed is reacted with sulfuric acid or SO_3 to give it water-soluble characteristics, and finally neutralized with sodium hydroxide to form the sodium salt. At each step, conditions of manufacture are carefully controlled to give a uniform and highly reproducible product. As described more fully in Sec. 3, *the safety of this surfactant, if ingested at the levels which have been found in waste water or drinking water, has been thoroughly established by research.* (See Appendix B.)

Alkyl Sulfate

The alkyl sulfate type of surfactant was introduced before World War II in the first synthetic detergent for hand dishwashing. Most alkyl sulfates now in use are, like soap, based on fats such as tallow or coconut oil. For these surfactants, however, the fats are first converted to the form of fatty alcohols, which are subsequently sulfated. Unlike soap, these alkyl sulfates do not form insoluble salts (or scum) in hard water. Some surfactants of this type, such as sodium lauryl sulfate, produce a generous foam at use concentrations and are particularly suitable for specialty products such as shampoos. However, due to cost and efficiency considerations, the alkyl sulfates do not have the wide range of uses or possibilities for universal application that exist for the ABS type.

Non-ionic Surfactants

This general family of surfactants is called non-ionic, because in solution the entire molecule remains associated. (Fig. 4.) It acts to orient itself with respect to soil, not by an electrical charge, but because of separate grease-solubilizing and water-soluble groups within the molecule. Non-ionics lend themselves particularly to special emulsifying and cleaning tasks in industry, where the solution may be either acid or alkaline.

Non-ionic surfactants have been developed from a wide range of chemical sources, ranging from straight chain materials such as natural fatty acids to aromatics such as phenols. The types used in some household detergents, and thus likely to find their way into domestic sewage, are typically alkyl phenols which have been given in-

creased affinity for water by a chemical reaction with several molecules of ethylene oxide.

In general, they exhibit less foam at washing concentrations than the ABS type and their use is thus one method of reducing foam-levels in automatic washers. It should be kept in mind, however, that foaming effects at *sewage* concentrations, for both non-ionics and other types of "low-foamers," does not necessarily reflect their sudsing properties during use. While non-ionics constitute about 28% of total surfactant production, according to U. S. Tariff Commission reports, their use in detergents finding their way into domestic sewage is substantially less, due to their proportionately higher industrial use.

Although public reference has been made to new sugar-based detergents, which are of the non-ionic type, these have so far confined to special industrial surfactant uses. In detergents for general household purposes, they have not yet, so far as we know, achieved acceptance as a practical answer to product improvement.

Why ABS Is Singled Out

You will note that considerably more attention is given to *alkyl benzene sulfonate* in this booklet than to the other surfactants. While this reflects the relative volume of use, it also stems from the fact that it is relatively easy to analyze for ABS when it is present in very minute amounts—even amounts that are completely undetectable in a water supply on the basis of tendency to foam. For some of the other surfactants, such as the non-ionics, no simple precise method has been found to determine the amounts still present in sewage or raw water at low concentrations. Recent carbon-adsorption and extraction techniques have revealed minute amounts of many soluble organic compounds which persist through conventional sewage treatment of waste water.⁴ Only a small portion of this total is identifiable as ABS, most being of non-detergent origin. If relative usage levels are any guide, the percentage from other detergent surfactants must be still smaller.

Degradability Defined

The fate of all waste material going down the drain and into a sewer system will depend on its amenability to decomposition or to physical removal from the "carrier" water. For waste matter which—unlike detergents—is dangerous to health, this breakdown and removal is the primary aim of sewage treatment. Breakdown of organic wastes may also take place, over some period of time or distance, in the "self-purification" of streams in which sewage is allowed to flow, and in septic tanks or the soil around them.

After a surfactant has done its job in the kitchen sink or washing machine, unreacted or unadducted residues will remain dissolved in the waste water with other soluble wastes, and some surface-active properties will persist until decomposition alters its structure to some degree, or

until it is removed.

While degradability, in some contexts, is used to mean its susceptibility to complete decomposition to compounds such as CO_2 and water, when a surfactant loses its surface-active properties, it can be considered to be degraded. This is the concept of degradability that is most useful when dealing with the effects of surfactants. Obviously, the rate at which a particular surfactant will degrade in waste water is not yet a quantitative concept, as the conditions of sewage handling and treatment will alter the relative speed and extent of degradation which takes place.

Since most conventional sewage treatment processes depend on biological action initiated by bacteria to bring about the breakdown of the other organic wastes, the term *biodegradability* has also come into use. With respect to detergents, this can be defined as the susceptibility of the surface-active properties of the product to destruction by purely biological processes.

Going beyond the elimination of surface-active effects, some consideration has also been given to the completeness of decomposition of the non-surface-active root structures of these and other organic compounds — down to the elemental level of oxidized carbon, oxidized hydrogen, etc. As indicated by British reports,⁵ the development of test methods in this area is still incomplete.

For the most part, concern for degradability (or biodegradability) has been aimed at avoiding the effects of foam. If a minute quantity of undegraded surfactant of confirmed non-toxicity derived from sewage persists at a level below that having any such objectionable effects, it becomes of secondary concern. At the same time, it may serve as an indicator of invisible concurrent pollution — such as that by hard-to-detect intestinal viruses.⁶

Degradability and Decomposition

Different surfactants vary in their rate of breakdown. Soap and other surfactants having a straight-chain structure characteristic of fats may be expected to have a fate similar to that of grease or fat from other sewage sources, so far as the action of bacteria is concerned. Because soluble soaps will also form insoluble metallic fatty acid salts in hard water, they may be precipitated, and be “degraded” in this sense, even though they are not fully decomposed.

Both degradation and decomposition are largely biological processes which certain bacteria can bring about in the presence of oxygen (aerobically) or in the absence of free oxygen (anaerobically), as in a septic tank.

For a molecule such as ABS, the breakdown is generally slower and less complete than for soap under the same conditions.⁷ Elimination of surface-active properties is more dependent on the extent and efficiency of the sewage treatment process, or time of exposure in a flowing stream. Efforts to find bacteria which will degrade or de-

compose ABS more rapidly than those commonly present in sewage treatment have not yet been successful.

Surfactants are sometimes colloquially referred to as being “soft” or “hard,” as if there were two distinct types, one quickly degradable and the other permanently resistant to breakdown. Actual die-away or biodegradability studies on ABS now show, however, that even this so-called “hard” material will be lowered by 50 to 60% in a typical activated sludge sewage plant,⁸ and that it will die away further in river water. Other persistent surfactants may be undetected by current test methods. On the other hand, in an overloaded plant or stream deficient in oxygen, the “softest” surfactant (along with grease and soil) may contribute to objectionable pollution effects.

Surfactant Analysis—A Key to the Facts

There is a natural tendency to assume that a high level of foam in a sewage plant, for example, is a measure of high levels of undegraded surfactant. Or, if well water shows signs of transient foam when drawn from the tap, its objectionable taste and odor arising from other sources may be attributed to high levels of “detergent content.”

To assess the problem scientifically, rather than by inference, the first requirement is an accurate way of knowing just how much of the materials originating in the detergent are present where undesirable effects are observed.

A constructive approach to this problem was launched in 1953 by an AWWA committee comprised of prominent scientists in the water works field. Early in its work this group focussed its attention on ABS, as the one material most likely to be identified in sewage and raw water supplies, if any residue from detergents at all is present, and they recommended that analytical methods for ABS be studied.⁹ The Soap Association's Technical Advisory Council¹⁰ took the initiative in developing such methods, and a second AWWA task group carried this work further.¹¹ (See Appendix, page 34.)

At the time, a colorimetric test using methylene blue dye had been applied here and there with somewhat questionable results. The method depends on the formation of a blue-colored salt when the methylene blue is reacted with ABS. The color of the dye, extracted in a chloroform layer, can be measured spectrophotometrically. The first job of the task groups was to standardize the method, providing a quantitative scale of values from 0.025 to 100 parts per million ABS.

Equally important was their work in establishing the extent and effect of various interfering substances, most of which were found to overstate apparent ABS levels. In most cases, ABS is not being determined in pure water, but in a complex mixture of concurrent pollutants from sewage and other sources. Just as foaming can be accentuated by components arising from sources other than detergents, so ABS readings made by colorimetric methods can give erratic or exaggerated results. In the work

of the AWWA task group, and in subsequent research, here and abroad, some of the possibilities of interference were eliminated by improvements in the colorimetric test procedure.

The real key to the facts, however, grew out of the development of a more elaborate method, using an unequivocal infra-red spectrometric technique, through the efforts of the Association's Technical Advisory Council.⁹ This method, which has come to be known as the "Infra-Red" or "Referee" Procedure, is not ordinarily used in the field. Water samples are first checked by the methylene blue test. If the apparent level is, say 0.2 parts per million* or below, no serious misjudgment is likely to result from assuming that this "apparent ABS" level is actual ABS. But if an exceptional or unexplained level of ABS is found by the simple color test, then the infra-red procedure can provide verification or correction. In several cases where colorimetric methods indicated rapidly rising levels of ABS, it was later shown by the more precise analysis that the real ABS levels gave no reason for concern. It is likely, too, that some of the exceptional levels reported in earlier literature would have been radically modified had the infra-red procedure then been in existence. The AWWA task group also recognized the value of the infra-red method, and in making its report¹¹ included both an improved methylene blue colorimetric procedure and the infra-red method. Both methods have been accepted as "tentative" in the 11th edition of Standard Methods for the Examination of Water and Wastewater.

Phosphate Builders

Aside from the surfactant present, a question naturally arises as to the fate and possible effects of the phosphate builders and the several minor ingredients present in synthetic detergents, after they have entered the waste water system.

First of all, do they persist in some form or other in the water entering a cycle of re-use? Do they affect the efficiency of sewage treatment or water treatment? Are they a factor in stream pollution, affecting fish life, algae growth, or reducing the "self-purification" of organic wastes? Finally, are phosphates from this particular source of a significant order of magnitude compared to other sources such as organic phosphates, fertilizer runoff, industrial process or natural phosphate rock or soil?

As previously mentioned, the phosphates normally employed in a detergent product are the so-called "condensed" or complex salts such as pentasodium tripolyphosphate or tetrasodium pyrophosphate. These are

known to break down to the simple orthophosphate form (salts of phosphoric acid— H_3PO_4) which are widely distributed in nature.¹² A wide range of phosphate salts—including sodium tripolyphosphate and sodium tetrapyrophosphate are included in a listing (as sequestrants) of "substances generally recognized as safe" by the Commissioner of Food and Drugs.¹³

Here again, the effort of our Association to get at the facts led to a program of research in which a study of analytical methods was the necessary first step. A test method was developed which distinguished between the natural organic phosphates and the inorganic phosphates, and between the "condensed" phosphates and the simple orthophosphate form.¹⁴

Following this program, two lines of inquiry were taken by scientists at the University of Illinois: (1) To measure the actual levels of phosphate content present in a number of typical Illinois lakes and streams, and (2) To determine the effects of these different phosphates on the coagulation and sedimentation of turbid waters—such as the raw water entering a treatment plant.

In general, the treatment project showed that the suspending power of the complex phosphates can cause a perceptible slow-down in treatment only when the amounts present exceed 0.5 ppm of P_2O_5 . Furthermore, the perceptible effect of phosphates above this level can be offset by a modest increase in the coagulant dosage.¹⁵ When the levels of complex phosphates in the Illinois lakes and streams were determined, 95% were found to be consistently below this 0.5 ppm level.¹⁶ In sewage there is a rapid conversion of the complex phosphates to the orthophosphate form, and "orthophosphate compounds produce no interference with coagulation and sedimentation."

The University of Illinois people, therefore, reported:

"The results of this investigation, which are in agreement with those reported by others, support the conclusion that troublesome interferences with coagulation and sedimentation of hard, turbid waters should not be caused by the condensed phosphate levels currently prevalent in water supplies."

So far as total stream phosphate is concerned, the work also suggests that, in many streams, other sources of phosphate such as agricultural land drainage will be an important source.

Minor Ingredients

As for the minor ingredients of packaged household detergents—perfumes, whiteners, anti-caking agents—they are largely reactive in waste water and are no more stable than the organic soil, grease and food particles that are concurrently present. Being present in very small quantities to begin with, after dilution and breakdown in the waste water, they cannot affect sewage plant or septic tank operation. Insoluble particles in scouring

*—Parts per million, or ppm, is a conventional method of expressing measurement of minor constituents in a solution. Milligrams per liter, or mg/l, is another expression which for practical purposes has the same numerical value and the terms may be used interchangeably.

cleaners, such as diatomaceous earth, are insignificant as compared to other sources of insoluble soil.

Problems Attributed to ABS

We come down, then, to the areas in which there are valid reasons to make a careful scientific study of any possible effect, direct or indirect, which one component of household synthetic detergents (alkyl benzene sulfonate) may have on the larger problem of protecting and extending America's supply of safe water.

These investigations have been brought to the fore by some of the following observations and allegations:

(1) The appearance of foam on some surface waters—particularly on streams and rivers that receive untreated sewage, or the effluent of sewage treatment plants. This is usually ascribed to detergents even though other foam-formers are present.

(2) The appearance of a slight transient foam—and measurable levels of ABS—in water from private wells, generally in areas in which household wastes are being handled in nearby septic tanks. Also, allegations of “detergent” taste and odors in well water.

(3) Increased foaming at the sewage treatment plants—along with the expressed belief on the part of some operators that plant efficiency is being lowered. In contrast, other plants are handling the same type of wastes without difficulty—indicating the need for further evaluation of plant design and operation.

(4) The presence, as revealed by sensitive chemical tests, of ABS in some public water supplies, at levels too low to have any observable effect, raising the question as to its safety from the chronic toxicity standpoint.

(5) Various allegations as to the effect of minute amounts of ABS on micro-organisms, fish and plant life.

(6) The possibility of a slow but continuing build-up of ABS from unobjectionable to objectionable levels in municipal wells and other water supplies.

(7) Septic tank troubles ascribed arbitrarily to the use of detergents.

(8) Difficulties observed in some apartment-house waste water systems (suds back-up).

(9) The problems of disposing of untreated laundry waste water in areas not served by public sewer systems.

To determine the responsibility for any such effects, the detergent manufacturers have sought out, from the start, the earliest reports of difficulties associated with or attributed to the presence of ABS. Even some isolated cases of foaming or of polluted private wells showing evidence of surfactant content, have stimulated study, on the chance that full knowledge of a single problem might help anticipate and forestall similar occurrences elsewhere. This approach is reflected in the attention which was given to obviously exceptional cases—such as that which occurred in Chanute, Kansas, in late 1956.¹⁷ Here,

prolonged drought had brought the stream which normally provides the water supply almost to a halt, and the city was forced to recycle its treated sewage effluent to the raw water intake to provide an emergency water supply. In this unusual situation, the treatment was inadequate, and ABS levels rose to 5 parts per million. Though no hazard resulted, this was well above the foam threshold, and esthetically objectionable.

Similarly, in a section of Suffolk County, Long Island, a considerable number of on-lot private shallow wells in close proximity to septic tanks and laundry establishments showed evidence of surfactant pollution as population density increased.¹⁸ The wide public attention drawn to transient foam on well waters contaminated by sewage effluent tended to obscure the fact that an essentially unsatisfactory system of water supply and waste disposal demanded correction, regardless of the surfactant content *per se*.

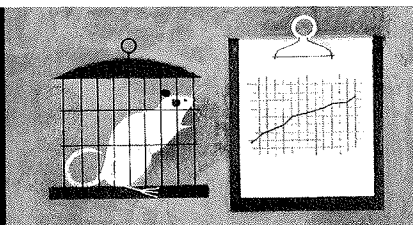
Incidents of this type cannot be taken as testimony for the existence of any nation-wide surfactant pollution problem. In 1959 and 1960, for example, the Association undertook a survey of drinking waters of 32 U. S. cities, representing one-eighth of the entire population of the country.¹⁹ Ninety-eight per cent of the samples did not exceed 0.1 ppm ABS, and the average was found to be 0.024 ppm ABS.

Reported “high-ABS-level” problems, or foaming problems, it will be noted, are the result of exceptional conditions at a relatively few locations. In some cases, they occurred some years ago^{20,21} and have never reoccurred.

Possible Solutions

In the product development work of individual companies and their suppliers, all the possibilities of adopting more easily degradable surfactants are being studied and assessed. Eventually, developments of this kind should serve to minimize the effects which have been troublesome in specific instances. *However, a “softer” surfactant, in itself, cannot make a water polluted with other wastes acceptable without treatment.* In the vast majority of cases, treatment essential to clear up gross pollution lowers even so-called “hard” surfactant residues to innocuous levels—having no significance to the acceptability of the water. Ultimately, then, we must rely on public sewage treatment and water treatment services for complete protection of our water resources. Certainly, immediate attention is needed in built-up areas where household wastes are still handled by cesspools or septic tanks, with the discharge from these units introducing pollution into the ground water—whether or not detergents are present. (See Sec. 8.) Sewage treatment services to handle any and all safe surfactants—along with removal of sewage pollution of a truly hazardous type—is the goal most likely to serve the public best.

SECTION 3



SAFETY OF WATER CONTAINING DETERGENT RESIDUES

Safety Factors

Totally aside from their possible entry into water supplies, practically all household detergents except specialties identified by a warning label are formulated so as to be non-hazardous. Their close association with food preparation and with dishes or utensils which may on occasion be improperly rinsed, precludes the use of any ingredients, residues of which would be dangerous if ingested.

With respect to alkyl benzene sulfonate in particular, a variety of investigations aimed at detecting any acute, subacute or chronic toxicity effects have been carried out with animals, and at least one with human beings. Freeman and coworkers²² fed an alkyl aryl sulfate to six men at a rate of 100 mg per day for four months, or the equivalent of 2 liters of water per day containing 50 ppm ABS. Even at this high intake, the men reported no change in weight, and only two reported any effect on their appetites.

Many other animal toxicity studies on guinea pigs, rats, dogs, etc., have been conducted and are summarized in the report, "ABS and the Safety of Water Supplies," appearing in the June 1960 issue of the *Journal, American Water Works Association*. (This report and its bibliography is reprinted as Appendix B of this publication.) As the report indicates, some studies have even shown that surfactants have a growth-promoting effect when added to animal feeds. None of these tests showed objectionable effects from ABS, even in a range of concentrations much higher than that associated with surfactant residues in water.

Generally, it has not been large accidental dosages of detergent materials which have been questioned from the health standpoint, but rather the possible effects of long-continued ingestion of trace amounts, undetectable by taste. This question has been met by several recent chronic toxicity studies.

One such study involved two separate two-year rat feeding tests on ABS.²³ Incidentally, two years is almost the full life span of the rat. In the first, levels of 0.5% and 0.1% (5,000 and 1,000 ppm) of alkyl benzene sulfonate derived from propylene tetramer, typical of that used in the manufacture of household detergents, were fed in

the diets of the test animals. In the second two-year test, the ABS was supplied in the drinking water of the rats at a level of about 0.05%. (The 0.05% level in drinking water is equivalent to 0.1% in the diet because the animals consume twice as much water as food.) The levels in both studies were administered with no significant effects and afford a more than adequate factor of safety, even assuming that as much as 10 ppm of ABS might be present in the drinking water. The authors conclude: "To the extent that animal tests provide a basis for the assay of toxicity of humans, it would appear that these investigations assure that considerable amounts of ABS (much in excess of the amounts that might find their way into the drinking water) could be consumed over long periods without harm."

Another chronic toxicity study reports the findings of two-year feeding studies of ABS at levels of 0.2% to 0.1% and 0.02% (2,000, 1,000 and 200 ppm) in the diet.²⁴ The results support those of the studies reported above, with the statement by the authors that: "No adverse effects were produced with respect to growth, food consumption, survival, hematological values, organ weights and organ: body-weight ratios. Gross and microscopic examination of tissues revealed no pathological changes attributable to the ingestions of the test material."

One further long-term feeding test, this one on dogs, is still in progress, using ABS typical of that used in the manufacture of several different brands of household detergents. This material is being fed to beagles at levels of 200, 500 and 1,000 ppm over a two-year period. At the end of twelve months the animals in the test group were comparable with the control animals in appearance, behavior, appetite and elimination.²⁵

In setting a recommended limit for ABS in water supplies at 0.5 ppm, the U. S. Public Health Service drew a clear distinction between toxic materials and ". . . substances such as chlorides and detergents that are not directly injurious to health, but might be objectionable and cause people to use other sources of supply that may not be properly protected."²⁶ In other words, they applied an esthetic rather than a health criterion to this type of material.

In time extensions and other regulations under the Food Additive Act, the U. S. Food and Drug Administration has dealt with ABS and similar surfactants employed for washing fruits and vegetables, and permits their use on the basis that, so used, they do not constitute a threat to public health.

Levels of ABS in Drinking Water

While tests of the safety of ABS have been conducted at levels of 200 ppm up to 5,000 ppm, the actual levels encountered in water intended for drinking, food preparation or recreation are of an entirely lower order of magnitude, one one-thousandth of the 200 ppm test level,

for example. Even here a distinction must be made between *typical* supplies, and the exceptional examples of water exposed to a high level of waste pollution—such as a well adjacent to the discharge of untreated laundry wastes. No one would drink waste-water, as such, for health and esthetic reasons entirely apart from detergent content.

As previously mentioned, the Association undertook a survey of drinking water of 32 U. S. cities, representing roughly one-eighth of the entire population of the country. Samples were taken in the summer during the period in which normal rainfall and run-off are low, during early winter when run-off is usually relatively low, and in the spring during the traditional high water period. Methylene blue analyses were carried out on all samples.¹⁹ The results are summarized as follows; and the locations surveyed are shown in Table I.

- 100% of the samples equal to or less than 0.14 ppm apparent ABS
- 98% of the samples equal to or less than 0.10 ppm apparent ABS
- 84% of the samples equal to or less than 0.05 ppm apparent ABS
- 68% of the samples equal to or less than 0.02 ppm apparent ABS
- 43% of the samples equal to or less than 0.01 ppm apparent ABS.

Average Apparent ABS, ppm

Summer Series	0.034
Winter Series	0.024
Spring Series	0.015

In none of these cases does the ABS at these minute levels downgrade the quality of the water in any significant or observable way. Taking 0.02 ppm as a typical ABS level, it would take 50 times this amount to show foam, and more than 1,000 times this level to be detectable by taste. Animals have been fed in their food an amount equivalent to 100,000 times this level in water each day over their life span of two years without effect.²³

These studies do not deal with shallow well-water supplies, particularly with private shallow-wells which may be located on the same lot with cesspools or septic tanks, or adjacent to streams in which raw sewage is being discharged. A few such wells have been reported with an ABS concentration of over 1 ppm, and in one location,¹⁸ some 20% of them were above 0.5 ppm—the limit recommended in the U. S. Public Health Service Water Standards. In another extensive test of well waters, 2,167 samples were tested. Sixty-eight per cent were free of ABS, 14% had trace amounts and 18% had significant amounts.⁶ Some of these wells were shown to be unsafe because of pollution not even associated with detergents,

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TABLE 1 / Occurrence of ABS in Drinking Waters

City	Approximate Population Served	Water Source	ppm Apparent ABS		
			Summer '59	Winter '59	Spring '60
Albuquerque, N. M.	97,000	Well	.04	.02	<.01
Baton Rouge, La.	126,000	Well	.02	.00	.00
Camden, N. J.	125,000	Well	.14	.02	<.01
Janesville, Wis.	25,000	Well	.01	.00	.00
Buffalo, N. Y.	580,000	Lake Erie	.01	.02	<.01
Chicago, Ill.	3,600,000	Lake Michigan	.03	<.01	<.01
Boulder, Colo.	20,000	Glacier	.01	.02	<.01
Little Rock, Ark.	105,000	Alum Fork of Saline River	.00	.00	.00
New York, N. Y.	8,100,000	Reservoirs (Catskill, Croton, Delaware River)	.00	.02	<.01
Los Angeles, Calif.	3,560,000	Colorado River	.00	.02	.00
Minneapolis, Minn.	540,000	Mississippi River	.02	.01	<.01
Burlington, Iowa	32,000	Mississippi River	.02	.04	.02
St. Louis, Mo.	860,000	Mississippi River	.02	.05	.04
Vicksburg, Miss.	28,000	Mississippi River	.03	.03	<.01
New Orleans, La.	570,000	Mississippi River	.02	.06	<.01
Great Falls, Mont.	44,000	Missouri River	.00	.00	<.01
Williston, N. D.	7,000	Missouri River	.02	.00	.00
Bismarck, N. D.	20,000	Missouri River	.01	.00	.00
Yankton, S. D.	11,000	Missouri River	.02	.02	<.01
Omaha, Nebraska	264,000	Missouri River	.05	<.01	<.01
Kansas City, Mo.	690,000	Missouri River	.00	.02	.06
St. Charles, Mo.	15,000	Missouri River	.02	.05	.06
East Liverpool, O.	31,000	Ohio River	.09	.04	.02
Huntington, W. Va.	120,000	Ohio River	.06	.02	<.01
Cincinnati, O.	634,000	Ohio River	.03	.04	.02
Louisville, Ky.	450,000	Ohio River	.06	.08	.03
Paducah, Ky.	37,000	Ohio River	.02	<.01	<.01
Hagerstown, Md.	30,000	Potomac River	.07	.02	.01
Washington, D. C.	1,000,000	Potomac River	.03	.02	.01
Pottstown, Pa.	30,000	Schuylkill River	.05	.04	.02
Norristown, Pa.	55,000	Schuylkill River	.07	.04	.04
Philadelphia, Pa.	1,100,000	Schuylkill River	.12	.04	<.01
Average			.034	.024	.015

Source: "ABS in Drinking Water in the United States" 19.

that is—bacteria present but detergent residues absent. As might be expected, where gross pollution from nearby cesspools occurs, ABS is usually one of the indicators that wastes of all types are entering the wells.

It is important to note that existence of a simple (though sometimes misleading) method of detection for ABS at levels well below 0.5 ppm has been a major factor in concentrating attention on this material. We all know that a highly acceptable drinking water is not "pure" water, in a chemical sense. Many minor constituents of such water are either undetectable or cannot be traced to a particular source. To the extent that they are (1) non-toxic; (2) non-detectable by taste, odor or appearance, they are usually overlooked or ignored. It is entirely probable that ABS below levels of 1-2 ppm would have remained in this class so far as nearly all drinking water supplies are concerned, except for the ease with which trace amounts are chemically identified.

Confirmation by Other Surveys

Another survey tending to put the problem into its proper perspective was recently (Summer 1961) completed by *Public Works* magazine. This survey was of water works officials and operators throughout the country, and 1,294 replies were received concerning their water treatment facilities and problems. Sixty of this group—less than 5% of those replying—reported that traces of synthetic detergents had been found in their supplies. Only 15 reported any observable interference with water treatment (1.2%), and only nine (0.7%) reported any consumer complaints relating to detergents.

Another questionnaire was made on individual household and farmstead water supplies. This questionnaire was distributed by the Water Treatment and Use Committee, American Society of Agricultural Engineers, and was compiled by Ronald D. Hill, Ohio Agricultural Experiment Station, Wooster, Ohio. It went to health officials, pollution control officials and sanitary engineers. Eighty-five answers to the questionnaire were received from 42 states.

In answer to the question, "What are the greatest research needs in this field?", 367 suggestions were recorded on some 20 different topics. *Only one out of this total group specifically cited "detergents."* This is in contrast to numerous votes concerning bacteriological quality, virus contamination, etc. Two other topics were: "chemical contamination" and "trace elements and their physiological effect on man." However, these topics got only 4 votes. "Detergents in well supplies" was mentioned once, but it received no particular emphasis in this list of 18 topics.

U. S. Public Health Drinking Water Standards

America faces a major problem in continuing to supply

a safe, palatable, high-quality water to a growing population. Considering all the services to which water must be put in its use and re-use, the quality of water supplies must be based on a practical standard of acceptability. As Dwight F. Metzler of the Kansas State Board of Health has stated²⁷: "Even as there is no justification for gross pollution of water, there is no need for requiring treatment far in excess of the requirements for the beneficial use of the receiving waters."

This rule of reason is of particular significance to ABS, the sensitive analytical methods for which make it possible to detect amounts insignificant from any measurable quality or health standpoint. This approach has been recognized and applied in the revision of Public Health Service Drinking Water Standards, issued July 21, 1961.²⁸

In this revision, two types of limits have been established: (1) Limits which, if exceeded, shall be grounds for rejection of the supply, and (2) Limits which should not be exceeded whenever more suitable supplies are, or can be made, available at reasonable cost.

The second of these standards has been applied to recommended limits for ABS, which are set at a level of 0.5 mg/l (ppm). While advising action to minimize the concentration of chemicals in drinking water, Omar C. Hopkins* has pointed out that "water containing as much as 0.5 mg/l of ABS would contain at least 5% water of sewage origin. The taste and odor difficulties are likely to arise from other wastes and their degradation products rather than from ABS."²⁶

Water which foams as a result of its ABS content should always be examined to be sure that it will meet acceptable standards of safety, i.e. free from sewage pollution that would be equally likely to be present, even if detergents had never been invented.

Safety of Detergent Residues Other than ABS

Although pollution by "detergents" has been cited from time to time in newspapers and other popular journals, evidence of such pollution has dealt almost exclusively with the surfactant—alkyl benzene sulfonate—because of its foam-producing effect. There are several reasons why, so long as traces of ABS in drinking water remain at an unobjectionable level, any other residues from household detergents will also be unobjectionable.

Naturally, ingredients that would be hazardous during use of the product will be excluded by the manufacturer. Additives such as perfumes, bleaches, whiteners, etc. are broken down or dissipated as quickly, if not more so, as waste matter present in sewage. Builders such as phosphates are innocuous in solution (see page 24) and other alkaline inorganic salts are quickly neutralized in

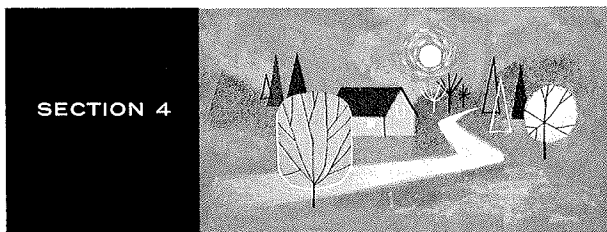
*—Chairman, Committee on Revision of Drinking Water Standards
U. S. Public Health Service
U. S. Dept. of Health, Education & Welfare

the mixed sewage, and are then indistinguishable from mineral salts naturally present in the water, or entering from surface water run-off or other sources. The mineral content from detergents carried over from sewage to a drinking water supply will be insignificant as compared to other mineral sources.

The term "foam-stabilizer," used in literature describing detergent composition, refers to certain additives generally comprising the alkylolamides (fatty acid-alkanol amine condensation products) which some producers use to stabilize the suds at washing concentrations in the presence of grease. They are relatively short-lived in waste water and are not a factor in stabilizing the foam found in sewage plants or rivers where surfactant content is 1/100 or less of that in use.

Non-ionic surfactants included in some household detergents constitute a smaller fraction of the total wastewater mixture than ABS. Here, too, types common in household products have been checked for toxicity. No reports of troublesome levels of non-ionic detergents in drinking water have come to the attention of the Association. A means of identifying low levels of non-ionics in waste water is still being sought.

The possible pollution of drinking water from a concentrated discharge of special surfactants used by laundries, textile mills, etc., is a separate question—paralleling that of any other industrial-plant waste problem, which may justify removal before the waste water is discharged. To the extent that these formulations are similar to household detergents in composition, they will constitute no threat to the safety of water supplies.



THE PROTECTION OF SURFACE WATERS

A few months ago, a prominent State Health official stated that accurate assessment of America's water pollution problem was perhaps as important as putting a man in space.¹ Part of the difficulty of assessment, no doubt, arises from the fact that our objectives are so complex.

The need to protect public health from unsafe water deserves top priority, of course, but what shall be the priorities for the conflicting industrial, recreational, agricultural and household requirements for its use and re-use? The function of water as a medium for the trans-

port and disposal of wastes is certainly a legitimate one—provided it can be accomplished without a pyramiding of objectionable effects.

The Sewage Pollution Problem

America has been slow to come to grips with the problems created by the discharge of untreated sewage directly into our streams, rivers and surrounding waters. In a recent national inventory, sewage from cities and towns occupied by 22 million persons was being so discharged. To this must be added the burden of industrial wastes entering these same waters. Voluminous evidence has been accumulated by the Senate Select Committee on National Water Resources to show the economic and social costs of this gross abuse of our surface waters.

In connection with this general problem, photographic evidence has been published showing foam on streams—particularly at the foot of a dam or elsewhere where agitation occurs. Often, the caption refers only to detergents as the pollutant. Yet, if *untreated sewage* is entering the stream, this cannot be regarded as an indictment of detergents, *per se*.

In the presence of untreated sewage, such water is concurrently polluted with bacteria, and unfit for recreational use, and the foaming (which may or may not arise from household detergents) simply provides visible confirmation of the overall abuse to which the stream is being subjected. It confirms to the public eye a danger of which health authorities were already well aware.

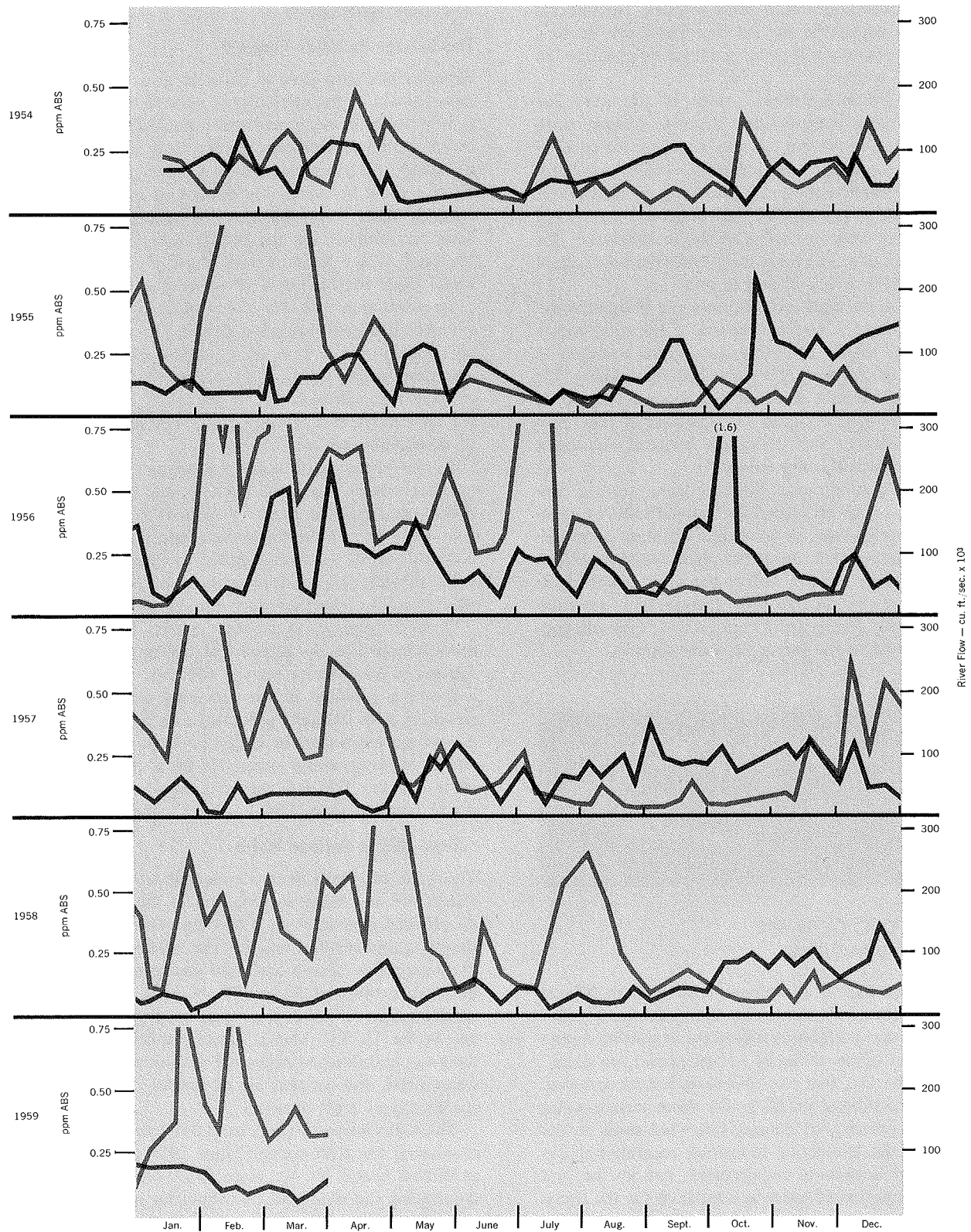
A more appropriate question is this: If sewage treatment effective in the *absence* of detergent wastes were applied to all entering sewage effluents, would there be a foaming problem in the receiving stream? In other words, is ABS uniquely persistent as a pollutant, in spite of sewage treatment, to a degree having objectionable effects in what would otherwise be a safe and wholesome stream? This is a question on which far less evidence prejudicial to ABS has been offered.

Fate of ABS in Surface Water

The bulk of available evidence indicates that surface waters are *not* being so menaced in the United States. As covered in Section 6, a modern sewage plant is not simply a transmission belt for the ABS which enters it. McGauhey has shown activated sludge treatment to remove an average of 50 to 60% of ABS, when its initial concentration is within the range occurring in raw sewage in the U. S.²⁰ This is entirely independent of the die-away and dilution occurring with time in the surface water itself, and without use of special processes aimed specifically at ABS removal.

The Ohio River at Cincinnati, for example, has been monitored for ABS content since 1954 and in addition at Willow Island, W. Va. since 1957. At the start of the monitoring the river and its tributaries received a great

FIGURE 5 / Weekly "apparent ABS" levels in Ohio River at Cincinnati, with comparable river flow data.



Source: "Monitoring the Ohio River for Synthetic Detergent Content," P. J. Weaver and F. J. Coughlin, JAWWA, 52, 607-612 (1960).

■ RIVER FLOW
■ ppm ABS

deal of untreated wastes from the populated areas it serves in addition to sewage plant effluents. The study was carefully set up at Anderson Ferry, just below Cincinnati after the river receives the effluent of the Cincinnati sewage plants, to monitor ABS at different points across the entire river.

As reported in the *Journal, American Water Works Association*,³⁰ the ABS content, as determined by the methylene blue procedure in weekly samplings over a five-year period, averaged 0.16 ppm. The variations in content of the 832 samples taken during this test are shown in Fig. 5. Ninety per cent of the time, the samples showed 0.32 ppm ABS or less. This is well below the level at which ABS can be made to cause foam, and at least 100 times less than the level at which tastes and odors attributable to ABS can be detected. There was no sign of a gradual build-up, as might be expected from increasing use of detergents during the period of observation.

The second monitoring station, set up at Willow Island in the Ohio River, furnished weekly results from December 1957 to January 1961. Here the average ABS level was also 0.16 ppm.

Other stream monitoring tests have been made on the Kaskaskia River in Illinois¹⁶ and along the Illinois Waterway, where Hurwitz studied the fate of ABS discharged from the Southwest Treatment plant of the Chicago Sanitary District.³¹ In the Kaskaskia, the ABS levels at different points were shown to be far below objectionable levels. In the Illinois Waterway, it was shown that an ABS level of 1.59 ppm in the plant effluent had died away to a level of 0.49 ppm by the time the water had reached Pekin, Illinois, some 160 miles downstream. Here, it should be noted, the plant effluent provides a substantial amount of the entire stream flow, so that die-away, rather than dilution, is clearly at work.

The U. S. Public Health Service's National Water Quality Network reports for 1958-1959-1960 include sections on "Organic Chemicals—Recovered by Carbon Filter Technique."³² Both chloroform and alcohol extractables are reported, generally on a monthly basis, for different monitoring stations. The alcohol-extractable portion from the carbon is stated to contain ABS (cited as "synthetic detergents")—though possibly only 20 to 30 per cent of it is extracted. However, since only 1 to 12 per cent of the total alcohol extractable is ABS, the preponderance of other persistent organic matter is indicated. The comparisons of the alcohol-extractable organics at seven stations on the Mississippi River, seven on the Missouri and five stations on the Ohio show that for all three rivers, a decrease occurred in 1959 from the comparable 1958 period; the decrease continued in 1960 on the Mississippi and Missouri Rivers, but showed some increase in the Ohio.

Some of the few recorded cases of surface water sup-

plies in which levels of ABS were sufficiently high to cause foam on drinking water occurred eight or ten years ago under highly exceptional conditions. These took place on the Marias des Cygnes River, in Kansas, at a time of severe drought³³ and at Chanute, Kansas, where sewage effluent was being recycled as a water supply.¹⁷

Under these special conditions, the coexisting poor color, taste and odor qualities of the water could be expected irrespective of the foaming difficulties ascribed to its ABS content. For example, the ABS content reported as responsible for foaming at Osawatimie, Kansas (1 ppm), was still well below its known taste threshold, and also below the levels which interfere with alum floc formation (see page 25). Similarly, a foaming incident at Wheeling, West Virginia, in 1953, proved to be a one-time occurrence newsworthy because of its exceptional nature, with many complicating factors suggesting that it is not reasonable to attribute the foaming effects there to detergents alone.

British Experience

Considerable attention has been drawn to the effects of synthetic detergents in sewage treatment plants and on streams from the report of the British Committee on Detergents³⁴ and subsequent progress reports of the Standing Technical Committee which has been conducting experiments to reduce the ABS concentration of the River Lee, one of the sources of London's water supply.³⁵

In Britain, the higher population density and more widespread re-use of water from streams carrying a heavy sewage-effluent load, increase the need for rapid die-away of surfactant residues. Foaming on the Lee and other such streams has occurred there even though untreated sewage is not being discharged, and levels of ABS are such as to indicate it is one source of the foaming effects. Even there, however, the problem is cited as being "limited and marginal, rather than widespread and acute" by competent technical advisors.^{34a} No foam has been detected on public water supplies as delivered to the consumer,^{34b} and no tastes are attributed to this source. Furthermore, the report states that "there is no evidence that the presence of synthetic detergent residues in raw water supplies has yet affected the purification processes at any water works in this country."^{34c}

ABS residues in streams carrying sewage effluent in the U. S. are well below the British levels. Consequently, the steps necessary to avoid objectionable effects in our streams or water supplies will not necessarily parallel British requirements. Gross pollution of our surface waters by untreated wastes remains America's big problem. As steps are taken to solve it, ABS residues as a visible sign of pollution of surface waters may be expected to drop to levels undetectable except by sensitive chemical tests, where they are not already below such levels.

Effects on Aquatic Life

So far as we can determine, there are no cases on record of fish kills in streams or lakes directly attributable to ABS or due to the toxic effects of other residues of detergents, even though extensive records of fish kills are compiled by the U. S. Public Health Service. Here again, because foam may be visible when streams are being polluted to a degree which makes fish life untenable, "detergents" rather than concurrent gross pollution have been made the whipping boy for dissolved oxygen deficiency, toxic industrial wastes, and the like.

Since 1950, a number of studies have been made of the effects of detergent residues on fish and marine organisms. A wide variation in results is shown, due to the fact that different species were used in water of different degrees of hardness, oxygen-level, etc., for various periods of time.

Direct toxic properties are expressed as the mean tolerance limit (TL_m)—the concentration which kills 50% of the fish over a 24 or 48 hour period. Reports by Henderson *et al.* of the U. S. Public Health Service;³⁶ and by Herbert *et al.* of the British Water Pollution Laboratories;³⁷ show 3.5 ppm at the TL_m limit under the most severe conditions. Herbert's tests, made on rainbow trout over a 3-month period, showed a limit in the 3 ppm range, but he pointed out that "the residues of these detergents which remain in the effluent after sewage has been treated biologically are very much less toxic than the original materials."

A recent report of the (British) Department of Scientific and Industrial Research, summarizing this work states: "It was concluded that under the conditions likely to be experienced in rivers in this country, detergent residues present no serious danger to fish."³⁸

In any event, the ABS concentrations having any lethal effect are of an entirely different order of magnitude than actually found in streams. As a typical example, 125 stream samples from the Kaskaskia River (Illinois) showed the average ABS content to be 0.078 ppm. Even the maximum ever reported in the Ohio River monitoring (0.59 ppm ABS) has an ample factor of safety.

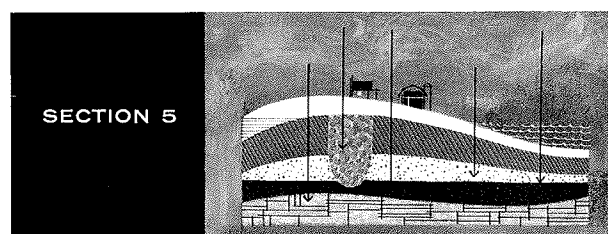
So far as the direct effects of other ingredients are concerned, Herbert reports that substances used as builders do not contribute to the toxicity of detergents, and Henderson³⁶ states that with respect to fish, "Their toxicity (ABS compounds) was apparently somewhat decreased in the presence of builders."

Effects on Algae Blooms

Still another aquatic-life problem has been the increased algae growth as a result of the fertilization effect of phosphates attributed to detergent residues.

Information is currently incomplete as to the situations in which phosphates—regardless of their source—

may act as nutrients to plant life in such a way as to reduce or eliminate fish population. It is clear, however, that the sources of this nutrient effect are necessarily far more widespread than detergent builders alone—and that here again the pollution problem cannot be dealt with on the basis of a single source. In a survey of phosphate concentration of Illinois streams,¹⁶ total phosphate concentrations were generally less than 0.2 ppm P_2O_5 in lakes and reservoirs, and less than 1.0 ppm P_2O_5 in streams receiving significant domestic sewage. The survey also showed that about one-half of stream phosphates came from land drainage, and substantial quantities from industrial sources.



THE PROTECTION OF GROUND WATER

Ground water from different sources may be as variable in its inherent quality, and in its susceptibility to pollution, as surface water. However, health authorities have been more greatly concerned with contamination of surface water—and less information is available on the factors influencing the safety and quality of underground supplies.

Contamination of Wells

Shallow wells (generally not over 50 feet in depth) may be dug, bored or driven into sand, gravel or other unconsolidated water-bearing formations. Their quality is closely interrelated with local surface water which seeps into the ground until it meets solid strata. Drilled wells which penetrate consolidated rock formations and go down to a depth of 1,000 feet may draw water from fractures or crevices in the rock, from rock basins or pores in water-bearing sandstone. While all of this water may not be of direct local surface origin, the concept of underground "rivers" flowing from sources hundreds of miles away is largely discounted today. Protection from contamination of both shallow and deep wells, whether it be a small private well or a municipal source, is thus a matter of increasing concern.³⁹

The bacteriological contamination of shallow wells is a classic field of public health study, to which many water-borne epidemics have been traced. Specific instances of the penetration of toxic chemicals, such as plating plant wastes, have also been observed—particu-

larly as they serve to establish the extent and direction of movement of water in the water-bearing sands. Innocuous dyes have been used as tracers—showing the rate and extent of the migration.

More recently, ABS has been found in well waters at several locations.⁴⁰ In some cases, the ABS content has been sufficient to result in the formation of transient foam as the water is drawn from the well or tap, and objectionable tastes and odors were said to have resulted from such ABS-containing well-water. It has been alleged, too, that well-pollution as a whole may have been stimulated by the presence of ABS or other surface-active residues.

How does the ABS enter the ground water and what is its fate in the underground water-bearing sands or rock? We know that in most of the “problem” areas, neither public sewers nor public water supplies are available. The conventional practice in these areas has been for individual households to operate septic tanks for sewage disposal on the same lots as wells used for water supply. Although standards have now been established by the Federal Housing Authority where such a combination is unavoidable,⁴¹ these standards do not apply to much past construction of shallow wells.

As vacant lots between houses are built-up, a concentration of four or more homes per acre may result—with one householder’s water well only 20 or 30 feet from his neighbor’s septic tank. This basically unsatisfactory situation comes to the attention of health authorities when householders begin to register complaints as to the declining quality of their water supply—as indicated by bad taste, odor, off-color, or tendency to foam. The latter, being visible and recognizable, is associated with detergents, which then may receive blame for all of the problems.

Due to the wide variation in septic tank design, capacity, and use, and in the sub-surface leaching system which distributes the effluent, no definite prediction is possible as to the extent to which detergent residues leave the system without having been broken down. It is true that ABS will be degraded or removed at a slower rate than soap or other materials more easily metabolized by soil bacteria. Typically, ABS may be present in the household waste water at, say, 20 ppm or more, and be detected in nearby well-water at levels of 1-2 ppm. Deepening of the well often reduces this below a level detectable by foaming.

Concurrent Tastes and Odors

The migration of ABS to wells from household septic tanks handling mixed sewage, however, cannot be considered by itself. As one report has stated: “The thought arises that even if syndets are eliminated there is no way of predicting what may next appear in the ground water.”¹⁸ This is borne out by the fact that—even where

bacteriological tests are negative—the presence of off-taste is the most commonly reported objection, *though ABS is at a level of one-twentieth of its taste threshold level*. In other words, consider a well water in which 1 ppm of ABS has been verified. Such water may, when shaken, reveal a transient foam. However, its oily, fishy or otherwise objectionable tastes and odors are no doubt due to soluble constituents other than ABS, since the taste threshold of ABS itself, even for sensitive individuals, is above 16 ppm,⁴⁰ and in some tests over 40 ppm.⁴² So far as other constituents of detergents are concerned (perfumes, for example), these may be detectable at a lower concentration than this when detergent is added to pure water, but they are no more persistent in sewage than all the other odorous organic wastes. Thus, the occurrence of bad-tasting water is evidence of *concurrent* pollution more objectionable than ABS, since—unlike ABS—its safety is unknown.

One of the reports on taste and odors due to ABS comes from the USPHS. G. Walton, Senior Sanitary Engineer, in a talk before the Annual Convention of the AWWA, May 1960, reported:⁴⁰ “Although taste or odor of water has frequently been attributed to ABS contamination, they are not due directly to this chemical. Panel tests made at the Sanitary Engineering Center showed that the odor of ABS is rarely detectable at concentrations below 1000 mg/l and that only sensitive individuals can taste it in water at concentrations as low as 16 mg/l.”

Levels of chemical content of such water—nitrate nitrogen, or chloroform extractable organics, for example—are often abnormal as well, and may point to organic contamination on a wide scale. Over 40 cases of infectious hepatitis were recently traced to an old well into which sewage had seeped.⁴³ This is a continuation of a condition existing long before detergents were invented.

One serious further question remains: Is it possible that ABS or other surface active constituents actually speed up or extend the migration of other pollutants through the ground water? Based on the physical chemistry of surfactants, at the concentrations here involved, this seems highly unlikely. Deliberate attempts to use surfactants underground, in water-flooding processes used to promote oil recovery, require far higher levels for a minimal effect. And in experiments conducted at the Robert A. Taft Sanitary Engineering Center of the U. S. Public Health Service⁵² the migration of bacteria and the migration of ABS appeared to be quite independent of one another. That is, the rate of migration of bacteria (when mixed with 10 ppm ABS solution) through a water-saturated sand column was no greater than the rate of migration of bacteria through a similar sand column, free of ABS.

So far as on-lot wells adjacent to householders’ septic tanks are concerned—while it is a fact that ABS may be

the first indicator of sewage pollution—removal of the indicator without attacking the basic problem is a questionable approach, to say the least. Furthermore, the easy assumption that any chance of foam can be eliminated from polluted well water by a change to a “softer” detergent does not necessarily stand up, if by “softer” we mean degradable under ordinary oxidative sewage-treatment processes. Even soap may not break down underground, but be precipitated out of solution as an insoluble metallic salt. Because of the inefficiency of septic tanks and cesspools, any surfactant, whether “hard” or “soft” could prove to be long-lived—even though the “softer” product was more amenable to aerobic degradation in a sewage plant.

As Professor Abel Wolman has written in the *Journal of the American Medical Association*:⁴⁴ “The current environmental problem in the thousands of private water supplies, many improperly sited and constructed, has been made more complex by the use of both on-lot water and sewerage systems in the limited space of semi-urban developments. No lasting solution to this problem exists short of public water and sewer services.”

Already in Suffolk County, Long Island, where the so-called “detergent problem” received wide publicity, the first step in establishing a public sewerage system has been taken on the basis of a 102-page need and feasibility report prepared by the County’s health and planning departments.⁴⁵

Overload of Livable Ground

An editorial by V. W. Langworthy in the November 1961 issue of *Water and Wastes Digest* is even more specific. Mr. Langworthy writes: “In metropolitan areas, such as Long Island, New York, ground water accumulation [of pollution] could get to be a serious problem, one requiring years to solve. We do not for one minute imagine that the cause of the problem is synthetic detergents, or soap, or whatever contaminant could be brought to mind. The real cause of the problem is gross overload of livable ground.”

Protecting Ground Water from Commercial Wastes

The problems resulting from disposal of household wastewater in cesspools or septic tanks have occurred in areas where population density requires a shift to public water supply and sewage systems. They are almost never exclusively detergent problems.

We have a somewhat different situation where the commercial or industrial use of detergents or other surface-active agents is involved, and a public sewer system is not available to handle it. This would be the case, for example, where a coin-operated laundry is located on an outlying highway—in the neighborhood of other homes or enterprises which depend on their own local

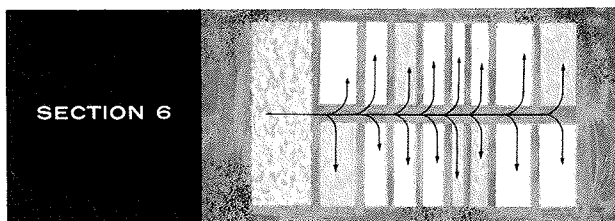
wells. A number of cases on Long Island have been cited where foaming apparently due to ABS content occurred in shallow-well water up to 400 feet from the laundry’s point of discharge.⁴⁶ Excessive alkalinity, chlorides and free ammonia, as well as ABS content, characterized these wastes.

As discussed in Section 8, the responsibility for protecting ground water from all forms of commercial pollutants, including detergent residues, must be shared by the establishment from which the wastes are being discharged. Here, means which are not available to the householder have been developed for removing excessive concentrations of any waste material prior to discharge to protect the ground water, and to comply with local regulations.⁴⁷

Ground Water Recharge

Another special situation, resulting from the exceptional water requirements of the area, can affect the quality of ground water if handled without proper precautions. This situation results when large volumes of polluted river water, or the effluent from sewage treatment plants, are deliberately returned to the ground, either by discharging into abandoned wells, or by the use of ponds from which water seeps into the ground. The purpose of such recharge is to help maintain falling water-table levels, or (along coast lines) to prevent the encroachment of salt water by reverse flow into the aquifer as wells are pumped down in times of low water.

Obviously, if the amount of ABS present in a sewage treatment plant effluent or river water which may be introduced into the ground water supply passes through the aquifers without breakdown or continuous underground dilution, then a gradual build-up of the ABS will occur, as well as a build-up of other organic or mineral constituents. At the present time, only a relatively small number of locations find it necessary to re-use sewage plant effluent directly, without permitting its movement and dilution in surface water over a sufficient time period to permit breakdown of the more slowly degradable constituents. As an exceptional, rather than a general problem, it may well call for a specially tailored solution, rather than any broad limitation on detergent composition affecting their use where no such problem occurs. Certain water reclamation processes, using high solids loading and extended aeration, give promise of an ABS reduction sufficient for this purpose. However, they are still experimental. It must be of equal concern that such plants also reduce the other refractory organics not of detergent origin which, while not a direct cause of foam, may be equally or even more objectionable to good-tasting, potable water.⁴ Special treatment methods to deal with the surfactant aspect of the problem are discussed in Section 6 (page 25).



DETERGENTS AND SEWAGE TREATMENT

The water-carriage of wastes, commonly called a sewer system, must necessarily terminate in some system of disposal. It is now agreed that some method of treatment, other than natural decomposition of sewage in water or on the ground surface, is essential to protect public health and to avoid causing a nuisance. The science of sewage treatment is currently making major advances, but the economics of paying for adequate sewage treatment facilities lags seriously behind. As a result, many sewage treatment plants are lacking in capacity or are obsolete for the population they serve. Partial treatment in an overloaded plant creates plant difficulties as well as an unsatisfactory effluent.

Effects of Inadequate Facilities

The introduction of synthetic detergents happened to coincide in time with the increase and concentration of population responsible for this overloading, and with many new types of industrial wastes. Thus, many operating difficulties that would have occurred, regardless of the type of washing products used in the home, have been attributed to the rise in the use of synthetic detergents.

Because synthetic detergents form suds so readily at dishpan concentrations (about 1,000-3,000 ppm as total product) and are known to have soil-suspending properties, there is an assumed link between these product characteristics, and the foaming and other operating difficulties which have plagued some treatment plants. It is not reasonable to extrapolate from usage concentrations to the low levels of residues which may be present in some sewage. The "high-sudgers" under one set of conditions are not necessarily the "foam-causers" under another. Fatty alcohols, for example, are foam stabilizers in certain detergent systems, but may be effective defoamers when used at lower concentrations.

Lack of knowledge about this apparent interrelationship became a matter of concern to the soap and detergent industry as early as 1954, when studies were first initiated to determine (1) the extent to which synthetic detergents might be affecting plant operation and (2) how any such problems might best be overcome.

Here again, the initial problem was to find the facts—

what were the levels of ABS and other detergent residues that sewage plants were actually handling? It was known, for example, that the methylene blue procedure for determining ABS content is subject to interferences, many of which tend to exaggerate the apparent ABS level. This is more pronounced in analyzing sewage than water. In 1956, the so-called "Referee" method for determining ABS in surface waters, using infra-red analysis, was developed.¹⁰ Later, modifications of the method were developed to arrive at an unequivocal way of determining ABS content in sewage.⁴⁸ This method is now employed as a check where methylene blue determinations are not sufficiently precise or reliable. Some of the more startling examples of apparent ABS content which continue to be cited in literature reviews occurred before it was possible to make this check.

In the course of this work, samples of raw domestic sewage from six different locations were examined, and showed a range from 3.3 to 13.8 ppm of ABS. Several other studies²⁸⁻⁴⁹ cite the typical amount present in raw sewage as 1 to 10 ppm. Polkowski *et al.*⁵⁰ reported that "A free ABS concentration of 10 mg/l is an unusually high value to expect in sewage treatment plants." These figures, of course, refer to the raw sewage, and not to the treated material.

Frothing at Sewage Plants

Do levels of ABS in the 1 to 10 ppm range cause frothing or foaming conditions in the sewage treatment plant that are more troublesome and difficult to cope with than cases of foaming that occurred prior to the introduction of synthetic detergents? A review of this situation indicated that activated sludge plants had reported that frothing had occurred from time to time before detergents were introduced, so the problem obviously cannot be attributable to detergent residues alone. Furthermore, at no time in the period after detergents were introduced did this survey show that a *majority* of activated sludge plants had a problem due to frothing in aeration tanks. Frothing appears to be a situation to which the growing use of detergents has contributed, but one which can be kept under control at most such plants handling the synthetic detergent levels resulting from household use of these products.

An extensive study of the frothing problem was conducted for the Association by Polkowski, Rohlich, *et al.*, at the University of Wisconsin, including both laboratory work and a survey of actual plant operating conditions.⁵⁰ In addition to ABS content, the following five factors were found to contribute to the frothing problem: low suspended solids concentration, protein degradation products, high temperatures, high pH, and high aeration rates.

It has been established that froth or foam "may form, or not form, under apparently identical conditions in

parallel aeration tanks”⁵¹ so that means of control other than a change in ABS content or composition can logically be sought. One test involved controlled addition of household synthetic detergent to the aeration tanks of an activated sludge plant, in amounts as high as 250 ppm over and above that normally in the sewage. No frothing or other harmful effects were evident, even with such high concentrations at this plant. On the other hand, in this plant frothing could be created at will, even in the *absence* of added synthetic detergent, by reducing mixed liquor solids to levels below 1,400 ppm.³

Control means include the maintenance of solids in the aerator at a concentration of 2,000 to 3,000 mg/l or higher; decrease in the volume or velocity of the air supplied; and the addition of oils or special defoamers to the surface of the liquid. Frequently, frothing problems have been brought under control by installing a sprinkling system over the aeration tank, using final effluent from the secondary settling tank.

It is apparent that foam, regardless of its cause, has nuisance value, particularly where plants are located adjacent to roads or populated areas—not to mention its photographic possibilities when operating difficulties due to under-capacity or other more basic causes become newsworthy, or a battle is on for more sewage-plant funds. For the most part, however, sewage plants have found ways to keep it under control, along with other potential nuisance factors that exist for this type of operation.

Of more serious concern is the impression held by some sewage plant operators that frothing in the plant is evidence of high detergent content which might mean interference with settling, thus reducing the capacity of the plant. This has been the subject of study, not only at activated sludge plants, but at smaller installations using primary sedimentation followed by trickling filters or rapid sand filters.²⁹ Primary purification processes are not affected.

So far as the effects of surfactants on sedimentation are concerned, these studies bear out the conclusions of the (British) “Report of the Committee on Synthetic Detergents,” as follows: “In practice . . . there is little evidence here or in the United States to suggest that at the concentrations at which any of these materials are normally present in sewage during sedimentation, their special properties have any adverse effect.”^{34d}

Effect of ABS on Sewage Bacteria

Studies on this question, under McKinney at MIT,⁴⁹ led to the reported conclusion that ABS, at concentrations much in excess of levels normally found in sewage, not only has no adverse effect on the bacteria in sewage-treatment plants, but may actually stimulate utilization by the bacteria of other nutrients available in the sewage. The University of California work independently came

to the same conclusion.²⁹ Furthermore, any additives of a bacteriostatic or germicidal nature included in soaps or detergents are so minute in amount compared to sewage volume that they cannot possibly affect the plant’s biological processes.

Effect of ABS on Sewage Plant Operation

McGauhey and Klein of the University of California, who studied the fate of ABS in sewage treatment, concluded: “No evidence was found in the investigation to indicate that the concentrations of ABS found in domestic sewage threaten to render the sedimentation, activated sludge or filtration units of a treatment plant incapable of performing the functions for which they are designed.”²⁹

How Treatment Reduces ABS Levels Downstream

While any effects of detergent residues on the sedimentation or digestion of *other* sewage constituents appear to be unobjectionable or correctable, the ability of the treatment to eliminate the ABS itself—rather than having it pass through into the effluent—is a matter of degree. In some instances, ABS has led to downstream problems—just as other characteristics of the effluent have done, entirely independent of ABS content. Each such problem-situation must be studied as a special case.

In a test based on radioactive tracer material,⁵³ a representative sewage plant was shown to produce the following results:

	ABS
Influent to plant.	10 mg/l
Primary effluent.	9.7 mg/l
Activated sludge effluent.	4.85 mg/l
	(4 hours retention).

Table 2 shows some other results at activated sludge plants indicating that 50 to 60% can be removed without modification of the treatment process. British results parallel this level of removal. As previously mentioned in connection with the foaming problem, the use of high solids concentrations in the aeration tanks has been the most effective step toward a lower ABS-content effluent.

Treatment involving sedimentation and trickling filters has not been found as effective in ABS removal—with 25% removal regarded as typical.

As previously discussed in Section 4, whether any problem will be presented by a sewage-plant effluent containing, say, 1 to 5 ppm of ABS, depends on the water-course into which it is discharged, the relationship of the volume of effluent to total flow, the time and distance for subsequent die-away before re-use of the water, and many other factors. Again, this is not exclusively an ABS problem, because the biochemical oxygen demand of the effluent as it enters a stream will also normally require dilution, or retention time prior to reuse in any case.

Except in highly unusual cases such as that at Chanute, Kansas, previously referred to,¹⁶ where sewage effluent was recycled to meet a drought emergency, dilution alone will bring the ABS level well below the point of foam formation, and substantial die-away will bring it to unobjectionable levels such as were determined in monitoring the Ohio River. In almost all persistent, high-foam situations on receiving streams—incompletely treated sewage appears to be the major contributory cause.

Special Treatment Requirements

One type of special situation—direct ground water recharge—has been referred to previously. Under these special conditions, more complete removal of ABS than is accomplished in a conventional plant may be economically justified. Several possibilities for such removal have been investigated, and efforts are continuing to advance their commercial practicality.

At the Los Angeles Hyperion Treatment Plant, a series of tests extending over 3 years was made to upgrade a portion of the plant effluent to make it acceptable for injection in a recharge well. ABS concentrations of about 10 ppm in the Hyperion plant influent were reduced to 4 ppm in the effluent after standard primary and secondary treatment. Then, an intermittent sand filter treatment (2 cycles per day) reduced the ABS approximately 75% to 1.12 ppm ABS. No foaming problem was encountered at this concentration.⁵⁴

It is significant that the tertiary treatment was primarily required to upgrade the water quality in other respects, to reduce BOD and avoid clogging of the injection sites.

Removal of ABS by activated carbon was studied by Renn and Barada.⁵⁴ Adsorption of ABS is effective, but the levels of carbon required suggest that treatment of raw water, rather than sewage effluent would be the preferred point, so far as municipal treating operations are concerned.

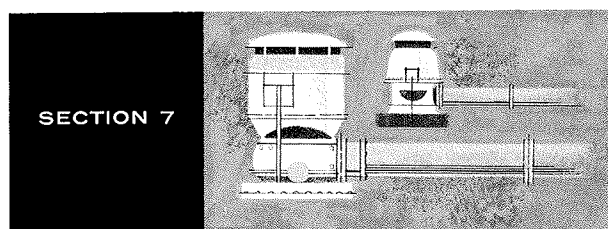
TABLE 2 / Removal of ABS³⁵ by Activated Sludge

Days	ABS In Sewage (mg/L)	Reduction (Percent)	
		BOD	ABS
1	2.25	66	75.9
4	3.8	87	48.6
6	3.8	95	54.3
7	4.0	91	54.2
8	2.2	93	57.6
11	3.8	91	68.4
13	3.9	..	58.7
14	2.6	83	47.6
18	4.0	56	37.7
19	9.0	85	48.0
20	..	85	56.3
21	8.0	..	52.3
25	4.0	96	46.2
26	3.6	90	54.6
27	4.6	74	57.6
28	..	92	60.4

From "The Removal of ABS from Sewage."⁸

By employing the well-known fact that a surface-active agent is concentrated in the froth, McGauhey and Klein¹ were able to reduce ABS levels by 85%. This procedure involves a deliberate aeration of the sewage to maximize frothing in a narrow tank, followed by stripping the froth from the surface, and its subsequent disposal. The procedure should have value in removing foam-causing constituents other than ABS. Projects sponsored by the U. S. Public Health Service⁵⁶ are continuing work on this process, and ABS removal as high as 95% has been reported.

Still another approach to the special problem is the use of ion exchange resins, in particular, a chloride cycle anion exchange resin which can remove about 350 grams of ABS per liter of resin.⁵⁷ The elution problem to regenerate the resin is currently under study.



DETERGENTS AND WATER TREATMENT

The presence of alkyl benzene sulfonate or other detergent residues in municipal drinking water supplies, or in surface water sources entering municipal water-treatment plants, has been troublesome only in a few instances where unusual circumstances existed. In water sources subject to sewage plant effluents upstream, ABS may generally be detected by chemical test, but the content is consistently below troublesome levels. This appears to be true even in Britain, where sewage loading of streams is considerably higher than in the United States. The report of the Committee on Synthetic Detergents³³ points out (p. 40) that "so far as observed effects are concerned there is no evidence that the presence of synthetic detergent residues in raw water supplies has yet affected the purification practices of any waterworks in the country."

Cohen and others studied the effect of synthetic detergents on water coagulation with ferric sulfate.⁵⁸ Their results were similar to those found with alum.⁵⁹ The surface-active agents caused no problem at concentrations of 8-32 mg/l — levels higher than those encountered except in completely untreated sewage and more than 100 times higher than any typical raw water.

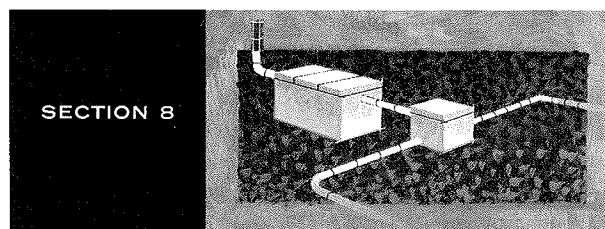
As developed in Section 5, even if ABS were to be present in raw water supplies at levels in the 0.01 to 0.5 ppm range, it has been shown to be innocuous from a health standpoint at these levels, and unrelated to taste

and odor problems arising from concurrent pollution, algae growths, etc. In dealing with such other taste and odor problems, the use of activated carbon has been developed to render water more acceptable from an esthetic point of view, in connection with the usual coagulation, filtration and chlorination processes. Extension of activated carbon dosage for the specific purpose of reducing ABS has been proposed⁶⁰ should it be necessary. This possibility is more appropriately dealt with in connection with polluted private-well water supplies, in view of the absence of actual cases of municipal raw water sources showing an ABS content having any detectable effect on taste, odor or tendency to foam.

Effects of Phosphates

The component of synthetic detergents which has been deemed most likely to have some effect on water coagulation is the complex phosphate. The University of Illinois project previously referred to was initiated to study this possibility. In addition to establishing the levels of phosphates which exist in Illinois waters, the project studied their effects on coagulation.

Laboratory jar tests and studies in a pilot coagulation unit constructed for the project showed that although complex phosphates at levels of 0.5 ppm P_2O_5 and greater may have a perceptible effect on normal coagulation and sedimentation, such interference is slight and can be overcome by simple and practical modifications, such as moderate increase in coagulant dosage or an increase in settling time. The University of Illinois study concluded: "The results of this investigation, which are in agreement with those reported by others, support the conclusion that troublesome interferences with coagulation and sedimentation of hard, turbid waters should not be caused by the condensed phosphate levels currently prevalent in water supplies."¹⁵



DETERGENTS AND SEPTIC TANKS

Two separate issues have been raised in connection with the disposal of detergent-containing wastes as a part of household sewage by means of cesspools and septic tanks. (1) To what extent, if any, do synthetic detergents interfere with the normal operation of the biological processes breaking down sewage wastes, or with the efficiency of the leaching system through which the outflow from

the septic tanks percolates into the ground? (2) To what extent do ABS or other detergent residues pass through the septic tank system unchanged, so as to enter the ground water which may subsequently convey the surfactant to wells or streams?

No Interference with Septic Tank Bacteria

While the amount of scientific information on septic tanks is limited, all of it 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, for bathing, or for other household tasks.

One of the most practical and thorough documents dealing with septic tanks is the "Manual of Septic Tank Practice"—Publication No. 326 of the U. S. Public Health Service. This booklet states: "Soaps, detergents, bleaches, drain cleaners, or other material, as normally used in the household, will have no appreciable adverse effect on the system."

The same conclusion has been reached by Harry L. Garver,⁶¹ author of "Safe Sewage Disposal for Rural Homes," and by Professor James E. Fuller, Department of Bacteriology and Public Health, University of Massachusetts,⁶² who writes: "There was no evidence that household detergents, in the concentrations likely to be present in sewage at any given time, would be detrimental to the proper functioning of septic tanks."

The May 31, 1961 "News Letter" of the National Association of Domestic and Farm Pump Manufacturers contains the following statement: "From the same source studies on synthetic detergents, the conclusion was drawn that household type syndets would not interfere with the proper functioning of septic tanks. The detergents did not interfere with the removal performance of suspended solids, nor the biological activity in the sludge, and the tendency to clog soil is about equal between soap and syndet laundry waters."

In view of the fact that a population of some 23 million is served by septic-tank installations, many of them inadequate in capacity for present-day washing practices and appliances (particularly garbage disposal units), many poorly maintained, it is not surprising that difficulties and failures will occur and be attributed to one type of waste material or another. Since heavier use of synthetic detergents has coincided with greater loading generally, a case has been made for their contribution to these troubles without specific evidence. This has been accentuated by those with "improvers" or other panaceas to dispose of who may wish to dramatize the need for their product.

Several investigators in the field have put emphasis on the need for adequate capacity to allow for increased loads of modern home appliances, such as automatic washing machines.⁶³ When this capacity factor has been

provided for, it is generally felt to be advisable to have all sanitary wastes from a household discharge to a single septic tank and disposal system. As the USPHS Manual previously referred to states: "Normal household waste, including that from the laundry, bath and kitchen, should pass into a single system."

Complaints unrelated to biological action in the tank, but attributing to detergents the scale and other insoluble deposits which tend to clog or seal off the tile fields or seepage pits, have also been made. This is difficult to accept, since detergent ingredients and their decomposition products are so largely soluble, and solubilizing in effect. Analysis of such deposits has been made and revealed no detergent solids, but rather a combination of insoluble fatty acid salts and mineral salts of hard-water origin.⁶⁴

Entry of ABS from Septic Tanks into Ground Water

At the present time, little scientific information is available which specifically traces the fate of ABS or other surfactants through the digestion system of a septic tank and in the subsurface tile fields or absorption trenches. The rate of decomposition of ABS under these anaerobic conditions is thought to be slow, on the basis of test drillings to the ground water in areas adjacent to the leaching system. As previously mentioned, because of the inefficiency of these systems even soap may not decompose completely, but simply lose its surface-active properties by forming insoluble metallic salts.

Assuming a relatively low rate of degradation of ABS in the septic tank and the soil immediately surrounding it, a question arises as to the extent of pollution of ground water to be expected from several households in close proximity having on-lot wells along with septic tanks. This is not a question of "detergent danger," but of the indication which the presence of ABS offers that sewage-polluted water is moving from tanks to wells. For even where the die-away rate of coliform bacteria may be such as to show no immediate evidence of well pollution of this type, virus migration may be potentially more dangerous than migration of the soluble constituents of organic origin detected at the well. To repeat, it is almost impossible to envision a situation in which troublesome levels of ABS are being encountered which will not also include taste and odor-producing contaminants and possibly more serious concurrent pollution, of a type which would be objectionable even in the complete absence of ABS. As Graham Walton of the Robert A. Taft Sanitary Engineering Center, U. S. Public Health Service, has stated: "Even the replacement of ABS with such biologically decomposable substances may not provide a solution to the ground-water contamination, as the major problem appears to be the other sewage substances present."⁶⁵

TABLE 3 / Minimum Safe Distances for Location of Wells

Source of Pollution	Minimum Distance (feet)
Septic tank	50
Absorption field	100 ¹
Seepage pit	100 ¹
Absorption bed	100 ¹
Sewer lines with permanent watertight joints	10
Other sewer lines	50
Drywell	50
Other	2

1 The horizontal separation between the sewage absorption system and the well may be reduced to 50 feet, only when the surface soil or subsoil receiving the sewage is effectively separated from the water supply formation by an extensive, continuous impervious strata of clay, hardpan, rock, etc. Also the well construction shall be such as to exclude surface water and sewage as effectively as did the undisturbed overlying impervious formation.

2 Recommendation of Health Authority.

The recommended minimum capacities for septic tanks are given as follows:

Number of Bedrooms	Minimum liquid capacity below outlet invert (gallons)
2 or less	750
3	900
4	1,000
Each additional bedroom, add	250

Sewage-Disposal Standards

As a part of a general delineation of minimum property standards for homes, the Federal Housing Authority⁶⁶ has recently issued specific requirements for individual water and sewage systems. This is far from being a "recommendation" for septic tanks. In fact, the general philosophy of such use is stated as follows:

"Whenever feasible connection shall be made to a public water and sewerage system."

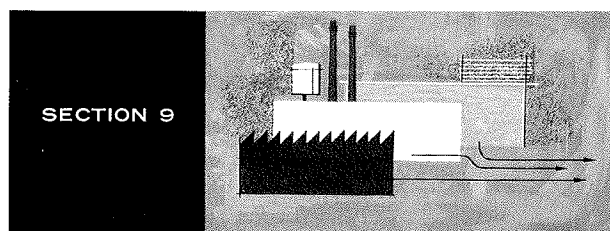
"When a public system is not available or connection thereto is not feasible, connection shall be made to a community system acceptable to the FHA field office."

"When service from an acceptable, public or community water or sewerage system is not available or feasible, and ground water and sub-soil conditions are found to be satisfactory, an individual system may be considered acceptable provided it is installed in accordance with the standards contained herein."

Minimum safe distances at which wells shall be located, relative to septic tanks and their absorption fields, are given as shown in Table 3.

Particular attention is given in the standards to the absorption beds, the type of soil in which they are located and the adequate percolation tests for these soils. It is significant that the FHA gives its grudging acceptance of this type of water supply and sewage disposal to one and two living units, and not to multiple-home subdivisions. Others⁶⁷ have gone so far as to say: "Septic tanks should be avoided whenever possible. In general, they should be used only in rural areas of large acreage, where suitable soil is available for disposal of the effluent by subsurface means."

Conformity with these principles is not predicated on difficulties caused solely by ABS, nor would their modification be expected to result from detergent materials having a higher rate of biodegradability. In fact, the indicator function of ABS, should it exceed the prescribed limit of 0.5 ppm, may be regarded as a safeguard against taste and odor-producing substances and other concurrent pollution whenever waste disposal and water systems of this kind are unavoidable.



DETERGENT WASTE DISPOSAL FROM COMMERCIAL OPERATIONS

Industrial plants or commercial establishments often have a waste problem distinct from household sewage disposal because of the unusual volume or character of the waste products involved. In general, there are advantages in combining this industrial waste with domestic sewage, and treating the combined product in a municipal plant. Where this can be done, it is becoming customary to make certain charges based on the volume and biochemical oxygen demand of the plant wastes, and also to limit, by regulation, any toxic chemicals or otherwise objectionable matter not amenable to conventional sewage treatment.

Responsibility of User Industries

Larger industrial plants, whether located within or beyond the areas served by municipal sewerage systems, of course, have invested millions of dollars in disposal systems of their own, tailored to the particular character of their waste water. Extensive information on such systems and their relation to pollution control have been compiled by the National Technical Task Committee on Industrial Wastes, Washington, D. C.⁶⁸

In fact, each major industry, such as textiles, paper, food processing, chemicals and the like, has an active program cooperating with Federal and State pollution control officials to develop and install such special systems. In some cases, such as the paper and mining industries, this activity is technically and economically a vital part of the industry's basic operations, in which millions have been spent for research on stream improvement.

To the extent that these plants utilize detergents or other surface-active products, or discharge wastes which have foam-producing effects of other origin, they may complicate or accentuate problems being ascribed to household detergent use.

Because of the wide variety of materials used in industrial plants, and their unusual concentration in some cases, it has been accepted that the responsibility here must rest with the waste creator. Technical studies in this specialized field of pollution control are beyond the scope of this volume.

However, we now find that some overlapping of effects, and of responsibility, arises with the widening use

of detergent products outside the home, and often beyond the limits of existing sewage-treatment plants. This applies, for example, to the commercial laundry, the coin-operated laundry, the car-wash establishment, etc., who may use products similar to those used in the home. The distinction here is that the relative volume of surfactant in the waste may result in hundreds of pounds per day being discharged in a concentrated area, unmixed with any comparable volume of domestic sewage.

Experience has shown that untreated waste water so discharged can cause troublesome pollution of streams or ground water, whether it contains ABS or some other surface-active agent.⁶⁹ Large industrial plants such as textile mills have found ways to cope with such problems; smaller commercial establishments such as coin-operated laundries are finding it necessary to accept a similar responsibility.

Treatment of Laundry Waste Water

According to one calculation,^{69a} a typical automatic laundry will use some 281 pounds of detergent per machine per year. Water systems are commonly designed on the basis of a flow of some 400 gallons per machine per day.^{69b} The "synthetic detergent" content as ABS of the effluents from laundramats has been estimated at 50 to 90 ppm. In most locations not served by sewers, most such laundries have discharged their waste water into various subsurface leaching systems. As can be seen from the above flow volume, this presents a percolation problem in many soils, regardless of what the waste water contains. Health Department regulations in Suffolk County, New York, now require a survey which indicates the ground water status in a strip 500 feet wide and 5,000 feet long extending from the proposed site in the direction of water flow for that area, including the location of all private wells within the area survey, as well as any public water supply wells.^{69c}

One proposed method of disposal when public sewers are not available, calls for use of tight waste tanks from which waste water is to be drawn and carted complete to approved dumping sites. This is obviously too impractical and costly for most operators.

Another study⁷⁰ showed that removals of ABS as high as 96 to 98 per cent, bringing the effluent concentrations to 1-2 ppm, could be accomplished by a combination treatment with activated carbon as an adsorbent and alum as a coagulant. However, the amount of carbon required was approximately 7 parts to 1 part ABS.

More recently, several commercial units specifically designed to filter, clarify and remove both insoluble and soluble material from laundry waste water have been introduced. Several states and certain other local health authorities have tested some of these units, and have approved their use on a basis of their removal of some 75% or more of the ABS. The pH value and biochemical

oxygen demand were also substantially reduced during the same treatment, according to these tests, upon which State approval of such units has been given.

Most of the units so far installed employ a combination of dosage with activated carbon and diatomaceous earth, subsequent filtration, or coagulation with alum, followed by clarification by flotation.

At least six companies have successful units operating in the field, and others have units under development. A list of such manufacturers as have brought their equipment to the attention of The Soap and Detergent Association will be supplied on request.

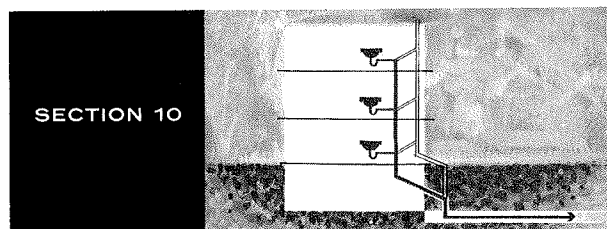
So far as laundry wastes are concerned, these are the key points which must be kept in mind:

(1) No change in detergent composition will in itself eliminate the need for laundry waste water treatment prior to discharge into ground water—particularly where well water sources are utilized nearby.

(2) Many of the so-called "detergent problems" such as the sludge formation in percolation basins or coating or blocking of tile fields are not due to the detergent composition—but to insoluble organic matter, finely divided solids, and mineral salts. This again will call for treatment—regardless of the soap or detergent used.

(3) The detergent components of laundry wastes are in themselves non-toxic and are less dangerous than accompanying pollutants of which they are an indicator.

(4) Removal of the less easily degradable detergent ingredients—along with other pollutants—from laundry wastes is becoming a practical procedure, the costs of which can be expected to decline as more efficient equipment becomes available.



SUDS BACK-UP IN PLUMBING

From time to time, apartment houses have reported the back-up of suds or waste water into sinks, laundry tubs or lavatories on the lower floors. This has been ascribed to the effects of synthetic detergents—particularly where individual apartments have automatic washing machines—but in some cases even where machines are not permitted.

Out of the many hundreds of thousands of apartment buildings throughout the country, the difficulty develops only in a relatively few cases. Thus, it more directly is

linked to the particular piping and plumbing layouts in the offending buildings than to detergent characteristics in themselves.

In most cases where this problem has been encountered previously, it has come to light due to suds backing up from soil stacks into fixtures on the first or second floor. Upon investigation of these problem installations, it has generally been found that the problem can be corrected by proper venting of the soil stack. It appears that foaming of the waste water occurs at sharp bends in the soil stack, and if this portion of the soil stack is not properly vented, a back-pressure results, causing backing-up of sanitary water into the lower floor fixtures. In quite a few instances where trouble occurred, the lower floor horizontal runs were not independently vented.

In most cases, the insertion of a vent line at the second bend where a horizontal connects into the vertical run to the main sewer may alleviate this back-up condition.

In another example, the problem was handled by inserting a 45° sloping pipe between the vertical stacks and the horizontal receiving pipes, thereby eliminating the 90° angle which previously existed.



A LOOK AHEAD

Product improvement is a tradition of the soap and detergent industry. Most of the products and ingredients now being used widely were not in existence ten or fifteen years ago. We can, therefore, expect that many of the products in use today will be displaced by further improvements in the future.

Among such improvements, a speed-up in the rate at which surface-active agents are biologically degraded under the influence of sewage bacteria would have beneficial effects, provided it could be accomplished without a serious sacrifice in cleansing efficiency or without excessive cost.

Recently, Graham Walton of the Robert A. Taft Sanitary Engineering Center, U. S. Public Health Service, put this approach in its proper perspective when he wrote: "Efforts are being made to produce biologically decomposable surfactants for use in place of ABS . . . Considerable development work on both composition and methods of manufacture will be needed before it can be determined whether such surface-active agents can compete, in detergent properties and cost, with ma-

terials in present use. Even the replacement of ABS with such biologically decomposable substances may not provide a solution to ground water contamination, as the major problem appears to be due to the other sewage substances present . . ."⁶⁵

Thus, there are some gains, but no panaceas, to be expected of this important research target of individual members of this industry. For some other pollution problems which have become associated with "detergents," few gains can be expected by any composition change—because the basic pollution problem would remain unaltered regardless of the particular cleaning compound in the waste water. Let us review each of these groups in turn: those related, and those unrelated, to the composition of the surfactant.

Factors Having Some Relation to Composition

(1) SEWAGE TREATMENT—Here, some improvement in reducing foaming on aeration tanks, etc., could be expected from products of faster rate of biodegradability where this foaming originates from detergents, although some foaming might continue to occur from other source materials. There would be no significant change in plant operating efficiency.

(2) SEWAGE PLANT EFFLUENT—More complete biodegradability of surfactants within the treatment plant would reduce the possibility or minimize the occurrence of foaming at the point where the effluent enters receiving waters. Occasionally, it might permit the earlier reuse of a raw water supply receiving such effluent, provided other "non-detergent" quality factors—taste, odor, BOD, etc.—were stepped up concurrently.

(3) GROUND WATER CONTAMINATION—A surfactant which would be degraded and lose its surface-active properties in a septic tank or other partial treatment, prior to discharge into the ground, would result in less surfactant reaching the ground water. However, even a surfactant readily degradable by conventional sewage treatment plants would probably not be entirely eliminated by the partial action of septic tanks. Nor would concurrent ground water contamination from other (non-detergent) sources be alleviated.

(4) ARTIFICIAL RECHARGE—The treatment requirements for sewage effluent to be used for artificial recharge or lagooning would be simplified so far as meeting specified limits of ABS is concerned. There would be less concern about the possibility of ABS entering municipal wells at a level detectable by transient foam at any location where recharge is necessary. Again, the potability of water from other standpoints would not be improved.

(5) COMMERCIAL LAUNDRY WASTES—Where disposal is made by underground leaching systems, costs of treat-

ment of wastes could possibly be cut. However, untreated wastes from this source could still not be acceptably discharged into cesspools, streams, etc.

Factors Having Little or no Relation to Composition

(6) ON-LOT SEPTIC TANKS AND WELLS—The danger of pollution of wells from nearby septic tanks would *not* be reduced or eliminated by a more easily biodegradable material. It would simply be the “indicator” that was being reduced or removed. Elimination of the so-called “detergent cocktail” could leave the “sewage cocktail” in its place.

(7) POLLUTION OF RECREATIONAL STREAMS AS EVIDENCED BY FOAMING—Whenever ABS reaches foam-causing levels (1-2 ppm), it is practically always an indication of (1) entry of untreated sewage or (2) sewage effluent loading levels so high as to make the stream unfit for fishing, swimming, etc. Even if the surfactant had been fully degraded within the sewage plant, and this did eliminate foaming from this source, other pollutants would still be present under these conditions.

(8) TASTE AND ODOR—A level of ABS causing taste and odor *from this source* (16 ppm or more) will never be found except in exceptional waste water or sewage unfit to drink in any case. In polluted water sources where taste and odor problems now exist, whether ABS is present at the levels which have actually been reported (say, 1 ppm) or whether it is absent, the taste and odor problem will continue.

(9) HEALTH AND SAFETY—The minute amounts of ABS in waters acceptable as raw water supplies have no chronic toxicity or other health effects. Being currently undetectable except by sensitive chemical tests, their elimination would make no significant change in water quality.

(10) AQUATIC LIFE—Present ABS is not toxic to fish or other aquatic life at levels which have ever been found in streams otherwise sufficiently unpolluted to support such life. Replacement of ABS with a more highly degradable product is not a factor of importance here. (The possible role of phosphates in stimulating algae or other plant growth is unrelated to surfactant degradability. Also, phosphates to a large measure come from sources other than detergents such as run-off from agricultural land.)

* * *

To sum up, there is a “philosophy of non-pollution” which takes the stand that any foreign material introduced into water-courses by man—regardless of its being innocuous or even undetectable by the user—is objectionable, *per se*.

The soap and detergent industry is not unsympathetic to this point of view even though its products may be

contributing only a small portion of the total load of persistent or “refractory” wastes.⁴ However, the economics of water use cannot suddenly ignore its familiar function as a vehicle for waste transport and disposal.

The responsibility for stream improvement and water quality is a joint one. Public and private efforts may make more gains by moving together toward minimization of all pollution rather than toward piecemeal elimination of a single pollutant, the elimination of which will leave the water no less objectionable for immediate re-use.

The extensive research continuing within each company in the detergent industry and within the laboratories of its suppliers, is aimed to advance this common objective along two lines: (1) to develop analytical and treatment procedures that will more successfully cope with the pollutants that have their origin in the use of water for cleaning purposes, including the removed soil and other non-detergent waste matter, and (2) to seek such improvements in composition as will more easily eliminate from treated sewage any residues of detergent products which may cause foam or be otherwise troublesome.

The protection of our water resources is a concomitant of industrial good citizenship that needs no public or legislative pressures to stimulate forward-looking soap and detergent producers. The answer lies rather in the fruits of their “research-mindedness”—applied to a difficult combination of goals: (1) New products should do the cleaning jobs for which they are designed better than their predecessor products. Any sacrifice of performance means “back to the lab” for the product’s developers. (2) Then, newly proposed products must be fully tested for safety under conditions of use or possible misuse before they are introduced. (3) Finally, the residues should ideally be as amenable to sewage treatment as anything else going down the drain.

As research work is continued—the makers of soaps and detergents and their suppliers can be expected to discharge their fully recognized responsibility to move ahead toward all of these goals as rapidly as improved technology shows the way.

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*—NOTE—The Soap and Detergent Association was formerly known as the Association of American Soap & Glycerine Producers, Inc. References to AASGP refer to the same organization.

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Journal American Water Works Association
Vol. 50, No. 10, October 1958

A / METHYLENE BLUE PROCESS

1. General Discussion

1.1. *Principle.* This process depends on the formation of a blue-colored salt when methylene blue reacts with ABS. The salt is soluble in chloroform and the intensity of color is proportional to the concentration. The intensity is measured by making spectrophotometric readings in this solvent at a wavelength of 652 m μ . The method is applicable in the 0.025–100 ppm (as ABS) range.

1.2. *Interference.* Both organic and inorganic compounds interfere with the determination of ABS. Some of the proved interferences can be predicted on the basis of chemical properties. Organic sulfates, sulfonates, carboxylates, phosphates, and phenols, which complex methylene blue, and inorganic cyanates, chlorides, nitrates, and thio cyanates, which form ion pairs with methylene blue, are among the positive interferences. Organic materials, especially amines which compete with the methylene blue in the reaction, can cause low results. Positive errors are much more common than negative when determining anionics in water.

2. Apparatus

2.1. *Graduated cylinders*, 250 ml, 100 ml, 25 ml.

2.2. *Beaker*, 600 ml.

2.3. *Separatory funnels*, 500 ml.

2.4. *Volumetric flask*, 100 ml.

2.5. *Glass wool*, pyrex filtering fiber.*

2.6. *Spectrophotometer*, either Coleman Junior,† or Beckman, Model B.‡ Refer to the instructions with the instruments. Calibration curves should be plotted by running a series of ABS solutions of known concentrations. Figure 1 shows an example of calibration curves for both types of spectrophotometer.

2.7. *Glass spectrophotometer cells.* For the Coleman, Selected Cuvettes, 6-300 A, 25 \times 105 mm; for the Beckman, Cortex Absorption Cells, 5.00 cm.

3. Reagents

3.1. *Standard ABS for calibration.*§

3.2. *Chloroform*, cp grade.

3.3. *Sodium hydroxide*, either approximately *N* NaOH, or approximately 20 per cent NaOH.

3.4. *Sulfuric acid*, either approximately *N* H₂SO₄, or cp concentrated H₂SO₄.

3.5. *Phenolphthalein*, 1 per cent in alcohol.

3.6. *Methylene blue chloride*, Eastman No. P573, or equivalent. Dissolve 0.1 g of methylene blue in 100 ml of distilled water. Transfer 30 ml of this solution to a 1-liter volumetric flask. Add 500 ml distilled water, 6.8 ml concentrated H₂SO₄, and 50 g of the monosodium phosphate. Shake until the solution is complete. Dilute to the 1-liter mark.

3.7. *Wash solution.* Add 6.8 ml of cp concentrated H₂SO₄ to 500 ml distilled water in a 1-liter flask. Introduce 50 g of monosodium dihydrogen phosphate monohydrate, ACS reagent grade, and shake until the solution is complete. Dilute to the 1-liter mark.

4. Procedure

4.1. *Preparation of calibration curve.* Prepare a standard solution by weighing an amount of the reference material equal

*Manufactured by Corning Glass Works, Corning, N. Y.

†Manufactured by Coleman Instruments, Maywood, Ill.

‡Manufactured by Beckman Instruments, Fullerton, Calif.

§Obtainable from The Soap and Detergent Association, New York.

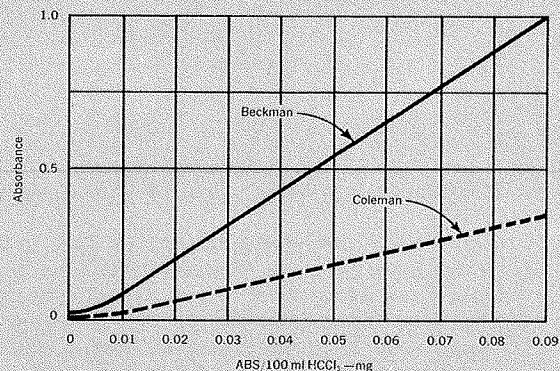


FIGURE 1 / Calibration Curves.

This figure shows an example of calibration curves plotted with the Beckman and the Coleman spectrophotometers. These curves are expressed in terms of mg ABS as the abscissa and absorbance, or optical density, as the ordinate.

to 1 g ABS on a 100 per cent active basis, dissolving in distilled water and diluting to 1 liter. Pipet 10 ml of this solution into a second 1-liter volumetric flask and dilute to volume with distilled water. Prepare a series of ten separatory funnels, with zero, 1, 3, 5, 7, 9, 11, 13, 15, and 20 ml of the dilute ABS solution, respectively. Add sufficient water to make the total volume 100 ml in each separatory funnel. Mg ABS (in 100 ml chloroform) = 0.01 \times ml of standard solution; plot mg ABS against absorbance.

4.2. *Volume of sample.* The volume of the water sample to be tested is based on the expected ABS concentration:

Expected ABS Concentration—ppm	Sample Taken ml
0.025-0.08	400
0.08-0.4	250
0.4-2.0	100
2.0-10.0	20
10.0-100.0	2

If a sample of less than 100 ml is indicated, dilute to 100 ml with distilled water; if 100 ml or more is used, extract the entire sample.

4.3. *Procedure for testing process:*

a. Make the solution alkaline by adding *N* NaOH, using phenolphthalein as the indicator. Then acidify with *N* H₂SO₄ and transfer to a separatory funnel.

b. Add 10 ml of chloroform and 25 ml of methylene blue. Rock vigorously for 30 sec and allow the phases to separate. Excessive agitation may cause emulsion trouble. Some samples require a longer period of phase separation than others.

c. Draw off the chloroform layer into a second separatory funnel. Rinse the delivery tube of the first separatory funnel with a small amount of chloroform. Repeat the extraction three times, using 10 ml of chloroform each time. If the blue color in the water phase becomes faint and disappears, add 25 ml more of dilute methylene blue.

d. Combine all extracts in the second separatory funnel. Add 50 ml of wash solution and shake vigorously for 30 sec. Emulsions do not form at this stage. Allow to settle and draw off the chloroform layer through the glass wool into the volumetric flask. Repeat the washing twice more with 10 ml of chloroform each time. Rinse the glass wool and the funnel with chloroform. Collect the washing in the volumetric flask, dilute to the mark, and mix well.

e. Determine the absorbance of the solution at 652 m μ , using a glass cell against a blank of chloroform, according to the instructions furnished with the spectrophotometer.

5. Calculation

The total apparent ABS of the sample may be calculated by the formula:

$$\text{ABS (ppm)} = \frac{\text{mg ABS from calibration curve} \times 1,000}{\text{sample taken (ml)}}$$

B/INFRARED PROCESS

1. General Discussion

1.1. *Principle.* This process involves the collection and isolation of a few milligrams of ABS and its quantitative determination based on infrared absorption of an amine complex of the ABS. Though lengthy this method is specific and accurate for low concentrations in water. When an infrared spectrophotometer is not available a colorimetric "finish" can be substituted by recovering the purified ABS and determining how much is present by the methylene blue process.

1.2. *Application.* This process is applicable to raw water samples only, not to sewage or industrial wastes.

1.3. *Precaution.* Most samples contain both solid and liquid phases, and the ABS is highly concentrated in the solid phases. For accurate analyses it is essential that the solids be either representatively sampled or excluded.

2. Apparatus

2.1. *Carbon adsorption tube.* This tube is a glass column, about 2 x 24 in., containing 100 g of carbon. Screens of stainless steel or brass, about 30 mesh, divide the carbon into sections of 20, 30, 40, and 10 g (see Fig. 2).

2.2. *Volumetric flasks,* either 2 or 5 ml.

2.3. *pH meter.*

2.4. *Buchner funnel,* 500 ml, medium porosity, sintered glass.

2.5. *Precaution.* All glassware used in the infrared process must be free of contamination. A thorough rinse with 1:1 hydrochloric acid must be used to remove adsorbed ABS.

3. Reagents

3.1. *Standard ABS for calibration.*[†]

3.2. *Carbon:*

a. *Solution for extracting carbon:* 500 ml thiophene-free benzene, 420 ml methanol, and 80 ml approximately 0.5 N alcoholic KOH.

b. *Test for impurities in carbon:* Extract 100 g of carbon by boiling 1 hr in 500 ml of thiophene-free benzene plus 500 ml of methanol. Filter the carbon, wash with 100 ml of methanol, add the washings to the remainder of the solvent mixture, evaporate to dryness on a steam bath, and weigh. The residue consists of soluble organic impurities and should be less than 10 mg, not including any residue from the solvent.

3.3. *1-methylheptylamine,* Eastman No. 2439.

3.4. *Solution for extracting ABS:* 400 mg (20 drops) of 1-methylheptylamine in 400 ml of CHCl_3 . This solution should be prepared fresh daily.

3.5. *Buffer solution:* Dissolve 6.8 g KH_2PO_4 in 1 liter of water. Adjust to pH 6.8-6.9 with 25 per cent KOH.

3.6. *Activated carbon,* unground.*

4. Procedure

4.1. *Preparation of calibration curve.* Place 25 mg of standard ABS in a 5-gal glass vessel and dilute with about 4 gal of distilled water. Mix thoroughly and, using synthetic rubber-like tubing, siphon the entire solution through the carbon column. Repeat with 20, 15, 10, 5, and zero mg ABS. Make two calibration curves by plotting the ABS added as the abscissa and the absorbances of the maxima at 9.6 and 9.9μ as the ordinate. The baseline technique is best used in determining the absorbance of the maxima.

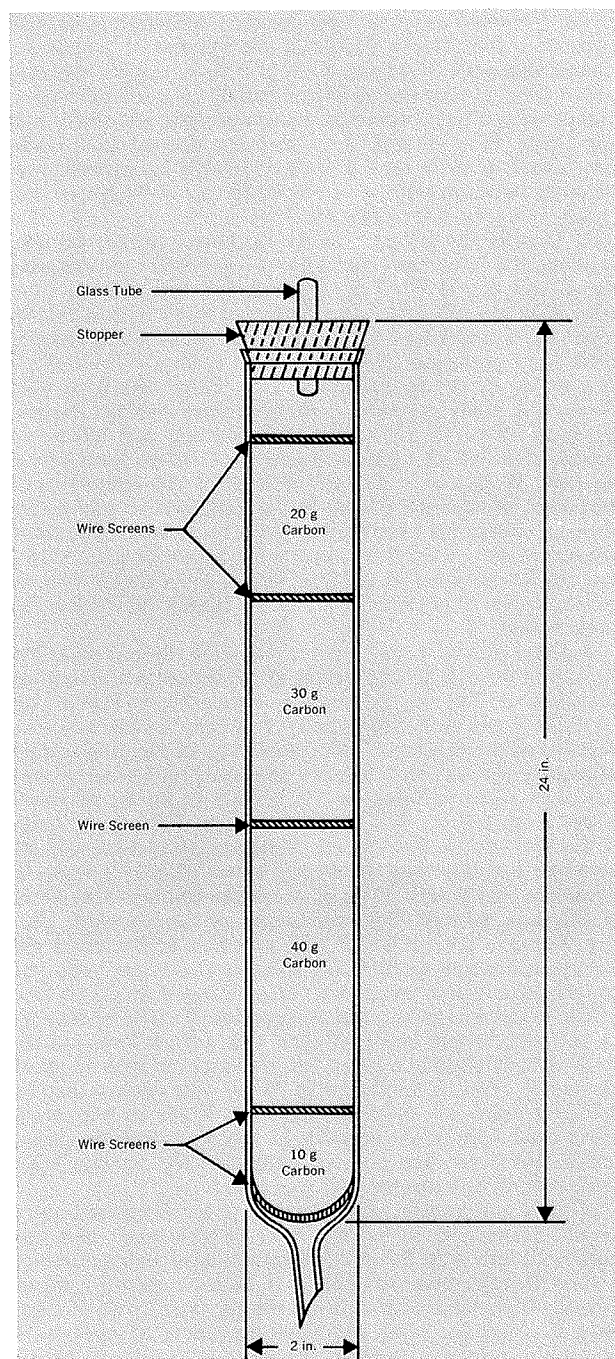


FIGURE 2/Carbon Adsorption Tube

This tube is made of glass and contains 100 g of carbon. It is used in the infrared process for determining ABS in water.

[†]Obtainable from The Soap and Detergent Association, New York.

*Obtainable from the West Virginia Pulp & Paper Co., New York.

4.2. *Volume of sample.* Estimate the concentration of ABS present in the sample. Calculate the volume of sample required to supply 10-25 mg ABS. If 2 liters or less, measure about 10 g of granular activated carbon into a 2-liter glass-stoppered graduated cylinder, add the sample, and shake well for 2 min. Filter on a medium-porosity, sintered-glass Buchner funnel. If more than 2 liters of sample is required, pass through the column of the carbon at the rate of 10 gph, or less.

4.3. *Procedure for testing process:*

a. Transfer the carbon from the Buchner funnel or column, treating the sections separately, to porcelain evaporating dishes and dry at 105-110°C. Brush the dried carbon from each dish into separate 2-liter bottles or flasks with standard-taper necks and add 1 liter of 1:1 benzene-alcohol which is 0.04 N in potassium hydroxide. Add boiling chips and reflux under an air condenser for 1 hr. Filter with a vacuum through a medium-porosity, sintered-glass Buchner funnel, draw off all liquid, release the vacuum, and add 100 ml of methanol. Stir with a glass rod and draw off the wash with a vacuum. Wash a second time with another 100-ml portion of methanol. Return the carbon to the flask, add solvent as before, and reflux for 1 hr. While making this second extraction, evaporate the solvent from the first extract and washes. Carry out this evaporation in a 2-liter beaker on a steam bath. A gentle stream of nitrogen or air on the surface will hasten the evaporation.

b. Filter off the second extract and wash the carbon as before. Add the extract and washes to the beaker containing the first extract. Discard the carbon. Evaporate sufficiently to combine in one beaker the extracts from the 20-, 30-, and 40-g sections of the column. Treat the extracts of the 10-g section separately throughout the entire procedure. After the solvent has been removed, take up the residue in 50 ml of warm water. Transfer to a 250-ml standard-taper Erlenmeyer flask. Rinse the beaker with 30 ml of concentrated hydrochloric acid and add slowly to the flask. Carbon dioxide is evolved. Rinse the beaker with 50 ml of water and combine with other washings in the flask. Reflux under an air condenser for 1 hr. c. Remove the condenser and continue boiling until the volume is reduced to 20-30 ml, transfer to a steam bath, and evaporate to near-dryness. A jet of air directed on the surface of the liquid will greatly aid evaporation. Take the solids up in 100 ml of water and neutralize with a 5 per cent sodium hydroxide solution to a pH of 8-9. Extract once with 50 ml of petroleum ether. A maximum of 70 per cent ethanol may be added, if necessary, to break emulsions. Wash the petroleum ether twice with 25-ml portions of water, discard the petroleum ether layer, and add the washes to the aqueous solution. Boil off any alcohol that was added.

d. Cool and transfer quantitatively to a 250-ml separatory funnel. Neutralize by adding dilute sulfuric acid until just acid to litmus. Add 50 ml of buffer solution and 2 drops of 1-methylheptylamine and shake vigorously. Add 50 ml of 1-methylheptylamine-chloroform solution and 25 ml of chloroform. Shake for 3 min and allow the phases to separate. If an emulsion forms, draw off the lower (chloroform) phase, including any emulsion, and filter through a plug of glass wool wet with chloroform, using suction if necessary, into a 250-ml separatory funnel. Draw off the chloroform phase into a 400-ml beaker and return any aqueous solution to the first separatory funnel. Wash the glass wool plug with 10 ml of chloroform and add to the chloroform extract.

e. Make an additional extraction with 50 ml of 1-methylheptylamine-chloroform solution and 25 ml of chloroform. Shake 2 min and separate the phases (see d), if necessary. Extract a third time with 5 ml of the amine solution and 45 ml of chloroform and a fourth time with 50 ml of chloroform.

Evaporate the combined chloroform extracts on a steam bath. With 10 ml of chloroform, quantitatively transfer the residue to a 50-ml beaker using three 5-ml portions of chloroform as rinses. Evaporate to dryness and continue heating on the steam bath for 30 min to remove excess amine. Take up the residue in about 1 ml of carbon disulfide or carbon tetrachloride and filter through a plug of glass wool in a funnel stem (2-mm bore) into a 2- or 5-ml volumetric flask. Dilute to volume through the filter with several rinsings from the beaker.

f. Transfer a portion of the sample to an infrared cell without further dilution. Run the infrared absorption curve from 9.0 to 10.5 μ against a solvent blank. Measure the absorbance of the 9.6- and 9.9- μ peaks, using base lines from 9.5 to 9.8 and 9.8 to 10.1 μ . From appropriate calibration curves calculate the concentration of ABS in the original sample. Report the values based on each wavelength separately. If infrared equipment is unavailable, a colorimetric "finish" can be used. The sulfonate-amine complex can easily be broken by boiling with aqueous alkali. After the amine has been boiled off, as indicated by a lack of amine odor, and suitable dilutions are made, colorimetric results should check well with infrared values.

g. Evaporate a 0.5-1.0-ml portion of the ABS solution on a sodium chloride flat. Record the absorption spectrum from 2 to 15 μ for positive qualitative identification of ABS.

Precaution. The carbon adsorption should be used on all samples. It separates the ABS from many of the materials present and reduces emulsion difficulties.

Note. From 10 to 50 ml of water may be lost through a 60 \times 1 cm air condenser during acid hydrolysis. This loss, while not affecting the hydrolysis, reduces the amount of water that needs to be boiled off after removal of the condenser.

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ABS AND THE SAFETY OF WATER SUPPLIES

AASGP Committee Report†

A contribution to the Journal by the Research Steering Committee of the Technical Advisory Council of the Assn. of Am. Soap & Glycerine Producers, Inc., New York, submitted by F. J. Coughlin, R. Bell, W. K. Griesinger, W. J. Jensen, J. D. Justice, W. A. Kline, E. Paulson, J. T. Rutherford, M. V. Trexler, and H. V. Moss (chairman).

Within the past 10-15 years, synthetic detergents have almost completely replaced soap in the field of heavy-duty washing products. One natural consequence of this has been the appearance of traces of detergent ingredients in sewage and, subsequently, in some surface and ground waters fed by sewage effluents. The substance most frequently encountered in water supplies is the commercial anionic surface-active agent, alkyl benzene sulfonate (ABS). Nor is this surprising, for, in terms of quantity manufactured and the number of detergent products containing it, ABS is the most important surface-active agent in use in detergents in the United States today.

The widespread use of ABS makes it appropriate to ask whether it will have any long-term effects on the health of man if consumed in trace amounts in food and water. Most of the available experimental data have been reviewed by responsible bodies or by individuals concerned with problems of public health and stream pollution. The general conclusion is typified by the views of the British Government's Committee on Synthetic Detergents,¹ who concluded that there was no evidence of ill effects from the concentrations of detergents normally found in food or water, but recommended that the possibility of long-term effects be kept under review.

It has long been known that ABS, like other anionic surface-active agents, has a low acute oral toxicity. This knowledge is based on experimentation with animals, as well as evidence of toxicity to humans through accidental ingestion. For example, the oral LD₅₀,* depending on the species of animal, is variously reported to be in the range of 1.0-2.3 g per kilogram of body weight.²⁻⁴ It is, however, the possibility of long-term or chronic effects of trace amounts of ABS which needs consideration. A possible household source of such traces, the residue left on unrinsed dishes, has been investigated.¹ Cups washed in common household detergents and drained without rinsing imparted 0.2-1.0 ppm of surface-active agent to water used to refill them. This is no more than is found in some water supplies⁵ and is below the level of detection by taste. Rinsing of the cups before they were refilled resulted in less than measurable concentrations of the surface-active agents.

Investigations With Animals

A variety of investigations aimed at detecting subacute and chronic effects of ABS have been carried out with animals, and at least one with human beings. Freeman and coworkers⁶ fed a purified alkyl aryl sulfonate to six men at a rate of 100 mg/day for 4 months, or the equivalent of 2 liters of water

per day containing 50 ppm ABS. The men experienced no change in weight, and only two reported any effect on their appetites. During the experiment, blood and urine analyses were normal. The same investigators fed ABS to dogs at a rate of 1 g/day for 6 months and to rats as 0.5 per cent of their diet for 65 days. Dosages as high as these produced no changes in weight, in the blood, or in other tissues of the animals. The ABS did not affect reproduction in the rats.

Woodward and Calvery⁴ gave ABS to guinea pigs at a 0.2 per cent concentration (2,000 ppm) in drinking water for 6 months. Although their findings were not presented in detail, the animals apparently did not exhibit toxic symptoms, and pathological examination of tissues revealed no damage due to toxic effect of the surface-active material.

Fitzhugh and Nelson⁷ made studies of both subacute and chronic toxicity to rats of several types of surface-active agents. The chronic-toxicity study did not include ABS, but when it was fed for 4 months as 0.5-1.0 per cent of the diet, the animals grew normally. Higher levels resulted in smaller weight gains, which were apparently due to decreases in the absorption of food resulting from a laxative effect induced by the ABS, rather than loss of appetite. In general, the animals showed no dislike for food containing anionic agents.

Hine and coworkers² have published the results of a variety of ABS toxicity studies, which include experiments with rats over a 6-month period. In concentrations of 1, 10, and 20 ppm in the diet, ABS had no effect on growth. In studies in which rats received up to half of the LD₅₀ dose daily for 45 days, food intake and weight gain were equal to or greater than those of controls. Histologic examinations of tissues gave normal findings.

Hopper and coworkers³ fed mice daily, 6 days a week, with one-tenth of the LD₅₀ dose of a C₁₂ and a C₁₀ ABS as well as with several other anionic, cationic, and nonionic surface-active agents. They reported one death in each group of ten mice after administration of 25 such doses of ABS. There was no comment by the authors on the possible significance of these deaths, which occurred early in the experiment. Of the various surface-active agents studied under these conditions, the ABS samples appeared to be the least toxic.

Almost all other published work on subacute effects of ABS has been done on domestic animals. These have been studies of the possible nutritional effects of detergents when added to the diet of swine or poultry. The results of work with swine are particularly relevant because of the similarity of this animal's digestive system to that of man.

The growth of weanling pigs was stimulated by 0.2 per cent of ABS in the diet over a 79-day period.⁸ Concentrations of 0.1 and 0.4 per cent ABS gave normal growth. Experiments in Germany^{9, 10} were run to test the common practice of preparing hog feed with dishwater from the kitchen.

†See note page 33.

*The LD₅₀ is the amount of substance (usually expressed in grams, milligrams, or milliliters) per unit of body weight which, on the average, will kill one-half of a group of animals of a given species under given conditions.

Groups of swine were daily fed rations mixed with 1 liter of water containing 0.15 or 0.375 per cent of one or the other of two ABS-alkyl sulfate detergent products. These concentrations were three times those recommended by the manufacturers for dishwashing. In comparison with a control group the experimental animals showed normal weight gain and feed consumption and utilization over a 5½-month period. Examination of the carcasses and internal organs and subjective analysis of the meat for any unusual taste revealed no abnormalities. In one experiment, hogs were given feed containing increasing concentrations of ABS-alkyl sulfate detergents until, at the end of approximately 7 months, they were consuming feed which had been mixed with water containing fourteen times the normal concentration of ABS in dishwater. These animals gained more weight than control animals that were given no detergent.

Metabolic studies with pigs¹¹ have shown that 99.5 per cent of an orally administered dose of S³⁵-labeled ABS was excreted within 8 days after ingestion, more than half of it appearing in the feces. Most of the ABS was excreted unchanged. The solubility of ABS is such that efficient excretion apparently does not require that it be metabolized.

There have been several articles on the growth-promoting effects of ABS in poultry rations.¹²⁻¹⁷ Workers in this area have fed ABS in concentrations up to 0.2 per cent in the diet of young chickens and turkeys, and, in some cases, they have reported growth increases of the order of 1 per cent over control fowl. None of the investigators has reported any adverse effect of ABS on the health or weight of the fowl.

Current Opinions

Several reviewers of the literature have expressed opinions on significance of trace amounts of ABS in water or food. Thus, Lehman,¹⁸ of the Food and Drug Administration, has stated that because of their low toxicity, anionic agents, including ABS, can be safely used for washing fruits and vegetables, provided that adequate rinsing follows their use. Heyroth¹⁹ stated in 1954 that the acute oral toxicities of anionics offer "no cause for alarm," but that long-term studies up to that time were inadequate to establish their safety as additives in foodstuffs. Smyth has reported the belief²⁰ that the present and anticipated levels of all the detergents that are found in rivers and streams offer a wide margin of safety, from the standpoint of any long-term effects of ingestion in drinking water. The British Government's Committee on Synthetic Detergents has concluded¹ that there is no evidence pointing to any serious acute toxic effects from anionic (or nonionic) detergents. The committee further stated that published experimental data do not show ill effects from chronic exposure to detergents in food or water — an exception being gastric irritation, which may interfere with food absorption when excessive levels are fed — but recommended that the possibility of long-term effects be kept under review. AWWA Task Group 2661 P, in reporting on detergents in water supplies,^{21, 22} has expressed a viewpoint similar to that of the British committee. The Food Protection Committee²³ has concluded that there are no toxic effects common to all surface-active agents, and that surface activity is not a measure of toxicity.

Stokinger and Woodward²⁴ have stated recently that the anionics, as a group, are practically nontoxic, although alkyl aryl sulfonates are more toxic than other anionics. The authors suggest that "mildly toxic" organic compounds should be assigned a limiting concentration of 500 ppm in water. Although the term "mildly toxic" was not defined by the authors, ABS might be put into this or some lower-toxicity category. It is interesting to note that maximum ABS levels in sewage reaching disposal plants are reported to be less than

one-thirtieth of this limit, or approximately 15 ppm,^{22, 25-27} and would therefore be much lower in rivers which receive sewage in either the raw or the treated form.

Conclusion

Various investigators have considered the possible oral toxicity of ABS from the standpoint of its short-term and long-term effects. The results all indicate that man and animals can tolerate relatively high concentrations of ABS in drinking water or food without ill effect. Even in feeding studies in which concentrations of ABS reached high enough levels to produce noticeable effects, the effects generally took the form of temporary gastrointestinal disturbances resulting rather from the irritant action common to all soaps and anionic detergents than from any true toxic effects.

Although future surveillance of the whole situation is, of course, desirable, it seems definite at this time that, based on a conservative assessment, ABS can be consumed at concentrations at least several times those presently found in drinking waters without producing any long-term, physiological effects.

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