

1930's (17) demonstrated the interconversion of saturated and monounsaturated acids by isotope labelling. These considerations make it conceivable that the difference between the abilities of land animals and fish to synthesize polyunsaturated acids is simply one of degree.

There still remains to be explained the differences between the level of the polyunsaturated fatty acids of fresh water and marine forms. Lovern (8) has indicated that this difference is also found in the zooplankton indigenous to those environments. The data in Table I indicate that within the limits imposed by normal variations between species and the limits of the analytical procedures no differentiation can be made between fresh water and marine forms after diets containing cottonseed and menhaden oil, that is, the differences within the two experiments with mullet and within the four species of fresh-water fish are as great as the differences between the mullet and the fresh-water fish. One can therefore conclude that, at least for the fish studied, the differences exhibited by the fresh-water and marine fish in their natural habitat are caused by differences in their natural diets. It is probable that this difference lies ultimately with the phytoplankton of those environments. A report of the work done in this laboratory on this problem is now in preparation.

### Summary

Four kinds of fresh water fish were captured in the young stage, maintained on a low-fat diet for about two months, and either continued on that diet or transferred to test diets containing 10% cottonseed or menhaden oil for about five weeks. The fish were then sacrificed, and their total body fatty acids were examined for relative amounts of 2, 3, 4, 5, and 6 double bonds. It was found that no significant change from the natural diet occurred in the fatty acids on

the low-fat or cottonseed oil diets while on the menhaden oil diet the fatty acid composition changed to resemble the composition of that oil.

These changes differed from those of the marine mullet in that the body fat of the latter lost much of its naturally occurring polyunsaturated acids, when placed on the low-fat regimen, and regained it on the menhaden oil diet.

### Conclusion

1. Both marine and fresh-water fish appear able to synthesize polyunsaturated though not necessarily essential fatty acids from nonfatty precursors.

2. The differences between the fatty acid composition of the body fat of marine and fresh-water fish largely result from differences in their dietary fatty acids.

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## Research on the Effects of Detergents (Alkylbenzenesulfonates and Phosphates) in Sewage Systems. A Progress Report<sup>1,2</sup>

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IN 1956 about 700 million pounds of synthetic surface-active agents were produced in the United States. Combined with the appropriate quantities of polyphosphates, the commercial syndets are eventually discharged into the country's sewers and sewage-treatment plants. Sewage-treatment plant operators occasionally see foam in the treatment basins. Aided by publicity in the lay press, the notion has come into being that the detergents seriously interfere with efficient treatment of sewage. The detergent question is only one of the many problems which have arisen during the past few years to challenge the water-works and sewage-treatment people. Detergents are only one of the many chemical, organic, and bacterial substances which find their way into surface waters from municipal sewage effluents or industrial wastes, or which might result from the natural plant and animal processes which take place in surface waters.

The program established by the American Associ-

ation of Soap and Glycerine Producers is aimed at learning something of the effects of formulated detergents on sewage and water treatment. Most of the formulated detergents consist of two principal components: the organic surfactant and inorganic phosphates. The most widely used organic active is sodium alkylbenzenesulfonate, ABS. The research projects have therefore been concerned with the effect of the two principal components, ABS and phosphates. In particular, the questions which these projects have sought to answer are these.

1. Do the complex phosphates find their way into natural water supplies? If so, does their presence interfere with the usual water-purification processes?
2. In addition to possible effects on drinking water, what effects, if any, do phosphates and ABS have on aquatic life?
3. What is the fate of ABS in the actual sewage-treatment process? How much is there in the effluent from the treatment plants?
4. Is the presence of ABS responsible for the frothing which is occasionally observed in treatment plants? If so, can the treatment be modified to reduce or eliminate this phenomenon?
5. Is there any truth to the belief that ABS interferes with

<sup>1</sup>This report covers work supported by the American Association of Soap and Glycerine Producers.

<sup>2</sup>Presented at the fall meeting of the American Oil Chemists' Society, September 30, 1957.

the biodegradation of sewage? Is the ABS itself subject to bacterial degradation?

6. Are there available reliable and practical methods for the analysis of ABS and phosphates in water at extremely low levels? If not, can they be developed?

A preliminary investigation of the analytical problem revealed that existing methods, which are still used to a large extent, are subject to naturally occurring positive interferences and hence do not give reliable results. These methods are based on colorimetric extraction techniques. A new and reliable method for the analysis of ABS in water is now available however as a result of the efforts of an AAS&GP subcommittee for the analysis of ABS. The concentration of ABS in surface water is rarely above 1 p.p.m. The new method works satisfactorily in this range. Unfortunately this method is rather time-consuming, involving adsorption of the ABS on a carbon column, removal from the column with alkali, followed by various extraction steps, which remove further interferences, and finally identification of an ABS-methyl heptyl amine complex by infrared absorption. A modification of this method, in which the adsorption on carbon has been eliminated is now under study by the committee. Both of these methods are long and require infrared equipment. A research project has therefore been initiated at the University of Southern California under O. H. Miller for the development of a short analytical method for the determination of ABS in sewage and water. The goal of this work is the development of a method which will be quick enough and simple enough to be used routinely in sewage-treatment plants.

In addition to the subcommittee on ABS, the AAS&GP formed a subcommittee for the analysis of phosphates. The importance of a reliable and practical method capable of measuring and differentiating between orthophosphate, inorganic condensed phosphates, and organic phosphates at fractional parts per million is self-evident. This is the concentration which may reasonably be expected in a study of the problems associated with phosphates from formulated detergents that enter surface waters. Such a method was not available at the time the various research projects were initiated. As a result of the efforts of the Phosphate Advisory Subcommittee of the AAS&GP such a method has now been developed and proved out by collaborative analyses on a variety of natural waters. This method is now being prepared for publication.

### Projects

To study the presence of phosphates in natural waters, an investigation at the University of Illinois was undertaken with the objective of determining first, the level and variety of phosphates that exist in natural Illinois waters and second, the effect of such levels upon water-purification procedures. A survey has been completed of one Illinois stream, a reservoir, and a typical drainage basin (the Kaskaskia). It showed that the over-all average phosphate content is surprisingly low—0.65 p.p.m., calculated as  $P_2O_5$ —with the Kaskaskia river averaging 0.37 p.p.m.  $P_2O_5$ , of which less than 50% is present as polyphosphates.

In order to estimate proportions of the total phosphate resulting from sewage effluent and land drainage, data were obtained at a number of sampling points above and below sewage-treatment plants. It was found that a considerable amount of phosphate

comes from agricultural land drainage. At times this far exceeds the amounts contributed by sewage effluents, consisting in part of detergent phosphate residues.

Since it was of interest to know in what form the phosphate exists, studies on the degradation of polyphosphates were undertaken. It was found that the degradation of polyphosphates proceeds faster in natural unfiltered waters than in filtered, natural, or distilled water. Reversion of polyphosphates has also been shown to take place faster in some natural waters than in others although both may have originated from the same sampling point at different times. Increasing temperature, as expected, accelerates reversion.

This information served to select realistic phosphate levels for the second part of the investigation which dealt with coagulation phenomena. Small-scale experiments were made by employing tripoly, pyro, monosodium, and disodium orthophosphates in concentrations of 1.37 to 5.48 p.p.m. as  $P_2O_5$ , which is considerably higher than the levels found in natural Illinois waters. In these studies it was found that it was never necessary to use more than 12 p.p.m. of alum to reduce residual turbidity to acceptable levels. As would be expected, at low alum dosages, polyphosphates interfere with coagulation somewhat more than simple orthophosphate. Many of these observations have been reported by Jesse C. Dietz at the Purdue Conference in May 1957.

Under the direction of P. H. McGahey and E. S. Crosby a study has been undertaken at the Sanitary Research Engineering Laboratory of the University of California of the fate of ABS during the sewage-treatment process. This has extended over roughly two years. In these experiments the ABS was tagged with sulfur-35, and its progress through the treatment was followed with the usual radiological monitoring instruments. It was found that only 2–4% of ABS is removed from sewage in the primary settling tanks but that considerable degradation of ABS is brought about by activated sludge. The maximum degree of reduction obtained with present methods is about 55–60%. Alkyl sulfate is more readily degraded by activated sludge than ABS. The studies at the University of California are sufficiently encouraging to give reason to hope that higher reduction of ABS may be possible by modification of the treatment process. The AAS&GP is continuing sponsorship of this research.

In a project at MIT, under the direction of Ross McKinney, the emphasis is somewhat more on the biological aspects. Thus far, no pure bacteria cultures have been found which are capable of completely degrading ABS. On the other hand, it has been firmly established that sewage bacteria decompose a portion of the ABS, and thereby a major part of the ABS entering a sewage plant can be made to disappear through biodegradation.

There is also some evidence that ABS induces or accelerates utilization by bacteria of other nutrients available in sewage. This is a significant factor in favoring growth of the many varieties of bacteria commonly present in sewage. These bacteria, it has been shown, are not detrimentally affected by ABS, in concentrations far in excess of levels normally found in raw sewage. Neither in a modified sewage-digesting system nor in Warburg studies was there

any evidence of build-up of an intermediate that blocked degradation of continuously added ABS.

Having established that ABS is not toxic to sewage bacteria, that there is no apparent build-up of an interfering residue, and that under favorable conditions a major portion of ABS can be biologically degraded, investigations have been undertaken to accomplish maximum ABS degradation in actual practice. These experiments were conducted in a modified activated sludge system in which biological population and activity are maintained at a constant and maximum level. Such a system depends upon continuous, uniformly distributed addition of waste to vigorously agitated sludge from which, by means of suitable design, waste solids are continuously removed. Such a system is referred to as a Hi-Lo system.

In laboratory experiments with natural as well as synthetic sewage, ABS removal efficiencies of 60–80% have been demonstrated. The higher efficiencies were achieved when a high level, 5,000–6,000 mg./l., of mixed liquor, suspended solids was maintained.

Because of these favorable findings, attention has been given to the proper hydraulic and biological design through study of small-scale models. Engineering data for design of a full-scale prototype have been developed, and MIT has, under independent study, an investigation of such a Hi-Lo system on a full scale.

### Frothing

The problem of frothing in sewage treatment tanks has often been ascribed to the presence of synthetic detergents. To study this problem the Soap Association maintains a project at the University of Wisconsin under the direction of G. A. Rohlich. The official title of the project is: "Frothing in Sewage Treatment, Its Causes and Elimination." This has been a most difficult problem to approach. As many plant operators have observed, local operating conditions and environment influence the degree of frothing. As a result, the variations within any plant and from plant to plant have made it difficult to separate the various physical, chemical, and biological conditions which might contribute to the frothing.

The project was started by attempting to determine whether a problem does indeed exist. A questionnaire was distributed to several hundred activated sludge-treatment plants in the United States. The majority of replies indicated that frothing occurs, to some degree, and that it is most prevalent during the periods of low flow and weak sewage strength. It is important to note however that a large majority of those who reported frothing felt that it had no effect on plant efficiency. In many plants the amount of frothing was not troublesome. Also a substantial number felt that factors other than detergents were involved.

As a first step in evaluating the problem on a small-scale laboratory basis, a foam meter was developed by which frothing persistency can be measured accurately and reproducibly. With this device several common chemical constituents of sewage were studied to determine which were the most important in their effect on froth formation.

A large proportion of the total amount of ABS present in a given mixed liquor sample is adsorbed or otherwise associated with the activated sludge solids. The remainder is "free" or in solution. It has

been assumed that the compounds most likely to contribute to frothing are those which are "free," consequently the evaluation of the various compounds has been restricted to those in solution. This does not, of course, preclude the possibility that certain physical properties, such as suspended solids concentration, might also influence the extent of frothing of a particular mixture.

These significant points were noted under laboratory conditions.

1. Certain organic solutions common to sewage, particularly those containing proteinaceous breakdown products, give a stable froth when aerated. ABS by itself will also produce some froth, if present in sufficiently high concentrations. The most stable froth however results from the combination of ABS with proteinaceous breakdown products; the total volume and the persistency are greater than the sum of the froth produced by each component alone. Concentrations of about 3 p.p.m. of each of "free" ABS and organic nitrogen would seem to be sufficient to produce a stable froth.
2. As the aeration of the activated sludge sewage-sample continues, the amount of "free" ABS present in the mixed liquor decreases.

### Field Investigations

As a follow-up to these laboratory studies a number of field investigations were undertaken at various activated sludge sewage-treatment plants. In addition, some larger bench-scale laboratory studies were made. In all of these tests the following determinations were made: ABS, pH, ammonia-nitrogen, organic nitrogen, biological oxygen demand, electrode potential, suspended solids, and temperature. Frothing of the various mixtures was evaluated under static and dynamic conditions. All of these findings were combined, and statistical evaluations were conducted on an IBM computer. Both simple and multiple correlations were obtained.

Preliminary interpretation of these data indicate correlation of frothing and ABS, also between frothing and the ammonia nitrogen. To a lesser extent there would appear to be a positive correlation between frothing and BOD, and frothing and temperature. There was no strong correlation between frothing and organic nitrogen, as was indicated by the preliminary laboratory tests. This could be explained, of course, if the nature and composition of the organic nitrogen were different in the two cases.

Low values of froth persistency correlated with high values of suspended solids, suggesting that increasing suspended solid levels should decrease frothing. This, of course, is an effect which has been observed in a number of plants.

Based on the experience gained on this project during the first two years of its existence, a third-year project has just been started with the emphasis on finding methods which make it possible to control or eliminate frothing.

There remains, at this point, one other aspect to be reported on, that is, the ABS which emerges as part of the effluent from sewage-disposal plants. Two problems are under study in this connection. One is the removal of ABS from potable waters by modification of conventional sewage- and water-treatment processes. This project is under the direction of Charles Renn of the Department of Sanitary Engineering and Water Resources of The Johns Hopkins University. While the project has not been underway very long, some very interesting results have been obtained. For example, it has been possible to demonstrate that fine

bubble aeration and the skimming away of the resulting foam will significantly reduce the ABS concentration in the mother liquor. This finding is presently being further investigated under varying conditions of aeration, using waters of different mineral content.

The second problem in connection with ABS in sewage-treatment plant effluents concerns the effect of ABS on aquatic life. This project is maintained at the Philadelphia Academy of Natural Sciences under the direction of John Cairns and Ruth Patrick. Their interest is the determination of the tolerance of aquatic life for alkylbenzenesulfonate. The organisms under test are bluegill fish, snails, and diatoms. This project, too, has been under way for a relatively short period only. Preliminary results indicate that the lethal dose of ABS in both hard and soft water is many times greater than maximum concentration ever recorded in any lakes or streams.

### Summary

Several university research programs on the effects of alkylbenzenesulfonate (ABS) and condensed phosphates on water-treatment plants and sewage-treatment plants are reviewed. Methods of analyzing for very small amounts of these materials have been developed. The concentration of condensed phosphates in surface waters was determined, and it was found that even at several times these levels the effect on normal water-treatment procedures is slight. In sewage treatment plants the presence of ABS is only one of the factors in the frothing problem. Ammonia nitrogen, BOD, and temperature are also involved. Most of the ABS entering an activated sludge process is biologically degraded, and it has no toxic effect on sewage bacteria. At the levels found in surface waters ABS does not have a toxic effect on aquatic life.

[Received April 10, 1958]

## Report of the Color Committee, 1957-1958

THE WORK of the Color Committee of the American Oil Chemists' Society during the 1957-58 year has been confined to the revision of Method Cc 13b-45 and to the acquiring of the necessary data for publishing an article on the standardization of Lovibond glasses, which appeared in the March, 1958, issue of the Journal of the American Oil Chemists' Society. The article appearing in the Journal is self-explanatory and resulted from a decision made at the New Orleans meeting in May, 1957. A copy of the revised method for the determination of color follows. The Color Committee recommends the amended procedure to the Uniform Methods Committee for adoption.

A meeting of the committee was held on April 20, 1958, to discuss a program for 1958-59.

R. C. STILLMAN, chairman

Sampling and Analysis of Commercial Fats and Oils  
A.O.C.S. Official Method Cc 13b-45

(Corrected Nov. 1947, revised Oct. 1952, revised Nov. 1953,  
revised Oct. 1955)

### COLOR

Wesson Method, Using Lovibond Glasses Calibrated in Accordance with N" Scale.

**Definition:** This method determines the color by comparison with glasses of known color characteristics.

**Scope:** Applicable to all normal fats and oils, providing no turbidity is present in the sample.

#### A. APPARATUS

- Colorimeter.** The instrument consists of a light-proof box with a dull black interior, illuminated by a 100-watt blue frosted Mazda electric light bulb. A block of magnesia  $1 \times 2\frac{3}{4} \times 3\frac{3}{4}$  in. is placed in the instrument at the proper angle to reflect the light from the electric bulb vertically upward through the color tube and color glasses. Thinner magnesia blocks may be used in combination with a spacer to give the 1-in. total thickness. An eye piece finished with a dull black interior is fitted over (outside) the rectangular top of the tube holder so that the light passes through the color tube and color glasses. Eye pieces with split fields are not permitted. The tube holder (1 in. i.d.) is fitted with  $\frac{1}{16}$  in. i.d. rings at the bottom. One ring is to retain the color tube containing the oil sample, and the other is to permit an equal amount of light to reach the color glasses.

- Wesson Type.** Wesson type of colorimeter, constructed as shown in the illustration.
  - Stevenson.** The Stevenson colorimeter conforms to the above specifications for the Wesson Colorimeter and is approved. See Oil and Soap, 13, 18-20 (1938).
  - Lovibond Tintometer, Model 14A.** The Lovibond Tintometer, Model 14A, conforms to these specifications and is approved when operated according to the manufacturer's instructions.
- Color Booth.** The colorimeter is maintained in a booth or cabinet, not less than 40 in. wide and 30 in. deep. The booth or cabinet is closed so that no external light can enter. The inside of the booth is painted a dull neutral gray of Munsell value 4. The booth is illuminated by a 15-watt daylight bulb, mounted 48 in. above the colorimeter box in an indirect fixture so that no direct rays strike the colorimeter or the eye of the reader. The level of illumination in the booth, at top of the box of the colorimeter, is to be not less than 1, nor more than 5 foot candles.
  - Color Glasses.** Color glasses shall be calibrated to conform to the National Bureau of Standards N" Scale. Glasses may be calibrated by the Electrical Testing Laboratories or may be compared against a standard set calibrated by the Electrical Testing Laboratories or the National Bureau of Standards. The method of comparison shall conform as nearly as possible with that outlined in Bureau of Standards Research Paper 653, p. 274. The minimum standard set shall consist of the following numbers of red and yellow glasses:

Red:

0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1.0	2.0	2.5	3.0	3.5	4.0	5.0	6.0	7.0
7.6	8.0	9.0	10.0	11.0	12.0	16.0	20.0	

Yellow:

1.0	2.0	3.0	5.0	10.0	15.0	20.0	35.0	50.0	70.0
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Glasses above 1.0 red need not have the exact value shown in the table but should cover the same range.

**Caution:** Keep the color glasses clean and free from oil film. Handle carefully and protect against scratches. It is especially important that every color glass be clean at the time of use.

#### 4. Color Tubes.

- Description.** Color tubes of clear, colorless glass with a smooth, flat polished bottom and of the following dimensions: length 154 mm. over-all, inside diameter 19 mm., outside diameter 22 mm.