pect of helping where individual septic tanks and cesspools are involved is not so bright for the near future.

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

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

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# Foreign Requirements and Developments in Biodegradability

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

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

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

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

Now the purification of river water to make it potable involves the removal of contaminants by methods such as flocculation and precipitation. It was conceivable, of course, that synthetic detergents if they were present in the intake to these river water works could act in opposition to the aims of such water treatment. The level of synthetic detergents in the intake in the early 1950's of water from the River Thames and the River Lee which are purified to provide public water supplies for much of the London area was in the order of one-half part per million, and at this level certainly the committee agreed was not sufficiently high to cause trouble. The 1956 final report of the Jephcott Committee so stated, and further stated that except as regards foam production at some sewage works, the risks and difficulties to which the use of synthetic detergents appeared to be giving rise at sewage works in rivers and at certain of the water works were limited and marginal rather than widespread and acute. Nonetheless, this committee recommended the establishment of a permanent standing technical committee in Great Britain on synthetic detergents. This recommendation was agreed to by the government, and in January 1957 such a committee was set up to "keep under review the difficulties or risks of difficulties arising in sewage works, rivers and water supplies in the use of synthetic detergents" (6). Under Committee sponsorship, full scale trials were run on various phases of the problem, the largest in scope being the trials begun at Luton in the summer of 1958. This ambitious trial was undertaken to test the value of the only inexpensive biodegradable material that their investigation had uncovered. The material was a development of the earlier work in Holland, and was a derivative of wax-cracking, a straight chain alkyl benzene sulfonate now familiar under the Shell name of DOBANE® JN. Many operational problems were encountered in these trials. For example, where every store in a large urban area was supplied with detergents based on a straight chain alkylate as contrasted with the previously used propylene tetramer based alkylate, it took much longer than anticipated to eliminate the propylene tetramer based product from use in the area. After almost a year it appeared that considerable quantities of propylene tetramer based material were still coming into the area and, therefore, upsetting the experiment.

Nonetheless, over a 2-year period in which time the use of 73% of detergent based on the hard alkylate in the area had been eliminated, the Luton effluent fell from 3 to 2 ppm of alkyl benzene sulfonate. This was sufficient to have a marked effect on the amount of foam observed on the river. It was calculated that with 100% replacement of hard alkylate by a partially soft alkylate, such as the DOBANE material used in the Luton trial, one could expect to reduce the concentration of detergent in the final effluent from the Luton sewage works to rather less than half the value observed when only hard detergents were present. It was estimated that this level would then be around 1.3 ppm. It was felt that this was sufficiently promising to issue a recommendation that as much as possible of this material should be used in preference to a hard propylene tetramer based alkylate throughout the U.K. An improved DOBANE JN grade is now being made and this, at present, accounts for about 70% of the total U.K. use of detergent alkylate.

In summary, the 1961 report of the committee states that in experimental treatment plants 68% of the detergents based on hard alkylate and 94% of that based on the soft alkylate can be removed. In a full scale plant it was shown that, although the removal of 68% of the hard material could be achieved on occasions when plants were operating under ideal conditions, the largest removal of the early type of soft DOBANE product was 80% and not the 94% expected. This is thought to be due to the fluctuation of flow through treatment plants during peak periods giving conditions far from ideal. It is worth remarking that the differences between the "hard" and the partially soft detergents have been much more marked in highly loaded and less efficient plants which appear unable to deal as well with detergents based on propylene tetramer alkylates as they are with those based upon soft alkylate.

The 1962 report went further still and this is an important point to illustrate how in the English situation there is a great deal of cooperation on the part of the government and industry, both the raw material suppliers and the soap and detergent manufacturers, and how this cooperation yielded concrete action. The 1962 report made a recommendation that the use of soft alkylate be extended to the present full capacity of the industry and there has indeed been a voluntary shift within the limit of product availability to the use of a straight chain alkylate in household products. As a result of this shift, the foaming problem in sewage in England has been greatly alleviated. It has not, however, been entirely eliminated and it can be anticipated that there will be continued cooperation on the same basis as in the past. It is also worth noting that the soft material used in England today is markedly more degradable than the early experimental/commercial products and that further significant improvements are already in sight as a result of additions to the original manufacturing plants.

The second country in Europe to take a leading role in the study of the use of soft synthetic detergents was Germany. The change from soap to syndets first created a problem in Germany when there was an extremely hot and dry summer in 1959 and many rivers carried only sewage or sewage effluent. Great publicity was given in the German newspapers to pictures of large mountains of foam that built up on the waterfalls and locks of medium-sized rivers such as the Neckar, the Main and the Ruhr. In a short time, the detergent foam problems became a political issue and a special industry/government committee was set up to study the problem (7). At the present time, the problem in Germany is much more serious than it is in England and far more serious than any similar type problem in the U.S. for two reasons. First, the per capita use of water in Germany is around 40 gal per day as compared with 150 gal in the U.S.; and second, the dilution capacity relative to household and industrial effluent is much lower in Germany. The streams serving the Ruhr area which contains about one-third of German industrial capacity are stated to have an annual low flow only about one-quarter as great as the Delaware's low flow record.

The river water situation in Germany shows a striking difference. For example, tests on the lower Ruhr River in the neighborhood of Essen showed the detergent concentrations to be as high as 3 mg per liter. In the U.S. the Ohio River at Cincinnati has been monitored since 1954. The sampling locations were set up below the point where the city sewage plants delivered their effluent. The average detergent content has been 0.16 mg per liter, and 90% of the samples showed 0.32 mg per liter or less. One exceptionally high reading during 1956 showed 1.6 milligrams per liter (8). A level of 1.6 mg per liter is about the same as was reached in Essen's drinking water during 1959 (9).

Again a point of difference, as a result of the low dilution factor in Germany whereas the ABS in raw sewage going to a U.S. treatment plant will generally run well under 5 mg per liter, in one large area of Germany with 90 treatment plants, one-quarter of the plants have an influent of over 10 mg and concentrations in the influent have been recorded as high as 20–25 mg per liter.

The Germans therefore had a problem which they felt was very severe and they chose to react to this problem with legislation. In November of 1960, legislation was proposed which, after several committee sessions, resulted in the "Law of Detergents in Washing and Cleaning Compounds" of September 5, 1961. A special German executive order was to establish by June 30, 1962, the test method for the determination of biodegradability, the minimum biodegradable requirements to be specified in these tests, and also fix the exact date of the switch-over to soft detergents. Regulations under this order were issued after a delay of five months and published in September 1962. As previously mentioned, a German detergents committee had constituted itself when the foam difficulties began. The government asked their assistance in developing a method for the determination of biodegradability. The method adopted is a fully standardized activated sludge process carried out on laboratory scale. The sewage in this case is a standardized artificial sewage solution to which such a quantity of the detergent is added until this "synthetic sewage" contains about 20 ppm methylene blue active substance. This is about the maximum amount of anionic detergents found in municipal sewage. One liter per hour of this "synthetic sewage" is pumped through the 3-liter unit where it remains for three hours; this corresponds to German sewage system practice. The 24 liters of effluent per day are composited and the percentage of the methylene blue active substance still present is determined on an aliquot sample.

The official test method is complicated in practice because in order to produce the activated sludge for testing, the apparatus must for each test be innoculated *by natural means* from the air with microbes present everywhere and allowed to cultivate by itself in the apparatus. It takes generally about two to four weeks until sufficient sludge has accumulated to start degradation. Therefore, one single determination of a product's biodegradability takes about seven weeks *if all goes well,* usually about four weeks for the sludge formation and three consecutive weeks of daily even degradation rates.

If, during three consecutive weeks, approximately the same value has been found every day then the average of these daily degradation rates in percent is the "biodegradability" in the sense of the German Detergent Law. For example, if in a period of three weeks 20 ppm MBAS are pumped into the unit and an average of 10 ppm MBAS is found in the daily effluents, then the substance tested is 50% degradable. If in the effluents only 4 ppm are found, then the product has the required degradability of 80%.

As regards the other countries in the free world, to date they have been interested bystanders. There is definite preliminary activity in Switzerland, France, Italy, Japan, and the Benelux countries. Switzerland and Japan are probably the most advanced among the other countries and are setting up study committees.

It will be interesting to see the ramifications of the two ways of handling the problem, namely the German method through legislation and the British method by committee and persuasion and, of course, it will be especially interesting to us here in the U.S. where we have not as yet decided on either course of action, although legislation has been proposed. Throughout Europe the government health authorities in the major countries have been asking their technical departments to study the detergent degradation problem and, of course, the type of action taken by the U.S. should be expected to have no slight influence on world thinking.

A few remarks on economics may be in order. The soft type of DOBANES produced in Europe by Shell are products based on olefins derived from the cracking of wax. This cracking step takes a long straight chain paraffin and produces shorter straight chain olefin fragments. The double bond in these olefins is predominately in the alpha position. The olefins are then used to alkylate benzene with standard acid catalysts. The economics of this operation are very complex depending as they do on total refinery economics and by-product utilization. To date the only large scale cracking of wax is by the Royal Dutch Shell group, whose through-put is several hundred thousand tons per year. To improve product quality Shell is now installing a plant utilizing Edeleanu's urea dewaxing process. Straight chain paraffins will be produced by their selective extraction from oil fractions, the extraction agent being a urea solution with which the straight chain products form an adduct.

As an example of another way to obtain straight chain product from petroleum, the plans of one German raw material producer namely the Huls Company are believed well known. The Gelsenberg refinery will extract normal paraffins from a refinery cut in the kerosene range utilizing the Molex molecular sieve process and sell this cut to Huls who will then take this straight chain paraffin and chlorinate it and then dehydrochlorinate. The resulting olefins can be used to produce a straight chain alkylate. It is expected that the straight chain product whether produced from wax cracking or from chlorination—dehydrochlorination should command a premium because of the increased cost over product based on propylene tetramer. The amount of this premium will, of course, be determined by competition.

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