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Alkylphenol ethoxylates – are they environmentally acceptable surfactants?

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Introduction

Most companies purchasing and using surfactants will be aware that the EEC has recently issued a Directive on the biodegradability of nonionic surfactants. The governments of the UK and other member countries must now issue their own national regulations based on this Directive. There appears to be some uncertainty in the UK about the likely impact of this Directive. A particular question is whether the use of alkylphenol ethoxylates (APEOs) will be permitted in future. This is one aspect of the rather broader question of the environmental impact of APEOs. Our object in this Bulletin is to summarise the facts as we see them, including the most recent technical developments.

The EEC Nonionics Biodegradability Directive (EEC/82/242)

This Directive does not pass or fail specific types of compounds. It simply states a biodegradability requirement (80% minimum in a single determination) and describes the permitted test procedures for obtaining the result. The onus is on the supplier or formulator to satisfy himself that the nonionic surfactants he uses meet the requirements of the Directive (certain speciality nonionics are at present excluded).

It is not possible to give a simple yes or no answer to the question "do APEOs meet the requirements of the Directive?". One also needs to consider an earlier and more general EEC Directive (EEC/73/404) which requires that surfactants should be biodegradable and not harmful to human or animal health under normal conditions of use. Again, this is not a simple issue and requires discussion in some detail.

For a clear understanding of the complexities of these issues, it is helpful to recall the early history of surfactants and the foaming problems which first focussed attention on the importance of biodegradation.¹

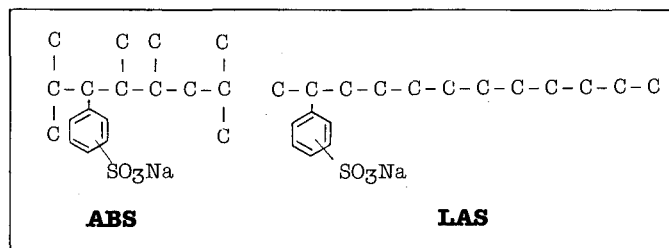
Historical background – the concept of biodegradability

The discovery that widespread use of certain synthetic detergents could lead to environmental problems dates from the early 1950s, when serious foaming occurred on waterways and in sewage treatment plants.² In the UK, the government set up a Standing Technical Committee under the Ministry of Housing and Local Government (later the Department of the Environment) to look into the problem; other countries took similar action.

Detailed studies in various laboratories, including those of Shell, established that branched alkylbenzene sulphonate (ABS), the main type of synthetic detergent then in use, was responsible for the problem.² Unlike 'natural' detergents such as soap, ABS was shown to be very slow to break down under the influence of bacteria, i.e. to biodegrade. Solutions containing as little as half of one part per million can foam strongly; hence, persistence of undegraded ABS during and after sewage treatment led to environmental problems.



BEFORE the change to biodegradable surfactants the highly branched alkyl chain in ABS, derived from a propylene polymer, was the cause of the trouble. A likely solution was to replace this branched carbon chain by an essentially linear (unbranched) chain, i.e. by a linear alkylbenzene sulphonate (LAS).



A field trial at Luton, using Shell's Dobane, confirmed the laboratory findings. As Shell already possessed the technology for manufacturing the long-chain linear olefins, commercial introduction of LAS soon followed, and indeed the foaming problem largely disappeared.³ In consequence, the Confederation of British Industry gave a voluntary undertaking to the UK government that synthetic detergents based on propylene tetramer, i.e. the old 'hard' material, would not be supplied to the UK domestic market after 1964². In other countries, e.g. France and Germany, use of ABS was prohibited by

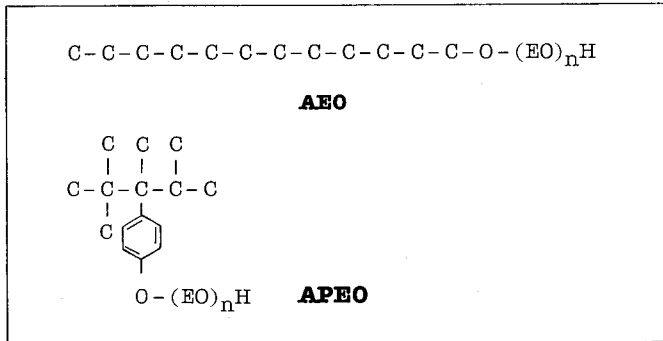


governmental statutes. These statutes are based on laboratory tests which aim to simulate sewage treatment processes as far as practicable. The test procedures are designed to give a clear distinction between:

- LAS** straight-chain, easily biodegradable (soft) and
- ABS** branched-chain, poorly biodegradable (hard)

Subsequently the EEC, in their role of harmonizing the legislation of member countries to reduce technical barriers to trade, issued a Directive (73/405/EEC) that all anionic surfactants should have a minimum biodegradability of 80% (in a prescribed test procedure). This Directive has caused no problems of interpretation in practice; LAS always gives results well above 80%, and ABS always much less than 80% (typically 20-50%). This fostered the belief that surfactants could be categorized as either 'good' (i.e. highly biodegradable) or 'bad' (i.e. poorly biodegradable).

This belief was strengthened when the accepted biodegradation tests were first applied to nonionic surfactants. It was found that alcohol ethoxylates (AEOs) were highly biodegradable (90%+) but APEOs much less so (20%-60%).¹ As the AEOs were based on linear alcohols, and the APEOs on highly branched alkylphenols derived from propylene trimer or diisobutylene, this caused no surprise. It reinforced the belief that highly branched carbon chains are associated with poor biodegradability.

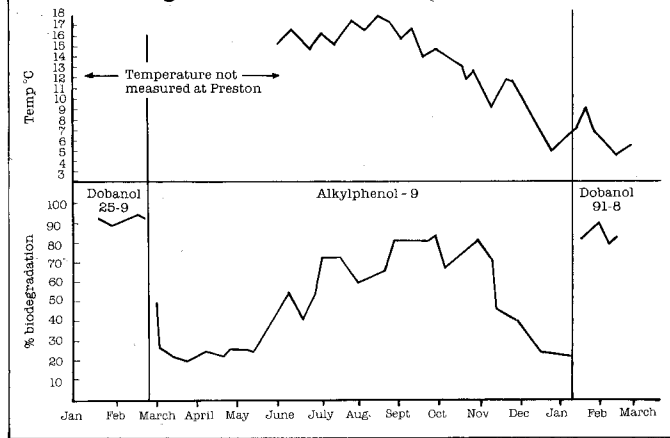


By the admittedly arbitrary standard of 80% minimum biodegradability, APEOs were accordingly regarded throughout the industry as 'hard'. The UK Standing Technical Committee stated in 1971 that "all branched-chain APEOs... are considered as being hard and not meeting the acceptable levels of biodegradability".⁴ The same Committee in its 1972 report "noted with satisfaction that the use of hard nonionics in domestic products in 1972 was negligible".⁵ From about 1970 onwards, these same laboratory tests began to give higher results than had been obtained in the 1960s, and many laboratories (including Shell) reported figures in excess of 80%. As far as we are aware, there has been no change in the composition of APEO or in the manufacturing processes which could account for this. It is generally assumed that it must be due to some change in the bacterial populations in the environment.

Laboratory tests represent an idealised situation in which most of the operating parameters can be held constant. In an actual sewage treatment plant, conditions are continuously varying; temperature, in particular, is subject to wide seasonal fluctuations, and can fall a long way below the ambient temperature of a laboratory.

To obtain information about the behaviour of surfactants under real world conditions, Shell Research carried out a field trial in the late 1960s at the village of Preston in Hertfordshire.⁶ Some 30 houses, linked to a small sewage works, were supplied with various experimental detergents over an extended period, while the performance of the sewage treatment plant was closely monitored. This trial included both AEO and APEO. It was found that AEO was consistently highly biodegradable in both summer and winter (80%+); APEO, on the other hand, only attained 80% in the height of

Fig 1 Biodegradation of nonionic detergents in trickling filter



Most laboratory studies of biodegradation until this time had been performed at ambient temperature (20-25°C). However, when the Water Pollution Research Laboratory at Stevenage (now the Water Research Centre) investigated the influence of temperature on the biodegradability of APEO in the laboratory, they found that it dropped from 80%+ at ambient temperature to only 60%-70% at 10°C.⁷ The biodegradability of AEO, on the other hand, was unaffected by such a drop in temperature.

At this point, it began to be realised that APEO was not 'hard' in the sense of ABS, nor 'soft' in the sense of LAS or AEO, but rather occupied an ill-defined intermediate position.

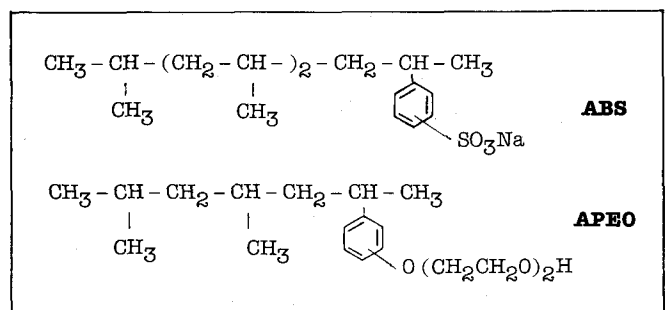
Recent developments - the concept of 'total' biodegradation or mineralisation

In the discussion so far, the term 'biodegradability' has always implied 'primary' biodegradability; this means some change in the original substance and its associated properties such as foaming or surface tension lowering. In the last decade, it has become clear that the issue of surfactants and water quality involves much more than just absence of foam. The ultimate fate of all chemicals which can enter the waterways is of concern. The nature of the intermediates which can be formed in the course of biodegradation, and the possible impact of these intermediates on the aquatic environment, are also questions which are being asked. In the UK, a Code of Practice to the Notification of New Substances Regulations 1982⁸ details the methods currently considered important for the determination of ecotoxicity. The concept of 'total' biodegradability, i.e. complete breakdown to CO₂, water and mineral salts is discussed, and appropriate laboratory methods are given in this Code of Practice.

It is already known that surfactants such as LAS, AEO and even APEO can be broken down in this way under bacterial action; however, the **rate** at which this happens is clearly of key importance.

In recent years, LAS has been studied in this way in great detail. Various intermediates have been characterised and their environmental properties established.⁹ In consequence, a large volume of solid evidence is now available to show that widespread use of LAS does not present a threat to the environment. The regulatory authorities appear to accept this conclusion. Studies on nonionics are not as far advanced. The most comprehensive study is that recently carried out by Shell Development Company in Houston, Texas. In this field trial, carried out with the cooperation of the local municipal authority, the progress of biodegradation of radio-labelled nonionic surfactants could be followed in their passage through a municipal sewage treatment plant.^{10, 11} The results of this trial showed that AEO was rapidly and completely broken down to carbon dioxide and water even at low temperatures (8°C). APEO did not persist long enough in summer conditions (25°C) but

temperatures (8°C), however, even primary biodegradation of APEO was incomplete, and foaming of the effluent was clearly noticeable.¹¹ This result is not surprising in view of earlier work¹² and the similarity in chemical structure between ABS and APEO.



Recent developments – concern about aquatic toxicity

Whilst not comparable with pesticides, cyanides, certain heavy metals, etc., many surfactants can have adverse effects on aquatic life. In the case of AEO (and also LAS), the toxic effects are apparently only associated with the original undegraded surfactant, and disappear as primary biodegradation proceeds. Our own laboratory studies¹³, a field trial carried out at the Water Research Centre, Stevenage¹⁴, and trials in the US¹⁵ have shown that any transient intermediates from AEO have a very low acute toxicity to fish. In the case of APEOs, the toxicity may be more persistent. This is partly because primary biodegradation is slower¹³, and partly because of the nature of the intermediates – APEOs with short EO chains or even free alkylphenols.¹⁶ These substances, detected in laboratory tests and recently also in the effluents from sewage treatment plants, are reported to be highly toxic to aquatic life. This is thus a cause for concern. It will also be recalled that the Thames Water Authority has recently expressed its concern about the presence of residues from the breakdown of various chemicals, including surfactants, in public water supplies.¹⁷ In comparison with the impressive dossiers of safety data which are now available for LAS and AEO¹⁸, less is known about the environmental impact of APEOs. More studies remain to be done to establish the conditions under which APEOs eventually break down, and to establish the environmental and toxicological properties of the intermediates involved.

Another point for future consideration is the possible impact of drinking water chlorination on any APEO residues. A recent article has pointed out that halogenation of APEO residues would 'render them even more refractory and lipophilic. Both of these characteristics are likely to cause greater persistence in the environment and possibly accumulation in the food chain. It seems necessary to address these questions as well as the public health significance of these residues in more detailed studies.'¹⁹

APEOs and the EEC Nonionics Directive – are they permitted?

To return to the question posed in the introduction, the EEC Nonionics Directive, despite its 1982 date, has actually been in preparation for almost 10 years. It simply describes a laboratory method for measuring the biodegradability of nonionics, as required to complement the Directive 404 of 1973. The latter gives legal effect to the Council of Europe Agreement of 1968, which requires surfactants of all types to be biodegradable and not harmful to human or animal health under normal conditions of use. The UK legislation to implement the EEC Nonionics Directive follows the EEC text very closely, that is it reflects the environmental attitudes of 1968 rather than those of 1982.²⁰ A better guide to future

the EEC is the Sixth Amendment to the Dangerous Substances Directive (EEC/79/831).

The UK Standing Technical Committee on synthetic detergents was dissolved as an economy measure in 1980. Until then, they had shown no inclination to modify their earlier recorded view that 'all branched-chain APEOs... are considered as being hard and not meeting the acceptable levels of biodegradability.'⁴

On the basis of laboratory tests carried out at 20-25°C, most manufacturers of APEO can now produce results to show that these products meet the EEC Directive requirements of 80% minimum biodegradability. Equally, it is probable that all manufacturers could also produce results to show that APEOs do **not** meet the minimum biodegradability requirements. We do not believe that there are any significant differences in APEOs from different manufacturers in this respect.

It is not strictly correct to say that the EEC regulations (and related national regulations) **permit** the use of APEOs in domestic products, because the regulations are concerned only with standards and methods and not with specific substances. Nevertheless, with the reservations noted above, manufacturers can claim that the present regulations do not prohibit the use of APEOs within the EEC.

At present, the use of APEO in domestic products in the UK is on a small scale and has not recently been linked to any specific environmental problems. The occasional severe foaming noted by the Standing Technical Committee in the 1970s and attributed to nonionics appears to have been caused by local factors such as overloaded sewage works.²¹ However, the available evidence indicates that extensive use of APEOs in the UK would be likely to lead to more general foaming problems, particularly in winter. Such a development would reflect adversely on the whole surfactants industry, and would be seen as a return to the situation of the 1950s. The Soap and Detergent Industry Association, at the behest of the Standing Technical Committee, gave a voluntary undertaking in 1976 to the UK Government. This undertaking covered 'the proposed use of new substances, or the increased use of existing components, in domestic detergents and related products, which in the industry's judgement may have a significant effect on the UK environment.'²² According to this undertaking, details of any such proposed changes would be supplied in advance to a special Scrutiny Group of experts who, after considering the evidence available, would in due course give their views on the environmental acceptability or otherwise of the proposed change. The demise of the Standing Technical Committee presumably does not affect the spirit of this voluntary undertaking, which is essentially between the members of the Soap and Detergent Industry Association and the UK government.

We are aware that the major UK suppliers of household detergent products, conscious of their responsibilities in regard to the environment, see any possibility of increased use of APEOs in such products as a retrograde step. On Shell's part, APEO was phased out of Teepol in the UK some years ago for environmental reasons, and will not be re-introduced. Many member companies of the Soap and Detergent Industry Association have given a voluntary undertaking not to use APEOs in their household products.

We believe that the Standing Technical Committee, had it still been active, would have been very reluctant to change its recorded views on APEOs, particularly in the light of the most recent scientific work. Within the UK industry, there is certainly a very considerable body of influential opinion which is set against any wider use of APEOs.

Conclusions

Biodegradability tests in the laboratory on APEOs give, and will probably continue to give, very diverse results. Most manufacturers have data which show greater than 80% biodegradability, and hence can claim that their products meet the requirements of the EEC Nonionics Directive. However, that Directive is based on the environmental situation of the 1960s. Current

they contain the highly branched carbon chain structure characteristic of ABS and are associated in the public mind with environmental problems caused by synthetic detergents;

primary biodegradability is sensitive to temperature; incomplete removal at sewage plants in winter; and therefore foaming problems, are to be expected;

mineralisation of APEOs is slow and incomplete, hence effluents containing soluble metabolites whose nature is incompletely known will be released into the waterways;

identification of toxic alkylphenols in effluents points to the need for further research into the intermediates which can be formed from APEOs, and their environmental impact.

Some years ago, the Standing Technical Committee set up by the UK government concluded that APEOs were environmentally unsatisfactory. Most members of the Soap and Detergent Industry Association agreed voluntarily not to use them in household detergent products. Whatever the outcome of current research, APEO is likely to remain a product which is environmentally less acceptable than other products in current use. We believe that any increased use of APEOs in the UK would give no performance improvement to the housewife, and environmentally would be a retrograde step. It could well lead to foaming and other environmental problems, and thereby attract unwelcome and adverse publicity to the whole industry.

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Glossary

APEO	Alkylphenol ethoxylate
ABS	Alkylbenzene sulphonate
LAS	Linear alkylbenzene sulphonate
AEO	Alcohol ethoxylate
EO	Ethoxylate

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Shell Chemical International Trading Company
Shell Centre, London SE1 7PG
Telephone: 01-934 1234 Telex: 919651