COUNCIL DIRECTIVE

of 31 March 1982

amending Directive 73/405/EEC on the approximation of the laws of the Member States relating to methods of testing the biodegradability of anionic surfactants

(82/243/EEC)

THE COUNCIL OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Economic Community, and in particular Article 100 thereof,

Having regard to the proposal from the Commission (1),

Having regard to the opinion of the European Parliament (2),

Having regard to the opinion of the Economic and Social Committee (3),

Whereas Council Directive 73/405/EEC (4) must be adapted to take account of the latest developments in science and technology, thus necessitating:

— the updating of the references relating to the methods listed in Article 2,

— the addition to Article 2 of a further method of measurement which is in use in the United Kingdom,

— the improvement of the 'confirmatory test procedure' provided for in the event of a dispute;

Whereas, pursuant to Article 4 of Council Directive 73/404/EEC of 22 November 1973 on the approximation of the laws of the Member States relating to detergents (5), suitable tolerances for the measurement of biodegradability should be determined in order to take due account of the unreliability of test methods which could result in rejection decisions with important economic consequences; whereas a rejection decision may therefore only be taken where the results obtained with a test method specified in Article 2 of Directive 73/405/EEC reveal a biodegradability of less than 80 %;

Whereas some confusion has arisen as to the scope of Directive 73/405/EEC and it is necessary to make quite clear that the Directive applies only to surfactants used in detergents; whereas it is also necessary to make quite clear that it is the level of biodegradability of the anionic surfactants contained in a detergent, and not the level of biodegradability of the detergent itself, which is dealt with in Article 2;

Whereas the necessary amendment and amplification of the Annex to Directive 73/405/EEC will be carried out under the procedure provided for in Article 3a thereof,

HAS ADOPTED THIS DIRECTIVE:

Article 1

Directive 73/405/EEC is hereby amended as follows:

1. The following is added to Article 1: 'present in detergents such as those referred to in Article 1 of Directive 73/404/EEC'.

2. Articles 2 and 3 are replaced by the following:

'*Article 2*

Pursuant to Article 4 of Directive 73/404/EEC relating to detergents, Member States shall prohibit the placing on the market and use on their territory of a detergent if the biodegradability of the anionic surfactants contained therein is less than 80 % determined in accordance with one of the following methods:

— the OECD method, published in the OECD technical report of 11 June 1976 on the "Proposed Method for the Determination of the Biodegradability of Surfactants used in Synthetic Detergents",

— the method in use in Germany, established by the "Verordnung über die Abbaubarkeit

(1) OJ No C 112, 14. 5. 1981, p. 4.
(2) OJ No C 172, 13. 7. 1981, p. 111.
(3) OJ No C 310, 30. 11. 1981, p. 7.
(4) OJ No L 347, 17. 12. 1973, p. 53.
(5) OJ No L 347, 17. 12. 1973, p. 51.

anionischer und nichtionischer grenzflächenaktiver Stoffe in Wasch- und Reinigungsmitteln" of 30 January 1977, published in the *Bundesgesetzblatt*, 1977, Part I, page 244, as set out in the Regulation amending that Regulation of 18 June 1980, published in the *Bundesgesetzblatt*, 1980, Part I, page 706,

— the method in use in France, approved by Decree of 28 December 1977 published in the *Journal officiel de la République française* of 18 January 1978, pages 514 and 515, and experimental standard T 73-260 of June 1981 published by the "Association française de normalisation" (AFNOR),

— the method in use in the United Kingdom called the "Porous Pot Test" and described in Technical Report No 70 (1978) of the Water Research Centre.

Article 3

Under the procedure laid down in Article 5 (2) of Directive 73/404/EEC, the laboratory opinion on anionic surfactants shall be based on the reference method (confirmatory test procedure) described in the Annex to this Directive.'

3. The following Article shall be inserted:

'Article 3a

The amendments required for adapting the Annex to technical progress shall be adopted in accordance with the procedure laid down in Article 7b of Directive 73/404/EEC.'

4. The Annex is replaced by the Annex to this Directive.

Article 2

Member States shall bring into force the provisions necessary to comply with this Directive within a period of 18 months following its notification and shall forthwith inform the Commission thereof.

Article 3

This Directive is addressed to the Member States.

Done at Brussels, 31 March 1982.

For the Council

The President

P. de KEERSMAEKER

ANNEX

DETERMINATION OF THE BIODEGRADABILITY OF ANIONIC SURFACTANTS

Reference method (confirmatory test)

CHAPTER 1

1.1. **Definition**

Anionic surface active agents in the sense of this Directive are those surface active agents which, after passage through cationic and anionic ion exchangers, are separated by fractional elution and determined as methylene blue active substance (MBAS) according to the analytical procedure described in Chapter 3.

1.2. **Equipment needed for measurement**

The method of measurement employs the small activated sludge plant shown in Figure 1, and in greater detail in Figure 2.

The equipment consists of a storage vessel A for synthetic sewage, dosing pump B, aeration vessel C, settling vessel D, air-lift pump E to recycle the activated sludge, and vessel F for collecting the treated effluent.

Vessels A and F must be of glass or suitable plastic and hold at least 24 litres. Pump B must provide a constant flow of synthetic sewage to the aeration vessel; this vessel, during normal operation, contains three litres of mixed liquor. A sintered aeration cube G is suspended in the vessel C at the apex of the cone. The quantity of air blown through the aerator should be monitored by means of a flowmeter H.

1.3. **Synthetic sewage**

A synthetic sewage is employed for the test.

Dissolve in each litre of tap water:

160 mg peptone,
110 mg meat extract,
30 mg urea $CO(NH_2)_2$,
7 mg sodium chloride (NaCl),
4 mg calcium chloride ($CaCl_2 \cdot 2H_2O$),
2 mg magnesium sulphate ($MgSO_4 \cdot 7H_2O$),
28 mg of dipotassium hydrogen phosphate (K_2HPO_4)
and 20 ± 2 mg MBAS

The MBAS is extracted from the product to be tested by the method given in Chapter 2. The synthetic sewage is freshly prepared daily.

1.4. **Preparation of samples**

1.4.1. Uncompounded surfactants may be examined in the original state. The MBAS content must be determined in order to prepare the synthetic sewage (1.3).

1.4.2. Formulated products are analyzed for MBAS and soap content. They must be subjected to an alcoholic extraction and separation of MBAS (see Chapter 2). The MBAS content of the extract must be known in order to prepare the synthetic sewage.

1.5. **Operation of equipment**

Initially fill aeration vessel C and settling vessel D with synthetic sewage. The height of vessel D should be so fixed that the volume contained in aeration vessel C is three litres.

Inoculation is made by introducing 3 ml of a secondary effluent of good quality, freshly collected from a treatment plant dealing with a predominantly domestic sewage. The effluent must be kept under aerobic conditions in the period between sampling and application. Then set aerator G, air lift E and dosing device B in operation. The synthetic sewage must pass through aeration vessel C at the rate of one litre per hour; this gives a mean retention time of three hours.

The rate of aeration should be so regulated that the contents of vessel C are kept constantly in suspension and the dissolved oxygen content is at least 2 mg/l. Foaming must be prevented by appropriate means. Anti-foaming agents which inhibit the activated sludge or contain MBAS must not be used. Air-lift pump E must be set so that the activated sludge from the settling vessel is continually and regularly recycled to aeration vessel C. Sludge which has accumulated around the top of aeration vessel C, in the base of settling vessel D, or in the circulation circuit must be returned to the circulation at least once each day by brushing or some other appropriate means. When sludge fails to settle, its density may be increased by the addition of 2 ml portions of a 5 % solution of ferric chloride, repeated as necessary.

The effluent from settling vessel D is accumulated in vessel F for 24 hours, following which a sample is taken after thorough mixing. Vessel F must then be carefully cleaned.

1.6. **Checking measuring equipment**

The MBAS content (in mg/l) of the synthetic sewage is determined immediately before use.

The MBAS content (in mg/l) of the effluent collected over 24 hours in vessel F should be determined analytically by the same method, immediately after collection; otherwise the samples must be preserved, preferably by freezing. The concentrations must be determined to the nearest 0·1 mg/l MBAS.

As a check on the efficiency of the process the chemical oxygen demand (COD), or the dissolved organic carbon (DOC) of the glass fibre filtered effluent accumulated in vessel F and of the filtered synthetic sewage in vessel A is measured at least twice per week.

The reduction in COD or DOC should level off when a roughly regular daily MBAS biodegradation is obtained, i.e. at the end of the running-in period shown in Figure 3.

The content of dry matter of the suspended solids in the activated sludge in the aeration tank should be determined twice a week (in g/l). If it is more than 2·5 g/l, the excess activated sludge must be discarded.

The test is performed at room temperature; this should be steady and kept between 292 and 297 K (19-24 °C).

1.7. **Calculation of biodegradability**

The percentage degradation of MBAS must be calculated every day on the basis of the MBAS content in mg/l of the synthetic sewage and of the corresponding effluent accumulated in vessel F. The degradability figures thus obtained should be presented graphically as in Figure 3.

The degradability of the MBAS should be calculated as the arithmetic mean of the figures obtained over the 21 days which follow the running-in period, during which degradation has been regular and the operation of the plant trouble-free. In any event the duration of the running-in period should not exceed six weeks.

The daily degradation values are calculated to the nearest 0·1 % but the final result is given to the nearest whole number.

In some cases it may be permissible to reduce the frequency of sampling but at least 14 results collected over the 21 days which follow the running-in period should be used in calculating the average.

CHAPTER 2

PRELIMINARY TREATMENT OF PRODUCTS TO BE TESTED

2.1. Preliminary notes

2.1.1. *Treatment of samples*

The treatment of anionic surface active agents and formulated detergents prior to the determination of biodegradability in the confirmatory test is:

Products	Treatment
Anionic surfactants	None
Formulated detergents	Alcoholic extraction followed by separation of the anionic surfactants by ion exchange

The purpose of the alcoholic extraction is to eliminate the insoluble and inorganic ingredients of the commercial product which in some circumstances might upset the biodegradability test.

2.1.2. *Ion-exchange procedure*

Isolation and separation of anionic surface active agents from soap, non-ionic and cationic surfactants is required for correct biodegradability tests.

This is achieved by an ion-exchange technique using a macro-porous exchange resin and suitable elutants for fractional elution. Thus soap, anionic and non-ionic surfactants may be isolated in one procedure.

2.1.3. *Analytical control*

After homogenizing, the concentration of anionic surfactants in the synthetic detergent is determined according to the MBAS analytical procedure. The soap content is determined by a suitable analytical method. This analysis of the products is necessary to calculate the quantities required to prepare fractions for the biodegradability test.

Quantitative extraction is not necessary; however, at least 80 % of the anionic surfactants should be extracted. Usually, 90 % or more is obtained.

2.2. Principle

From an homogeneous sample (powders, dried pastes and dried liquids) an ethanol extract is obtained which contains the surfactants, soap and other alcohol-soluble constituents of the synthetic detergent sample.

The ethanol extract is evaporated to dryness, dissolved in an isopropanol/water mixture and the solution obtained is passed through a strongly acidic cation exchange/macro-porous anion exchange combination heated to 323 K (50 °C). This temperature is necessary to prevent the precipitation of any fatty acids which may be present in acidic media.

Any non-ionic surfactants remain in the effluent.

Soap fatty acids are separated by elution with ethanol containing CO_2. The anionic surfactants are then obtained as ammonium salts, by elution with an aqueous isopropanolic solution of ammonium bicarbonate. These ammonium salts are used for the degradation test.

Cationic surfactants which might upset the biodegradability test and the analytical procedure, are eliminated by the cation exchanger placed above the anion exchanger.