

## **P5\_TA(2003)0184**

### **Detergents \*\*\*I**

**European Parliament legislative resolution on the proposal for a European Parliament and Council regulation on detergents (COM(2002) 485 – C5-0404/2002 – 2002/0216(COD))**

**(Codecision procedure: first reading)**

*The European Parliament,*

- having regard to the Commission proposal to the European Parliament and the Council (COM(2002) 485)<sup>1</sup>,
  - having regard to Article 251(2) and Article 95 of the EC Treaty, pursuant to which the Commission submitted the proposal to Parliament (C5-0404/2002),
  - having regard to Rule 67 of its Rules of Procedure,
  - having regard to the report of the Committee on the Environment, Public Health and Consumer Policy and the opinion of the Committee on Industry, External Trade, Research and Energy (A5-0105/2003),
1. Approves the Commission proposal as amended;
  2. Calls on the Commission to refer the matter to Parliament again if it intends to amend its proposal substantially or replace it with another text;
  3. Instructs its President to forward its position to the Council and Commission.

---

<sup>1</sup> OJ not yet published.

**Position of the European Parliament adopted at first reading on 10 April 2003 with a view to the adoption of European Parliament and Council Regulation (EC) No ..../2003 on detergents**

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 95 thereof,

Having regard to the proposal from the Commission<sup>1</sup>,

Having regard to the opinion of the Economic and Social Committee<sup>2</sup>,

Acting in accordance with the procedure laid down in Article 251 of the Treaty<sup>3</sup>,

Whereas:

- (1) *As set out in Article 174 of the Treaty, the Community's environment policies shall contribute to pursuit of the objectives of preserving, protecting and improving the quality of the environment through, inter alia, encouraging the prudent and rational utilisation of natural resources, and shall be based on the precautionary principle and on the principles that preventive action should be taken and that environmental damage should, as a priority, be rectified at source, and that the polluter should pay for such rectification.*

---

<sup>1</sup> OJ C ...

<sup>2</sup> OJ C ...

<sup>3</sup> *Position of the European Parliament of 10 April 2003.*

- (2) Council Directive 73/404/EEC of 22 November 1973 on the approximation of the laws of the Member States relating to *detergents*<sup>1</sup>, Council Directive 73/405/EEC of 22 November 1973 on the approximation of the laws of the Member States relating to methods of testing the biodegradability of anionic *surfactants*<sup>2</sup>, and Council Directive 82/242/EEC of 31 March 1982 on the approximation of the laws of the Member States relating to methods of testing the biodegradability of non-ionic surfactants and *amending Directive 73/404/EEC*<sup>3</sup> *should*, for reasons of clarity and *efficiency*, *be* modernised and replaced by a single *text*; *labelling* provisions concerning detergents and cleaning products of Commission Recommendation 89/542/EEC of 13 September 1989 for the labelling of detergents and cleaning products<sup>4</sup> are to be included.
- (3) In accordance with the principles of subsidiarity *and proportionality*, as stated in Article 5 of the Treaty, the objectives of the envisaged action to ensure the internal market in detergents cannot be achieved individually by Member States if there are no common technical criteria throughout the Community, and can therefore be better achieved by Community action; this action should be limited to the minimum required to achieve these objectives and should not exceed what is necessary to this end; a regulation is the appropriate legal instrument as it imposes directly on manufacturers precise requirements to be implemented at the same time and in the same manner throughout the Community; in the area of technical legislation, uniformity of application in the Member States is needed, and this can only be guaranteed by a regulation.
- (4) A new definition of "*detergent*" is needed to cover equivalent uses and be in line with developments at Member State level.
- (5) It is necessary to introduce a *definition of "surfactant"*, which was lacking in the existing legislation.
- (6) It is important to give a clear and precise description of the relevant types of biodegradability.
- (7) Measures concerning detergents should be adopted to ensure the functioning of the internal market and avoid *restricting competition* in the Community.

---

<sup>1</sup> OJ L 347, 17.12.1973, p. 51. *Directive as last amended by Directive 86/94/EEC (OJ L 80, 25.3.1986, p. 51).*

<sup>2</sup> OJ L 347, 17.12.1973, p. 53. *Directive as last amended by Directive 82/243/EEC (OJ L 109, 22.4.1982, p. 18).*

<sup>3</sup> OJ L 109, 22.4.1982, p. 1.

<sup>4</sup> OJ L 291, 10.10.1989, p. 55.

- (8) As confirmed by the Commission White Paper on the strategy for a future *Chemicals Policy*<sup>1</sup> these measures should ensure a high level of environmental protection, especially of the aquatic environment.
- (9) Detergents are already subject to certain Community provisions concerning the manufacture, proper handling, usage and labelling, in particular with reference to *Recommendation 89/542/EEC* and *Commission Recommendation 98/480/EC* of 22 July 1998 concerning good environmental practice for household laundry detergents<sup>2</sup>; *European Parliament and Council Directive 1999/45/EC* of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations<sup>3</sup> applies to detergents.
- (10) Ditolow-dimethyl-ammonium-chloride (DTDMAC) and Nonylphenol (including ethoxylates derivatives - APEs) are priority substances undergoing risk assessment *at Community level*, in accordance with *Council Regulation (EEC) No 793/93* of 23 March 1993 on the evaluation and control of the risks of existing substances<sup>4</sup>, **and adequate** strategies to limit the risks of exposure to these substances will **therefore** be recommended and implemented in the framework of other relevant EC instruments.
- (11) The existing legislation on biodegradability of surfactants in detergents only covers primary *biodegradability* and is only applicable to *anionic and non-ionic surfactants*; therefore it needs to be replaced by new legislation *in which the* main emphasis *is* on ultimate biodegradability and *which responds to* the important concerns *as to* the potential toxicity of persistent metabolites.
- (12) This requires the introduction of a new set of tests, based on EN ISO standards and OECD guidelines, which governs the granting of direct permission for placing detergents on the market.

---

<sup>1</sup> COM(2001) 88.

<sup>2</sup> OJ L 215, 1.8.1998, p. 73.

<sup>3</sup> OJ L 200, 30.7.1999, p. 1. *Directive amended by Commission Directive 2001/60/EC (OJ L 226, 22.8.2001, p. 5).*

<sup>4</sup> OJ L 84, 5.4.1993, p. 1.

- (13) To provide a high level of *environmental protection*, *detergents* not fulfilling *the* requirements laid down by this *Regulation shall* not be placed on the market.
- (14) On 25 November 1999 the Scientific Committee on Toxicity, Ecotoxicity and the *Environment* issued an opinion on *the* biodegradability of surfactants in detergents and *the* relevance of test methods for regulatory control in this area.
- (15) The existing requirements regarding primary biodegradability ***and the complementary risk assessment*** are to *remain in* second *position in the hierarchy* for those surfactants failing “ultimate biodegradability” tests; furthermore, surfactants failing primary biodegradability tests cannot obtain marketing authorisation by way of derogation.
- (16) The primary biodegradability requirements need to be extended to all surfactants, in particular cationic and amphoteric, whilst allowing *for the option* of applying instrumental analyses *in cases where* semi-specific analytical methods are not suitable.
- (17) The determination of biodegradability ***test methods and*** the record-keeping of lists of derogations are technical matters. ***The setting of criteria for derogations is a political matter. These matters*** need to be revised taking into account technical and scientific developments as well as regulatory ***and political*** developments.
- (18) Test methods should produce data that give sufficient assurance of *the* aerobic biodegradability of surfactants in detergents.
- (19) Test methods to test *the* biodegradability of surfactants in detergents may produce variable results. ***In such cases they*** need to be complemented by additional assessments in order to determine the risks of continued use.
- (20) *In exceptional cases*, provisions should also be set out to place on the *market surfactants* in detergents failing “ultimate biodegradability” tests. *This* should take place on the basis of all relevant information to ensure environmental protection and on a case by case basis.
- (21) Since the measures necessary for the implementation of this Regulation are measures of general scope within the meaning of Article 2 of Council Decision 1999/468/EC of 28 June 1999 laying down the procedures for the exercise of implementing powers conferred on the Commission<sup>1</sup>, they should be adopted by use of the regulatory procedure provided for in Article 5 of that Decision.

---

<sup>1</sup> OJ L 184, 17.7.1999, p.23.

- (22) It is appropriate to refer to other horizontal legislation applicable to detergent surfactants, in particular Council Directive 76/769/EEC of 27 July 1976<sup>1</sup> by which the marketing and use of dangerous substances covered by this Regulation might be banned or restricted, Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances<sup>2</sup>, Commission Directive 93/67/EEC of 20 July 1993 on assessment of risks to man and the environment of new substances<sup>3</sup> or Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 of 28 June 1994 laying down the principles for the assessment of risks to man and the environment of existing substances<sup>4</sup>.
- (23) ***Detergents must not be harmful under normal or foreseeable conditions of use. Given the special risks that the substances classified as carcinogenic, mutagenic or toxic for reproduction - categories 1, 2 and 3 pursuant to Directive 67/548/EEC - may entail for human health, their use in detergents should be prohibited. As an exception, a substance classified in category 3 may be used in detergents if it has been evaluated by the Scientific Committee on Cosmetics and Non-Food Products and found to be acceptable for such use.***
- (24) It should be the responsibility of manufacturers to refrain from marketing detergents not complying with the provisions of this Regulation and to *hold* at the disposal of the national authorities the corresponding technical files for all substances and preparations covered by this Regulation; this should also apply to surfactants that have failed to pass the tests mentioned in Annex III.
- (25) Manufacturers ***may*** request a derogation ***which*** the Commission ***may*** grant in accordance with the Committee procedure of this Regulation ***if the criteria set out in Article 6 are met.***
- (26) Competent authorities *in the Member States may* apply control measures to detergents on the market, but should avoid repeating tests made by the competent laboratories ***and must ensure, in particular, that animal tests are not repeated.***

---

<sup>1</sup> OJ L 262, 27.9.1976, p. 201. *Directive as last amended by European Parliament and Council Directive 2003/11/EC (OJ L 42, 15.2.2003, p. 45).*

<sup>2</sup> OJ 196, 16.8.1967, p. 1. *Directive as last amended by Commission Directive 2001/59/EC (OJ L 225, 21.8.2001, p. 1).*

<sup>3</sup> OJ L 227, 8.9.1993, p. 9.

<sup>4</sup> OJ L 161, 29.6.1994, p. 3.

- (27) Labelling provisions should be continued, including those in Recommendation 89/542/EEC for the labelling of detergents and cleaning *products*, in order to fulfil the objective of *updating* the rules on detergent products. Specific labelling is introduced to inform consumers about fragrance substances and preservation agents that are present in detergents. **Medical personnel** should be able to obtain from the manufacturer upon request a full listing of all ingredients of a detergent to assist them *in investigating* whether a causal link exists between the development of an allergic response and exposure to a particular chemical substance.
- (28) All the above points call for new legislation replacing the existing legislation; however, for a period not exceeding eighteen months, Member States *may* continue to apply their existing laws.
- (29) The technical **parts of the** Annexes to this Regulation are to be adapted by Committee procedure.
- (30) Detergents complying with this Regulation should be allowed to be placed on the market without prejudice to other relevant ***national or*** Community provisions.
- (31) In order to ensure the protection of man and the environment from unforeseen risks of detergents, a safeguard clause is needed.
- (32) The tests specified for the biodegradability of surfactants should be carried out in laboratories meeting an internationally recognised standard, namely EN/ISO/IEC/17025. *It would not be justified to ask that this requirement apply* to existing surfactants, *as* the available tests on them *were* performed before the *entry* into force of the *above-mentioned* standard and still provide a comparable level of scientific quality.
- (33) The issues relating to anaerobic biodegradation, the biodegradation of the main non-surfactant organic detergent *ingredients and* phosphate content should be ***evaluated*** and, where this is justified, a ***legislative*** proposal should be presented to the European Parliament and the Council *by ...\* at the latest. The review of phosphate content should include the evaluation of a gradual phase-out.*

---

\* ***Three years after the entry into force of this Regulation.***

- (34) *In accordance with its White Paper, 'Strategy for a Future Chemicals Policy', the Commission should promote research into the development and validation of alternative non-animal test methods at Community and national level and promote the competitiveness of the chemical industry to encourage innovation and, in particular, the development of safer chemicals.*
- (35) *In accordance with Council Directive 86/609/EEC of 24 November 1986 on the approximation of laws, regulations and administrative provisions of the Member States regarding the protection of animals used for experimental and other scientific purposes<sup>1</sup>, it is important to ensure that conventional test methods are replaced first and foremost by validated alternative methods that do not involve the use of animals or, should no such methods exist, by methods intended significantly to reduce the number of animals used or methods that enable the suffering caused to animals to be significantly reduced.*
- (36) *The long-term aim of replacing all animal-based toxicity testing must be actively pursued, and the Commission should set out a targeted timeframe for such replacement.*
- (37) *Directives 73/404/EEC, 73/405/EEC and 82/242/EEC and Recommendation 89/542/EEC, which are replaced by this Regulation, should be repealed,*

HAVE ADOPTED THIS REGULATION:

#### Article 1

##### Objectives and scope

1. This Regulation establishes rules designed to achieve the free movement of detergents and surfactants for detergents in the internal market while, at the same time, ensuring a high degree of protection of the environment *and human health*.
2. For this purpose, this Regulation lays down rules for:
  - the biodegradability of surfactants in *detergents*
  - the labelling of detergents *and*
  - *restrictions on the use of certain substances or preparations in detergents.*

---

<sup>1</sup> *OJ L 358, 18.12.1986, p. 1.*

## Article 2

### Definitions

For the purpose of this Regulation:

1. “Detergent” means any substance or preparation containing soaps or other surfactants intended *to be dissolved or dispersed in water or in other liquids for* washing processes. Detergents may be in any form (liquid, powder, paste, bar, cake, moulded piece, shape, etc.) and used for household, and/or institutional and/or industrial purposes. Other products to be considered as covered within the meaning of this definition are listed in Annex I.A;
2. “Washing” means the cleaning of laundry, fabrics, *dishes, kitchen* utensils, *floors, windows or sanitary facilities*;
3. “Cleaning” has the meaning defined by EN ISO 862;
4. **“Industrial and institutional use” means washing and cleaning outside the domestic sphere, carried out by specialised personnel using specific products;**
5. “Substance” means chemical elements and their compounds in *a* natural state or obtained by any production process, including any additive necessary to preserve the stability of the products and any impurity deriving from the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition;
6. “Preparation” means *a* mixture or solution composed of two or more substances;
7. “Surfactant” means any organic substance and/or preparation used in detergents which *has* surface-active properties, and which consists of one or more hydrophilic and one or more hydrophobic groups of such a nature and size that it is capable of *reducing the surface tension of water, forming spreading or adsorption monolayers at the water-air interface, forming emulsions and/or microemulsions, forming micelles and adsorption at water-solid interfaces*;
8. “Primary biodegradation” means the structural change (transformation) of a surfactant by micro-organisms resulting in the loss of its surface-active properties due to the degradation of the parent substance and consequential loss of the surface-active property as measured in *the* test methods listed in Annex II;

9. “Ultimate aerobic biodegradation” means the level of biodegradation achieved when the surfactant is totally *degraded* by micro-organisms in the presence of oxygen resulting in its breakdown *into* carbon dioxide, water and mineral salts of any other elements present (mineralisation), as measured *via the* test methods listed in Annex III, and new microbial cellular constituents (biomass);

10. “Placing on the market” means introducing onto the Community market, thereby making available to third parties whether in exchange for payment or not. Importation into the Community customs territory shall be deemed to be placing on the market;

11. “Manufacturer” means the natural or legal person (including importers) placing a detergent and/or a surfactant for detergents on the market.

### Article 3

#### *Placing on the market*

1. Detergents and surfactants for detergents referred to in Article 1 shall conform with the conditions, characteristics and limits laid down in this Regulation and its Annexes when placed on the Community market.

2. Manufacturers of detergents and/or of surfactants for detergents shall be established within the Community.

3. Manufacturers shall be responsible for the conformity of detergents and of surfactants for detergents *with this* Regulation and its Annexes.

### Article 4

#### Limitations to the placing on the market

**1. *Substances and preparations whose use is prohibited in detergents are listed in Annex VII.***

2. If a detergent contains surfactants for which the level of ultimate aerobic biodegradation is less than **60% within 28 days**, manufacturers of detergents containing surfactants, and/or of surfactants for detergents may ask for a derogation. Requests for derogation shall be made **and granted** in accordance *with Articles 5, 6 and 9*.

3. The level of primary biodegradability shall be measured for all surfactants in detergents failing ultimate aerobic biodegradation tests. Detergent *surfactants for* which the level of primary biodegradability is less than **80% shall** not be granted derogation.

## Article 5

### Granting of derogation

1. The request by a manufacturer for derogation shall be made by sending an application to the competent authorities of the Member State concerned, referred to in Article 8(1), and to the Commission, providing evidence relating to the criteria mentioned *in* Article 6(1).

2. Applications shall include a technical file supplying all the information and justifications necessary for evaluating the safety aspects related to the specific use of surfactants in detergents failing to comply with the biodegradability **limit** as set out in **Article 4(2)**.

In addition to the results of tests stipulated in Annex III, the technical file shall include results of *the tests specified* in Annexes II and IV.

3. ***The tests specified in Annex IV(4) shall be carried out on the basis of a graded risk assessment (tiered approach). By ...\* at the latest, the Commission shall lay down an appropriate technical guideline in accordance with the procedure referred to in Article 12(2).***

4. The competent authorities of the Member States receiving applications for derogation according to paragraphs 1 and 2 above, shall examine the requests, evaluate their compliance with the conditions for derogation and inform the Commission of the results without delay.

If the competent authority of the Member State deems it *necessary for* the evaluation of the risk which may be caused by a substance and/or a preparation, it **shall** ask for further information, verification and/or confirmatory tests concerning these substances and/or preparations or their transformation *products of* which they have been notified or have received information under this Regulation. ***If the necessary information is not provided within a timeframe to be clearly specified, the application shall be considered incomplete and thus invalid.***

***If further information on metabolites is sought, stepwise testing strategies should be employed to ensure maximum use of in-vitro and other non-animal test methods.***

---

\* ***Twelve months after the entry into force of this Regulation.***

5. ***On the basis of the evaluation carried out by the Member States***, the Commission may grant derogation in accordance with the procedure set out in Article 12(2). If necessary, before granting derogation the Commission ***shall*** evaluate further the matters indicated in *paragraph 4* above.

6. Such derogations may allow, limit or severely restrict the placing on the market and the use of surfactants in detergents, depending on the results of the complementary risk assessment, as defined in Annex IV. *They* may include a phase-out period for *the* placing on the market and the use of surfactants in detergents. ***A derogation must be reviewed after 5 years and the applicant must provide information to demonstrate that he is developing alternatives which fulfil the requirements for ultimate aerobic biodegradation.***

7. The Commission shall publish the list of surfactants that have obtained derogation, with the corresponding conditions or limitations of use, as provided in Annex V.

## Article 6

### ***Conditions for granting a derogation***

1. Where the Commission intends ***to grant*** a derogation it may do so on the basis of the following criteria, ***provided that such a course of action is justified on the basis of the further checks carried out pursuant to Article 5(4):***

- ***the surfactant in question is for specific industrial and/or institutional use only, provided that the volume of sales and use throughout whole EU territory is below that which would pose a threat to the environment and health, and***
- ***an overall environmental benefit for its use has been shown, while social benefits such as food safety and hygiene standards are ensured.***

2. As long as the Commission has not decided on a request for derogation, the use of the surfactant in question may be maintained, provided *that* the manufacturer can show that the surfactant was already in use on the Community market at the date of entry into force of this Regulation and that the request for derogation was made within two years *of* that date. If the Commission refuses to grant a derogation for a surfactant, it ***shall*** set a transitional period during which the use of the surfactant in question shall be *phased out*. This transitional period shall not exceed two years.

## Article 7

### Testing of surfactants and listing of those that are banned or restricted for use

1. All tests referred to in Articles 3 and 4 and in Annexes II, III, IV and IX shall be conducted in compliance with the standard mentioned in Annex I.B.1. In cases where surfactants are used in detergents which were marketed before the entry into force of the above standard, existing *tests performed* using the best scientific knowledge *available, to* a standard comparable to *that mentioned* in Annex I.B.1, may be accepted on a case-by-case basis. The manufacturer or the Member State may submit to the Commission any case over which there is doubt or dispute. A decision will then be taken in accordance with the procedure laid down in Article 12(2).

**2. *The use of the following substances shall be banned unless they are recognised as safe by the competent scientific committee and the results of the tests referred to in Annexes II, III and IV are satisfactory:***

- ***ditallow-dimethyl-ammonium-chloride (DTDMAC),***
- ***alkylphenol (including ethoxylates derivatives - APEs).***

3. *Surfactants which are banned or restricted for use because they do not comply with this Regulation are listed in Annex VI.*

4. Surfactants listed in Annex VII are also banned or restricted for use in detergents, *regardless of the results of the tests performed pursuant to Annexes II, III, and IV, and under other Community legislation, in particular Directive 76/769/EEC.*

## Article 8

### Duties of the Member States

1. Member States shall appoint the competent authority or authorities responsible for communicating and exchanging information relating to the management of this Regulation and *shall* inform the Commission of the name and full address of these authorities.

2. Each Member State shall notify the other Member States and the Commission *of* the list of approved laboratories, *including full names and addresses*, that are competent and authorised to carry out the tests required by this Regulation and its Annexes. Member States shall demonstrate the competence of the above laboratories according to the standards mentioned in Annex I.B.

3. Where a Member State competent authority has grounds for believing that an approved laboratory does not possess the competence referred to in *paragraph 2*, it shall raise the matter in the Committee referred to in Article 12. If the Commission decides that the laboratory does not possess the required competence referred to in paragraph 2, the name of the approved laboratory shall be removed from the list referred to in paragraph 4. *Article 16(2)* shall apply.

4. The Commission shall publish the lists of competent authorities, mentioned in paragraph 1, and of approved laboratories, mentioned in paragraph 2, in the Official Journal of the European *Union*.

## Article 9

### Duties of Manufacturers

1. Manufacturers placing on the market the preparations *and/or substances* covered by this Regulation shall hold at the disposal of the competent authorities of the Member States:

- information on one or more results of the tests mentioned in Annex III;
- for those surfactants failing to pass tests stipulated in Annex III, and for which a request for derogation was made as referred to in Article 5:
  - (i) a technical file on results of tests as stipulated in Annex II,
  - (ii) a technical file on results of tests as stipulated in Annex IV.

2. Whenever substances and preparations covered by this Regulation are placed on the market, the manufacturer shall be responsible for *the performance* of the relevant tests mentioned above. He shall also have available documentation on the testing carried out to demonstrate compliance with the Regulation, and to show that he is allowed to benefit from the property rights concerning the test results, other than for those test results already in the public domain.

3. Manufacturers placing on the market the preparations covered by this Regulation *shall make* available, without delay and free of charge to *the authorities appointed by the Member States pursuant to Article 8(1)*, a datasheet listing all ingredients as stipulated in Annex VIII.C.

*The manufacturer or the authority shall, upon request, make such a datasheet available without delay and free of charge to medical staff bound by professional secrecy.*

## Article 10

### Control measures

1. Member State competent authorities may apply, as appropriate, control measures to detergents on the market by using the test and analytical methods referred to in Annex IX. These control measures shall not oblige manufacturers to repeat tests made by laboratories fulfilling the conditions indicated in Article 8(2), or to pay for any repeat or additional test, provided *that* the initial test has shown *the* compliance of detergents, or *of* surfactants used in detergents, with this Regulation.
2. *Where there is* concern that the test methods in Annex II, III, IV or IX have produced false positive results, the Member State competent authorities shall notify the Commission, *which may*, in accordance with the procedure laid down in Article 12(2), verify those results and take the necessary measures.

## Article 11

### Labelling

1. The provisions of this Article are without prejudice to the provisions relating to the classification, packaging and labelling of dangerous substances and preparations in Directive 67/548/EEC and Directive 1999/45/EC.
2. The following information must appear in legible, visible and indelible characters on the packaging in which the detergents are put up for sale to the consumer:
  - (a) the name of the product;
  - (b) the name or trade name and address or trademark of the party responsible for placing the product on the market;
  - (c) the address from which the datasheet referred to in Article 9(3) can be obtained.

The same information must appear on all documents accompanying detergents transported in bulk.

***Products covered by a derogation pursuant to Article 5 must be suitably labelled.***

3. The packaging of detergents shall indicate the content according to the specifications provided for in Annex VIII.A.

4. Additionally, the packaging of detergents sold to the general public intended *for use* as laundry detergents shall bear the information *mentioned* in Annex VIII.B.

5. In cases where a Member State has a national requirement to label in the national language(s) it shall notify the Commission thereof, and the manufacturer shall comply with *such a* requirement for the information specified in paragraphs 3 and 4 above.

***6. If a detergent product carries a label, other than the Community Eco-label, claiming that it is environmentally friendly, it must indicate clearly which of the Community Eco-label criteria it does not meet. This information must appear on the packaging adjacent to, and in characters of the same size as, the claim that the product is environmentally friendly.***

## Article 12

### Committee procedure

1. The Commission shall be assisted by a committee, composed of representatives of the Member States and chaired by the representative of the Commission.

2. Where reference is made to this paragraph, Articles 5 and 7 of Decision 1999/468/EC shall apply in compliance with Article 8 thereof.

3. The period provided for in Article 5(6) of Decision 1999/468/EC shall be three months.

4. The committee shall adopt its rules of procedure.

## Article 13

### Adaptation of the annexes

The amendments necessary for adapting Annexes ***I.B***, II, III, IV, V, VI, ***VII and IX to technical progress*** shall be adopted in accordance with the procedure laid down in Article 12(2), and shall, wherever possible, use European Standards.

## Article 14

### Sunset clause

*Without prejudice to the implementing measures already adopted, on the expiry of an eight-year period following its entry into force, the application of the provisions of this Regulation stipulating the adoption of technical rules and decisions in accordance with the procedure referred to in Article 13 by the Committee referred to in Article 12(2) shall be suspended. On a proposal from the Commission, the European Parliament and the Council may renew the provisions concerned in accordance with the procedure laid down in Article 251 of the Treaty and, to that end, they shall review them prior to the expiry of the period referred to above.*

## Article 15

### Free movement clause

*Member States shall not prohibit, restrict or impede the placing on the market of detergents, and/or of surfactants for detergents, which comply with the requirements of this Regulation.*

*Without prejudice to the Treaty, and in particular Articles 28 and 30 thereof, paragraph 1 shall not affect national provisions on detergents which are applicable in the absence of Community harmonisation measures adopted by the European Parliament and the Council.*

## *Article 16*

### *Safeguard clause*

1. Where a Member State has justifiable grounds for believing that a specific detergent, although satisfying the requirements of this Regulation, constitutes a risk to safety or health of humans or of animals or a risk to the environment, it may temporarily prohibit the placing on the market of that detergent in its territory or make it temporarily subject to special conditions.

It shall immediately inform the other Member States and the Commission thereof, giving the reasons for its decision.

2. After consultation of the Member States, or if appropriate of the relevant technical or scientific committee of the Commission, a decision shall be taken on the matter within ninety days in accordance with the procedure referred to in Article 12(2).

## *Article 17*

### *Review*

1. *By ...\* at the latest, the Commission shall carry out an evaluation and submit to the European Parliament and the Council a report and, where justified, a legislative proposal to regulate the issues relating to:*

- *anaerobic biodegradation*
- *the biodegradation of main non-surfactant organic detergent ingredients*
- *the use of phosphates with a view to the gradual phase-out or a restriction to specific applications.*

2. *By ...\*\* at the latest, the Commission shall carry out a review of the application of this Regulation, paying particular regard to the biodegradability of surfactants, and shall present appropriate legislative proposals in accordance with Article 251 of the Treaty for the revision of this Regulation.*

---

\* *Three years after the entry into force of this Regulation.*

\*\* *Five years after the entry into force of this Regulation.*

**Article 18**  
**Further development**

***By ...\* at the latest, the Commission shall submit a proposal seeking to regulate methods and analyses of ecotoxicological tests on all detergent substances and/or preparations and their metabolites.***

**Article 19**  
**Legislation to be replaced**

1. The following Directives are hereby repealed with effect from the date of entry into force of this Regulation:
  - Directive 73/404/EEC;
  - Directive 73/405/EEC;
  - Directive 82/242/EEC.
2. References to the above Directives shall be construed as being references to *this* Regulation.
3. Recommendation 89/542/EEC for the labelling of detergents falling under the scope of this Regulation is hereby repealed.

**Article 20**  
**Sanctions for non-compliance**

1. No later than the day of the entry into force of this Regulation, Member States shall establish:
  - appropriate legal or administrative measures in order to deal with any non-compliance with the provisions of this Regulation and
  - dissuasive, effective and proportionate sanctions for any such non-compliance.
2. They shall immediately inform the Commission thereof.

---

\* ***Twelve months after the entry into force of this Regulation.***

*Article 21*

Entry into force

This Regulation shall enter into force 18 months after its publication in the Official Journal of the European Union.

This Regulation shall be binding in its entirety and directly applicable in all Member States.

Done at

For the European Parliament  
The President

For the Council  
The President

## ANNEX I

### A. List of products that are covered within the meaning of detergent

The following products containing soap or other surfactants are also covered within the meaning of the detergent definition as set out in Article 2(1):

- “Auxiliary washing preparation”, as intended for soaking (pre-washing), rinsing or bleaching clothes, household linen, etc.;
- “Laundry fabric-softener”, as intended to modify the feel of fabrics in processes which are to complement the washing of fabrics;
- “Cleaning preparation”, as intended for domestic all purposes cleaners and/or other water based cleaning of surfaces (e.g.: materials, products, machinery, mechanical appliances, means of transport and associated equipment, instruments, apparatus, etc.);
- “Other cleaning and washing preparations”, as intended for any other water-based processes.

### B. Standards of accreditation concerning the laboratories that are competent and authorised to provide the necessary service for checking compliance of EC detergents with the requirements of this regulation and its annexes

#### 1. Standards applicable at the level of the laboratories:

EN ISO/IEC 17025, General requirements for the competence of testing and calibration laboratories.

#### 2. Standards applicable at the level of the accreditation bodies:

EN 45003, Calibration and testing laboratory accreditation system, general requirements for operation and recognition.

## ANNEX II

### “Primary biodegradability” test methods for surfactants in detergents

Primary biodegradability is measured by the determination in biodegraded liquors of the remaining level of parent surfactants. This Annex begins with a list of the test methods common to all classes of surfactants, and then lists under headings A to D the analytical test procedures specific to each class of surfactant.

The pass criterion for primary biodegradability shall be *as laid down in Article 4(3), and* as measured according to the tests below.

The reference method for the laboratory testing of surfactants in this Regulation is based on the “Confirmatory test procedure” in the OECD method, described in Annex IX.1. Changes to the Confirmatory test procedure are permissible provided that they comply with EN ISO 11733.

#### Test methods

1. The OECD method published in the OECD's technical report of 11 June 1976 on the “Proposed Method for the Determination of the Biodegradability of Surfactants in Synthetic Detergents”.
2. The method in use in France, approved by the “arrêté du 24 décembre 1987” published in the Journal officiel de la République française of 30 December 1987, p. 15385, and by standard NF 73-260 of June 1981, published by the Association française de normalisation (AFNOR).
3. The method in use in Germany, established by the “Verordnung über die Abbaubarkeit anionischer und nichtionischer grenzflächenaktiver Stoffe in Wasch- und Reinigungsmitteln,” of 30 January 1977, published in the Bundesgesetzblatt, Part I, p. 244, as set out in the Regulation amending that Regulation of 18 June 1980, published in the Bundesgesetzblatt, Part I, p. 706.
4. 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.
5. The “Confirmatory test procedure” in the OECD method, described in Annex IX.1 (including possible changes in operating conditions as proposed in EN ISO 11733). This is also the reference method used for the settlement of litigation.

#### A. Analytical Methods for Anionic Surfactants

The determination of anionic surfactants in the tests shall be done by the Methylene Blue Active Substance (MBAS) analysis according to the criteria established in Annex IX.2.

For those anionic surfactants not reacting to the above-mentioned MBAS *method, appropriate specific* instrumental analyses *such as HPLC (high performance liquid chromatography) and GC (gas chromatography)* are to be applied. Samples of the pure surfactant *concerned* shall be provided by the manufacturer to the competent national authorities of the Member States upon request.

#### B. Analytical Methods for Non-ionic Surfactants

The determination of non-ionic surfactants in the tests shall be done by the Bismuth Active Substance (BiAS) method, according to the analytical procedure established in Annex IX.3.

For those non-ionic surfactants not reacting to the above-mentioned BiAS *method, appropriate specific* instrumental analyses *such as HPLC (high performance liquid chromatography) and GC (gas chromatography)* are to be applied. Samples of the pure surfactant *concerned* shall be provided by the manufacturer to the competent national authorities of the Member States upon request.

#### C. Analytical Methods for Cationic Surfactants

The determination of cationic surfactants in the tests shall be done by the Disulfine Blue Active Substance (DBAS) analysis according to the following DBAS procedures:

The method in use in the Federal Republic of Germany, (1989) DIN 38 409 – Ausgabe: 1989-07.

For those cationic surfactants not reacting to the above-mentioned test *method, appropriate specific* instrumental analyses *such as HPLC (high performance liquid chromatography) and GC (gas chromatography)* are to be applied. Samples of the pure surfactant *concerned* shall be provided by the manufacturer to the competent national authorities of the Member States upon request.

#### D. Analytical Methods for Amphoteric Surfactants

The determination of amphoteric surfactants in the tests shall be done by analysis following the procedures listed below:

1. If cationics *are* absent:

the method in use in the Federal Republic of Germany, (1989) DIN 38 409-Teil 20.

2. Otherwise:

*the* Orange II method (Boiteux, 1984).

For those amphoteric surfactants not reacting to the above-mentioned *tests, appropriate specific* instrumental analyses *such as HPLC (high performance liquid chromatography) and gas chromatography (GC)* are to be applied. Samples of the pure surfactant *concerned* shall be provided by the manufacturer to the competent authorities of the Member States upon request.

## ANNEX III

### “Ultimate biodegradability” (mineralisation) test methods for surfactants in detergents

- A. The reference method for laboratory testing of surfactant ultimate biodegradability in this Regulation is based on the EN ISO Standard 14593: 1999 (CO<sub>2</sub> headspace test).

Surfactants in detergents shall be considered as biodegradable if the level of biodegradability (mineralisation) measured according to one of the *following five tests*<sup>1</sup> is ***as laid down in Article 4(2) and the remainder (maximum 40%) is shown not to contain very persistent and/or very bio-accumulative chemicals and/or chemicals with endocrine disrupting properties, and/or not to contain any chemicals that have these properties:***

1. EN ISO Standard 14593: 1999. Water quality. – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium. – Method by analysis of inorganic carbon in sealed vessels (CO<sub>2</sub> headspace test). Pre-adaptation is not to be used. The *ten-day window* principle is not applied. (Reference method.)
2. Method Directive 67/548/EEC Annex V.C.4.C [Carbon dioxide (CO<sub>2</sub>) Evolution Modified Sturm Test]: Pre-adaptation is not to be used. The *ten-day window* principle is not applied.
3. Method Directive 67/548/EEC Annex V.C.4.E (Closed Bottle): Pre-adaptation is not to be used. The *ten-day window* principle is not applied.
4. Method Directive 67/548/EEC Annex V.C.4.D (Manometric Respirometry): Pre-adaptation is not to be used. The *ten-day window* principle is not applied.
5. Method Directive 67/548/EEC Annex V.C.4.F (MITI: Ministry of International Trade and Industry-Japan): Pre-adaptation is not to be used. The *ten-day window* principle is not applied.

---

<sup>1</sup> These five tests are identified as the most suitable for surfactants.

- B. Depending on the physical characteristics of the surfactant, one of the methods listed below might be used if appropriately justified<sup>1</sup>. It should be noted that the pass criterion of at least 70 % of these methods is to be considered as equivalent to the pass criterion of at least 60 % referred to in methods listed in point A above. The adequacy of the choice of the methods listed below shall be decided on a case by case confirmation, in accordance with Article 5 of this Regulation.
1. Method Directive 67/548/EEC Annex V.C.4.A (Dissolved Organic Carbon DOC Die-Away): Pre-adaptation is not to be used. The *ten-day window* principle is not applied. The pass criteria for biodegradability measured according to the test shall be at least 70 % within twenty-eight days.
  2. Method Directive 67/548/EEC Annex V.C.4.B (Modified OECD Screening-DOC Die-Away): Pre-adaptation is not to be used. The *ten-day window* principle is not applied. The pass criteria for biodegradability measured according to the test shall be at least 70 % within twenty-eight days.

N.B. All the above-mentioned methods from Council Directive 67/548/EEC can also be found in the publication Classification, Packaging and Labelling of Dangerous Substances in the European Union. Part 2: "Testing Methods", European Commission 1997, ISBN 92-828-0076-8.

---

<sup>1</sup> The DOC methods could give results on the removal and not on the ultimate biodegradation. The Manometric Respirometry and the MITI would not be appropriate in some cases because the high initial test concentration could be inhibitory.

## ANNEX IV

### Complementary risk assessment for surfactants in detergents

For those surfactants for which environmental risk assessment is available in the context of Directive 93/67/EEC, or Regulation (EEC) No 793/93 and Regulation (EC) No 1488/94, and Technical Guidance Documents, this risk assessment shall be considered together with the complementary risk assessment run in the scope of this Regulation.

The complementary risk assessment run in the scope of this **Regulation shall** be considered in the context of assessments made on the basis of Directive 93/67/EEC and Regulation (EEC) **No 793/93**.

The study shall cover the aquatic environmental compartment. Additional information relating to specific risk assessment concerns might be required by the Committee on a case by case basis. Additional information might include other environmental compartments such as sewage sludge and soil.

As noted in Articles 12(2) and 13 the guidelines included in this Annex for the Decisions on derogation may be adapted as appropriate on the basis of the accumulated experience.

The technical file referred to in Articles 5 and 9 shall contain at least the information described here below.

1. Identity of the surfactant (in accordance with the provisions laid down by Annex VII.A of Directive 67/548/EEC.)
  - 1.1. Name
    - 1.1.1. Names in the IUPAC nomenclature
    - 1.1.2. Other names
    - 1.1.3. CAS number and CAS name (if available)
    - 1.1.4. EINECS <sup>1</sup> or ELINCS <sup>2</sup> numbers (if available)
  - 1.2. Molecular and structural formula
- 1.3. Composition of the surfactant

---

<sup>1</sup> European Inventory of Existing Chemical Substances.

<sup>2</sup> European List of Notified Chemical Substances.

2. Information on the surfactant

2.1. Quantities of the surfactant used in detergents

2.2. The information on use patterns given in this section shall be sufficient to allow an approximate but realistic estimate of function and environmental exposure to the surfactant as associated with its use in detergents. It shall include the following:

- importance of the application (societal value);
- use conditions (release scenario);
- use volume;
- availability and suitability of alternatives (performance and economic considerations);
- assessment of relevant environmental information.

3. Information on the potential recalcitrant metabolite

Toxicity information on test liquors shall be provided. If no data are available on residue identity, the information referred to in point 4.2.1 below may be requested, depending on the potential risk, the importance and the quantity of the surfactant used in detergents. In conflicting cases concerning this information, a Decision may be taken in accordance with Article 12(2).

***Information shall be provided on contents of chemicals that are very persistent and/or very bio-accumulative and/or persistent, bio-accumulative and toxic, and/or of chemicals with endocrine-disrupting properties and/or of any chemicals that have these properties.***

#### 4. Additional studies

##### 4.1. Biodegradability tests

###### 4.1.1. Pre-adapted inoculum

Any of the preferred tests described in Annex III, may be run with pre adapted inoculum in order to provide evidence of the relevance of pre-adaptation for the surfactant.

###### 4.1.2. Inherent Biodegradability Tests

At least one of the *following tests shall* be included:

- method *mentioned in* Directive 67/548/EEC Annex V.C.12 (Modified SCAS test);
- method *mentioned in* Directive 67/548/EEC Annex V.C.9 (Zahn-Wellens).

Failure to pass the inherent biodegradability test would indicate potential for persistency which may be considered, in general terms, as sufficient to prohibit the placing on the market of such a surfactant unless, as stated in Article 5, there are other justifiable reasons for granting a derogation.

###### 4.1.3. Activated Sludge Simulation Biodegradability Tests

The following *tests shall* be included:

- method Directive 67/548/EEC Annex V.C.10;

(including possible changes in operating conditions as proposed in EN ISO 11733).

Failure to pass the activated sludge simulation biodegradability *test would* indicate potential for the release of the metabolites by sewage treatment, which may be considered, in general terms, as evidence of *the* need for a more complete risk assessment.

## 4.2. Toxicity testing of biodegradation test liquors

Toxicity information on test liquors is to be provided on:

### 4.2.1. Chemical and physical information, such as:

- identity of the metabolite (and analytical means by which it was obtained);
- key physical chemical properties (water solubility, Octanol: Water partition coefficient (Log Po/w, etc.).

### 4.2.2. Effects on organisms:

Fish: the test recommended is that in Annex V.C.1 of Directive 67/548/EEC

Daphnia: the test recommended is that in Annex V.C.2 of Directive 67/548/EEC

Algae: the test recommended is that in Annex V.C.3 of Directive 67/548/EEC

Bacteria: the test recommended is that in Annex V.C.11 of Directive 67/548/EEC

### 4.2.3. Degradation:

Biotic: the test recommended is that in Annex V.C.5 of Directive 67/548/EEC

Abiotic: the test recommended is that in Annex V.C.7 of Directive 67/548/EEC. The information to be provided will *also concern* the potential of metabolites for bio-concentration and their partitioning to the sediment phase.

Moreover, if some metabolites are suspected for endocrine disrupting activity, it is recommended to determine *whether* these have *the* potential to result in adverse affects as soon as validated testing schemes to assess such adverse effects are available.

N.B. All the *above-mentioned* methods from Directive 67/548/EEC can also be consulted in the publication Classification, Packaging and Labelling of Dangerous Substances in the European Union; Part 2: "Testing Methods"; European Commission 1997; ISBN 92-828-0076-8.

## ANNEX V

### List of surfactants that have obtained a derogation

The following detergent surfactants passing tests stipulated in Annex II, but not passing tests stipulated in Annex III, may be placed on the market by means of derogation stipulated in Article 5 and in accordance with the procedure laid down in *Article 12(2)*:

NAME in the IUPAC NOMENCLATURE	EINECS or ELINCS NUMBER	CAS NUMBER and CAS NAME	LIMITATIONS

EINECS means the European Inventory of Existing Commercial Substances. This inventory contains the definitive list of all substances deemed to be on the Community market on 18 September 1981.

ELINCS means the list of new substances as defined in Council Directive 92/32/EEC of 30 April 1992 amending for the seventh time Directive 67/548/EEC on the approximation of the laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances<sup>1</sup>.

---

<sup>1</sup> OJ L 154, 5.6.1992, p. 1.

## ANNEX VI

### List of banned or restricted detergent surfactants

The following detergent surfactants have been identified as not complying with the provisions of this Regulation:

NAME in the IUPAC NOMENCLATURE	EINECS or ELINCS NUMBER	CAS NUMBER and CAS NAME	LIMITATIONS

EINECS means the European Inventory of Existing Commercial Substances. This inventory contains the definitive list of all substances deemed to be on the Community market on 18 September 1981.

ELINCS means the list of new substances as defined in Directive 92/32/EEC.

## ANNEX VII

### List of banned or restricted detergent surfactants, *including* in the implementation of other Community legislation

The following list of detergent surfactants<sup>1</sup> incorporates substances and preparations covered by this Regulation and banned or restricted by other Community legislation, in particular *the substances and preparations listed in points 29, 30 and 31 of Annex I of Directive 76/769/EEC and the substances classified as carcinogenic, mutagenic or toxic to reproduction, category 3 pursuant to Directive 67/548/EEC*:

NAME in the IUPAC NOMENCLATURE	LEGISLATION ENFORCED	EINECS or ELINCS NUMBER	CAS NUMBER and CAS NAME	LIMITATIONS

EINECS means the European Inventory of Existing Commercial Substances. This inventory contains the definitive list of all substances deemed to be on the Community market on 18 September 1981.

ELINCS means the list of new substances as defined in Council Directive 92/32/EEC.

---

<sup>1</sup> It may refer as appropriate to the enforcement of international agreements and/or organisations.

## ANNEX VIII

### Labelling and ingredient datasheet

#### A. Labelling for contents

As prescribed in Article 11(3) of this Regulation, the following provisions on labelling shall apply to the packaging of detergents sold to the general public.

The following weight percentage ranges:

- less than 5 %,
- 5 % or over but less than 15 %,
- 15 % or over but less than 30 %,
- 30 % and more,

shall be used to indicate the content of the constituents listed below where they are added in a concentration above 0.2 weight %:

- *total surfactants,*
- *other chelating agents,*
- *oxidants,*
- *fabric softening ingredients,*
- *dirt redepositing inhibitors,*
- *oxidant activators,*
- *colour protectors,*
- *other solvents,*
- *other hardness sequestering agents,*

*they shall also be used to indicate the content of the constituents listed below, if added, irrespective of their concentration:*

- *EDTA,*
- *phosphates,*
- *phenols.*

For other constituents, if added, neither the above percentage ranges nor the concentration threshold of 0.2 % shall be applied. The following classes of constituent, if added, shall be listed irrespective of their concentration:

- enzymes,
- disinfectants,
- *preservatives,*
- *perfumes,*
- *optical brighteners.*

If added, preservation agents shall be listed, irrespective of their concentration, using where possible the common nomenclature established under Article 8 of Directive 76/768/EEC.

If added, fragrances that appear on the list of allergenic perfume ingredients first established by the Scientific Committee on Cosmetics and Non Food Products in its opinion SCCNFP/0017/98<sup>1</sup>, shall be listed using the nomenclature established by that *Committee*.

*By ...\* at the latest, the Scientific Committee on Cosmetics and Non-Food Products shall give an opinion on whether, based on scientific knowledge, a concentration limit shall be established for listing such fragrances. On the basis of that opinion, the Commission shall put forward, if necessary, a proposal establishing a concentration limit.*

---

<sup>1</sup> [http://europa.eu.int/comm/food/fs/sc/sccp/out98\\_en.html](http://europa.eu.int/comm/food/fs/sc/sccp/out98_en.html)

\* *Eighteen months after the entry into force of this Regulation.*

For detergents intended to be used in the industrial sector, and not made available to members of the general public, the above-mentioned requirements do not have to be fulfilled if the equivalent information is provided by means of technical data sheets, safety data sheets, or in a similar appropriate manner.

*A full list of the substances added to the detergent shall be made readily accessible to consumers and shall be published by the manufacturer on appropriate web sites, made available via a freephone number, and supplied in writing on demand and within a reasonable period. To this end, the Commission shall adopt, by ...\* at the latest, a common ingredients nomenclature for detergents.*

*The web site address, telephone number, and postal address of the information service shall be indicated on the primary packaging.*

#### B. Labelling for Dosage information

As prescribed in Article 11(4) of this Regulation, the following provisions on labelling shall apply to the packaging of detergents sold to the general public. The packaging of detergents sold to the general public intended to be used as laundry detergents shall bear the following information:

- The recommended quantities and/or dosage instructions expressed in millilitres or grams appropriate to a standard washing machine load, for specified water hardness classes and making provision for one or two cycle washing processes.
- ***For normal detergents***, the number of standard washing machine loads of ‘normally soiled’ fabrics, ***and, for detergents for delicate fabrics, the number of standard washing machine loads of ‘lightly soiled’ fabrics*** that can be washed with the contents of the package using water of medium hardness, corresponding to 2.5 millimoles CaCO<sub>3</sub>/l.
- The capacity of any measuring cup, if provided, shall be indicated in millilitres or grams.

The standard washing machine loads are 4.5 kg dry fabric for heavy-duty detergents and 2.5 kg dry fabric for low-duty detergents in line with the definitions of Commission Decision 1999/476/EC of 10 June 1999 establishing the ecological criteria for the award of the Community Eco-label to laundry detergents<sup>1</sup>. A detergent shall be considered to be a heavy-duty detergent unless the claims of the manufacturer or importer predominantly promotes fabric care i.e. low temperature wash, delicate fibres and colours.

---

\* ***One year after the entry into force of this Regulation.***

<sup>1</sup> OJ L 187, 20.7.1999, p. 52. Decision amended by Decision 2003/200/EC (OJ L 76, 22.3.2003, p. 25).

### C. Ingredient datasheet

The following provisions shall apply to the listing of ingredients on the datasheet referred to in Article 9(3) of this Regulation.

The datasheet shall list the name of the detergent and of the manufacturer.

All ingredients shall be listed; they shall be listed in order of decreasing abundance by weight, and the list shall be sub-divided into the following weight percentage ranges:

- 10 % or more,
- 1 % or *more*, but less than 10 %,
- 0.1 % or *more*, but less than 1 %,
- less than 0.1 %.

Impurities shall not be considered to be ingredients.

The common chemical name or IUPAC<sup>1</sup> name, the CAS number, and, where available, the INCI<sup>2</sup> name and the European Pharmacopoeia name shall be given for each ingredient.

---

<sup>1</sup> International Union of Pure and Applied Chemistry

<sup>2</sup> International Nomenclature Cosmetic Ingredient

## ANNEX IX

### Test methods and analytical methods

The following test and analytical methods apply to control procedures of detergents on the market made by Member States:

#### 1. Reference method (confirmatory test)

##### 1.1. Definition

This method describes a laboratory model of the activated sludge + secondary settler which is designed to simulate municipal sewage treatment. The conditions described are those from Directives that preceded this Regulation. Improved state-of-the-art operating conditions can be applied to this test method as described in EN ISO 11733.

##### 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 sewage 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 twenty-four 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 shall be monitored by means of a flow meter 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,  $\text{CO}(\text{NH}_2)_2$ ;
- 7 mg sodium chloride,  $\text{NaCl}$ ;
- 4 mg calcium chloride,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ;
- 2 mg magnesium sulphate,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ;
- 28 mg of di-potassium hydrogen phosphate,  $\text{K}_2\text{HPO}_4$ ;
- and  $10 \pm 1$  mg of the surfactant.

The synthetic sewage is freshly prepared daily.

### 1.4. Preparation of samples

Uncompounded surfactants are examined in the original state. Active content of surfactant samples must be determined in order to prepare the synthetic sewage (1.3).

### 1.5. Operation of equipment

Initially, fill aeration vessel C and settling vessel D with synthetic sewage. The height of the vessel D should be so fixed that the volume contained in the 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 the aerator G, air-lift E and dosing device B in operation. The synthetic sewage must pass through the aeration vessel C at a 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 that inhibit the activated sludge or contain surfactants must not be used. The 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 the aeration vessel C, in the base of the 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 the sludge fails to settle, its settleability may be increased by the addition of 2 ml portions of a 5 % solution of ferric chloride, repeated as necessary.

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

#### 1.6. Checking measuring equipment

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

The surfactant content (in mg/l) of the effluent collected over twenty-four 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 surfactant

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 surfactant degradation is obtained at the end of the running-in period shown in Figure 3.

The content of dry matter in the activated sludge contained in the aeration vessel 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 degradation test is performed at room temperature; this should be steady and kept between 19-24°C.

### 1.7. Calculation of biodegradability

The percentage degradation of surfactant must be calculated every day on the basis of the surfactant content in mg/l of the synthetic sewage and of the corresponding effluent accumulated in vessel F.

The degradability values thus obtained should be presented graphically as in Figure 3.

The degradability of the surfactant should be calculated as the arithmetic mean of the values obtained over the twenty-one days that follow the running-in and acclimatisation 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 fourteen results collected over the twenty-one days which follow the running-in period should be used in calculating the average.

## 2. Determination of anionic surfactants in biodegradability tests

### 2.1. Principle

The method is based on the fact that the cationic dye methylene blue forms blue salts with anionic surfactants [MBAS<sup>1</sup>], which can be extracted with chloroform. To eliminate interference, the extraction is first effected from alkaline solution and the extract is then shaken with acidic methylene blue solution. The absorbency of the separated organic phase is measured photometrically at the wavelength of maximum absorption of 650 nm.

---

<sup>1</sup> MBAS means Methylene Blue Active Substances.

## 2.2. Reagents and equipment

### 2.2.1. Buffer solution pH 10

Dissolve 24g sodium bicarbonate,  $\text{NaHCO}_3$  AR, and 27g anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) AR in deionised water and dilute to 1 000 ml.

### 2.2.2. Neutral methylene blue solution

Dissolve 0.35 g methylene blue AR in deionised water and dilute to 1 000 ml. Prepare the solution at least twenty-four hours before use. The absorbency of the blank chloroform phase, measured against chloroform must not exceed 0.015 per 1 cm of layer thickness at 650 nm.

### 2.2.3. Acidic methylene blue solution

Dissolve 0.35 g methylene blue AR in 500 ml deionised water and mix with 6.5 ml  $\text{H}_2\text{SO}_4$  ( $d = 1.84 \text{ g/ml}$ ). Dilute to 1 000 ml with deionised water. Prepare the solution at least twenty-four hours before use. The absorbency of the blank chloroform phase, measured against chloroform must not exceed 0.015 per 1 cm of layer thickness at 650 nm.

### 2.2.4. Chloroform (trichloromethane) AR freshly distilled

### 2.2.5. Dodecyl benzene sulphonic acid methyl ester

### 2.2.6. Ethanolic potassium hydroxide solution, KOH 0.1 M

### 2.2.7. Ethanol pure, $\text{C}_2\text{H}_5\text{OH}$

### 2.2.8. Sulphuric acid, $\text{H}_2\text{SO}_4$ 0.5 M

### 2.2.9. Phenolphthalein solution

Dissolve 1g phenolphthalein in 50 ml ethanol and add 50 ml deionised water while stirring continuously. Filter off any precipitate obtained.

- 2.2.10. Methanolic hydrochloric acid: 250 ml hydrochloric acid AR and 750 ml methanol
- 2.2.11. Separating funnel, 250 ml
- 2.2.12. Graduated flask, 50 ml
- 2.2.13. Graduated flask, 500 ml
- 2.2.14. Graduated flask, 1 000 ml
- 2.2.15. Round-bottomed flask with ground glass stopper and reflux condenser, 250 ml; boiling granules
- 2.2.16. pH meter
- 2.2.17. Photometer for measurements at 650 nm, with 1 to 5 cm cells
- 2.2.18. Qualitative grade filter paper

### 2.3. Procedure

The samples for analysis must not be taken through a layer of foam.

After thorough cleaning with water, the equipment used for the analysis must be thoroughly rinsed with methanolic hydrochloric acid (2.2.10) and then with deionised water before using.

Filter the activated sludge plant influent and effluent to be examined immediately on sampling. Discard the first 100 ml of the filtrates.

Place a measured volume of the sample, neutralised if necessary, into a 250 ml separating funnel (2.2.11). The volume of sample should contain between 20 and 150  $\mu\text{g}$  of MBAS. At the lower MBAS content, up to 100 ml of sample may be used. When using less than 100 ml, dilute to 100 ml with deionised water. Add to the sample 10 ml of buffer solution (2.2.1), 5 ml of neutral methylene blue solution (2.2.2) and 15 ml of chloroform (2.2.4). Shake the mixture uniformly and not too vigorously for one minute. After phase separation, run the chloroform layer into a second separating funnel, containing 110 ml of deionised water and 5 ml of acidic methylene blue solution (2.2.3). Shake the mixture for one minute. Pass the chloroform layer through a cotton-wool filter previously cleaned and wetted with chloroform into a graduated flask (2.2.12).

Extract the alkaline and acid solutions three times, using 10 ml of chloroform for the second and third extractions. Filter the combined chloroform extracts through the same cotton wool filter and dilute to the mark in the 50 ml flask (2.2.12) with chloroform used for rewashing the cotton wool. Measure the absorbency of the chloroform solution with a photometer at 650 nm in 1 to 5 cm cells against chloroform. Run a blank determination through the whole procedure.

#### 2.4. Calibration curve

Prepare a calibration solution from the standard substance dodecylbenzene sulphonic acid methyl ester (tetrapropylene type mol. wt. 340) after saponification into the potassium salt. The MBAS is calculated as sodium dodecyl benzene sulphonate (mol. wt. 348).

From a weighing pipette, weigh 400 to 450 mg of dodecyl-benzene-sulphonic-acid-methyl-ester (2.2.5) to the nearest 0.1 mg in a round-bottomed flask and add 50 ml of ethanolic potassium hydroxide solution (2.2.6) and some boiling granules. After mounting the reflux condenser, boil for one hour. After cooling, wash the condenser and ground glass joint with about 30 ml of ethanol, and add these washings to the contents of the flask. Titrate the solution with sulphuric acid against phenolphthalein until it becomes colourless. Transfer this solution to a 1 000 ml graduated flask (2.2.14), dilute to the mark with deionised water and mix.

Part of this surfactant stock solution is then further diluted. Withdraw 25 ml, transfer to a 500 ml graduated flask (2.2.13), dilute to the mark with deionised water and mix.

This standard solution contains:

$$\frac{E \times 1,023}{20\,000} \text{ mg MBAS per ml,}$$

where: E is the sample weight in mg.

To establish the calibration curve, withdraw 1, 2, 4, 6, 8 ml portions of the standard solution and dilute each to 100 ml with deionised water. Then proceed as stated under item 2.3 including a blank determination.

## 2.5. Calculation of results

The amount of anionic surfactant (MBAS) in the sample is read from the calibration curve (2.4). The MBAS content of the sample is given by:

$$\frac{\text{mg MBAS} \times 1\,000}{V} = \text{MBAS mg/l}$$

where: V = ml volume of the sample used.

Express the results as sodium dodecylbenzene sulphonate (MW 348).

## 2.6. Expression of results

Express the results as MBAS mg/l to the nearest 0.1.

# 3. Determination of non-ionic surfactants in biodegradation test liquors

## 3.1 Principle

Surface active agents are concentrated and isolated by gas stripping. In the sample used, the quantity of non-ionic surfactant should be in the range 250-800 µg.

The stripped surfactant is dissolved in ethyl acetate.

After phase separation and evaporation of the solvent, the non-ionic surfactant is precipitated in aqueous solution with modified Dragendorff reagent ( $\text{KBiI}_4 + \text{BaCl}_2 + \text{glacial acetic acid}$ ).

The precipitate is filtered, washed with glacial acetic acid and dissolved in ammonium tartrate solution. The bismuth in the solution is titrated potentiometrically with pyrrolidinedithiocarbamate solution at pH 4-5 using a bright platinum indicator electrode and a calomel or silver/silver chloride reference electrode. The method is applicable to non-ionic surfactants containing 6-30 alkylene oxide groups.

The titration result is multiplied by the empirical factor of 54 for conversion to the reference substance nonylphenol condensed with 10 mols ethylene oxide (NP 10).

### 3.2. Reagents and Equipment

Reagents are to be made up in deionised water.

3.2.1. Pure ethyl acetate, freshly distilled

3.2.2. Sodium bicarbonate,  $\text{NaHCO}_3$  AR

3.2.3. Dilute hydrochloric acid [20 ml concentrated acid ( $\text{HCl}$ ) diluted to 1 000 ml with water]

3.2.4. Methanol AR, freshly distilled, stored in a glass bottle.

3.2.5. Bromocresol purple, 0.1 g in 100 ml methanol.

3.2.6. Precipitating agent: the precipitating agent is a mixture of two volumes of solution A and one volume of solution B. The mixture is stored in a brown bottle and can be used for up to one week after mixing.

#### 3.2.6.1. Solution A

Dissolve 1.7 g bismuth nitrate,  $\text{BiONO}_3 \cdot \text{H}_2\text{O}$  AR, in 20 ml glacial acetic acid, and make up to 100 ml with water. Then dissolve 65 g potassium iodide AR in 200 ml water. Mix these two solutions in a 1 000 ml measuring flask, add 200 ml glacial acetic acid (3.2.7) and make up to 1 000 ml with water.

#### 3.2.6.2. Solution B

Dissolve 290 g barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  AR, in 1 000 ml of water.

3.2.7. Glacial acetic acid 99-100 % (lower concentrations are unsuitable).

3.2.8. Ammonium tartrate solution: mix 12.4 g tartaric acid AR and 12.4 ml of ammonia solution AR ( $d = 0.910 \text{ g/ml}$ ) and make up to 1 000 ml with water (or use the equivalent amount of ammonium tartrate AR).

3.2.9. Dilute ammonia solution: 40 ml ammonia solution AR ( $d = 0.910 \text{ g/ml}$ ) diluted to 1 000 ml with water.

- 3.2.10. Standard acetate buffer: dissolve 40 g solid sodium hydroxide AR, in 500 ml water in a beaker and allow to cool. Add 120 ml glacial acetic acid (3.2.7). Mix thoroughly, cool and transfer to a 1 000 ml volumetric flask. Make up to the mark with water.
- 3.2.11. Pyrrolidinedithiocarbamate solution (known as “carbate solution”): dissolve 103 mg sodium pyrrolidinedithiocarbamate,  $C_5H_8NNaS_2 \cdot 2H_2O$ , in about 500 ml water, add 10 ml of n-amyl alcohol AR and 0.5 g  $NaHCO_3$  AR, and make up to 1 000 ml with water.
- 3.2.12. Copper sulphate solution (for standardisation of 3.2.11).

#### STOCK SOLUTION

Mix 1 249 g copper sulphate,  $CuSO_4 \cdot 5H_2O$  AR, with 50 ml 0.5 M sulphuric acid and make up to 1 000 ml with water.

#### STANDARD SOLUTION

Mix 50 ml stock solution with 10 ml 0.5 M  $H_2SO_4$  and make up to 1 000 ml with water.

- 3.2.13. Sodium chloride AR
- 3.2.14. Gas-stripping apparatus (see Figure 5).  
The diameter of the sintered disc must be the same as the internal diameter of the cylinder.
- 3.2.15. Separating funnel, 250 ml.
- 3.2.16. Magnetic stirrer with magnet 25-30 mm.
- 3.2.17. Gooch crucible, diameter of the perforated base = 25 mm, Type G4.
- 3.2.18. Circular glass-fibre filter papers, 27 mm diameter with fibre diameter 0.3-1.5  $\mu m$ .
- 3.2.19. Two filter flasks with adapters and rubber collars, 500 and 250 ml respectively.

3.2.20. Recording potentiometer fitted with a bright platinum indicator electrode and a calomel or silver/silver chloride reference electrode with a 250 mV range, with automatic burette of 20-25 ml capacity, or alternative manual equipment.

### 3.3. Method

#### 3.3.1. Concentration and separation of the surfactant

Filter the aqueous sample through a qualitative filter paper. Discard the first 100 ml of the filtrate.

Into the stripping apparatus, previously rinsed with ethyl acetate, place a measured quantity of the sample, such that it contains between 250-800 µg non-ionic surfactant.

To improve the separation add 100 g sodium chloride and 5 g sodium bicarbonate.

If the volume of the sample exceeds 500 ml, add these salts to the stripping apparatus in solid form, and dissolve by passing nitrogen or air through.

If a smaller-sized sample is used, dissolve the salts in 400 ml water and then add to the stripping apparatus.

Add water to bring the level to the upper stopcock.

Cautiously add 100 ml ethyl acetate on top of the water.

Fill the wash-bottle in the gas-line (nitrogen or air) two-thirds full with ethyl acetate.

Pass a gas stream of 30-60 l/h through the apparatus; the use of a flowmeter is recommended. The rate of aeration must be increased gradually at the beginning. The gas rate must be so adjusted that the phases remain noticeably separate to minimise the mixing of the phases and the solution of the ethyl acetate in the water. Stop the gas flow after five minutes.

If there is a reduction of more than 20 % in the volume of the organic phase through solution in water, the sublation must be repeated paying special attention to the rate of gas flow.

Run off the organic phase into a separating funnel. Return any water in the separating funnel from the aqueous phase - it should only be a few ml - to the stripping apparatus. Filter the ethyl acetate phase through a dry qualitative filter paper into a 250 ml beaker.

Put a further 100 ml ethyl acetate into the stripping apparatus and again pass nitrogen or air through for five minutes. Draw off the organic phase into the separating funnel used for the first separation, reject the aqueous phase and run the organic phase through the same filter as the first ethyl acetate portion. Rinse both the separating funnel and the filter with about 20 ml ethyl acetate.

Evaporate the ethyl acetate extract to dryness using a water-bath (fume cupboard). Direct a gentle stream of air over the surface of the solution to accelerate the evaporation.

### 3.3.2. Precipitation and filtration

Dissolve the dry residue from 3.3.1 in 5 ml methanol, add 40 ml water and 0.5 ml dilute HCl (3.2.3) and stir the mixture with a magnetic stirrer.

To this solution add 30 ml of precipitating agent (3.2.6) from a measuring cylinder. The precipitate forms after repeated stirring. After stirring for ten minutes leave the mixture to stand for at least five minutes.

Filter the mixture through a Gooch crucible, the base of which is covered with a glass-fibre filter paper. First wash the filter under suction with about 2 ml glacial acetic acid. Then thoroughly wash the beaker, magnet, and crucible with glacial acetic acid, of which about 40-50 ml is necessary. It is not necessary to quantitatively transfer the precipitate adhering to the sides of the beaker, to the filter, because the solution of the precipitate for the titration is returned to the precipitating beaker, and the remaining precipitate will then be dissolved.

### 3.3.3. Dissolution of the precipitate

Dissolve the precipitate in the filter crucible by the addition of hot ammonium tartrate solution (about 80 °C) (3.2.8) in three portions of 10 ml each. Allow each portion to stand in the crucible for some minutes before being sucked through the filter into the flask.

Put the contents of the filter flask into the beaker used for the precipitation. Rinse the sides of the beaker with a further 20 ml of tartrate solution to dissolve the rest of the precipitate.

Carefully wash the crucible, adapter and filter flask with 150-200 ml water, and return the rinsing water to the beaker used for the precipitation.

### 3.3.4 *Titration*

Stir the solution using a magnetic stirrer (3.2.16), add a few drops of bromocresol purple (3.2.5) and add the dilute ammonia solution (3.2.9) until the colour turns violet (the solution is initially weakly acid from the residue of acetic acid used for rinsing).

Then add 10 ml standard acetate buffer (3.2.10), immerse the electrodes in the solution, and titrate potentiometrically with standard “carbate solution” (3.2.11), the burette tip being immersed in the solution.

The titration rate should not exceed 2 ml/min.

The endpoint is the intersection of the tangents to the two branches of the potential curve. It will be observed occasionally that the inflection in the potential curve becomes flattened; this can be eliminated by carefully cleaning the platinum electrode (by polishing with emery paper).

### 3.3.5. Blank determinations

At the same time run a blank determination through the whole procedure with 5 ml methanol and 40 ml water, according to the instructions in 3.3.2. The blank titration should be below 1 ml, otherwise the purity of the reagents (3.2.3, 3.2.7, 3.2.8, 3.2.9, 3.2.10) is suspect, especially their content of heavy metals, and they must be replaced. The blank must be taken into account in the calculation of the results.

### 3.3.6. Control of the factor of the “carbate solution”

Determine the factor for the carbate solution on the day of use. To do this, titrate 10 ml of the copper sulphate solution (3.2.12) with “carbate solution” after the addition of 100 ml water and 10 ml standard acetate buffer (3.2.10). If the amount used is  $a$  ml, the factor  $f$  is:

$$f = \frac{10}{a}$$

and all the results of the titration are multiplied by this factor.

### 3.4. Calculation of results

Every non-ionic surfactant has its own factor, depending on its composition, particularly on the length of the alkene oxide chain. The concentration of non-ionic surfactant is expressed in relation to a standard substance – a nonyl phenol with ten ethylene oxide units (NP 10) – for which the conversion factor is 0.054.

Using this factor the amount of surfactant present in the sample is found expressed as mg of NP 10 equivalent, as follows:

$$(b - c).f.0.054 = \text{mg non-ionic surfactant as NP 10}$$

where:

b = volume of “carbate solution” used by the sample (ml),

c = volume of “carbate solution” used by the blank (ml),

f = factor of the “carbate solution”.

### 3.5 Expression of results

Express the results in mg/l as NP 10 to the nearest 0.1.

## 4. Preliminary treatment of anionic surfactants to be tested

### 4.1. Preliminary notes

#### 4.1.1. Treatment of samples

The treatment of anionic surface-active agents and formulated detergents prior to the determination of primary 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.

#### 4.1.2. Ion-exchange procedure

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

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

#### 4.1.3. Analytical control

After homogenising, 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 for preparing 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.

#### 4.2. Principle

From a 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 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 extraction with ethanol containing CO<sub>2</sub>. 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 that might upset the biodegradability test and the analytical procedure are eliminated by the cation exchanger placed above the anion exchanger.

### 4.3. Chemicals and equipment

#### 4.3.1. Deionised water

#### 4.3.2. Ethanol, 95 % (v/v) $\text{C}_2\text{H}_5\text{OH}$ (permissible denaturant: methyl ethyl ketone or methanol)

#### 4.3.3. Isopropanol/water mixture (50/50 v/v):

- 50 parts by volume isopropanol,  $\text{CH}_3\text{CHOH.CH}_3$ , and
- 50 parts by volume water (4.3.1)

#### 4.3.4. Solution of carbon dioxide in ethanol (approximately 0,1 % $\text{CO}_2$ ): using a delivery tube with a built-in sinter, pass carbon dioxide, $\text{CO}_2$ , through the ethanol (4.3.2) for ten minutes . Use fresh solutions only

#### 4.3.5. Ammonium bicarbonate solution (60/40 v/v): 0,3 mol $\text{NH}_4\text{HCO}_3$ in 1 000 ml of an isopropanol/water mixture consisting of 60 parts by volume isopropanol and 40 parts by volume water (4.3.1)

#### 4.3.6. Cation exchanger (KAT), strongly acidic, resistant to alcohol (50-100 mesh)

#### 4.3.7. Anion exchanger (AAT), macro-porous, Merck Lewatit MP 7080 (70-150 mesh) or equivalent

#### 4.3.8. Hydrochloric acid, 10 % $\text{HCl}$ (w/w)

#### 4.3.9. 2 000 ml round-bottomed flask with ground glass stopper and reflux condenser

#### 4.3.10. 90 mm diameter suction filter (heatable) for filter papers

#### 4.3.11. 2 000 ml filter flask

#### 4.3.12. Exchange columns with heating jacket and tap: inner tube 60 mm in diameter and 450 mm in height (see Figure 4)

4.3.13. Water-bath

4.3.14. Vacuum drying oven

4.3.15. Thermostat

4.3.16. Rotary evaporator

4.4. Preparation of extract and separation of anionic active agents

4.4.1. Preparation of extract

The quantity of surfactants necessary for the biodegradation test is about 50 g MBAS.

Normally, the quantity of product to be extracted will not exceed 1 000 g, but it may be necessary to extract further quantities of sample. For practical reasons, the quantity of product used should in most cases be limited to 5 000 g in preparing extracts for the biodegradation test.

Experience has shown that there are advantages in using a number of small extractions rather than one large extraction. The exchanger quantities specified are designed for a working capacity of 600-700 mmoles of surfactants and soap.

4.4.2. Isolation of alcohol-soluble constituents

Add 250 g of the synthetic detergent to be analysed to 1 250 ml ethanol, heat the mixture to boiling point and reflux for one hour with stirring. Pass the hot alcoholic solution through a coarse-pored suction filter heated to 50 °C and filter rapidly. Wash the flask and suction filter with approximately 200 ml hot ethanol. Collect the filtrate and filter washings in a filter flask.

In the case of pastes or liquid products to be analysed, make sure that not more than 55 g anionic surfactants and 35 g soap are contained in the sample. Evaporate this weighed sample to dryness. Dissolve the residue in 2000 ml ethanol and proceed as described above.

In the case of powders of low apparent density (< 300 g/l) it is recommended to increase the ethanol ratio in the relation 20:1. Evaporate the ethanolic filtrate to dryness, preferably by means of a rotary evaporator. Repeat the operation if a greater quantity of extract is required. Dissolve the residue in 5 000 ml isopropanol/water mixture.

#### 4.4.3. Preparation of ion-exchange columns

##### CATION-EXCHANGE COLUMN

Place 600 ml cation-exchange resin (4.3.6) in a 3 000 ml beaker and cover by adding 2 000 ml hydrochloric acid (4.3.8). Allow standing for at least two hours, with occasional stirring. Decant the acid and transfer the resin into the column (4.3.12) by means of deionised water. The column should contain a glass-wool plug. Wash the column with deionised water at a rate of 10-30 ml/min until the eluate is free of chloride. Displace the water with 2 000 ml isopropanol/water mixture (4.3.3) at a rate of 10-30 ml/min. The exchange column is now ready for operation.

##### ANION-EXCHANGE COLUMN

Place 600 ml anion-exchange resin (4.3.7) in a 3 000 ml beaker and cover by adding 2 000 ml deionised water. Allow the resin to swell for at least two hours. Transfer the resin into the column by means of deionised water. The column should contain a glass-wool plug.

Wash the column with 0,3 M ammonium bicarbonate solution (4.3.5) until free of chloride. This requires about 5 000 ml solution. Wash again with 2 000 ml deionised water. Displace the water with 2 000 ml isopropanol/water mixture (4.3.3) at a rate of 10-30 ml/min. The exchange column is now in the OH-form and ready for operation.

#### 4.4.4. Ion-exchange procedure

Connect the exchange columns so that the cation-exchange column is placed on top of the anion-exchange column. Heat the exchange columns to 50 °C using thermostatic control. Heat 5 000 ml of the solution obtained in item 4.4.2 to 60 °C and pass the solution through the exchanger combination at a rate of 20 ml/min. Wash the columns with 1 000 ml hot isopropanol/water mixture (4.3.3).

To obtain the anionic surface active agents (MBAS), disconnect the KAT column. Using 5 000 ml ethanol/CO<sub>2</sub> solution at 50 °C (4.3.4), elute the soap fatty acids out of the KAT column. Reject the eluate.

Then elute the MBAS out of the AAT column with 5 000 ml ammonium bicarbonate solution (4.3.5). Evaporate the eluate to dryness using a steam bath or in a rotary evaporator. The residue contains the MBAS (as ammonium salt) and possible non-surfactant anionics that have no detrimental effect on the biodegradation test. Add deionised water to the residue until a definite volume is obtained and determine the MBAS content in an aliquot. The solution is used as a standard solution of the anionic synthetic detergents for the biodegradation test. The solution should be kept at a temperature below 5 °C.

#### 4.4.5. Regeneration of ion exchange resins

The cation exchanger is rejected after use.

Passing an additional quantity of ammonium bicarbonate solution (4.3.5) down the column at a flow rate of approximately 10 ml/min until the eluate is free from anionic surfactants (methylene blue test) regenerates the anion-exchange resin. Then pass 2 000 ml isopropanol/water mixture (4.3.3) down the anion exchanger to wash. The anion exchanger is again ready for operation.

### 5. Preliminary treatment of non ionic surfactants to be tested

#### 5.1. Preliminary notes

##### 5.1.1 Treatment of samples

The treatment of non-ionic surface-active agents and formulated detergents prior to the determination of primary biodegradability in the confirmatory test is:

PRODUCTS	TREATMENT
Non-ionic surfactants	None
Formulated detergents	Alcoholic extraction followed by separation of the non-ionic 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.

##### 5.1.2. Ion-exchange procedure

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

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

### 5.1.3. Analytical control

After homogenising, the concentration of anionic and non-ionic surfactants in the detergent is determined according to the MBAS and BiAS analytical procedure. The soap content is determined by a suitable analytical method.

This analysis of the product is necessary to calculate the quantities required preparing fractions for the biodegradability tests.

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

## 5.2. Principle

From a homogeneous sample (powders, dried paste and dried liquids) an ethanol extract is obtained which contains the surfactants, soap and other alcohol-soluble constituents of the 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 50 °C. This temperature is necessary to prevent the precipitation of any fatty acids which may be present in acidic media. The non-ionic surfactants are obtained from the effluent by evaporation.

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

## 5.3. Chemicals and equipment

### 5.3.1. Deionised water

### 5.3.2. Ethanol, $C_2H_5OH$ 95 % (v/v) (permissible denaturant: methyl-ethyl ketone or methanol)

### 5.3.3. Isopropanol/water mixture (50/50 v/v):

- 50 parts by volume isopropanol,  $CH_3CHOH.CH_3$ , and
- 50 parts by volume water (5.3.1)

- 5.3.4. Ammonium bicarbonate solution (60/40 v/v):  
0,3 mol  $\text{NH}_4\text{HCO}_3$  in 1 000 ml of an isopropanol/water mixture consisting of 60 parts by volume isopropanol and 40 parts by volume water (5.3.1)
- 5.3.5. Cation exchanger (KAT), strongly acidic, resistant to alcohol (50-100 mesh)
- 5.3.6. Anion exchanger (AAT), macro-porous, Merck Lewatit MP 7080 (70-150 mesh) or equivalent
- 5.3.7. Hydrochloric acid, 10 % HCl w/w
- 5.3.8. 2 000 ml round-bottomed flask with ground glass stopper and reflux condenser
- 5.3.9. 90 mm diameter suction Filter (heatable) for filter papers
- 5.3.10. 2 000 ml filter flask
- 5.3.11. Exchange columns with heating jacket and tap: inner tube 60 mm in diameter and 450 mm in height (see Figure 4)
- 5.3.12. Water-bath
- 5.3.13. Vacuum drying oven
- 5.3.14. Thermostat
- 5.3.15. Rotary evaporator
- 5.4. Preparation of extract and separation of non-ionic active agents
  - 5.4.1. Preparation of extract

The quantity of surfactant necessary for the degradation test is about 25 g BiAS.

In preparing extracts for the degradation tests, the quantity of product to be used should be limited to a maximum of 2 000 g. Therefore it may be necessary to carry out the operation two or more times in order to obtain sufficient quantity for the degradation tests. Experience has shown that there are advantages in using a number of small extractions rather than one large extraction.

#### 5.4.2. Isolation of alcohol-soluble constituents

Add 250 g of the synthetic detergent to be analysed to 1 250 ml ethanol and heat the mixture to boiling point and reflux for one hour with stirring. Pass the hot alcoholic solution through a coarse-pored suction filter heated to 50 °C and filter rapidly. Wash the flask and suction filter with approximately 200 ml hot ethanol. Collect the filtrate and filter washings in a filter flask.

In the case of pastes or liquid products to be analysed, make sure that not more than 25 g anionic surfactants and 35 g soap are contained in the sample. Evaporate this weighed sample to dryness. Dissolve the residue in 500 ml ethanol and proceed as described above.

In the case of powders of low apparent density (< 300 g/l) it is recommended to increase the ethanol ratio in the relation 20:1.

Evaporate the ethanolic filtrate to complete dryness, preferably by means of rotary evaporator. Repeat the operation if a greater quantity of extract is required. Dissolve the residue in 5 000 ml isopropanol/water mixture.

#### 5.4.3 Preparation of ion-exchange columns

##### CATION-EXCHANGE COLUMN

Place 600 ml cation-exchange resin (5.3.5) in a 3 000 ml beaker and cover by adding 2 000 ml hydrochloric acid (5.3.7). Allow to stand for at least two hours, with occasional stirring. Decant the acid and transfer the resin into the column (5.3.11) by means of deionised water. The column should contain a glass-wool plug. Wash the column with deionised water at a rate of 10-30 ml/min until the eluate is free of chloride. Displace the water with 2 000 ml isopropanol/water mixture (5.3.3) at a rate of 10-30 ml/min. The exchange column is now ready for operation.

##### ANION-EXCHANGE COLUMN

Place 600 ml anion-exchange resin (5.3.6) in a beaker and cover by adding 2 000 ml deionised water. Allow the resin to swell for at least two hours. Transfer the resin into the column by means of deionised water. The column should contain a glass-wool plug.

Wash the column with 0,3 M ammonium bicarbonate solution (5.3.4) until free of chloride. This requires about 5 000 ml solution. Wash again with 2 000 ml deionised water. Displace the water with 2 000 ml isopropanol/water mixture (5.3.3) at a rate of 10-30 ml/min. The exchange column is now in the OH form and ready for operation.

#### 5.4.4. Ion-exchange procedure

Connect the exchange columns so that the cation-exchange column is placed on top of the anion-exchange column. Heat the exchange columns to 50 °C using thermostatic control. Heat 5 000 ml of the solution obtained in item 5.4.2 to 60 °C and pass the solution through the exchanger combination at a rate of 20 ml/min. Wash the columns with 1 000 ml hot isopropanol/water mixture (5.3.3).

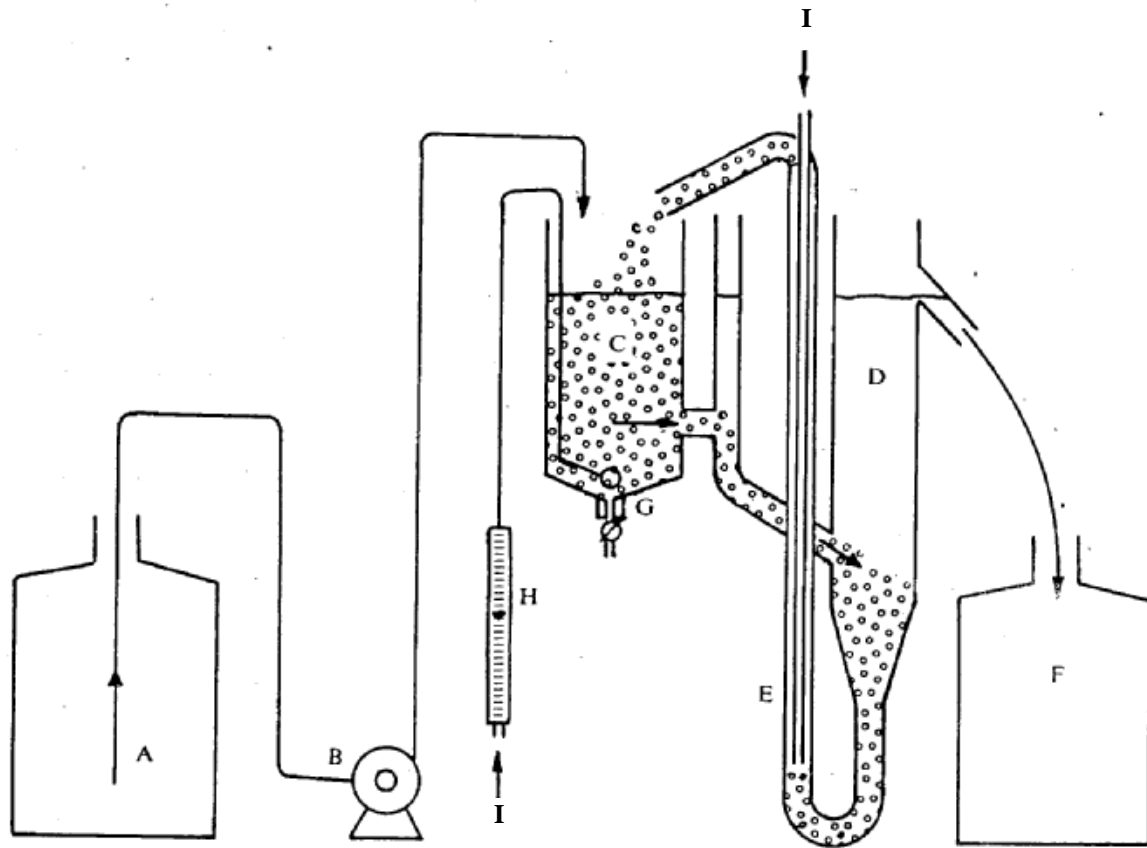
To obtain the non-ionic surfactants collect the filtrate and filter washings and evaporate to dryness, preferably by means of a rotary evaporator. The residue contains the BiAS. Add deionised water until a defined volume is obtained and determine the BiAS content in an aliquot. The solution is used as a standard solution of non-ionic surfactants for the degradation test. The solution should be kept at a temperature below 5 °C.

#### 5.4.5. Regeneration of ion exchange resins

The cation exchanger is rejected after use.

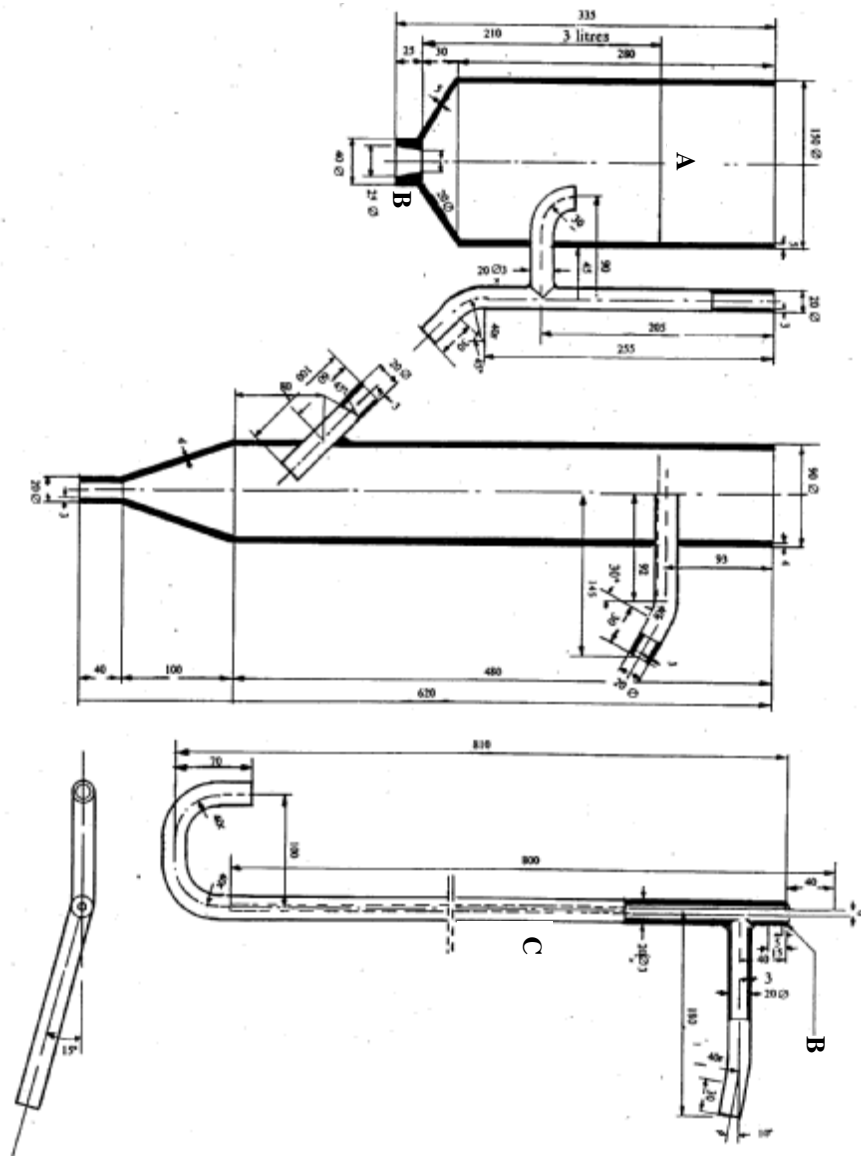
Passing about 5 000-6 000 ml of ammonium bicarbonate solution (5.3.4) down the column at a flow rate of approximately 10 ml/min until the eluate is free from anionic surfactants (methylene blue test) regenerates the anion-exchange resin. Then pass 2 000 ml isopropanol/water mixture (5.3.3) down the anion exchanger to wash. The anion exchanger is again ready for operation.

Figure 1  
Activated sludge plant: overviews



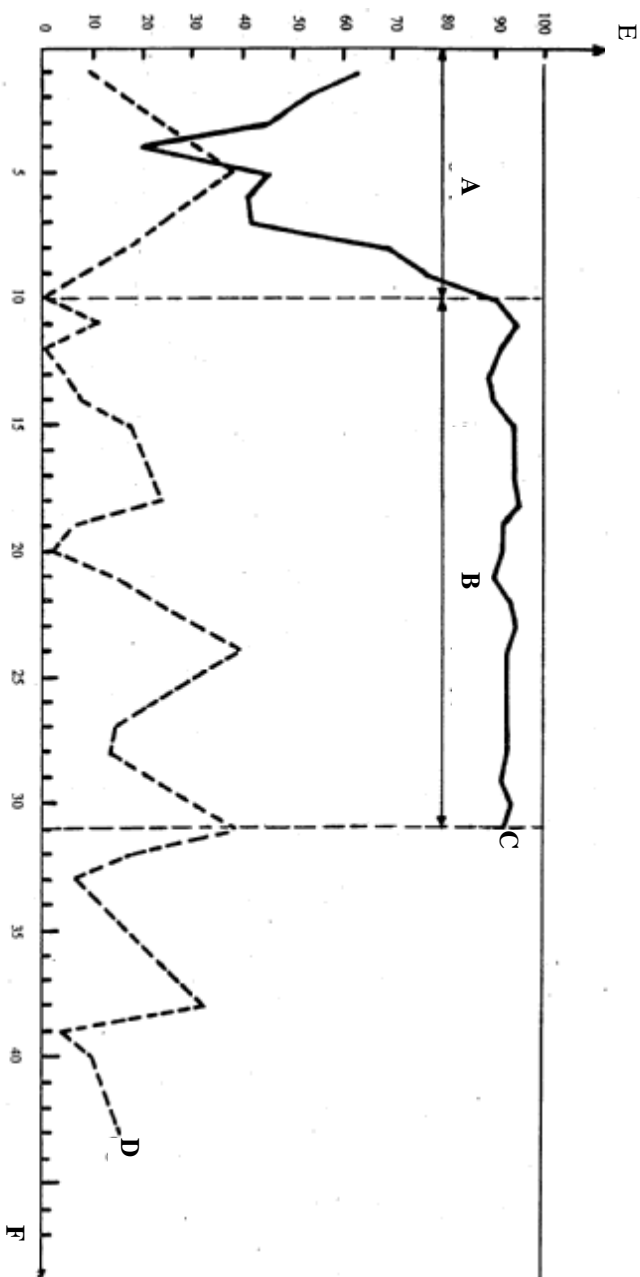
- A. Storage vessel
- B. Dosing device
- C. Aeration chamber (*three litres capacity*)
- D. Settling vessel
- E. Air-lift pump
- F. Collector
- G. Sintered aerator
- H. Air-flow meter
- I. Air

Figure 2  
Activated sludge plant: detail  
(dimensions in millimetres)



- A. Liquid level
- B. Hard PVC
- C. Glass or waterproof plastic (hard PVC)

Figure 3  
Calculation of biodegradability – Confirmatory test



- A. Running-in period
- B. Period used for calculation (*twenty-one days*)
- C. Readily biodegradable surfactant
- D. Surfactant not readily biodegradable
- E. Biodegradation (%)
- F. Time (days)

Figure 4  
Heated exchange column  
(dimensions in millimetres)

