COMMITTEE OF EXPERTS ON THE TRANSPORT OF DANGEROUS GOODS AND ON THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS

Sub-Committee of Experts on the Globally Harmonized System of Classification and Labelling of Chemicals

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UPDATING OF THE SECOND REVISED EDITION OF THE GLOBALLY HARMONIZED SYSTEM OF CLASSIFICATION AND LABELLING OF CHEMICALS (GHS)

Environmental hazards

Proposal for amendment to Chapter 4.1 (section 4.1.2.10.3)

Transmitted by the European Chemical Industry Council (CEFIC) and the International Association for Soaps, Detergents and Maintenance Products (AISE)

Introduction

1. Chapter 4.1, section 4.1.2.10.3 specifies the criteria which substances have to meet in order to be considered rapidly degradable in the environment.

2. These criteria are based on the outcome of ready biodegradability tests. The rationale behind the ready biodegradability tests is that any chemical passing these tests would be rapidly broken down during sewage treatment and in most aerobic ecosystems. For such an approach to be valid, tests have to be extremely stringent. The stringency of the ready biodegradability tests is primarily ensured by precluding the use of acclimatised micro-organisms (even though this is a natural phenomenon) and by using a low initial biomass concentration (which may delay the onset of biodegradation and limit the microbial diversity).

3. Ready biodegradability tests use batch cultures, and initial concentration of the test substance is in the range of 2 to 100 mg/L. In these tests, degradation of an organic chemical can only be brought about by micro-organisms which are capable of growing on the test substance. Growth of micro-organisms on a single chemical typically results in a smooth S-shaped biodegradation curve composed of a lag period, a logarithmic growth phase and a stationary phase (Schlegel, 1993[1]). (NB: In microbiology, the logarithmic growth-phases are generally specified with maximum specific growth rates (μmax) or doubling times ($t_{½} = \ln 2/\mu max$)).

[1] *Schlegel HG (1993) General Microbiology 7th edition. Cambridge University Press.*

4. In ready biodegradability tests, **the time window concept** has been introduced as a simple criterion to quantify the rate of biodegradation. In order to pass the test, over 60% O_2 uptake or CO_2 formation, or 70 % DOC removal has to be achieved within a period of 10 days immediately following the attainment of 10% biodegradation. The 10 day window can only be interpreted correctly if a normal S-shaped degradation pattern is observed, as this would typically be the case for a single water-soluble chemical substance.

Multi-constituent substances and the 10-day window

5. Many commercial surfactants derived from petroleum or renewable resources occur as substances of multi-constituent character, i.e. with different chain lengths (the so-called homologues), degree and / or site of branching or stereo-isomers, even in their most purified commercial forms. (NB: a surfactant is a chemical in which a hydrophilic group is linked to a lipophilic moiety).

6. As mentioned above, many common surfactants are mixtures of homologues. The biodegradation kinetics (lag period, growth rate, yield etc.) of the individual compounds in a mixture are not necessarily the same. The biodegradation curve of a surfactant consisting of homologues is therefore an addition of different individual biodegradation curves. It is thus possible that some individual compounds do meet the 10-day time window criterion whereas the biodegradability curve of the mixture of homologues suggests that the surfactant is not readily biodegradable (Richterich and Steber, 2001[2]). It has also been observed that for multi-constituent substances sequential biodegradation of the individual structures can take place (e.g. the biodegradation of one compound or functional group is delayed until another one has been fully degraded). In such cases, the 10-day window is a poor indicator of the biodegradation kinetics and should not be applied to interpret the results of the test.

7. In summary, the 10-day window criterion should not be considered as a requirement for determining the desired stringency for multi-constituent substances. There are several technical reasons to support this statement:

(a) Multi-constituent substances such as many commercial surfactants will lead to a degradation curve characterised by multiphase kinetics (i.e. not smooth S shape)

(b) It is known that intermediate metabolites can have degradation kinetics different from the parent product. Some metabolites interfere with the degradation process by inhibiting transformation of the parent molecule.

(c) Some components of mixtures show sequential degradation.

The ultimate aim of ready biodegradability tests is to assess the capability (in percentage terms) of a product to be fully degraded into simple compounds during a 28-day period.

8. The above scientific arguments therefore suggest that the 10-day window should be disregarded for the evaluation of the ready biodegradability of surfactants representing mixtures of closely related homologues and isomers with a very similar biodegradability profile. Importantly, this proposal is supported by the fact that the EU Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE; now SCHER[3]) adopted an "opinion on the proposed ready biodegradability approach to update the detergents legislation (2004/648/EC[4])" stating that keeping the 10-day window is not deemed

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[2] *Richterich K and Steber J (2001) The time-window – an inadequate criterion for the ready biodegradability assessment of technical surfactants. Chemosphere 44 1649-1654.*

[3] *Scientific Committee on Health and Environment Risks*

[4] Regulation 2004/648/EC of the European Parliament and of the Council of 31 March 2004 on detergents.

necessary for assessing ready ultimate biodegradability of surfactants in detergents (CSTEE, 1999[5]). The rationale behind this statement was recognition of the fact that surfactant degradation is generally characterised by multiphase kinetics resulting from the multi-component nature of substrate.

9. As the application of the 10-day window criterion is not scientifically justified for surfactants (CSTEE, 1999; OECD, 2005[6]), it is recommended that surfactants surpassing the 60 % (resp. 70 %) limit value within the standard test duration of 28 days are considered as readily (bio)degradable substances, and a modification should be made in the UN GHS text and/or associated guidance.

Proposal

11. Add a new paragraph to 4.1.2.10.3 as follows *(new text is shown in bold)*:

"4.1.2.10.3 Substances are considered rapidly degradable in the environment if the following criteria hold true:

(a) if in 28-day ready biodegradation studies, the following levels of degradation are achieved;

(i) tests based on dissolved organic carbon: 70%;

(ii) tests based on oxygen depletion or carbon dioxide generation: 60% of theoretical maxima;

These levels of biodegradation must be achieved within 10 days of the start of degradation which point is taken as the time when 10% of the substance has been degraded; or

(b) if, in those cases where only BOD and COD data are available, when the ratio of BOD_5/COD is ≥ 0.5; or

(c) if other convincing scientific evidence is available to demonstrate that the substance can be degraded (biotically and/or abiotically) in the aquatic environment to a level > 70% within a 28 day period.

Multi-constituent substances *(e.g.* surfactants consisting of mixtures of homologues and isomers) do not need to fulfil the specified levels of biodegradation within 10 days of the start of biodegradation. Such samples surpassing the 60 % (resp. 70 %) limit value within the standard test duration of 28 days are considered as readily (bio)degradable substances."

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[5] European Commission (1999) Scientific Committee on Toxicity, Ecotoxicity and the Environment. Opinion on proposed 'ready biodegradability" approaches to update detergents legislation. Opinion adopted at the 12th CSTEE plenary meeting 25-11-1999.

[6] Annex I to OECD Guideline for Testing of Chemicals, Proposal for revised introduction to the OECD guidelines for testing of chemicals, section 3, April 2005: *"43. Although these tests are intended for pure chemicals, it is sometimes relevant to examine the ready biodegradability of mixtures of structurally similar chemicals like oils and surface-active substances (surfactants). Such substances often occur as mixtures of constituents with different chain-lengths, degree and/or site of branching or stereo-isomers, even in their most purified commercial forms. Testing of each individual component may be costly and impractical. If a test on the mixture is performed and it is anticipated that a sequential biodegradation of the individual structures is taking place, then the 10-day window should not be applied to interpret the results of the test. A case by case evaluation should however take place on whether a biodegradability test on such a complex mixture would give valuable information regarding the biodegradability of the mixture as such (i.e. regarding the degradability of all the constituents) or whether instead an investigation of the degradability of carefully selected individual components of the mixture is required".*