**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

Sixteenth session,
Geneva, 10 – 12(a.m) December 2008
Item 2 (c) of the provisional agenda

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

Environmental hazards

Proposed amendment to Chapter 4.1 (section 4.1.2.10.3)

10-Day window: Technical support document to ST/SG/AC.10/C.4/2008/27

Transmitted by the European Chemical Industry Council (CEFIC),
the International Association for Soaps, Detergents and Maintenance Products (A.I.S.E.)
and the Soap and Detergent Association (SDA)

1. Introduction and background

Chapter 4.1 of the GHS (Rev.2) section 4.1.2.10.3 specifies the criteria which substances have to meet in order to be considered rapidly degradable in the environment. These criteria are mainly based on the outcome of ready biodegradability tests. The rationale behind ready biodegradability tests is that any chemical achieving the pass level in these tests would be rapidly broken down during sewage treatment and in most aerobic ecosystems. 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 % removal of dissolved organic carbon (DOC) has to be achieved within a period of 10 days immediately following the attainment of 10% biodegradation. This condition is termed the "*10-day window*".

In document ST/SG/AC.10/C.4/2008/27 submitted to the Secretariat on 19 September 2008, CEFIC, AISE and SDA propose a small addition to paragraph 4.1.2.10.3 of the GHS, related to the criteria for classifying a chemical as "readily biodegradable", specifically for the class of multi-component substances (such as most commercial surfactant types). The amendment states that the 10-day window does not apply to multi-component substances because the test method can lead to misleading results. This flaw is such that multi-component substances may be incorrectly classified as not readily biodegradable, while the individual components are readily biodegradable. More information on this issue is provided below.

2.   Consequences of an incorrect classification for industry

A false-negative rapidly biodegradable reading for a substance could lead to classification of the substance or mixtures containing it in a chronic category. Such classifications have not only labelling consequences but also potential downstream consequences both at regional level (for example in Europe: regulatory duties under the Seveso Directive, potential market restrictions such as Ecolabel requirements, change to the waste classification) and at global level (e.g. additional transport-related requirements).

Furthermore it is critical that substances and mixtures be assigned the appropriate classification which truly reflects their environmental properties in order to avoid misleading labelling information for consumer products and be consistent with other pieces of legislation (e.g. EU Detergent Regulation, under which the 10-day window principle is not applied to surfactants).

3.   Technical rationale for the suggested amendment for multi-component substances

3.1   *Concept of the ready biodegradability test*

Ready biodegradability tests use batch cultures, and the 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 (because no other organic substrate is provided). 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 ($t\frac{1}{2} = \ln2/\mu$max)). 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).

The 10-day window can only be interpreted correctly if a normal S-shaped degradation pattern is observed, as would typically be the case for a single water-soluble chemical substance.

3.2   *Empirical observations with multi-component substances*

Many commercial surfactants derived from petroleum or renewable resources occur as substances of multi-component character, i.e. with different chain lengths (the so-called homologue series), 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).

The biodegradation kinetics (lag period, growth rate, yield etc.) of the individual components in a multi-component substance are not necessarily the same. The biodegradation curve of a surfactant consisting of homologues is therefore an addition of different individual biodegradation curves, superimposed on one another. It is thus possible - and this has been observed in practice - 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]).

---

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

It has also been observed that for multi-component substances, sequential (instead of concurrent) 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 partially or fully degraded). The different solubilities of individual components can also play a role in delayed degradation (Richterich and Steber, 2001). In such cases, the 10-day window becomes a poor indicator of the biodegradation kinetics of the individual components and should not be applied to interpret the results of the test. This phenomenon is illustrated with an example (Figures 1 and 2). Figure 2 represents the results for an equimolar solution of surfactant components 1 and 2, which, individually (as shown in Figure 1), are readily biodegradable.

A significant number of fragrance ingredients are multi-component substances. Synthetic fragrance ingredients are usually structural isomers; naturally occurring substances (natural extracts and essential oils) may also be multi-component substances. In a review of the biodegradability of dozens of multi-component fragrance substances including both synthetic and natural examples the same ten-day window issue arose with a quarter of the examples (16 of 64) examined, i.e. they reached at least 60% degradation in the 28 days but failed the 10-day window criterion.

4.   Review of the argument by third party experts

The above scientific arguments therefore suggest that the 10-day window criterion should be disregarded for the evaluation of the ready biodegradability of surfactants representing multi-component substances consisting of closely related homologues and/or isomers with a very similar biodegradability profile.

4.1.   *CSTEE opinion*

Already in 1999, 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 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 the substrate.

4.2.   OECD Guidelines

In addition, Annex I to the OECD Guideline for Testing of Chemicals, 'Proposal for revised introduction to the OECD guidelines for testing of chemicals, section 3, April 2005': states *"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*

---

[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.*
[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.*

the constituents) or whether instead an investigation of the degradability of carefully selected individual components of the mixture is required".

5. Summary and recommendations

The 10-day window criterion should not be considered as a requirement for assuring the desired stringency for multi-component substances. There are several technical reasons to support this statement:

(a) Multi-component substances such as many commercial surfactants will lead to a degradation curve characterised by multiphase kinetics (i.e. not the 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 (Richterich and Steber, 2001);

(c) Some constituents of multi-component substances 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.

As the application of the 10-day window criterion is not scientifically justified for surfactants (CSTEE, 1999; OECD, 2005[6]), it is <u>recommended that multi-component substances exceeding the 60 % (resp. 70 %) pass level within the standard test duration of 28 days are considered as readily (bio)degradable substances.</u> Therefore, a modification of the UN GHS text has been proposed for section 4.1.2.10.3 as described in ST/AG/SC.10/C.4/2008/27.
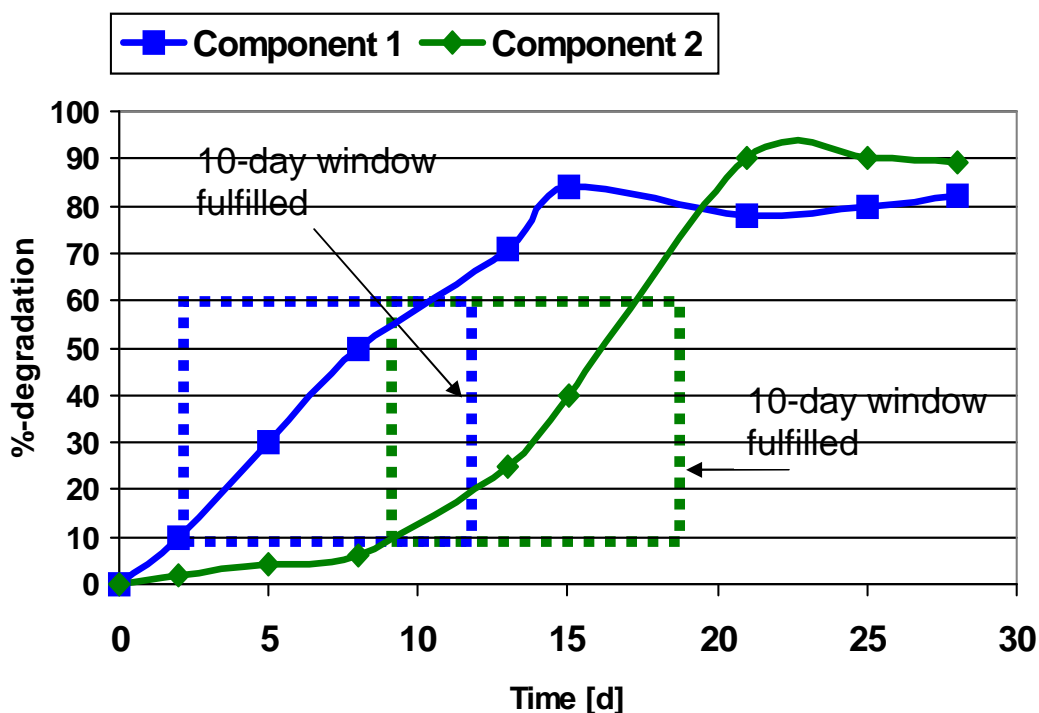
Figure 1: Results of separate ready biodegradability tests (OECD 301 B, CO2 production test) on two pure surfactants components. NB: The blue line represents a linear alcohol ethoxylate (1) and the green line a mono-branched alcohol ethoxylate (2).
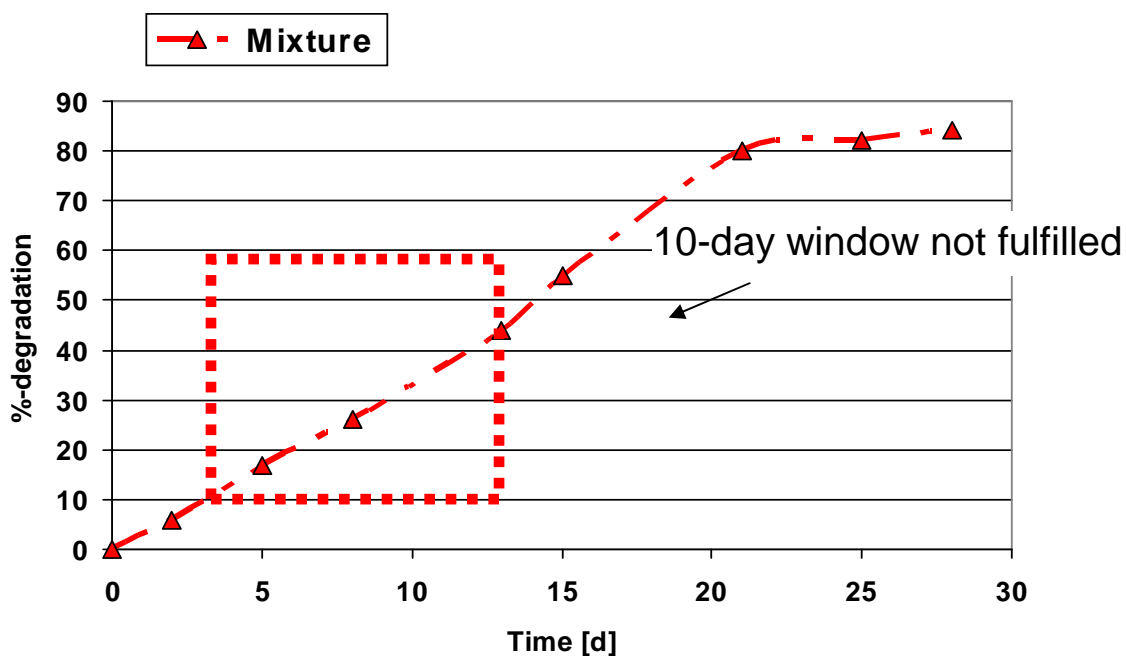

Figure 2: Results of the ready biodegradability test (OECD 301B) for the equimolar solution of components 1 and 2.