

GUIDE TO

THE CLASSIFICATION & LABELLING OF UV/EB ACRYLATES

Impact of European chemical legislation on Classification & labelling of UV/EB Acrylates

Fourth edition, August 2011 (Update table 7 June 2014)

1 CEFIC and the UV/EB sector group

Cefic, the European Chemical Industry Council (http://www.cefic.org), represents an industry which makes an invaluable contribution to the welfare and quality of life of European citizens.

The chemical industry is a responsible industry, holding itself accountable to society and committed to addressing its concerns actively and transparently, ensuring that chemical products manufactured and developed in Europe meet the most demanding safety criteria.

The Industry Sectors of CEFIC

Industry sectors exist alongside the Cefic horizontal programmes in order to address issues and pursue initiatives which are specific to individual industries

A vast majority of individual sector groups are clustered together under the Fine, Specialty and Consumer Chemicals (FSCC) industry sector. This diverse grouping serves the purpose of bringing together a range of product groups in a way that enables their management in a cost effective manner by sharing resources and working jointly on shared issues raising the profile of such issues to the Cefic policy centre.

The UV/EB acrylate manufacturers and importers, representing more than 90% of the European market, work together in the sector group UV/EB Acrylate resins within the FSCC industry sector in order to jointly follow questions of common interest regarding regulatory and health, safety and environmental (HSE) issues.

Members of the UV/EB sector group: ARKEMA (FR), BASF (DE); Bayer (DE), Cytec Surface Specialities (BE), IGM Resins (NL), RAHN AG (CH)

Contact UV/EB sector group: <u>UV/EB Acrylate Resins | Cefic</u> (for the complete web address refer to annex II).

Representative of the sector group: Dominique de Halleux deh@cefic.be

The member companies of the UV/EB sector group act in compliance with the Responsible Care® guidelines in which the chemical industry worldwide commits to continuously improve

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services in the areas of safety, health and environmental protection and also to demonstrate this progress.

The most important objective of our quality policy is to offer products and services that meet



For further details see the following websites:

http://www.responsiblecare.org/

UV/EB curable resins - Uses and properties -

UV/EB-curing is a drying technology for coatings, inks and adhesives. It uses light of a certain wavelength (UV) or high speed electrons (<u>E</u>lectron <u>beam</u>) to give almost instantaneous dry films. It allows formulators to develop products for a wide variety of applications and substrates without using volatile organic compounds as solvents.

UV/EB acrylate resins, bearing one or several acrylate groups, are derived from various chemical backbones such as polyol, polyester, polyurethane, polyether, epoxies and acrylics. Their unsaturated acrylate functionalities have the unique property of instantaneously polymerising under ultra-violet radiation when mixed with an adequate photoinitiator or when treated with a beam of high energy electrons.

The so called UV/EB curable resins are mainly used as solventless binders in inks, varnishes, adhesives and decorative and protective coatings and paints. They can be applied on almost any substrate - paper, wood, plastics, glass and metal.

Typical applications are inks and over-print varnishes, hard coatings, protective coatings used on CD's and DVD's and optical fibres, and finally, in solder and etch resistant coatings for printed circuit boards.

Purpose of the guide to classification & labelling of acrylates

There have been major changes in the European legislation with regards to registration, classification & labelling of chemicals. The guide shortly summarizes the current legislation and describes the impact on the classification & labelling of UV/EB acrylates.

It should be a guideline for the downstream user to illustrate which classification & labelling is applicable for acrylates and which rules have to be followed, when preparing mixtures containing these acrylates.

In addition to this guide, the most recommended source for information on classification and labelling, other than the actual legislation, is the SDS provided by the supplier.

Disclaimer:

This Classification and Labelling Guide has been compiled in good faith and is believed to be accurate and reliable, but may well be incomplete and/or not applicable to all conditions or situations that may exist or occur. Neither the UV/EB Acrylate Resins Sector Group nor any of its members does assure any legal responsibility for the given information to be correct. Readers are cautioned to satisfy themselves as to the suitability of said information for the purposes intended prior to use. It is the user's responsibility to ensure that existing laws are observed.

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UV/EB ACRYLATE RESINS SECTOR GROUP



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2 Current legislation in the EU

2.1 Regulation (EC) No. 1907/2006 (REACH)

REACH is the Regulation for **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emicals. It entered into force on 1st June 2007 to streamline and improve the former legislative framework on chemicals in the European Union (EU). REACH places greater responsibility on industry to manage the risks that chemicals may pose to the health and the environment.

REACH is based on the principle that manufacturers, importers and downstream users must ensure they manufacture, place on the market or use such substances that do not adversely affect human health or the environment.

The responsible agency in Europe is ECHA, the European Chemicals Agency, located in Helsinki (http://echa.europa.eu/).

The mission of the European Chemicals Agency is to manage all REACH and CLP tasks by carrying out or co-coordinating the necessary activities, by ensuring a consistent implementation at Community level and by providing Member States and the European institutions with the best possible scientific advice on questions related to the safety and the socio-economic aspects of the use of chemicals.

REACH applies to the manufacture, placing on the market or use of substances on their own, in preparations or in articles and to the placing on the market of preparations. REACH follows a substance based approach: the obligations do not directly apply to preparations and articles and polymers are for the time being exempt from registration.

All manufacturers and importers of chemicals must identify and manage risks linked to the substances they manufacture and market. For substances produced or imported in quantities of 1 tonne or more per year per company, manufacturers and importers need to demonstrate that they have appropriately done so by means of a registration dossier, which shall be submitted to ECHA. Only companies with a legal entity located within the EU can take the necessary measures (preregistration/registration) under REACH. Companies located outside the EU can release their downstream users located within in the EU by assigning an only representative in the EU. The only representative can take the necessary actions on behalf of the outside EU manufacturer.

2.1.1 Substance definition and registration timeline under REACH

Substances

Regarding the registration process REACH distinguishes between two categories of substances:

a) Phase-in substances

Substances listed in EINECS or in NLP or qualify for NLP, for these substances a preregistration could have been filed. With the preregistration the respective notifier benefits from a transition period until a final REACH registration is required.

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b) Non-phase-in substances

Substances formerly listed in ELINCS are automatically regarded as registered under REACH with the tonnage band they have been registered before.

New substances, which do not qualify as phase-in substances are subject to "immediate" (no transition period) registration if the manufactured or imported volume exceeds 1 t/year for the specific manufacturer/importer.

Depending on the chemical nature of the substance the distinction within both groups is made between the following three types of substances:

- mono-constituent substances
- multi-constituent substances
- UVCB substances:

A <u>mono-constituent substance</u> is a substance, defined by its quantitative composition, in which one main constituent is present to at least 80% (w/w)

A <u>multi-constituent substance</u> is a substance, defined by its quantitative composition, in which more than one main constituent is present in a concentration $\geq 10\%$ (w/w) and < 80% (w/w). A multi-constituent substance is the result of a chemical reaction in a manufacturing process. A multi-constituent substance is named as a reaction mass of two or more main constituents.

A <u>UVCB</u> substance (substances of Unknown or Variable composition, Complex reaction products or Biological materials) cannot be sufficiently identified by its chemical composition, because: the number of constituents is relatively large and/or the composition is, to a significant part, unknown and/or the variability of composition is relatively large or poorly predictable. As a consequence, UVCB substances require other types of information for their identification, in addition to what is known about their chemical composition.

Detailed guidance on substances and substance identity can be found in the Guidance on registration (REACH Navigator - Guidance on registration).

UV/EB acrylates regarded as substances under REACH are either monoconstituent, or multiconstituent, or UVCB substances depending on their chemical nature or fulfill the polymer definition.

Polymers

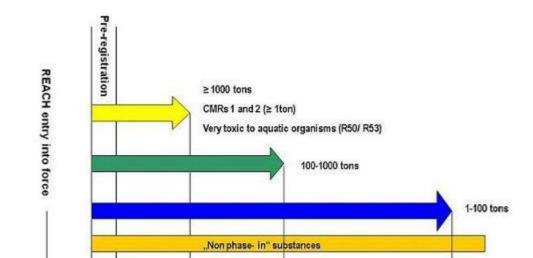
Polymers are exempt from REACH, but the respective monomers need to follow the rules for substances and are therefore subject to preregistration and/or registration.

Acrylates of the UV/EB industry are regarded as substances under REACH or are exempt under the the polymer definition given in the regulation and explained in the ECHA guidance document on polymers. REACH Navigator - Guidance.

Registration of the UV/EB acrylate substances will follow the timeline given by the REACH regulation. Most relevant deadlines for registration are set for 2010, 2013, 2018 depending on the manufactured/imported volume.

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31 May

Fig. 1 Registration time line under REACH

1 June

2008

1 June

2.1.2 Registration requirements/ information down the supply chain

30 Nov 2010

A registration under REACH is only valid for the respective notifier and for the uses covered by the registration dossier. This is in contrast to most other inventories, where the inventory listing of a specific substance allows the manufacture/import of this substance no matter who the manufacturer/importer is (e.g., TSCA).

The aim of REACH is to have only one registration per substance. Therefore it is foreseen to do the registration by a joint submission. All parties filing a preregistration for a substance are automatically members of the respective SIEF (Substance information exchange forum).

In a joint submission the lead registrant (which is elected out of the SIEF) is to prepare the basic registration dossier including all data on intrinsic properties of the substance. The technical dossier prepared by the lead registrant typically contains information on identity of the substance, classification & labelling of the substance, robust study summaries of the toxicological and ecotoxicological properties, information on use, and guidance for safe use of the substance.

The dossiers of the other members of the joint submission for this substance refer to the information given in the lead dossier and add member specific information, for example, the identity of the manufacturer/importer, information on manufacture of the substance and a company-specific chemical safety report if necessary. A member of a joint submission also has to prove by analytical data that the substance identity provided in the lead dossier covers their own substance.

The preparation of the lead registration dossier is sometimes done within a consortium. A consortium is a voluntary association with the objective to have joined efforts for REACH compliance activities. Often these consortia for REACH activities are born out of long time existing industry associations such as the sector groups of CEFIC. For the REACH compliance of UV/EB

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acrylates, a consortium has been formed. It is called PARAD (Polymerisable Acrylate Resins and Derivatives REACH consortium (PARAD consortium).

A registration dossier following the REACH regulation also requires comprehensive knowledge and information about the use of a substance downstream by the supply chain because a REACH registration takes into account the exposure to the respective substance during its whole life cycle. To ensure REACH compliance of substances or articles it is necessary to enforce the communication upwards and downwards in the supply chain. Not only manufacturers and importers, but also downstream users should have enough information to use chemical substances safely. The main tool to communicate down the supply chain is the Safety Data Sheet (SDS).

Safety data sheet (SDS) / extended safety data sheet (eSDS)

A registration dossier for a specific substance includes a detailed description of the use of the substance, the expected exposure and the necessary risk management measures to ensure the safe use of the substance.

In a SDS prepared according to Annex II of the Regulation (EC) No. 1907/2006, the downstream user can find all relevant data for the products on the European market to ensure their safe use.

For substances and mixtures containing substances which have already been fully registered under REACH, section 1 of the SDS includes the registration number of the registered substance, information about identified uses and uses advised against. Additionally, for hazardous substances registered for more than 10t/year, an extended safety data sheet (eSDS) has to be provided. The eSDS includes exposure scenarios and related risk reduction measurements. Also, the relevant DNELs and PNECs will be reported in section 8 of the eSDS.

When an eSDS with the registration number(s) is received, the clock starts running for the obligations of the downstream user set in articles 37-39 of REACH.

Basically it is the obligation of the downstream user to ensure that its use of the substance is covered by the uses identified in the exposure scenarios and that the risk reduction measures recommended in the eSDS of the suppliers are applied.

If the downstream user's use of the substance is not covered by the use and risk management measures registered by the supplier, the downstream user has several options:

- Adapt to the conditions of uses described in the eSDS
- Ask the supplier to adapt the chemical safety report in order to cover the use
- Find another supplier that is already covering the use in his eSDS
- Perform his own chemical safety assessment for that particular use and record it in a Chemical Safety Report (CSR) if the total amount used is 1 tonne/year or more. Notify the use, including the information specified in Article 38(2) of the REACH regulation to ECHA

According to article 39 of the REACH regulation, the downstream user has 12 months to ensure he complies with these requirements (article 37) but only 6 months to notify the ECHA in case he does not comply with the uses registered by its supplier and wants makes his own CSR or does not need to do a CSR because he uses the substance in a total quantity less than 1 tonne /year (article 38).

When the downstream user produces a preparation, he must also ensure that the eSDS for that preparation includes all relevant information received from the suppliers of the individual components (uses covered, uses advised against, risk management measures, etc.).

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2.1.3 Substances of very high concern (SVHC)

The European Chemical Agency (ECHA) has current and future substances identified as Substances of Very High Concern (SVHC). The list of SVHCs is updated continuously by ECHA in the form of a so-called SVHC candidate list. This is a list of chemicals fulfilling any of the following criteria: categorized as CMR cat. 1or 2, or being PBT or vPvB (as specified in REACH annex VII) or for which there is scientific evidence of probable serious impact on human health or the environment with similar degree of concern of the above mentioned substances.

If further evaluation confirms very high concern, these substances will be part of a list of substances that require special action - REACH annex XIV - without being deleted from the candidate list.

Substances on the list in REACH annex XIV need approval by ECHA if used as single chemical or in mixtures, or in articles that are manufactured in EU (authorisation process). The purpose is to achieve: Full control of all risks arising from production or use of that SVHC, and substitution of this SVHC where ever economically and technically feasible.

Once a substance is added to the Candidate List, REACH imposes immediate obligations on manufacturers and importers to declare the substances if present. Article 33(1) of the REACH Regulation states that manufacturers and importers of articles (products) are required to notify their customers of the presence of any Substances of Very High Concern (SVHC) in their products exceeding 0.1% by weight and provide instructions on safe use of the product.

None of the acrylates used in the UV/EB industry today is currently listed on the SVHC list.

In case you need information about the presence of SVHCs in UV/EB acrylates supplied to you, refer to the SDS provided by the supplier. In the case where a mixture contains > 0.1% of a SVHC substance, it will be mentioned on the SDS.

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2.2 Regulation (EC) No. 1272/2008 (CLP)

2.2.1 Background - The Globally Harmonised System of Classification and Labelling of Chemicals (GHS)

The GHS is a global system for standardizing and harmonizing the classification and labelling of chemicals, which has been developed and agreed at UN level. It defines physical, health and environmental hazards of chemicals and creates classification processes that use available data on chemicals and mixtures for comparison with the defined hazard criteria. Further it comprises communication of hazard information with symbols, signal words ("danger" or "warning," depending on the severity of the hazard), hazard statements as well as protective measures on labels and Safety Data Sheets (SDS).

Although the GHS Document establishes agreed hazard classification and communication provisions with explanatory information on how to apply the system, implementation of GHS will not necessarily result in a uniform classification of substances all over the world. One reason will be that the current form of GHS enables Competent Authorities to adapt the system to their individual needs. Countries can determine which of the GHS building blocks will be applied in their national systems. For example, some options for implementing the GHS include: Not using a specific GHS class (e.g., cancer, hazardous to the aquatic environment, etc.) as well as not using a specific GHS category (normally at the beginning or end of a class, e.g., Acute Toxicity Cat. 5). A second reason will be that already existing classification lists (e.g., harmonized classification & labelling as per Regulation (EC) No. 1272/2008, Annex VI, Part 3 (formerly: Annex I of 67/548/EEC) will also be part of national GHS.

Whereas GHS has already been implemented widely for Transport of Dangerous Goods, implementation of GHS for other sectors currently is focused at European and Asian-Pacific countries. Activities in other countries are ongoing. The following UNECE website provides information about the GHS implementation status on a country by country basis: GHS implementation - UNECE

2.2.2 Regulation (EC) No. 1272/2008

On 20 January 2009 the Regulation (EC) No. 1272/2008 on the classification, labelling and packaging of substances and mixtures (CLP) entered into force <u>ECHA Website - Legislation</u>.

The CLP Regulation aligns existing EU legislation to the United Nations Globally Harmonized System (GHS).

The CLP Regulation will, after a transitional period, replace the rules on classification, labelling and packaging of substances (Directive 67/548/EEC, Dangerous Substances Directive, DSD) and mixtures (Directive 1999/45/EC, Dangerous Preparations Directive, DPD).

When the CLP Regulation entered into force in 2009, it also repealed the EU harmonized classification and labelling of Directive 67/548/EEC, Annex I. The harmonized classifications, as well as most of the specific concentration limits of substances listed in Annex I to DSD, have been transferred to Part 3 of Annex VI to CLP: in Table 3.1 the substances are classified according to CLP while Table 3.2 contains the original classifications based on the DSD criteria.

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The CLP Regulation is further subject to revision by so-called adaptions to technical and scientific progress (ATP). The legal text of the ATPs can be found on ECHA Website - Legislation.

A first revision of the tables containing the harmonized classification was done in 2009 by Regulation (EC) No. 790/2009.

A second adaption to technical and scientific progress, Regulation (EC) No. 286/2011 is mainly revising classification and labelling rules in line with the 3rd revised edition of United Nations GHS was published on 30 March 2011.

The 2nd ATP contains the following significant items:

- Regarding acute toxicity, combinations of hazard statements are introduced.
- For respiratory and skin sensitizing substances and mixtures, new sub-categories are introduced. Regarding sensitizing components in mixtures the application of the supplemental hazard information is extended in accordance with Annex II Part 2 Section 2.8 of the CLP Regulation.
- The classification criteria for long-term hazards (chronic toxicity) to the aquatic environment are revised.
- The additional EU hazard class "Hazardous to the Ozone Layer" (EUH059) is transferred into a corresponding GHS hazard class.
- In Annex VI Part 1 of the CLP regulation, Note H is deleted. Further, in both tables of Annex VI Part 3 of the CLP Regulation containing the harmonized classification and labelling, all references to Note H are deleted. By that step it is clarified that for all substances specifically listed in the tables of Annex VI Part 3 of the CLP Regulation, their hazards and properties, which are not given as harmonized, are to be self classified on the basis of available information. This obligation applies also for the classifications made in accordance to the old classification rules of the Dangerous Substances Directive 67/548/EEC (obligation for completion of classification for all listed substances).
- In respect of substances, the provisions shall apply from 1 December 2012 and in respect of mixtures from 1 June 2015 at the latest. The rules may be already voluntarily applied before these dates
- Substances and mixtures duly classified, labelled and packaged according to the Regulation (EC) 1272/2008 and placed on the market before the individual application dates of the 2nd ATP, are in each case not required to be re-labelled and repackaged in accordance with the provisions of the 2nd ATP before the expiration of a further two year period (Sell-off period).

2.2.2.1 Timelines of Regulation (EC) No. 1272/2008

Important timelines are mentioned below:

2009, January 20

- CLP entered into force
- Substances and mixture may be classified and labelled according to CLP
- Repeal of Annex I to DSD

2010. December 1

- Obligation to apply CLP to substances. For certain substances a prolonged deadline may apply: Substances classified, labelled and packaged in accordance with Directive 67/548/EEC and already placed on the market before 1 December 2010, are not required to be re-labelled and repackaged in accordance with CLP until 1 December 2012.
- Obligation to apply harmonized classification of the 1st ATP

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2012, December 1

Obligation to apply CLP as amended by the 2nd ATP to substances. For certain substances a prolonged deadline may apply: Substances classified, labelled and packaged in accordance with Regulation (EC) No 1272/2008 (CLP) and placed on the market before 1 December 2012, are not required to be re-labelled and repackaged in accordance with Regulation (EC) No. 286/2011 (2nd ATP) until 1 December 2014.

2014, December 1

Obligation to apply CLP as amended by the 2nd ATP to all substances

2015, June 1

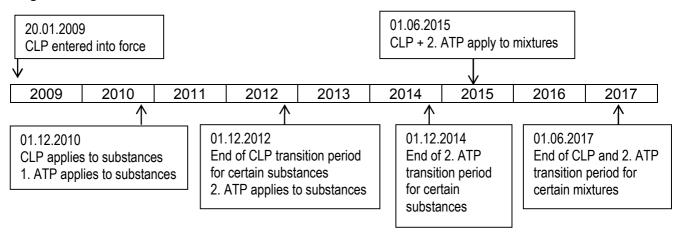
Obligation to apply CLP as amended by 2nd ATP to mixtures. For certain mixtures a
prolonged deadline may apply: Mixtures classified, labelled and packaged in accordance
with Directive 1999/45/EC and already placed on the market before 1 June 2015 are not
required to be re-labelled and repackaged in accordance with CLP until 1 June 2017.

2017, June 1

Obligation to apply CLP as amended by 2nd ATP to all mixtures

From 1 December 2010 until 31 May 2015, substances are classified under both DSD as well as CLP, but they are labelled and packaged according to CLP only. Classification of substances according to DSD is still required for the classification of mixtures and published in the safety data sheet. Until 31 May 2015, mixtures are classified, labelled and packaged under DPD. If CLP is applied to mixtures in full as well, mixtures will not be labelled and packaged according to DPD. From 1 June 2015, substances and mixtures are classified, labelled and packaged according to CLP only. Please note that for certain substances / mixtures (as outlined above) the 2012 / 2014 / 2017 deadline for re-labelling and re-packaging may apply (cf. Article 61(4) of CLP and article 2(2) and 2(3) of 2nd ATP to CLP).

Fig. 2 Timelines of CLP



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2.2.2.2 Elements of Regulation (EC) No. 1272/2008

In general, the classification and labelling system for substances and mixtures according to the CLP Regulation and according to the provisions of the Dangerous Substances Directive 67/548/EEC, Dangerous Preparations Directive 1999/45/EC, and Safety Data Sheet Directive 91/155/EEC (as amended) are conceptually similar. Nevertheless, the implementation of GHS involves also significant changes.

Regulation (EC) No. 1272/2008 (CLP) (ECHA Website - Legislation) comprises 62 articles and 7 annexes.

- Annex I Classification and labelling requirements for hazardous substances and mixtures
- Annex II Special rules for labelling and packaging of certain substances and mixtures
- Annex III List of Hazard Statements, supplemental Hazard Information and supplemental Label Elements
- Annex IV List of Precautionary Statements
- Annex V Hazard pictograms
- Annex VI Harmonised classification and labelling for certain hazardous substances
- Annex VII Translation table from classification under Directive 67/548/EEC to classification and assignment of hazard statements under this (note: i.e. CLP) Regulation

In contrast to the 15 categories of danger in DSD, the CLP Regulation comprises the following 28 Hazard Classes (see table 1). 'Hazard class' means the nature of the physical, health or environmental hazard.

'Hazardous for the Ozone Layer' is an additional EU Hazard Class not contained in the original GHS document ('EU left-over') but, in the meantime (refer to 2nd ATP), has been transferred to a corresponding GHS hazard class.

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Tab. 1 Hazard classes of the CLP Regulation

| | Physical Hazards | | Health Hazards |
|---------|--|------|---|
| 2.1 E | Explosives | 3.1 | Acute Toxicity |
| 2.2 F | Flammable Gases | 3.2 | Skin Corrosion / Irritation |
| 2.3 F | Flammable Aerosols | 3.3 | Serious Eye Damage / Eye Irritation |
| 2.4 (| Oxidising Gases | 3.4 | Respiratory or Skin Sensitisation |
| 2.5 | Gases under Pressure | 3.5 | Germ Cell Mutagenicity |
| 2.6 F | Flammable Liquids | 3.6 | Carcinogenicity |
| 2.7 F | Flammable Solids | 3.7 | Reproductive Toxicity |
| 2.8 | Self-reactive Substances and Mixtures | 3.8 | Specific Target Organ Toxicity – Single |
| | | | Exposure |
| 2.9 F | Pyrophoric Liquids | 3.9 | Specific Target Organ Toxicity – Repeated |
| | | | Exposure |
| | Pyrophoric Solids | 3.10 | Aspiration Hazard |
| | Self-heating Substances and Mixtures | | |
| 2.12 \$ | Substances and Mixtures which in contact | | Environmental Hazards |
| \ | with water emit flammable Gases | | |
| | Oxidising Liquids | 4.1 | Hazardous to the Aquatic Environment |
| 2.14 (| Oxidising Solids | | |
| 2.15 (| Organic Peroxides | | Additional EU Hazard Class |
| 2.16 (| Corrosive to Metals | 5.1 | Hazardous for the Ozone Layer |

Each of these hazard classes may be further divided into 'hazard categories' specifying the hazard severity (see table 2).

According to the 'Building Block Approach', the following GHS Hazard Categories are not part of the CLP regulation:

- Flammable Liquids Category 4
- Acute Toxicity Category 5
- Skin Corrosion / Irritation Category 3
- Aspiration Hazard Category 2
- Acute Aquatic Toxicity Category 2
- Acute Aquatic Toxicity Category 3

CLP further introduces 9 new 'hazard pictograms' replacing the black/orange hazard symbols of the Dangerous Substances Directive. Three of the pictograms, GHS04 'Gas cylinder, GHS 07 'Exclamation mark' and GHS08 'Health hazard' are completely new.

The DSD hazard symbols related to the indications of danger 'Harmful' and 'Irritant' ('X', St. Andrew's cross) no longer exist under CLP. Depending on the CLP hazard classification, the pictograms GHS05 'Corrosion', GHS08 'Health hazard', GHS07 'Exclamation mark', or GHS06 'Skull and crossbones' may now apply.

The CLP hazard pictograms have a black symbol on a white background with a red frame. They are in the shape of a square set at a point (see table 2).

In addition, CLP introduces 2 'signal words', Danger and Warning, to indicate the relative level of severity of hazards and to alert the reader to a potential hazard.

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Tab. 2 Hazard Pictograms according to Annex V of CLP (Amendments by Regulation (EC) No. 286/2011 in *italic*)

| Pictogram | Hazard class / category | Signal word | Hazard code |
|-----------|---|-------------|-------------|
| GHS01 | Explosives | | |
| Exploding | Unstable explosives | Danger | H200 |
| bomb | Explosives of Division 1.1 | Danger | H201 |
| | Explosives of Division 1.2 | Danger | H202 |
| 1/2 | Explosives of Division 1.3 | Danger | H203 |
| -30 | Explosives of Division 1.4 | Warning | H204 |
| | Self reactive substances and mixtures | | |
| | Type A | Danger | H240 |
| | Type B (see also GHS02) | Danger | H241 |
| | Organic peroxides | 3 | |
| | Type A | Danger | H240 |
| | Type B | Danger | H241 |
| GHS02 | Flammable gases, hazard category 1 | Danger | H220 |
| Flame | Flammable aerosols | Danigo. | |
| | hazard category 1 | Danger | H222 |
| | hazard category 2 | Warning | H223 |
| (63) | Flammable liquids | VVarring | 11220 |
| | hazard category 1 | Danger | H224 |
| • | hazard category 2 | Danger | H225 |
| | hazard category 2 | Warning | H226 |
| | Flammable solids | vvarriing | 11220 |
| | | Danger | H228 |
| | hazard category 1 | Danger | |
| | hazard category 2 | Warning | H228 |
| | Self-reactive substances and mixtures | D | 11044 |
| | Type B (see also GHS01) | Danger | H241 |
| | Type C | Danger | H242 |
| | Type D | Danger | H242 |
| | Type E | Warning | H242 |
| | Type F | Warning | H242 |
| | Pyrophoric liquids, hazard category 1 | Danger | H250 |
| | Pyrophoric solids, hazard category 1 | Danger | H250 |
| | Self-heating substances and mixtures | | |
| | hazard category 1 | Danger | H251 |
| | hazard category 2 | Warning | H252 |
| | Substances and mixtures, which in contact with water, | | |
| | emit flammable gases | | |
| | hazard category 1 | Danger | H260 |
| | hazard category 1 | Danger | H261 |
| | hazard category 3 | Warning | H261 |
| | Organic peroxides | | |
| | Type B | Danger | H241 |
| | Type C | Danger | H242 |
| | Type D | Danger | H242 |
| | Type E | Warning | H242 |
| | Type F | Warning | H242 |
| <u> </u> | 1 170 | | |

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Tab. 2 Hazard Pictograms according to Annex V of CLP (continued)

| Pictogram | Hazard class / category | Signal word | Hazard code |
|--------------|--|-------------|-------------------|
| GHS03 | Oxidising gases, hazard category 1 | Danger | H270 |
| Flame over | Oxidising liquids | | |
| circle | hazard category 1 | Danger | H271 |
| | hazard category 2 | Danger | H272 |
| 100 | hazard category 3 | Warning | H272 |
| \U/ | Oxidising solids | | |
| | hazard category 1 | Danger | H271 |
| | hazard category 2 | Danger | H272 |
| | hazard category 3 | Warning | H272 |
| GHS04 | Gases under pressure: | | |
| Gas cylinder | Compressed gases | Warning | H280 |
| | Liquefied gases | Warning | H280 |
| | Refrigerated liquefied gases | Warning | H281 |
| | Dissolved gases | Warning | H280 |
| | | | |
| GHS05 | Corrosive to metals, hazard category 1 | Warning | H290 |
| Corrosion | Skin corrosion, hazard categories 1A, 1B, 1C | Danger | H314 |
| | Serious eye damage, hazard category 1 | Danger | H318 |
| | | | |
| GHS06 | Acute toxicity (oral, dermal, inhalation), hazard | Danger | H300, H310, H330, |
| Skull and | categories 1, 2 | | H300+H310, |
| crossbones | | | H300+H330, |
| | | | H310+H330, |
| 2 | | | H300+H310+H330 |
| 2000 | Acute toxicity (oral, dermal, inhalation), hazard | Danger | H301, H311, H331, |
| | categories 3 | | H301+H311, |
| | | | H301+H331, |
| | | | H311+H331, |
| | | | H301+H311+331 |
| GHS07 | Acute toxicity (oral, dermal, inhalation), hazard | Warning | H302, H312, H332, |
| Exclamation | category 4 | | H302+H312, |
| mark | | | H302+H332, |
| | | | H312+H332, |
| 〈! 〉 | | | H302+H312+H332 |
| | Skin irritation, hazard category 2 | Warning | H315 |
| | Eye irritation, hazard category 2 | Warning | H319 |
| | Skin sensitisation | | |
| | hazard category 1 | Warning | H317 |
| | sub-category 1A, 1B | Warning | H317 |
| | Specific Target Organ Toxicity - Single exposure hazard category 3 | | |
| | - Respiratory tract irritation | Warning | H335 |
| | - Narcotic effects | Warning | H336 |
| | Hazardous to the ozone layer | Warning | H420 |

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Tab. 2 Hazard Pictograms according to Annex V of CLP (continued)

| Pictogram | Hazard class / category | Signal word | Hazard code |
|--------------|---|----------------|----------------|
| GHS08 | Respiratory sensitisation, | | |
| Health | hazard category 1 | Danger | H334 |
| hazard | sub-category 1A, 1B | Danger | H334 |
| | Germ cell mutagenicity | | |
| | hazard categories 1A, 1B | Danger | H340 |
| | hazard category 2 | Warning | H341 |
| | Carcinogenicity | | |
| | hazard categories 1A, 1B | Danger | H350 |
| | hazard category 2 | Warning | H351 |
| | Reproductive toxicity | | |
| | hazard categories 1A, 1B | Danger | H360 |
| | hazard category 2 | Warning | H361 |
| | Specific Target Organ Toxicity - Single exposure | | |
| | hazard category 1 | Danger | H370 |
| | hazard category2 | Warning | H371 |
| | Specific Target Organ Toxicity - Repeated exposure | | |
| | hazard categories 1 | Danger | H372 |
| | hazard categories 2 | Warning | H373 |
| 011000 | Aspiration hazard, hazard category 1 | Danger | H304 |
| GHS09 | Hazardous to the aquatic environment | | |
| Environment | - Acute hazard category 1 | Warning | H400 |
| NV. | - Chronic hazard categories 1 | Warning | H410 |
| (*2) | - Chronic hazard categories 2 | No signal word | H411 |
| | | | |
| No pictogram | Explosives | | |
|] ' " | Explosives of Divisions 1.5 | Danger | H205 |
| | Explosives of Divisions 1.6 | No signal word | No hazard code |
| | Flammable gases, hazard category 1 | Warning | H221 |
| | Self-reactive substances and mixtures, Types G | No signal word | No hazard code |
| | Additional category for effects on or via lactation | No signal word | H362 |
| | Hazardous to the aquatic environment | _ | |
| | - Chronic hazard categories 3 | No signal word | H412 |
| | - Chronic hazard categories 4 | No signal word | H413 |
| | Hazardous to the ozone layer | Danger | EUH059 |
| | (will be replaced by H420 in line with 2 nd ATP) | | |

Hazard statements

Under CLP, 71 basic 'hazard statements' (H-Statements), plus 1 additional hazard statement introduced by the 2nd ATP, which are assigned to a hazard class and category describe the nature of the hazards of a hazardous substance or mixture, including, where appropriate, the degree of hazard.

The 2nd ATP further introduces 12 combinations of hazard statements for acute toxicity.

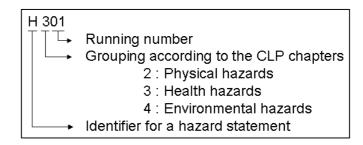
These hazard statements will replace the 66 basic DSD risk phrases (R-Phrases) and their 57 R-Phrase combinations.

The hazard statements are accomplished by supplemental hazard information and supplemental label elements for certain mixtures originating from DSD risk phrases and special labelling provisions of the DPD. As these statements are not part of GHS, they are assigned to EUH codes.

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Currently the codification system for hazards statements is as follows:



Tab. 3 Hazard statements

| Hazard statements for physical hazards according Annex III, Part 1 and Annex VI, Part 1 of CLP |
|--|
| |
| H200: Unstable Explosive |
| H201: Explosive; mass explosion hazard |
| H202: Explosive; severe projection hazard |
| H203: Explosive; fire, blast or projection hazard |
| H204: Fire or projection hazard |
| H205: May mass explode in fire |
| H220: Extremely flammable gas |
| H221: Flammable gas |
| H222: Extremely flammable aerosol |
| H223: Flammable aerosol |
| H224: Extremely flammable liquid and vapour |
| H225: Highly flammable liquid and vapour |
| H226: Flammable liquid and vapour |
| H228: Flammable Solid |
| H240: Heating may cause an explosion |
| H241: Heating may cause a fire or explosion |
| H242: Heating may cause a fire |
| H242: Heating may cause a fire |
| H250: Catches fire spontaneously if exposed to air |
| H251: Self-heating; may catch fire |
| H252: Self-heating in large quantities; may catch fire |
| H260: In contact with water releases flammable gases which may ignite spontaneously |
| H261: In contact with water releases flammable gases |
| H270: May cause or intensify fire; oxidiser |
| H271: May cause fire or explosion; strong oxidiser |
| H272: May intensify fire; oxidiser |
| H280: Contains gas under pressure; may explode if heated |
| H281: Contains refrigerated gas; may cause cryogenic burns or injury |
| H290: May be corrosive to metals |

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Tab. 3 Hazard statements (continued)

of exposure cause the hazard)

| Hazard | statements for health hazards according Annex III, Part 1 and Annex VI, Part 1 of CLP |
|--------|--|
| Hazara | otatomonto for notata nazardo docording / uniox in, r are r and / uniox vi, r are r or ozi |
| H300: | Fatal if swallowed |
| H301: | Toxic if swallowed |
| H302: | Harmful if swallowed |
| H304: | May be fatal if swallowed and enters airways |
| | Fatal in contact with skin |
| H311: | Toxic in contact with skin |
| H312: | Harmful in contact with skin |
| H314: | Causes severe skin burns and eye damage |
| H315: | Causes skin irritation |
| H317: | May cause an allergic skin reaction |
| H318: | Causes serious eye damage |
| H319: | Causes serious eye irritation |
| H330: | Fatal if inhaled |
| H331: | Toxic if inhaled |
| H332: | Harmful if inhaled |
| H334: | May cause allergy or asthma symptoms or breathing difficulties if inhaled |
| H335: | May cause respiratory irritation |
| | May cause drowsiness or dizziness |
| | May cause genetic defects (state route of exposure if it is conclusively proven that no other |
| | routes of exposure cause the hazard) |
| | Suspected of causing genetic defects (state route of exposure if it is conclusively proven |
| | that no other routes of exposure cause the hazard |
| | May cause cancer (state route of exposure if it is conclusively proven that no other routes |
| | of exposure cause the hazard) |
| | Suspected of causing cancer (state route of exposure if it is conclusively proven that no |
| | other routes of exposure cause the hazard) |
| | May damage fertility or the unborn child (state specific effect if known)(state route of |
| 11004 | exposure if it is conclusively proven that no other routes of exposure cause the hazard) |
| | Suspected of damaging fertility or the unborn child (state specific effect if known) (state |
| | route of exposure if it is conclusively proven that no other routes of exposure cause the hazard) |
| | |
| | May cause harm to breast-fed children. |
| | Causes damage to organs (or state all organs affected, if known) (state route of exposure if it is conclusively proven that no other routes of exposure cause the hazard) |
| | May cause damage to organs (or state all organs affected, if known) (state route of |
| | exposure if it is conclusively proven that no other routes of exposure cause the hazard |
| | May cause damage to organs (state all organs affected, if known) through prolonged or |
| | repeated exposure (state route of exposure if it is conclusively proven that no other routes |
| · ' | for the control of th |

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Tab. 3 Hazard statements (continued)

| Hazard statements for health hazards, as amended by Regulation (EC) No. 286/2011 | | | | | | | | |
|--|---|--|--|--|--|--|--|--|
| | | | | | | | | |
| H300 + H310: | Fatal if swallowed or in contact with skin | | | | | | | |
| H300 + H330: | Fatal if swallowed or if inhaled | | | | | | | |
| H310 + H330: | Fatal in contact with skin or if inhaled | | | | | | | |
| H300 + H310 + H330: | Fatal if swallowed, in contact with skin or if inhaled | | | | | | | |
| H301 + H311: | Toxic if swallowed or in contact with skin | | | | | | | |
| H301 + H331: | Toxic if swallowed or if inhaled | | | | | | | |
| H311 + H331: | Toxic in contact with skin or if inhaled | | | | | | | |
| | Toxic if swallowed, in contact with skin or if inhaled | | | | | | | |
| H302 + H312: | Harmful if swallowed or in contact with skin | | | | | | | |
| H302 + H332: | Harmful if swallowed or if inhaled | | | | | | | |
| H312 + H332: | Harmful in contact with skin or if inhaled | | | | | | | |
| H302 + H312 + H332: | Harmful if swallowed, in contact with skin or if inhaled | | | | | | | |
| | | | | | | | | |
| Hazard statements for e | environmental hazards according Annex III, Part 1 and Annex VI, Part 1 of CLP | | | | | | | |
| | | | | | | | | |
| H400: Very toxic to aq | | | | | | | | |
| | uatic life with long lasting effects | | | | | | | |
| | life with long lasting effects | | | | | | | |
| | tic life with long lasting effects | | | | | | | |
| H413: May cause long | lasting harmful effects to aquatic life | | | | | | | |
| | | | | | | | | |
| Hazard statements for environmental hazards as amended by Regulation (EC) No. 286/2011 | | | | | | | | |
| 11100 11 | | | | | | | | |
| H420: Harms public he | ealth and the environment by destroying ozone in the upper atmosphere | | | | | | | |
| | " A M D (4 N 4 4 0 4 0 1 0 1 D | | | | | | | |
| Hazard Statement codes | s according Annex VI, Part 1, No. 1.1.2.1.2 of CLP | | | | | | | |
| H350i: May cause | cancer by inhalation. | | | | | | | |
| H360F: May damag | • | | | | | | | |
| , | e the unborn child. | | | | | | | |
| | of damaging fertility. | | | | | | | |
| | of damaging the unborn child. | | | | | | | |
| | e fertility. May damage the unborn child | | | | | | | |
| | of damaging fertility. Suspected of damaging the unborn child. | | | | | | | |
| | e fertility. Suspected of damaging the unborn child. | | | | | | | |
| | e the unborn child. Suspected of damaging fertility. | | | | | | | |
| | | | | | | | | |

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Tab. 4 Supplemental hazard information

| Supplemental hazard information according to Annex III, Part 2 of CLP | | | | | |
|---|---|--|--|--|--|
| | | | | | |
| Physical P | roperties | | | | |
| | | | | | |
| EUH001: | Explosive when dry | | | | |
| EUH006: | Explosive with or without contact with air | | | | |
| EUH014: | Reacts violently with water | | | | |
| EUH018: | In use, may form flammable/explosive vapour-air mixture | | | | |
| EUH019: | May form explosive peroxides | | | | |
| EUH044: | Risk of explosion if heated under confinement | | | | |
| | | | | | |
| Health pro | perties | | | | |
| | | | | | |
| EUH029: | Contact with water liberates toxic gas | | | | |
| EUH031: | U | | | | |
| EUH032: | Contact with acids liberates very toxic gas | | | | |
| EUH066: | Repeated exposure may cause skin dryness or cracking | | | | |
| EUH070: | Toxic by eye contact | | | | |
| EUH071: | Corrosive to the respiratory tract | | | | |
| | | | | | |
| Environme | ental properties | | | | |
| | | | | | |
| EUH059: | Hazardous to the Ozone Layer (replaced by H420 according to Regulation (EC) No. 286/2011) | | | | |

Tab. 5 Supplemental label elements on certain substances and mixtures according to Annex III, part 3 of CLP

| EUH201: | Contains lead. Should not be used on surfaces liable to be chewed or sucked by children |
|---------|--|
| EUH201A | : Warning! Contains lead |
| EUH202: | Cyanoacrylate. Danger. Bonds skin and eyes in seconds. Keep out of the reach of children |
| EUH203: | Contains chromium (VI). May produce an allergic reaction |
| EUH204: | Contains isocyanates. May produce an allergic reaction. |
| EUH205: | Contains epoxy constituents. May produce an allergic reaction. |
| EUH206: | Warning! Do not use together with other products. May release dangerous gases |
| | (chlorine) |
| EUH207: | Warning! Contains cadmium. Dangerous fumes are formed during use. See information |
| | supplied by the manufacturer. Comply with the safety instructions |
| EUH208: | Contains (name of sensitising substance). May produce an allergic reaction |
| EUH209: | Can become highly flammable in use |
| EUH209A | : Can become flammable in use |
| EUH210: | Safety data sheet available on request |
| EUH401: | To avoid risks to human health and the environment, comply with the instructions for |
| | use |

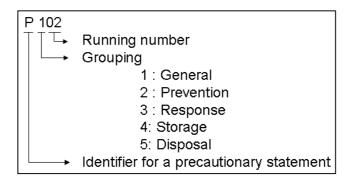
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Precautionary statements

Under CLP, 104 basic precautionary statements and 32 combinations of precautionary statements are introduced. A 'precautionary statement' (P-Statement) describes recommended measure(s) to minimise or prevent adverse effects resulting from exposure to a hazardous substance or mixture due to its use or disposal. The measures are coded for general, prevention, response, storage and disposal. The 2nd ATP introduces 1 additional precautionary statement related to disposal. These precautionary statements will replace the 54 basic DSD safety phrases (S-Phrases) and their 19 S-Phrase combinations.

Currently the codification system for precautionary statements is as follows:



Precautionary statements and their wording are available in Annex IV of the CLP regulation.

2.2.2.3 A brief highlight of differences between CLP and DSD

Some differences between the classification and labelling have already been described in the chapter 2.2.2.2 Elements of Regulation (EC) No. 1272/2008.

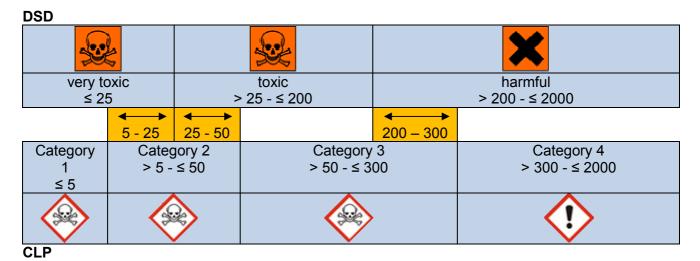
This chapter will highlight in brief important differences with relevance for classification of acrylates.

There are minor changes in classification criteria for flammable liquids (flash point) as well as for those of serious eye damage/eye irritation and skin irritation. More significant may be the fact that the classification intervals for acute toxicity are not congruent in the two classification systems. Substances, which are classified 'Xn' (harmful) under the DSD system may now possibly be reclassified with a 'skull and crossbones' pictogram under CLP. This is illustrated with the LD_{50} [mg/kg] criteria of acute oral toxicity (see figure 3)

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Fig. 3 Difference in classification for acute oral toxicity between DSD and CLP



As the symbol 'X' (St. Andrew's cross) disappears under CLP, some substances classified as irritant (DSD) may now bear the corrosive pictogram.

There are also changes in the classification of mixtures (see also chapter 3.3). Concentration limits that trigger classification under CLP are often lower than under DPD. For instance, the general threshold for classification as a skin or eye irritant has been diminished from 20 % (DPD) to 10 % (CLP). Some mixtures not classified for irritation under DPD may possibly be classified as a skin or eye irritant under CLP.

Classification of mixtures for acute toxicity is no longer derived by calculation using the risk phrase classification of a substance. Calculation under CLP is based on the so-called 'acute toxicity estimate' (ATE), which is derived either from the LD_{50}/LC_{50} (where available) or from an appropriate conversion value based on the classification category or experimentally obtained acute toxicity range estimate (see CLP, Table 3.1.2).

If the total concentration of the ingredient(s) with unknown toxicity is > 10 %, the calculation formula will be modified to adjust for the total percentage of the unknown ingredient(s).

In addition, for acute toxicity, all relevant routes of exposure have to be considered under CLP.

On the other hand, the threshold of concern for N R51/53 (Aquatic chron. 2 H411) rises from 0.1 % (DPD) to 1.0 % (CLP).

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3 Classification & labelling of acrylates

Classification and labelling (C&L) involves an evaluation of the intrinsic hazard of a substance or mixture and a communication of that hazard via SDS and label. This evaluation must be made for any substance or mixture manufactured within or imported into the EU and results in classification of the substance/mixture as hazardous concerning physico-chemical properties, health or environmental effects.

Irrespective of the quantity, all marketed substances in the EU must be classified and labelled. The labelling is often the first and only information on the hazards of a substance/mixture that reaches the downstream user.

The classification and labelling of substances or mixtures has a large number of downstream consequences within the EU legislation. For example, applying the classification & labelling of products made thereof and risk reduction measures to be applied when handling these substances/mixtures.

3.1 Classification & labelling of acrylates regarded as substances

Based on the chemical nature of UV/EB acrylates they can be split into two different groups, which can be assigned to one of the substance definitions given in the REACH regulation (details on substance definition under REACH are given in chapter 2.1.1).

Stenomeric acrylates

Stenomeric acrylates (derived from the Greek prefix $\sigma\tau\epsilon\nu o$, meaning narrow and $\mu\epsilon\rho\iota\sigma$, meaning part) are well-defined substances that are listed in EINECS or have been notified as new substances (ELINCS). Under REACH, many of these acrylates are defined as monoconstituent substances. Stenomeric acrylates differ little in chemical composition when comparing a product from one supplier to another.

The classification & labelling of these acrylates is either set in Annex VI of Regulation (EC) No. 1272/2008 (see also table 6) or subject to industry self classification.

Eurymeric acrylates

Eurymeric acrylates (derived from the Greek prefix $\epsilon\nu\rho\nu$, meaning large and $\mu\epsilon\rho\iota\sigma$, meaning part) are products with higher molecular weight and a wider molecular weight distribution. Eurymeric acrylates often differ significantly in chemical composition between different suppliers and, because of this, for most of the eurymeric acrylates no classification & labelling is set in the relevant regulations.

Eurymeric acrylates are divided in various categories, based on their chemistry:

- Oligoether acrylates
- Urethane acrylates
- Melamine acrylates
- Amine modified acrylates
- Chlorinated polyester acrylates
- Epoxy acrylates
- Polyester acrylates
- Silicone acrylates
- Acrylated acrylates
- Polybutadiene acrylates

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UV/EB ACRYLATE RESINS SECTOR GROUP



Formerly Eurymeric acrylates have been reported as NLP (no longer polymers) to the respective European inventory or they have been exempt if meeting the polymer definition.

Under REACH, acrylates formerly qualified as NLP are regarded as multiconstituent or UVCB substances. Acrylates meeting the polymer definition are exempt from a registration under REACH but their monomers are subject to registration.

3.1.1 Legally binding classification & labelling of UV/EB acrylates

Regulation (EC) No. 1272/2008 (CLP) is amending and repealing directives 67/548/EEC and 1999/45/EC and amending Regulation (EC) No. 1907/2006. Annex VI of the CLP regulation lists hazardous substances for which harmonized classification and labelling have been established at the community level. More details can be found in chapter 2.2.2 of this document.

It is mandatory to use the Annex VI classifications as a minimum. Manufacturers and suppliers should evaluate the substance in order to decide whether the harmonized classification is sufficient or whether further hazards should be added. Manufacturers or importers should apply the minimum classification but must classify in a more severe hazard category in cases where they have further information which shows that this is more appropriate. Such information might become available during the preparation of a REACH registration dossier for the members of a joint submission.

The classification & labelling of some UV/EB acrylates is regulated in Annex VI to Regulation (EC) No. 1272/2008. The following table (table 6) lists the UV/EB acrylates for which a harmonized, legally binding minimum classification & labelling exists.

As some of the UVEB acrylates are manufactured or imported in high tonnages, the UVEB industry has already registered them in 2010 according to REACH guidelines. Therefore the toxicological and ecotoxicological data of these acrylates have been extensively evaluated. As a result of the assessment, the classification and labelling of some acrylates now differs from the one listed in Annex VI. For example, the classification & labelling for PETA CAS 4986-89-4/PETIA CAS 3524-68-3 goes beyond the minimum classification given in Annex VI.

As mentioned above, in cases where new data are available and indicate a more stringent classification, this has to be applied by all parties knowing the information.

UV/EB Acrylate producers, as members of the joint submissions for these acrylates, strongly recommend to follow the classification & labelling indicated by the data evaluated for the registration. This classification & labelling will be communicated down the supply chain with the SDS/eSDS.

The classification and labelling for high volume acrylates proposed with the REACH registration dossier is summarized in table 7.

Most of the changes are related to the ecotoxicological properties of the acrylates resulting in an ecotox labelling, which might also have an impact on the dangerous good transport classification. Regarding human hazards, the most obvious change is related to the sensitizing porperties of acrylates.

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Tab. 6 Classification & labelling of UV/EB acrylates as regulated in Annex VI of 1272/2008 (= minimum classification)

| Substance | Abbrev. | Annex I number | CAS no | EC number | Symbol | Risk Phrases | CLP symbol | Hazard statements | Signal word | Transport classification (ADR) |
|---|---------|-------------------|------------|-----------|--------|---------------------------|----------------------------------|--|-------------------|--------------------------------|
| Monoalkyl or monoaryl or monoalkylaryl esters of acrylic acid with the exception of those specified elsewhere in this annex | | 607-133-00-9 | | | Xi; N | 36/37/38- 51/53 | GHS07 GHS09 | H319 H335 H315 H411 | Warning | Class 9 VGr: III UN3082 |
| Monoalkyl or monoaryl or monoalkylaryl esters of methacrylic acid with the exception of those specified elsewhere in this Annex | | 607-134-00-4 | | | Xi | 36/37/38 | GHS07 | H319 H335 H411 | Warning | Class 9 VGr: III UN3082 |
| Acrylic acid | AA | 607-061-00-8 | 79-10-7 | 201-177-9 | C; N | 10- 20/21/22- 35-50 | GHS02 GHS05 GHS07 GHS09 | H226 H332 H312 H302 H314 H400 | Warning Danger | Class 8 VGr: II UN2218 |
| 2-ethylhexyl acrylate | 2-EHA | 607-107-00-7 | 103-11-7 | 203-080-7 | Xi | 37/38-43 | GHS07 | H335 H315 H317 | Warning | - |
| Isooctyl acrylate | | 607-244-00-2 | 29590-42-9 | 249-707-8 | Xi; N | 36/37/38- 50/53 | GHS07 GHS09 | H319 H335 H315 H400 H410 | Warning | Class 9 VGr: III UN3082 |
| 1,3-butylene glycol diacrylate | | 607-118-00-7 | 19485-03-1 | 243-105-9 | С | 21-34-43 | GHS05 GHS07 | H312 H314 H317 | Warning Danger | Class 8 VGr: II UN1760 |
| Cyclohexyl acrylate | | 607-116-00-6 | 3066-71-5 | 221-319-3 | Xi; N | 37/38- 51/53 | GHS07 GHS09 | H335 H315 H411 | Warning | Class 9 VGr: III UN3082 |
| 1,4-butylene glycol diacrylate | | 607-119-00-2 | 1070-70-8 | 213-979-6 | С | 21-34-43 | GHS05 GHS07 | H312 H314 H317 | Warning Danger | Class 8 VGr: II UN1760 |
| Diethylene glycol diacrylate | DEGDA | 607-120-00-8 | 4074-88-8 | 223-791-6 | Т | 24-36/38- 43 | GHS06 | H311 H319 H315 H317 | Warning Danger | Class 6.1 VGr: II UN2810 |

Continued Tab. 6: Classification & labelling of UV/EB acrylates as regulated in Annex VI of 1272/2008 (= minimum classification)

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| Substance | Abbrev. | Annex I number | CAS no | EC number | Symbol | Risk Phrases | CLP symbol | Hazard statements | Signal word | Transport classification (ADR) |
|-----------------------------------|---------|-------------------|------------|-----------|--------|-----------------------|-------------------------|--------------------------------------|-------------------|------------------------------------|
| 1,6-hexanediol diacrylate *** | HDDA | 607-109-00-8 | 13048-33-4 | 235-921-9 | Xi | 36/38-43 | GHS07 | H319 H315 H317 | Warning | - |
| Pentaerythritol triacrylate ** | PETIA | 607-110-00-3 | 3524-68-3 | 222-540-8 | Xi | 36/38-43 | GHS07 | H319 H315 H317 | Warning | - |
| Pentaerythritol tetraacrylate ** | PETA | 607-122-00-9 | 4986-89-4 | 225-644-1 | Xi | 36/38-43 | GHS07 | H319 H315 H317 | Warning | - |
| Trimethylolpropane triacrylate*** | ТМРТА | 607-111-00-9 | 15625-89-5 | 239-701-3 | Xi | 36/38-43 | GHS07 | H319 H315 H317 | Warning | - |
| Triethylene glycol diacrylate | TEGDA | 607-126-00-0 | 1680-21-3 | 216-853-9 | Xi | 36/38-43 | GHS07 | H319 H315 H317 | Warning | - |
| Neopentyl glycol diacrylate | NPDGA | 607-112-00-4 | 2223-82-7 | 218-741-5 | Т | 24-36/38- 43 | GHS06 | H311 H319 H315 H317 | Warning Danger | Class 6.1 VGr: III UN2810 |
| Tripropylene glycol diacrylate | TPGDA | 607-249-00-X | 42978-66-5 | 256-032-2 | Xi; N | 36/37/38- 43-51/53 | GHS07 GHS09 | H319 H335 H315 H317 H411 | Warning | Class 9 VGr: III UN3082 |
| 2-norbornyl acrylate | | 607-121-00-3 | 10027-06-2 | | Xn | 21-38-43 | GHS07 | H312 H315 H317 | Warning | - |
| 2-hydroxyethyl acrylate | 2-HEA | 607-072-00-8 | 818-61-1 | 212-454-9 | T; N | 24-34-43- 50 | GHS06 GHS05 GHS09 | H311 H314 H317 H400 | Warning Danger | Class 8 (6.1) VGr: II UN2922 |
| Hydroxypropyl acrylate | НРА | 607-108-00-2 | 25584-83-2 | 247-118-0 | Т | 23/24/25- 34-43 | GHS06 GHS05 | H331 H311 H301 H314 H317 | Warning Danger | Class 6.1 (8) VGr: II UN2927 |

^{**} more stringent classification & labelling than Annex VI, due to new data developed for 2010 REACH registration (see table 7 below)

*** classification & labelling confirmed with data developed for 2010 REACH registration (see table 7 below)

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Tab. 7: updated June 2014

Tab. 7.1 Classification & labelling of UV/EB acrylates <u>evaluated by a 2010 REACH registration done by PARAD</u>

| Substance | Abbrev. | Index number | CAS No | EC No | CLP Symbol | Hazard Statement | Signal Word | Transport classification (ADR) |
|--|----------------|-----------------|--|---|-------------------------|--------------------------------------|----------------|--------------------------------|
| 1,6-hexanediol diacrylate | HDDA | 607-109-00-8 | 13048-33-4 | 235-921-9 | GHS07 | H315 H317 H319 H412 | Warning | - |
| _ b. c b c | PETIA/ PETA | - | 1245638-61-2 | 629-850-6 | GHS09 GHS07 GHS05 | H302 H315 H318 H317 H411 | Danger | Class 9 VGr: III UN3082 |
| Pentaerythritol triacrylate | PETIA | 607-110-00-3 | 3524-68-3 | see above CAS no 12456-38-61-2 | | | | |
| Pentaerythritol tetraacrylate | PETA | 607-122-00-9 | 4986-89-4 | | see | above CAS no | 12456-38-6° | 1-2 |
| Trimethylolpropane triacrylate | ТМРТА | 607-111-00-9 | 15625-89-5 | 239-701-3 | GHS07 | H315 H319 H317 | Warning | - |
| Propylidynetrimethanol, ethoxylated, esters with acrylic acid | TMP(EO)TA | - | 28961-43-5 | 500-066-5 | GHS07 | H319 H317 | Warning | - |
| Propylidynetrimethyl trimethacrylate | ТМРТМА | - | 3290-92-4 | 221-950-4 | GHS09 | H411 | Warning | Class 9 VGr: III UN3082 |
| Glycerol, propoxylated, esters with acrylic acid (1 - 6.5 moles propoxylated) | GPTA | - | 52408-84-1 | 500-114-5 | GHS07 | H319 H317 | Warning | - |
| 4,4'-Isopropylidenediphenol, oligomeric reaction products with 1-chloro-2,3-epoxypropane, esters with acrylic acid | BADGDA | - | 55818-57-0 (37625-93-7 merged with above CAS) | 500-130-2 (500-100-9 merged with above EC) | GHS07 | H317 | Warning | - |

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Continued Tab. 7.1 Classification & labelling of UV/EB acrylates <u>evaluated by a 2010 REACH registration done by PARAD</u>

| Substance | Abbrev. | Index number | CAS No | EC No | CLP Symbol | Hazard Statement | Signal Word | Transport classification (ADR) |
|--|----------------|-----------------|--|---|-------------------------|--------------------------------------|----------------|--------------------------------|
| 1,6-hexanediol diacrylate | HDDA | 607-109-00-8 | 13048-33-4 | 235-921-9 | GHS07 | H315 H317 H319 H412 | Warning | - |
| 2-propenoic acid reaction products with pentaerythritol | PETIA/ PETA | - | 1245638-61-2 | 629-850-6 | GHS09 GHS07 GHS05 | H302 H315 H318 H317 H411 | Danger | Class 9 VGr: III UN3082 |
| Pentaerythritol triacrylate | l | 607-110-00-3 | 3524-68-3 | | see | above CAS no | 12456-38-6 | 1-2 |
| Pentaerythritol tetraacrylate | PETA | 607-122-00-9 | 4986-89-4 | | see | above CAS no | 12456-38-6 | 1-2 |
| Trimethylolpropane triacrylate | ТМРТА | 607-111-00-9 | 15625-89-5 | 239-701-3 | GHS07 | H315 H319 H317 | Warning | - |
| Propylidynetrimethanol, ethoxylated, esters with acrylic acid | TMP(EO)TA | - | 28961-43-5 | 500-066-5 | GHS07 | H319 H317 | Warning | - |
| Propylidynetrimethyl trimethacrylate | ТМРТМА | - | 3290-92-4 | 221-950-4 | GHS09 | H411 | Warning | Class 9 VGr: III UN3082 |
| Glycerol, propoxylated, esters with acrylic acid (1 - 6.5 moles propoxylated) | GPTA | - | 52408-84-1 | 500-114-5 | GHS07 | H319 H317 | Warning | - |
| 4,4'-Isopropylidenediphenol, oligomeric reaction products with 1-chloro-2,3-epoxypropane, esters with acrylic acid | BADGDA | - | 55818-57-0 (37625-93-7 merged with above CAS) | 500-130-2 (500-100-9 merged with above EC) | GHS07 | H317 | Warning | - |
| Oxybis(methyl-2,1-ethanediyl) diacrylate | DPGDA | - | 57472-68-1 | 260-754-3 | GHS05 | H315 H318 H317 | Danger | - |
| (1-methyl-1,2-ethanedyl)bis[oxy(methyl-2,1-ethanediyl)] | TPGDA | 607-249-00-X | 42978-66-5 | 256-032-2 | GHS07 GHS09 | H315 H319 H317 H335 H411 | Warning | Class 9 VGr: III UN3082 |

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Tab 7. 2 Classification & labelling of UV/EB acrylates <u>evaluated by a 2013 REACH registration done by PARAD</u>

| Substance | Abbrev. | CAS No | EC No | CLP Symbol | Hazard Statement | Signal Word | Transport classification (ADR) |
|---|---|-------------|-----------|----------------|-----------------------|-------------|--------------------------------|
| 2-Propenoic acid, (1-methyl-1,2- ethanediyl)bis[oxy(methyl-2,1-ethanediyl)] ester, reaction products with diethylamine | | 111497-86-0 | 601-101-8 | GHS07 | H315 H317 H319 | Warning | - |
| 2-[2-[2-(1-methyl-2-prop-2-enoyloxy-ethoxy)ethoxymethyl]-2-[2-(2-prop-2-enoyloxypropoxy)ethoxymethyl]butoxy]ethoxy]propyl prop-2-enoate | TMP(PO)EOTA | 118800-30-9 | 601-566-7 | none | None | - | - |
| Esterification product of 2,2-bis(hydroxymethyl)-1,3-propanediol, ethoxylated and propoxylated and prop-2-enoic acid. | Pentaerythritol, alkoxylated, esters with acrylic acid | 144086-02-2 | 604-394-0 | GHS07 GHS09 | H319 H411 | Warning | Class 9 VGr: III UN3082 |
| 2-(2-hydroxyethoxy)propyl prop-2-enoate; 2-[2- [2-[2-(1-methyl-2-prop-2-enoyloxy- ethoxy)ethoxymethyl]butoxy]ethoxy]propyl 3- (dibutylamino)propanoate | TMP(PO)EOTA (DBA) | 173011-06-8 | 605-658-8 | GHS07 | H317 | Warning | - |
| 2-[2,2-bis(2-prop-2- enoyloxyethoxymethyl)butoxy]ethyl 3- (dibutylamino)propanoate | TMPEOTA-DBA | 195008-76-5 | 606-330-7 | GHS07 | H317 H319 | Warning | - |
| Esterification products of 4,4'- isopropylidenediphenol, ethoxylated and 2-methylprop-2-enoic acid. | BPA(EO)4DMA | 41637-38-1 | 609-946-4 | none | H413 | - | - |
| 2-Propenoic acid, 2-phenoxyethyl ester | POEA | 48145-04-6 | 256-360-6 | GHS07 GHS09 | H317 H411 | Warning | Class 9 VGr: III UN3082 |
| Pentaerythritol, ethoxylated, esters with acrylic acid | PPTTA | 51728-26-8 | 500-111-9 | GHS07 GHS09 | H315 H319, H411 | Warning | Class 9 VGr: III UN3082 |

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Continued Tab 7. 2 Classification & labelling of UV/EB acrylates evaluated by a 2013 REACH registration done by PARAD

| Substance | Abbrev. | CAS No | EC No | CLP Symbol | Hazard Statement | Signal Word | Transport classification (ADR) |
|---|---|--|-----------|----------------|------------------------------|-------------|--------------------------------|
| 1,4-butanediylbis[oxy(2-hydroxy-3,1- propanediyl)] diacrylate | BDGDA | 52408-42-1 | 257-900-3 | GHS05 GHS07 | H302 H317 H318 H412 | Danger | - |
| Propylidynetrimethanol, propoxylated, esters with acrylic acid | TMP(PO)3TA | (53879-54-2) 68890-85-7 | 676-712-6 | GHS07 | H315 H319 | Warning | - |
| [[2-[2-[2-(3-chloro-2-hydroxy-propoxy)propoxymethyl]-3-(2-prop-2-enoyloxypropoxy)-2-(2-prop-2-enoyloxypropoxymethyl)propoxy]-1-methyl-ethyl] | PETA-EPI-TA | 57903-73-8 | 611-591-5 | GHS07 GHS09 | H317 H411 | Warning | Class 9 VGr: III UN3082 |
| 2-Propenoic acid, reaction products with dipentaerythritol | DPPA (DPHA) | 1384855-91-7 (60506-81-2 29570-58-9) | 800-838-4 | GHS07 | H315 H317 H412 | Warning | - |
| Esterification products of 4,4'- isopropylidenediphenol, ethoxylated and prop-2-enoic acid. | BPA(EO)nDA | 64401-02-1 | 613-584-2 | none | H411 | - | Class 9 VGr: III UN3082 |
| (5-ethyl-1,3-dioxan-5-yl)methyl acrylate | TMPFA | 66492-51-1 | 266-380-7 | GHS07 GHS09 | H315 H317 H411 | Warning | Class 9 VGr: III UN3082 |
| Esterification product of poly[oxy(methyl-1,2-ethanediyl)], .alpha.,.alpha.'-(2,2-dimethyl-1,3-propanediyl)bis[.omegahydroxy- and prop-2-enoic acid | NPG(PO)nDA | 84170-74-1 | 617-546-6 | GHS07 GHS09 | H317 H411 | Warning | Class 9 VGr: III UN3082 |
| Soybean oil, epoxidised, acrylate | Soybean oil, epoxidised, acrylate | 91722-14-4 | 294-415-6 | none | none | - | - |

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Continued Tab 7. 2 Classification & labelling of UV/EB acrylates evaluated by a 2013 REACH registration done by PARAD

| Substance | Abbrev. | CAS No | EC No | CLP Symbol | Hazard Statement | Signal Word | Transport classification (ADR) |
|--|------------------|-------------|-----------|----------------|----------------------|-------------|--------------------------------|
| 2-[[2,2-bis[[(1- oxoallyl)oxy]methyl]butoxy]methyl]-2-ethyl-1,3- propanediyl diacrylate | DTMPTTA | 94108-97-1 | 302-434-9 | GHS07 GHS09 | H319 H411 | Warning | Class 9 VGr: III UN3082 |
| Reaction product of poly(oxy-1,2-ethanediyl), .alphahydroomega[(1-oxo-2-propenyl)oxy]-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (3:1) and N-ethylethanamine | TMPEOTA + DEA | 159034-91-0 | 500-425-6 | GHS07 | H317 H319 H412 | Warning | - |
| 2-Propenoic acid, monoester with 1,2- propanediol, polymer with 2- (chloromethyl)oxirane, dihydro-2,5-furandione and 4,4'-(1-methylethylidene)bis[phenol] | | 68958-77-0 | 500-240-0 | GHS07 | H317 | Warning | - |
| 2-Propenoic acid, isodecyl ester | IDA | 1330-61-6 | 1330-61-6 | GHS07 GHS09 | H317 H335 H411 | Warning | Class 9 VGr: III UN3082 |

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3.1.2 Harmonized Classification and Labelling (C & L) of Acrylates

For acrylates widely used in the UV/EB industry which are not listed in Annex VI of the CLP regulation and not yet registered under REACH, the sector group companies have considered the available toxicological data for each substance and agreed voluntarily on a common, harmonized labelling.

When these acrylates are finally evaluated and registered under REACH (in the years 2013 or 2018) or when new data becomes available, this voluntarily agreed classification & labelling might change. Therefore please consult the UV/EB website for the most current information about voluntarily agreed classification and labelling of UV/EB acrylates.

UV/EB sector group within CEFIC

http://www.cefic.org/About-us/How-Are-We-Organised/Cefic-Headquarter/The-Industry-Sectors/Fine-Speciality-and-Consumer-Chemicals/UVEB-Acrylate-Resins/?cat=Acrylate+Resins+(UV/EB)

Also the photoinitiator group organized in RadTech Europe has published a list of widely used photoinitiators with their harmonized classification & labelling.

RADTECH Europe

http://www.radtech-europe.com/templates/mercury.asp?page_id=1963

http://www.radtech-europe.com/files_content/hse/final%20CLP%20table%20v2.pdf

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3.2 Acrylates regarded as polymers

According to CLP, Article 4, there is a general obligation for manufacturers, importers and downstream users to classify substances or mixtures in accordance with CLP Title II before placing them on the market. According to REACH, Article 3 ("Definitions"), and CLP, Article 2 ("Definitions"), a polymer will also be a substance. Consequently, polymers are exempted from REACH registration obligations, but not from classification obligations. It will be necessary to identify the relevant available information for the purposes of determining whether the polymer entails a physical, health or environmental hazard.

As long as there is no information available for skin irritation or eye irritation, the UV/EB Sector Group recommends to classify for these endpoints as follows:

Tab. 8 Recommendation of classification of polymeric acrylates

| Skin irritation | Eye irritation | labelling |
|--------------------------|--------------------------|--|
| No information available | No information available | DSD: Xi, R36/38 CLP: Warning H315: Causes skin irritation H319: Causes serious eye irritation |
| No skin irritant *) | No information available | DSD: Xi, R36 CLP: Warning H319: Causes serious eye irritation |
| No information available | No eye irritant *) | DSD: Xi, R38 CLP: Warning H315: Causes skin irritation |
| No skin irritant *) | No eye irritant *) | Not labelled for skin and eye irritation |

^{*) &#}x27;No skin irritant' or 'no eye irritant' means there is information available that the polymer is not an irritant. If there would be instead information available that the polymer is an irritant, then the corresponding classification as skin or eye irritant, respectively, has to be used in addition to the recommended classification/labelling.

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3.3 Classification & Labelling of mixtures

Although classification of mixtures under CLP is to some extent similar to classification of mixtures under DPD, CLP puts less emphasis on simple calculations and instead asks for more expert judgement.

The approach for classification of mixtures is as follows:

- 1. Classification based on test data for the specific mixture
- 2. Application of bridging principles
- 3. Estimation of hazard properties based on the composition of the mixture

Just as under DPD, priority is given to classification based on test data obtained by testing the specific mixture. Where tests always have to be performed for the mixture itself in order to determine its physical hazards, test data from toxicological and eco-toxicological testing may often not be available.

Where the mixture itself has not been tested to determine its hazardous properties but its composition is known and sufficient data on a similar tested mixture are available, it may be possible to classify the untested mixture by using bridging principles (dilution, batching, concentration of highly hazardous mixtures, interpolation within one toxicity category, substantially similar mixtures, review of classification where the composition of a mixture has changed, aerosols) as described in Annex I, No. 1.1.3 of the CLP Regulation.

For health and environmental hazards, the classification of a mixture may be estimated based on data for the components contained in the mixture. Such estimate is based on calculation principles, which can be based either on an additivity approach or a non-additivity approach.

Additivity approach

If the hazard properties of every ingoing substance or at least for some of them are known, it is possible to classify the mixture by using the substance concentration and additivity formulas. The additivity approach applies to the following hazard classes:

- Acute toxicity
- Skin corrosion/Irritation*)
- Serious damage to eyes/eye irritation*)
- Hazardous to Aquatic Environment

If the total concentration of the ingredients with unknown acute toxicity is > 10 %, then the additivity formula for this hazard class has to be corrected to adjust for the total percentage of the unknown ingredients.

*) For some mixtures containing ingredients that are corrosive or irritating, the additivity approach is made unworkable due to the chemical characteristics of the ingredients. This may possibly apply to mixtures containing substances such as acids and bases, inorganic salts, aldehydes, phenols, and surfactants. In such an event, the non-additive approach applies. Thresholds may differ between the additivity and non-additivity approaches.

Non-additive approach

If any ingredient in the mixture exceeds the concentration limit for classification (general limit or

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substance specific limit, respectively) the mixture shall be classified in the respective hazard class. The non-additive approach applies to the following hazard classes:

- Respiratory or skin sensitization
- Germ Cell Mutagenicity
- Carcinogenicity
- Reproductive Toxicity
- Specific Target Organ Toxicity Single Exposure
- Specific Target Organ Toxicity Repeated Exposure
- Aspiration Hazard
- Hazardous to the ozone layer
- Skin corrosion/Irritation (where the additivity approach is not applicable)
- Serious damage to eyes/eye irritation (where the additivity approach is not applicable)

In general, the concentration limits that trigger classification for a certain hazard class are lower under CLP compared to those under DPD. As a consequence, a mixture may be not classified as hazardous for a specific toxicological endpoint under DPD but may possibly be classified under CLP.

The following example of a hypothetical formulation shall illustrate the differences when classified according to DPD and CLP. Please note that physical hazards need to be determined by testing the mixture. For the following example, it is assumed that the mixture is not tested for toxicological or ecotoxicological properties and there are no data available which would allow to apply bridging principles.

Tab. 9 Example of a mixture classified according to DSD and CLP

| Component | Content | Classification DPD | Classification CLP | Remarks |
|----------------|---------|--------------------|------------------------|----------------------------------|
| Α | 9 % | Xn R22 | Acute Tox. 4 H302 | |
| | | 52/53 | Aquatic Chronic 3 H412 | |
| В | 3 % | Xn R22 | Acute Tox. 3 H301 | LD ₅₀ oral: 250 mg/kg |
| | | N R51/53 | Aquatic Chronic 2 H411 | |
| С | 12 % | - | - | No information on acute |
| Acrylate resin | | | | oral toxicity available |
| D | 17 % | Xi R36/38 | Eye Irrit. 2 H319 | Skin/eye irritation not |
| Acrylate resin | | | Skin Irrit. 2 H315 | tested, polymer classified |
| | | | | according to the |
| | | | | recommendations of |
| | | | | labelling guide |
| E | 2 % | Xi R37/38 | STOT SE 3 H335 | |
| | | R43 | Skin Irrit. 2 H315 | |
| | | | Skin Sens. 1 H317 | |
| F | 0.5 % | Xi R43 | Skin Sens. 1 H317 | |
| G | 56.5 % | - | - | Not classified as |
| Acrylate resin | | | | hazardous based on |
| | | | | available information |

The classification and labelling according to the rules of the Dangerous Preparations Directive is:

Acute oral toxicity: $(9/25) + (3/25) = 0.48 \rightarrow \text{not classified for acute toxicity (<1)}$ Eye irritation: below threshold $(20 \%) \rightarrow \text{not classified for eye irritation}$

Respiratory irritation: below threshold (20 %) → not classified for respiratory irritation

Skin irritation: $(17/20) + (2/20) = 0.95 \rightarrow \text{not classified for skin irritation}$

Skin sensitisation: above threshold (1 %) \rightarrow R43 Environmental hazard: (3/2.5) + (9/25) = 1.56 \rightarrow R52/53

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UV/EB ACRYLATE RESINS SECTOR GROUP



Classification: R43, R52/53

Labelling:

×

Symbol: R-Phrases:

R43-52/53

Name of substance E appears on the label

Note: For this example the selection of S-Phrases was set aside.

The classification according to the rules of the <u>CLP Regulation</u> is

Acute oral toxicity: Additivity formula, ATE(A): 500; ATE(B): 250; Data not available (C)

 $ATE_{Mix} = (100 - 12) / [(9/500) + (3/250)] = 2933.3$

→ not classified for acute oral toxicity

Eye irritation: Additivity formula, $(17/10) = 1.7 \rightarrow \text{Eye irritation 2 H319}$

Respiratory irritation: Non-additivity, below threshold (20 %, but may require expert judgement)

→ not classified for respiratory irritation

Skin irritation: Additivity formula, $(17/10) + (2/10) = 1.9 \rightarrow \text{Skin Irrit. 2 H315}$ Skin sensitisation: Non-additivity, above threshold $(1 \%) \rightarrow \text{Skin Sens. 1 H317}$

Environmental hazard Additivity formula, (3/2.5) + (9/25) = 1.56 → Aquatic Chronic 3 H412

Classification:

Eye irritation 2 H319 Skin Irritation 2 H315 Skin Sens 1 H317 Aquatic Chronic 3 H412

Labelling:

!>

Pictogram:

Warning

Signal word: Hazard Statements:

H315 Causes skin irritation

H317 May cause an allergic skin reaction

H319 Causes serious eye irritation

H412 Harmful to aquatic life with long lasting effects

Name of substance E appears on the label Name of substance F appears on the label

For the classification according to CLP, the extent of information published in the SDS may influence the classification of the mixture. For instance, if the LD_{50} of substance B would not be known, then the applicable ATE(B) is 100. This would alter the ATE_{Mix} to 1833.3 (88/0.048) and the mixture needs to be classified also as Acute Tox. 4 H302. On the other hand, if there is also information available that substance C is not classified for oral toxicity because the LD_{50} is > 2000 mg/kg, this would alter the additivity formula to 100/0.048 = 2083.3 and the mixture does not need to be classified for oral toxicity.

Note: For this example the selection of P statements was set aside.

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4. Various Topics

4.1 Influence of environmental labelling on ADR transport / dangerous goods

The classification as a dangerous good for transport is closely related to the hazardous properties of the transported materials. There have been some changes regarding the classification & labelling of UVEB acrylates. Quite a few changes are in the area of ecotoxicological hazard classification and labelling and this also has impacts on the classification as a dangerous good.

The criteria for environmentally hazardous substances (for aquatic life) are harmonized between ADR, IMDG and IATA since 1.1.2010, based on the ecotox criteria given in the 2nd UN GHS.

But (according to ADR 2011) the provisions of 2.2.9.1.10.3 and 2.2.9.1.10.4 concerning the classification on environmentally hazardous substances, applicable until 31 December 2010, may be applied until 31 December 2013 because the UN GHS ecotox criteria for sea transport will only be in force with the 36 amendment of the IMDG code.

More details can be found here:

UN model regulation Rev. 13 (2003) - UNECE

ADR: About the ADR - UNECE

ADR classification of UV/EB acrylates

Except for 2-hydroxypropyl acrylate (UN2927), none of the UV/EB acrylates has a specific entry on the alphabetic index of ADR.

The ADR classification of UV/EB acrylates is included in tables 6 and 7 in chapter 3.1.1 Most common transport classes for UV/EB acrylates are:

Class 6.1 UN 2810 Toxic, liquids, organic, n.o.s.

CORECGIVE



Class 8 UN 1760 Corrosive liquids, n.o.s.

Class 9 UN 3077 Environmentally hazardous substance, solid, n.o.s. Class 9 UN 3082 Environmentally hazardous substance, liquid, n.o.s.





How to classify UV/EB acrylates and mixtures thereof:

One applicable method is to use the translation table given in Annex VII of the CLP regulation and classify with regard to dangerous goods transport accordingly:

The following R-Phrases or H-Statements of acrylates trigger a classification as environmentally hazardous goods class 9 (UN3077 or UN 3082):

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| Tab.10 ADR | classification class | s 9 related to | ecotoxicological | hazard classification |
|------------|----------------------|----------------|------------------|-----------------------|
|------------|----------------------|----------------|------------------|-----------------------|

| R-Phrases of a substance | H-Statements of a substance | R-Phrases and H-Statements | | | |
|--------------------------|-----------------------------|--|--|--|--|
| R 50 N; Class 9 | H400 N; Class 9 | R50: Very toxic to aquatic organisms R51: Toxic to aquatic organisms R52: Harmful to aquatic organisms R53: May cause long-term adverse effects in the aquatic environment R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment R51/53: Toxic to aquatic organisms, may cause long-term | | | |
| N; Class 9 | N; Class 9 | adverse effects in the aquatic environment R51/53: Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment R52/53: Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment H400 very toxic to aquatic life | | | |
| R 51/53 N; Class 9 | H411 N; Class 9 | H410 very toxic to aquatic life with long lasting effects H411 toxic to aquatic life with long lasting effects H412 harmful to aquatic life with long lasting effects H413 may cause long lasting harmful effects to aquatic life | | | |
| R 52/53 R 53 | H412; H413 | | | | |

ADR has changed with respect to classification of environmental hazards. This means that all dangerous goods meeting the relevant criteria, not just those directly assigned UN 3077 (solids) or UN 3082 (liquids), will be regarded as environmentally hazardous substances and are required to show the "dead fish and tree" mark.

Example HEA, CAS 818-61-1

ADR transport: class 8 and 6.1 and additionally environmentally hazardous



UN2922 corrosive liquid, toxic, n.o.s. (2-hydroxyethyl acrylate)

The other applicable method is to classify according CLP/ADR based on available data. The basic elements for classification of environmentally hazardous substances (aquatic environment) are:

- Acute aquatic toxicity;
- Chronic aquatic toxicity;
- Potential for or actual bioaccumulation; and
- Degradation (biotic or abiotic) for organic chemicals.

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Take into consideration that a classification according to the first mentioned method, using the translation table, may lead to a worst case classification regarding transport due to some differences in the classification criteria for hazard classification according 67/548/EC and the criteria applied in CLP/ADR regulation.

e.g. n-Pentane

a) Using the classification given in Annex VI and translation table Annex VII: According to 67/548/EEC Annex V n-pentane is classified as: N, R51/53 chronic cat. 2 (aquatic environment), using the translation table Annex VII of CLP:

N, R51/53 chronic cat. 2 → chronic cat. 2 H411 → classified as dangerous good on ADR transport.

b) Classification based on available data:

n- pentane has a log Kow <4:

according to 67/548/EEC this triggers the classification as: N, R51/53 chronic cat. 2

but according CLP and ADR criteria the classification with Kow > 4 results only in acute cat. 2 (aquatic environment) → no dangerous good on ADR transport

Table 11: Categories for substances hazardous to the aquatic environment (see Note 1)

- **NOTE 1:** The organisms fish, crustacea and algae are tested as surrogate species covering a range of trophic levels and taxa and the test methods are highly standardized. Data on other organisms may also be considered, however, provided they represent equivalent species and test endpoints.
- **NOTE 2:** When classifying substances as Acute 1 and/or Chronic 1 it is necessary at the same time to indicate an appropriate M factor (see 2.2.9.1.10.4.6.4) to apply the summation method.
- **NOTE 3:** Where the algal toxicity ErC₅₀ (= EC₅₀ (growth rate)) falls more than 100 times below the next most sensitive species and results in a classification based solely on this effect, consideration shall be given to whether this toxicity is representative of the toxicity to aquatic plants. Where it can be shown that this is not the case, professional judgment shall be used in deciding if classification shall be applied. Classification shall be based on the ErC₅₀. In circumstances where the basis of the EC₅₀ is not specified and no ErC₅₀ is recorded, classification shall be based on the lowest EC₅₀ available.
- **NOTE 4:** Lack of rapid degradability is based on either a lack of ready biodegradability or other evidence of lack of rapid degradation. When no useful data on degradability are available, either experimentally determined or estimated data, the substance shall be regarded as not rapidly degradable.
- **NOTE 5:** Potential to bioaccumulate, based on an experimentally derived BCF \geq 500 or, if absent, a log $K_{OW} \geq 4$ provided log K_{OW} is an appropriate descriptor for the bioaccumulation potential of the substance. Measured log K_{OW} values take precedence over estimated values and measured BCF values take precedence over log K_{OW} values.

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Table 11 Categories for substances hazardous to the aquatic environment (see Note 1) (ADR regulation chapter 2.9)

(a) Acute (short-term) aquatic hazard

| Category Acute 1: (see Note 2) | |
|--|-----------------------|
| 96 hr LC ₅₀ (for fish) | ≤ 1 mg/l and/or |
| 48 hr EC ₅₀ (for crustacea) | ≤ 1 mg/l and/or |
| 72 or 96hr ErC ₅₀ (for algae or other aquatic plants) | ≤ 1 mg/l (see Note 3) |

(b) Long-term aquatic hazard (see also Figure 2.2.9.1.10.3.1)

 Non-rapidly degradable substances (see Note 4) for which there are adequate chronic toxicity data available

Category Chronic 1: (see Note 2)

Chronic NOEC or EC_x (for fish) ≤ 0.1 mg/l and/or Chronic NOEC or EC_x (for crustacea) ≤ 0.1 mg/l and/or Chronic NOEC or EC_x (for algae or other aquatic plants) ≤ 0.1 mg/l

Category Chronic 2:

(ii) Rapidly degradable substances for which there are adequate chronic toxicity data available

Category Chronic 1: (see Note 2)

Chronic NOEC or EC_x (for fish) ≤ 0.01 mg/l and/or Chronic NOEC or EC_x (for crustacea) ≤ 0.01 mg/l and/or Chronic NOEC or EC_x (for algae or other aquatic plants) ≤ 0.01 mg/l ≤ 0.01

Chronic NOEC or EC_x (for fish) $\leq 0.1 \, \text{mg/l} \, \text{and/or}$ Chronic NOEC or EC_x (for crustacea) $\leq 0.1 \, \text{mg/l} \, \text{and/or}$ Chronic NOEC or EC_x (for algae or other aquatic plants) $\leq 0.1 \, \text{mg/l}$

(iii) Substances for which adequate chronic toxicity data are not available

Category Chronic 1: (see Note 2)

96 hr LC_{50} (for fish) \leq 1 mg/l and/or 48 hr EC_{50} (for crustacea) \leq 1 mg/l and/or 72 or 96hr ErC_{50} (for algae or other aquatic plants) \leq 1 mg/l (see Note 3)

and the substance is not rapidly degradable and/or the experimentally determined BCF is \geq 500 (or, if absent the log $K_{ow} \geq$ 4) (see Notes 4 and 5).

Category Chronic 2:

96 hr LC50 (for fish)>1 but \leq 10 mg/l and/or48 hr EC50 (for crustacea)>1 but \leq 10 mg/l and/or72 or 96hr ErC50 (for algae or other aquatic plants)>1 but \leq 10 mg/l (see Note 3)

and the substance is not rapidly degradable and/or the experimentally determined BCF is ≥ 500

(or, if absent the log $K_{ow} \ge 4$ (see Notes 4 and 5).

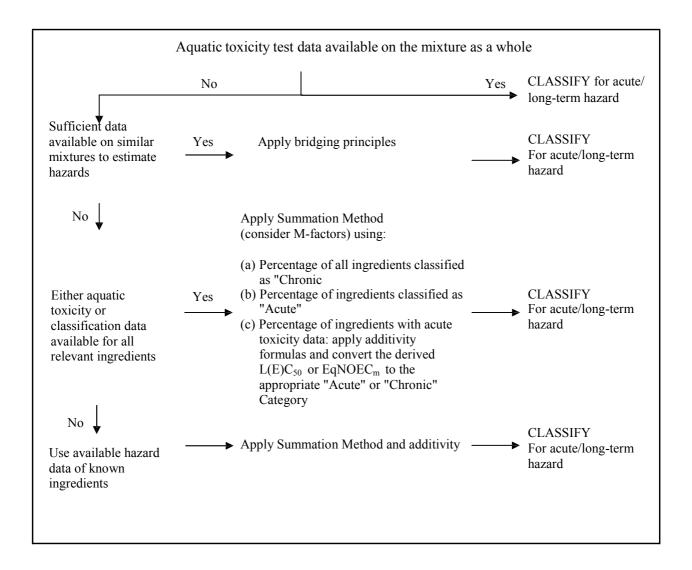
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ADR classification of mixtures follows the CLP criteria for the classification of mixtures.

For further details of classification of mixtures, please refer directly to the relevant documents (CLP regulation and ADR). Below find a simplified scheme taken out of ADR 2011.

Figure 4: Tiered approach to classification of mixtures for acute and long-term aquatic environmental hazards



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4.2 Recommendation on gloves

Legal background

COMMISSION DIRECTIVE 2001/58/EC of 27 July 2001, amending for the second time Directive 91/155/EEC defining and laying down the detailed arrangements for the system of specific information relating to dangerous preparations in implementation of Article 14 of European Parliament and Council Directive 1999/45/EC and relating to dangerous substances in implementation of Article 27 of Council Directive 67/548/EEC (safety data sheets). In the annex you will find the "GUIDE TO THE COMPILATION OF SAFETY DATA SHEETS", which list the recommendations for the compilation of the safety data sheets:

Exposure control: Hand protection

Specify clearly the **type of gloves** to be worn when handling the substance or preparation, including:

- the type of material
- **the breakthrough time** of the glove material, with regard to the amount and duration of dermal exposure.
- If necessary indicate any additional hand protection measures.

General recommendations for some acrylates

In general recommended glove materials depend on the chemistry of the material they get in contact with and on the duration of exposure. In case none of the general recommendations match your use, e.g. long handling of HDDA or DPGDA, acrylates with solvents containing high amounts of acetates and/or ketones, it is highly recommended to use laminated multilayer gloves.

The SDS and especially the eSDS provided by the supplier is the first source for information about safe use of substances and mixtures and the risk measurements necessary for handling. Only if the information given there is not sufficient, refer to the following general recommendations:

General recommendations: Protective gloves to handle UV/EB-Acrylates

Polyester acrylate

Nitrile rubber (NBR) gloves (0,1 mm) Give adequate protection up to 30 minutes

Nitrile rubber (NBR), NRL (latex) free; < 0.45 mm Give adequate protection for most acrylates up to 4 hours

Nitrile rubber (NBR), NRL (latex) free; > 0.56 mm

Give adequate protection for most acrylates in combination with commonly used solvents up to 8 hours

HDDA / DPGDA and other low molecular weight monomers

Laminated multilayer gloves

Give adequate protection to low molecular weight monomers for more than 1 hour.

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Tab. 12 Type of gloves versus exposure conditions

| Go | na | rai | l wa | rni | na: |
|----|----|-----|------|-----|-----|
| Ge | пе | ıaı | ı wa | | HU. |

DO NOT USE LATEX GLOVES! ONLY USE RECOMMENDED GLOVES! USING THE WRONG GLOVES MAY INCREASE THE RISK!

| ONLY USE RECOMM | ENDED GLOVES! USING THE WRONG GLOVES MAY INCREASE THE RISK! |
|--|---|
| Exposure condition: Short time use; (few minutes; less than 0.5 hour) Little physical stress | Use of thin nitrile rubber gloves Nitrile rubber (NBR) (0,1 mm) Excellent tactibility ("feel"), powder-free Disposible Inexpensive (€7.25/100 gloves) Gives adequate protection up to 30 minutes Does not give adequate protection to low molecular weight monomers (e.g. 2-PEA, HDDA, probably DPGDA) |
| Exposure condition: Medium time use; less than 4 hours Physical stress (opening drums, using tools, etc.) | Use of medium thick nitrile rubber gloves Nitrile rubber (NBR), NRL (latex) free; < 0.45 mm Moderate tactibility ("feel"), powder-free Disposible Moderate price Gives adequate protection for most acrylates up to 4 hours Does not give adequate protection to low molecular weight monomers (e.g. 2-PEA, HDDA, probably DPGDA) at exposures longer than 1 hour) |
| Exposure condition: Long time Cleaning operations | Use of thick nitrile rubber gloves Nitrile rubber (NBR), NRL (latex) free; > 0.56 mm low tactibility ("feel"), powder-free High price (€ 4.30/pair) Gives adequate protection for most acrylates in combination with commonly used solvents up to 8 hours Does not give adequate protection to low molecular weight monomers (2-PEA, HDDA, probably DPGDA) at exposures longer than 1 hour; Avoid the use of ketones and acetates in wash-up solvents) |

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ANNEX II Links used in the document

CEFIC

http://www.cefic.org

UV/EB sector group within CEFIC

http://www.cefic.org/About-us/How-Are-We-Organised/Cefic-Headquarter/The-Industry-Sectors/Fine-Speciality-and-Consumer-Chemicals/UVEB-Acrylate-Resins/?cat=Acrylate+Resins+(UV/EB)

Responsible care

http://www.responsiblecare.org/

ECHA

http://echa.europa.eu/).

ECHA REACH Navigator: Guidance on polymers:

http://quidance.echa.europa.eu/docs/guidance_document/polymers_en.htm?time=1309858514

ECHA REACH Navigator: Guidance on registration including substance definition http://guidance.echa.europa.eu/docs/guidance_document/registration_en.htm?time=130866765

PARAD consortium

http://www.reachcentrum.eu/en/consortium-management/consortia-under-reach/parad-reachconsortium.aspx

SVHC candidate list on ECHA

http://echa.europa.eu/chem_data/authorisation_process/candidate_list_table_en.asp

UN GHS

http://live.unece.org/trans/danger/publi/ghs/implementation e.html.

Regulation (EC) No. 1272/2008 CLP regulation incl. ATP

http://echa.europa.eu/legislation/classification_legislation_en.asp http://ec.europa.eu/enterprise/reach/ghs_en.htm

UN Model Regulation (Transport of dangerous good)

http://live.unece.org/trans/danger/publi/unrec/rev13/13files e.html

ADR applicable as from 1 January 2011

http://live.unece.org/trans/danger/publi/adr/adr e.html

RADTECH Europe

http://www.radtech-europe.com/templates/mercury.asp?page_id=1963 http://www.radtech-europe.com/files_content/hse/final%20CLP%20table%20v2.pdf

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ANNEX III List of abbreviations

ADR European Agreement concerning the International Carriage of Dangerous Goods by

Road

ATE Acute Toxicity Estimate

ATP Adaption to technical and scientific progress

1st ATP (to CLP) Regulation (EC) No. 790/2009 2nd ATP (to CLP) Regulation (EC) No. 286/2011 CEFIC European Chemical Industry Council

CLP Regulation (EC) No. 1272/2008 on the classification, labelling and packaging of

substances and mixtures

CMR Carcinogen, mutagen, reproductive toxin

CSR Chemical Safety Report DNEL Derived no effect level

DPD Dangerous preparations directive, Directive 1999/45/EC DSD Dangerous substances directive, Directive 67/548/EEC

ECHA European Chemicals Agency

EINECS European Inventory of Existing Commercial Chemical Substances

ELINCS European List of Notified Chemical Substances

EU European Union

FSCC Fine, Specialty and Consumer Chemicals

GHS Globally harmonized system of classification and labelling of chemicals

H-Statement
NBR
Nitrile-Butadiene-Rubber
NLP
NRL
Natural rubber latex
OR
Only representative

PARAD Polymerisable Acrylate Resins and Derivatives

PBT Persistent, bioaccumulative and toxic

PNEC Predicted no effect level Precautionary statement

REACH Registration, evaluation, authorisation, and restriction of chemical substances

R-Phrase Risk phrase

SDS/eSDS Safety data sheet /extended safety data sheet SIEF Substance Information Exchange Forum

S-Phrase Safety phrase

SVHC Substances of very high concern (i.e. substances on the 'candidate list of

substances of very high concern for authorisation')

TSCA United States Toxic Substances Control Act

UN United Nations

UV/EB Ultraviolet/Electon Beam

vPvB Very persistent, very bioaccumulative

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