

HARRPA Statement on Fortified Rosin Esters: Classification Packaging & Labelling

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Background

As a part of the compliance with the REACH Regulation (EC Regulation 1907/2006¹) the H4R consortium² was formed to address the issues arising from REACH, and to collaborate in the testing programs necessary to compile and complete the registration dossiers. Owing to the large number of rosin based derivatives on the market, the management was facilitated by grouping substances into “families” with similar chemistry, referred to as “categories” under REACH. Rosin derivatives employing fumaric acid and/or maleic anhydride together with polyols, such as glycerol, pentaerythritol and glycols fell into one such category – “No.4 Fortified Rosin Esters.”

The original members of this family were as follows:

CASRN	Chemical name
65997-11-7	Rosin, fumarated, oligomeric reaction products with pentaerythritol
68188-53-4	Rosin, fumarated esters with sorbitol
71243-68-0	Resin acids and Rosin acids, fumarated, decyl esters
91081-25-3	Resin acids and Rosin acids, maleated, mixed esters with diethylene glycol, glycerol and phthalic anhydride
92202-14-7	Rosin, fumarated, reaction products with glycerol and pentaerythritol
94581-15-4	Resin acids and Rosin acids, fumarated, esters with pentaerythritol
94581-16-5	Resin acids and Rosin acids, maleated, esters with glycerol
94581-17-6	Resin acids and Rosin acids, maleated, esters with pentaerythritol
97489-11-7	Resin acids and Rosin acids, fumarated, esters with glycerol
161074-62-0	Rosin, tall-oil, fumarated, oligomeric reaction products with pentaerythritol
193293-72-0	Resin acids and Rosin acids, maleated, esters with diethylene glycol and triethylene glycol

Note that the list only contains non-polymeric substances. As polymeric substances are REACH exempt they were excluded from the scope of this testing activity. However, further investigation by HARRPA has revealed that also polymeric versions of the members belonging to this family should also be classified as skin sensitisers³ (see table at the end of this position).

After having conducted a thorough investigation it was found that the members with most information on skin sensitisation and eye irritancy were:

CASRN 94581-15-4, the reaction product from Rosin, fumaric acid and pentaerythritol
 CASRN 92202-14-7, the reaction product from Rosin, fumaric acid, glycerol and pentaerythritol
 CASRN 68038-41-5, the polymer formed from Rosin, maleic anhydride and glycerol
 CASRN 68333-69-7, the polymer formed from Rosin, maleic anhydride and pentaerythritol
 CASRN 82228-97-5, the reaction product formed from Rosin, maleic anhydride and pentaerythritol

These were then selected to be the “models” for all other members, as far as toxicology (and eco-toxicology) was concerned. Rather than make tests on all the individual members the approach adopted was to “read across” from the “model” compounds.

According to CLP Regulation⁴ Article 41, notifiers and registrants shall make every effort to come to an agreed entry to be included in the inventory. The purpose of this document is to align the classification of all notifiers, importers and manufacturers for the substances within the scope of this category or family.

Notifiers, importers and manufacturers are therefore advised to use the classification in this document.

Case of rosin esters 'slightly' fortified

Rosin esters to which fumaric acid or maleic anhydride are added - even in small proportions - so as to increase the softening point of the resins, are to be considered as fortified rosin esters and thus should be classified accordingly.

Skin Sensitisation and Eye Irritation

The REACH data gap analysis showed the need to conduct skin sensitization tests among others. Tests were commissioned by the H4R Consortium at Harlan Laboratories using OECD Protocol 429. The result showed these substances gave a positive test result meaning it to be a skin sensitiser. Also discovered during the data gap analysis was the existence of studies showing eye irritancy.

Earlier, the HARRPA trade association had commissioned testing at a number of laboratories on the polymeric versions.

The impact of these results is that products previously considered as "un-classified" according to the former Dangerous Substances Directive (DSD) (EC Directive 67/548/EEC - as amended) now become classified. Until 30th November 2010, the DSD required to be labelled as "Xi, R36 and R43" which translates to the familiar St. Andrews Cross with the word "IRRITANT" and bear the text "Irritating to eyes" and "May cause sensitisation by skin contact".

For Eye irritation the classification becomes eye irritation Category 2 under the new CLP Regulation⁶.

For skin sensitization, animal studies for identification of skin sensitisation hazard, have been validated and are commonly used.

When assessing potency, cut-off values are applied to animal test results (mainly guinea pig tests or local lymph node assay). However, this sub-categorisation can only be applied where sufficient data exist to make the distinction; where the data are insufficient, the classification in Category 1 should be maintained.

Following the criteria used in CLP, the respective classifications for skin sensitisation are summarised in the following table:

Skin sensitisation	category 1	Sub-category 1A
		Sub-category 1B

Skin sensitizer classification is dependent on whether sufficient data exist. 1B is the classification of a substance showing a low to moderate potency.

following H-statements are required for skin sensitizer category 1, 1A or 1B and eye irritation category 2:

H317 "May cause an allergic skin reaction", and

H319 "Causes serious eye irritation"

Based on the available test data the following substances are justified for a skin sensitization classification category 1B:

CASRN	Chemical name
94581-15-4	Resin acids and Rosin acids, fumarated, esters with pentaerythritol
94581-17-6	Resin acids and Rosin acids, maleated, esters with pentaerythritol

All other substances will require a skin sensitizer category 1 classification.

There is no difference in generic concentration limit nor label elements for the different category classification 1 and 1B.

The symbol is the GHS07 pictogram depicting the exclamation mark, and is accompanied by the signal word "WARNING" as shown below.

Environmental Classification

No effects were observed at the highest loading rate tested in any of the acute toxicity studies for fish, daphnia or algae. Substances in this category would be therefore not classified for acute environmental hazards.

However as these substances are of low solubility, are not readily biodegradable and have log Kow values of >4, a "safety net" classification of aquatic Chronic Category 4 is assigned to substances in this category, according to the point number 4.1.2.4, and table 4.1.0 Part 4, Annex I of the CLP Regulation (EC) 1272/2008 (amended by the Commission Regulation (EU) 286/2011 of 10 March 2011).

Under DSD, a classification of R53 "May cause long-term adverse effects in the aquatic environment" is also considered to be appropriate for substances in this category.

Under CLP the H413 statement needs to be applied "May cause long lasting harmful effects to aquatic life"

All members of this family now also need to be so classified and labelled, regardless of whether they are polymeric or not.

Classification and Labelling according to Classification Labelling & Packaging Regulation 1272/2008

Pictogram:



Signal word: Warning

Hazard Statements:

H317 - May cause an allergic skin reaction

H319 - Causes serious eye irritation

H413 – May cause long lasting harmful effects to aquatic life.

Precautionary Statements:

P261 - Avoid breathing dust

P273 – Avoid release to the environment

P280 - Wear protective gloves/protective clothing (eye protection/face protection.)

P302+P352 - IF ON SKIN: Wash with plenty of soap and water.

P305+P351+P338 - IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P301 Immediately call a POISON CENTER or doctor/physician

P501 - Dispose of contents/container in compliance with all local and national regulations

Validity:

From 1st December 2010

Note: the H-statements are mandatory, however the P-Statements are voluntary and this selection has been agreed within the H4R Consortium.

Legal Obligations

Classification

According to Art 4 of the CLP Regulation, “Manufacturers, importers and downstream users shall classify substances or mixtures before placing them on the market.”

This means that all products being sold to customers must be classified and labeled in accordance with the rules described in the regulation. From the 1st December 2010, the new CLP scheme must be used. This involves the use of pictograms displayed in a red bordered diamond with associated H- and P-statements.

A CLP notification must be made to ECHA, if not already registered. This includes classified polymers that fall within the scope of this position. They are not exempt from the requirement to submit a CLP notification.

Pursuant to Art 40.2 of the CLP Regulation there is the requirement by suppliers to update the CLP inventory with the changed classification. It also recommended to refer in the CLP platform to this HARRPA document.

Formulations containing more than 1% of the classified substance also need to be classified and labeled as a skin sensitizer, in accordance with the CLP Regulation.

Formulations containing $\geq 0.1\% - < 1\%$ need not be labelled as a skin sensitizer, but the following text must be displayed on labels and SDS's: “Contains (substance name) – may produce an allergic reaction”, and the substance must be released in section 3 of the SDS.

Labelling

According to Art 30 of the CLP Regulation, “The supplier shall ensure that the label is updated, without undue delay, following any change to the classification and labelling of that substance or mixture, where the new hazard is more severe taking into account the nature of the change as regards the protection of human health and the environment.”

The meaning of this is that products shall be labelled according to the new classification as soon as practicably possible.

Safety Data Sheets

According to Art 31 of REACH Regulation, suppliers shall update the safety data sheet without delay. Further it shall be provided to all former recipients to whom they have supplied the product within the preceding 12 months.

This means that the new information shall be included in the revised SDS as soon as practicably possible and sent to all customers who were supplied with that product in the last 12 months.

In section 3 of the SDS it is mandatory to disclose the identification of the component in the product giving rise to the hazard classification. The CASRN, EC No. and chemical name of the substance must be displayed on both labels and SDS's.

Substances Affected

A list of substances originally affected by this was already given in the introduction.

There may be others not listed but are the reaction products of fumaric acid, maleic anhydride or similar compounds forming a Diels-Alder adduct with rosin and/or tall oil rosin and further esterified with an alcohol. Typically such alcohols employed in commercial products are glycerol and pentaerythritol, although other alcohols, polyols and glycols may be used.

Listed here is a collection of such substances and polymers fitting this description. It is not to be taken as a definitive list, but indicative only.

CASRN	EC No.	Name
68153-44-6	none, polymer	Rosin, fumarated, maleated, polymer with glycerol
68152-48-7	none, polymer	Rosin, fumarated, polymer with diethylene glycol
68152-49-8	none, polymer	Rosin, fumarated, polymer with diethylene glycol and ethylene glycol
68152-50-1	none, polymer	Rosin, fumarated, polymer with diethylene glycol and pentaerythritol
72230-81-0	none, polymer	Rosin, fumarated, polymer with dipentaerythritol and pentaerythritol
68152-53-4	none, polymer	Rosin, fumarated, polymer with dipropylene glycol
68152-56-7	none, polymer	Rosin, fumarated, polymer with ethylene glycol and glycerol
68152-57-8	614-317-2	Rosin, fumarated, polymer with ethylene glycol and pentaerythritol
65997-10-6	613-867-0	Rosin, fumarated, polymer with glycerol
68424-99-7	none, polymer	Rosin, fumarated, polymer with glycerol and pentaerythritol
68152-58-9	none, polymer	Rosin, fumarated, polymer with glycerol and sorbitol
65997-11-7	none, polymer	Rosin, fumarated, polymer with pentaerythritol
65997-11-7	500-164-8	Rosin, fumarated, oligomeric reaction products with pentaerythritol
68152-59-0	none, polymer	Rosin, fumarated, polymer with pentaerythritol and tripentaerythritol
68188-53-4	614-369-6	Rosin, fumarated, polymer with sorbitol
68082-94-0	none, polymer	Rosin, fumarated, polymer with trimethylolethane
92202-14-7	296-047-1	Rosin, fumarated, reaction products with glycerol and pentaerythritol
161074-62-0	500-495-8	Rosin, tall-oil, fumarated, oligomeric reaction products with pentaerythritol
68458-24-2	none, polymer	Tall-oil rosin, fumarated, polymer with glycerol
193293-72-0	none, polymer	Rosin, maleated, polymer with diethylene glycol and triethylene glycol
68554-22-3	none, polymer	Rosin, maleated, polymer with diethylene glycol, methyl ester
68514-97-6	none, polymer	Rosin, maleated, polymer with ethylene glycol and methanol
68038-41-5	614-235-7	Rosin, maleated, polymer with glycerol
68152-64-7	none, polymer	Rosin, maleated, polymer with glycerol and pentaerythritol
68309-58-0	none, polymer	Rosin, maleated, polymer with glycerol and trimethylolpropane
188958-72-7	none, polymer	Rosin, maleated, polymer with glycerol, esters with polyethylene glycol
68333-69-7	614-421-8	Rosin, maleated, polymer with pentaerythritol
82228-97-5	617-307-6	Rosin-maleic anhydride reaction product, pentaerythritol ester
68458-65-1	none, polymer	Rosin, maleated, polymer with pentaerythritol and polymerized rosin
68188-54-5	none, polymer	Rosin, maleated, polymer with propylene glycol
68152-67-0	none, polymer	Rosin, maleated, polymer with tripentaerythritol
127820-98-8	none, polymer	Rosin, maleic anhydride adduct, reaction products with polyethylene glycol and maleic anhydride
68188-28-3	none, polymer	Tall-oil rosin, maleated, polymer with pentaerythritol

CASRN	EC No.	Name
258342-84-6	Not listed	Resin acids and rosin acids, fumarated, C9-11-isoalkyl esters, C10-rich
71243-68-0	275-288-6	Resin acids and rosin acids, fumarated, decyl esters
97489-11-7	307-051-0	Resin acids and rosin acids, fumarated, esters with glycerol
94581-15-4	305-514-1	Resin acids and rosin acids, fumarated, esters with pentaerythritol
94581-16-5	305-515-7	Resin acids and rosin acids, maleated, esters with glycerol
94581-17-6	305-516-2	Resin acids and rosin acids, maleated, esters with pentaerythritol

References

¹ Regulation 1907/2006 on REACH, OJ L396 30.12.2006, p1

² Hydrocarbon Resins and Rosin Resins REACH (H4R) Consortium: <http://h4rconsortium.com/>

³ Private communication Dr. P Illing "Skin sensitization properties of a series of rosin adducts and adduct esters November 2011

⁴ Regulation 1272/2008 on CLP, OJ L353, 31.12.2008, p1

⁵ Regulation 286/2011 OJ L83 30.3.2011, p.1, amending for the second time Regulation 1272/2008 on the classification labeling and packaging of substances and mixtures

⁶ Regulation 1272/2008 OJ L353 31.12.2008, p.1, on the classification labeling and packaging of substances and mixtures
