

PR&S Committee



Guidance Document

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CLASSIFICATION OF ROSIN ADDUCT ESTERS

PURPOSE

The purpose of this guidance document is to provide an opinion from the Pine Chemicals Association (PCA) Product Regulatory & Stewardship Committee concerning how rosin adducts esters should be classified and labeled. It should not be considered legal guidance.

INTRODUCTION

Rosin adduct esters are substances that result from the reaction of rosin with dienophiles such as maleic anhydride and fumaric acid, followed by esterification with polyols such as glycerol and pentaerythritol. A complete listing of all the known members of this class is appended to the attached HARRPA document incorporated into this Guidance Document. Note that both non-polymers and polymeric versions have been shown to be skin sensitizers and should be labeled in the same way.

The Hydrocarbon Resins, Rosin Resins and Pine Chemicals Producers Association (HARRPA) conducted significant hazard testing for registration in Europe under the REACH regulations and the results were evaluated thoroughly. The HARRPA position is summarized in the attached document dated March 31, 2014 and should be reviewed carefully.

OPINION

It is the opinion of the Product Regulatory & Stewardship Committee of the

Pine Chemicals Association (PCA) that the classifications of HARRPA should be adopted by the members of the PCA and adapted to Safety Data Sheets in those countries to which the products are shipped ***with the possible exception of the following:***

R53: “May cause long-term adverse effects in the aquatic environment”,
and

H413: “May cause long-lasting harmful effects to aquatic life”

HARRPAs test results showed that that rosin adducts esters had NO acute hazards to aquatic life. Due to the low solubility and low biodegradability HARRPA gave them all the default classifications shown above to avoid testing that might cause the European Chemicals Agency (ECHA) to rethink its approach to the equivalency of the substances in this family, possibly requiring additional, extensive and expensive hazard testing. There is no reason to label them in non-European countries as causing long-term or long-lasting adverse effects on aquatic life.

On behalf of the Product Regulatory & Stewardship Committee of the Pine Chemicals Association

A handwritten signature in black ink that reads "Nelson Lawson". The signature is written in a cursive style with a large, looping initial 'N'.

Nelson Lawson



HARRPA

**Hydrocarbon Resins, Rosin Resins and Pine Chemicals
Producers Association**

Fortified Rosin Esters:

Classification Packaging & Labelling

Impact of new test data.

HARRPA

31st March, 2014





HARRPA

**Hydrocarbon Resins, Rosin Resins and Pine Chemicals
Producers Association**

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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 programmes 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.

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.



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.

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".

The classification becomes skin sensitisation Sub-category 1B⁵ and eye irritation Category 2 under the new CLP Regulation⁶. Skin sensitiser 1B is the classification of a substance showing a low to moderate potency and this attracts the following "H-statements":

H317 "May cause an allergic skin reaction", and
H319 "Causes serious eye irritation"

The symbol is replaced by 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.

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



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Hydrocarbon Resins, Rosin Resins and Pine Chemicals
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**Classification and Labelling according to the Dangerous
Substances Directive (DSD) 67/548/EEC⁷ (as amended)**

Symbol: Xi



Signal word: IRRITANT

Risk Phrases:

R36 – Irritating to eyes

R43 – May cause sensitisation by skin contact

**R53 – May cause long-term adverse effects in the aquatic
environment**

Safety Phrases:

S24/25 – avoid contact with skin and eyes

S37 – wear suitable gloves

**S60 – this material and its container must be disposed of
as hazardous waste.**

**S61 – avoid release to the environment, refer to special
instructions / safety data sheet**

Validity:

Until 31ST May 2015 for mixtures:

Labels

Safety Data Sheets

Classification

Packaging

⁷ Directive 67/548/EEC on the Classification Packaging and Labelling of Dangerous substances, OJ 196, 16.8.1967,
p. 1–98 (as amended)

**Classification and Labelling according to Classification
Labelling & Packaging Regulation 1272/2008⁸****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.****P312: Call a POISON CENTER or doctor/physician if you
feel unwell.****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.*

⁸ Regulation 1272/2008 OJ L353 31.12.2008, p.1, on the classification labeling and packaging of substances and mixtures



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. Prior to 1st December 2010, the scheme to be used for substances is the “old” European system involving the familiar symbols on orange square and the associated R- and S- Phrases. From the 1st December 2010, the new CLP scheme must be used. This involves the use of new pictograms displayed in a red-bordered diamond with associated H- and P- statements. Prior to the change-over date the use of CLP pictograms and text is optional. After the change-over date the use of the “old” scheme becomes optional.

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 is 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 “Dangerous Preparations Directive” 1999/45/EC⁹ and the CLP Regulation.¹⁰

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

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.

⁹ OJ L200 30.7.1999, p.1 EC Directive relating to the classification, packaging and labelling of dangerous preparations

¹⁰ Regulation 1272/2008 OJ L353 31.12.2008, p.1, on the classification labeling and packaging of substances and mixtures



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Practicalities:

The purchase of labels and new printed packaging obviously takes time and it is impracticable to stop production until the changes can be implemented. It is also impracticable to re-package all affected material in inventory whether it be at the manufacturer's facilities or at the customers or distributors. A practical solution is for affected material to be segregated and the necessary instructions on safe handling and storage be given to all concerned. This information is contained in the revised SDS's. Segregated material should be clearly marked on fences for example. This approach has been accepted by at least the French authorities in a similar situation previously.



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 |

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| CASRN | EC No. | Name |
|--------------|---------------|---|
| 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 |
| 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 |