## **REACH** registrations of Rosin, Rosin Salts and Rosin Esters

## H4R Position Statement on One Substance Registration

Historically, various names, CAS, and EINECS numbers have existed for rosin. REACH<sup>1</sup> mandates "One Substance – One Registration". This obliged the Rosin registrants to carefully examine the composition of their substances of interest. They concluded that, although Rosin is historically listed under different names and EINECS and CASRNs (e.g. Rosin; Tall-oil rosin; Resin acids and rosin acids; etc.), it needed to be considered as one and the same substance. In addition, the registrants concluded that rosin is a chemical substance of Unknown or Variable Composition, Complex Reaction Products and Biological Materials (UVCB).

In other words, rosin was listed on EINECS and CAS under different names, but the rosin registrants determined that differentiation was not justified and appropriate as these are the same UVCB substances. Therefore, Rosin with CAS 8050-09-7 was chosen. Appendix 1 to this document outlines the registrations that cover each of these substances. This decision and its rationale for one rosin registration is well documented in two papers:

- "Justification for grouping rosin and rosin derivatives into families" by Gary McCallister (Hercules), Bert Lenselink (Hexion), Jerrold Miller (Arizona Chemical), Bill Grady (Arizona Chemical) and Leon Rodenburg (Eastman Chemical), 24 August 2010<sup>2</sup>
- "Justification for considering Rosin as a Single Substance" by H4R Consortium, 22 February 2010<sup>3</sup>

Based on these papers, it was concluded that, for rosin and the derived rosin salts, fortified rosin, fortified rosin salts, rosin esters and fortified rosin esters, the starting rosin is not relevant. Therefore, during SIEF discussions in the H4R Consortium in 2010, H4R members concluded that the individual SIEFs needed to be merged to come to single registrations for rosin and its derived rosin salts and esters. This one rosin approach is not new, as it has been recognized and adopted by:

- The US Environmental Protection Agency (EPA), who no longer distinguish between rosin and tall oil rosin. (as indicated in a 1992 EPA letter to the Pulp Chemicals Association and later confirmed by the EPA in 2007). The Toxic Substance Control Act (TSCA) contains only one entry (CASRN 8050-09-7) for rosin and tall oil rosin.
- The grouping was used in the EPA's HPV challenge program (managed by PCA) in the early 2000's.
- The US Food and Drug Administration (FDA) in 2009, when considering rosin and derivatives (FDA, 2009), accepted that wood rosin is not distinguished from gum rosin.
- The European Chemical Bureau (ECB) who decided in 1992 that "one notification would be sufficient for the derivative made from the two rosins if the notifier could prove, to the satisfaction of the Competent Authorities, that both substances derived from the two entries were the same" (as published in the July 2006 ECB Manual of Decisions).

<sup>&</sup>lt;sup>3</sup> Attached as Appendix 3 to this position paper.

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<sup>&</sup>lt;sup>1</sup> REGULATION (EC) No 1907/2006 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

<sup>&</sup>lt;sup>2</sup> Attached as Appendix 2 to this position paper.



• The ECB, who published in June 2008 a Summary Fact Sheet from the PBT Working Group TC NES Subgroup on Identification of PBT and vPvB Substances. This factsheet presents several substances that can be considered corresponding substances to Tall Oil Rosin.

#### Appendices

- 1 Rosin, Rosin salts and Rosin Ester Registrations
- 2 Justification for grouping rosin and rosin derivatives into families H4R consortium February 2010
- 3 Justification for considering rosin as a single substance H4R Consortium February 2010

	REACH registered as		
REACH registered as	CAS Number EC Number Name		
	8050-09-7	232-475-7	Rosin
Rosin	8052-10-6	232-484-6	Tall-oil rosin
CAS Number 8050-09-7	73138-72-6	277-299-1	Resin acids and rosin acids
EC Number 232-475-7	94114-23-5	302-657-1	Resin acids and rosin acids, tall-oil
Desta setenda e el	61790-50-9	263-142-4	Resin acids and rosin acids, potassium
Rosin, potassium salt CAS 61790-50-9			salt
EC 263-142-4	84776-85-2	284-011-8	Resin acids and rosin acids, tall-oil,
EC 205-142-4			potassium salt
Rosin, sodium salt	61790-51-0	263-144-5	Resin acids and rosin acids, sodium
CAS 61790-51-0			salt
EC 263-144-5	85409-26-3	287-093-3	Resin acids and rosin acids, tall-oil,
LC 203-144-5			sodium salt
Rosin, aluminium salt	61789-65-9	263-075-0	Resin acids and Rosin acids,
CAS 61789-65-9			aluminium salts
EC 263-075-0			
Rosin, triethylene glycol	8050-25-7	232-478-3	Resin acids and rosin acids, esters
ester			with triethylene glycol
CAS 8050-25-7	84776-84-1	287-093-3	Resin acids and rosin acids, tall-oil,
EC 232-478-3			esters with triethylene glycol
Rosin, pentaerythritol	8050-26-8	232-479-9	Resin acids and rosin acids, esters
ester			with pentaerythritol
CAS 8050-26-8	85566-49-0	287-660-5	Resin acids and rosin acids, tall-oil,
EC 232-479-9			esters with pentaerythritol
Rosin, glycerol ester	8050-31-5	232-482-5	Resin acids and rosin acids, esters
CAS 8050-31-5			with glycerol
EC 232-482-5	85566-48-9	287-658-4	Resin acids and rosin acids, tall oil,
	esters with glycerol		
Rosin, fumarated	65997-04-8	266-040-8	Rosin, fumarated
CAS 65997-04-8	85631-69-2	288-017-1	Tall-oil rosin, fumarated
EC 266-040-8	01001 22 0	202 625 5	Design estide and particulate
Rosin, fumarated,	91081-22-0	293-625-5	Resin acids and rosin acids,
compounds with			fumarated, compounds with
triethanolamine	01081 30 0	202 (22.0	triethanolamine
CAS 91081-22-0	91081-30-0	293-633-9	Resin acids and rosin acids, tall-oil, fumarated, compounds with
EC 293-625-5			triethanolamine
	65997-11-7	500-164-8	Rosin, fumarated, oligomeric reaction
	03337-11-7	500-104-0	products with pentaerythritol
Rosin, fumarated,	94581-15-4	305-514-1	Resin acids and rosin acids,
esters with	54301 13 4	505 517 1	fumarated, esters with
pentaerythritol			pentaerythritol
CAS 94581-15-4	161074-62-0	500-495-8	Rosin, tall-oil, fumarated, oligomeric
EC 305-514-1			reaction products with
			pentaerythritol
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## Appendix 1: Rosin, Rosin salts and Rosin Ester Registrations



REACH registered as	Substance names, CAS and EC numbers covered			
REACH registered as	CAS Number	EC Number	Name	
Rosin, maleated CAS 8050-28-0	8050-28-0	232-480-4	Rosin, maleated	
EC 232-480-4	85409-30-9	287-098-0	Tall-oil rosin, maleated	
Rosin, maleated, sodium salt	68201-60-5	269-228-8	Resin acids and rosin acids, maleated, sodium salts	
CAS 68201-60-5 EC 269-228-8	85736-82-9	293-637-0	Resin acids and rosin acids, tall-oil, maleated, sodium salts	
Rosin, maleated, potassium salt	85409-27-4	287-094-9	Resin acids and rosin acids, maleated, potassium salt	
CAS 85409-27-4 EC 287-094-9	91081-33-3	293-637-0	Resin acids and rosin acids, tall-oil, maleated, potassium salts	
Rosin, maleated, esters with pentaerythritol	68333-69-7	614-421-8	Rosin, maleated, polymer with pentaerythritol	
CAS 94581-17-6 EC 305-516-2	94581-17-6	305-516-2	Resin acids and rosin acids, maleated, esters with pentaerythritol	
Rosin, maleated, esters with glycerol	68038-41-5	614-235-7	Rosin, maleated, polymer with glycerol	
CAS 94581-16-5 EC 305-515-7	94581-16-5	305-515-7	Resin and rosin acids, maleated, esters with glycerol	
Tall oil fatty acids, oligomeric reaction	160901-14-4	500-451-8	Fatty acids, tall oil, oligomeric reaction products with maleic anhydride and rosin, calcium magnesium zinc salts	
products with maleic anhydride and rosin, calcium, magnesium, zinc salts	160901-15-5	500-452-3	Fatty acids, tall oil, oligomeric reaction products with maleic anhydride and tall-oil rosin, calcium magnesium zinc salts	
CAS 160901-14-4 EC 500-451-8	160901-16-6	500-453-9	Fatty acids, tall oil, oligomeric reaction products with maleic anhydride, rosin and tall oil rosin, calcium magnesium zinc salts	



REACH pre-registered	Substance names, CAS and EC numbers covered		
as CAS Number EC Number Name			Name
Rosin, fumarated, sodium salt	68201-59-2	269-227-2	Resin acids and rosin acids, fumarated, sodium salt
CAS 68201-59-2 EC 269-227-2	85736-81-8	288-493-0	Resin acids and rosin acids, tall-oil, fumarated, sodium salts
Rosin, fumarated, potassium salt CAS 68649-83-2	68649-83-2	272-035-1	Resin acids and Rosin acids, fumarated, potassium salts
EC 272-035-1	84776-94-3	284-020-7	Resin acids and rosin acids, tall-oil, fumarated, potassium salts
Rosin, maleated, reaction product with	98219-66-0	308-735-1	Rosin, maleated, reaction product with formaldehyde
formaldehyde CAS 98219-66-0 EC 308-735-1	94114-24-6	302-658-7	Resin acids and rosin acids, tall-oil, maleated, reaction products with formaldehyde



## Appendix 2

Justification for Grouping Rosin and Rosin Derivatives into Families

## Justification for grouping rosin and rosin derivatives into families

Disclaimer:

It is the individual responsibility for each co-registrant to register its dossier individually. The information contained in the following document intends to serve as a practical guidance only, and whilst the information is provided in good faith and has been based on the information currently available at that time, is to be relied upon at the user's own risk. No representations or warranties are made with regards to its completeness or accuracy and does not state any liability of the lead registrant/members of the H4R consortium. The lead registrant/members of the H4R consortium will not accept any liability for damages of any nature whatsoever resulting from the uses of or reliance on the information for any purpose including but not limited to REACH registration purpose.

<u>Authors</u>: Gary McCallister (Hercules), Bert Lenselink (Hexion), Jerrold Miller (Arizona Chemical), Bill Grady (Arizona Chemical) and Leon Rodenburg (Eastman Chemical)

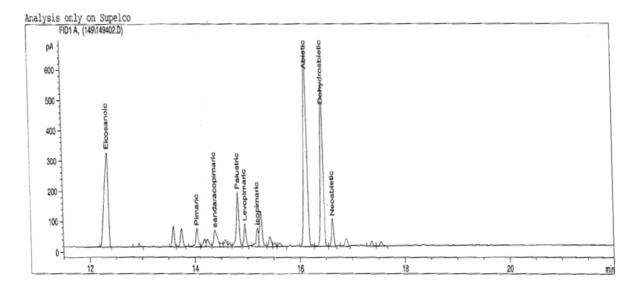
Date: 24 August 2010

#### Introduction to Rosin and Rosin Chemistry

Rosin is a complex naturally occurring mixture of diterpenic structures containing carboxylic acid and unsaturation functionality. Rosin is obtained from trees, typically pine trees. It is light amber and glassy in appearance. See picture below.



There are more than 20 different isomeric structures of resin acids, most of which have the general formula of  $C_{19}H_{29}COOH$ . Below is a typical chromatogram of rosin illustrating the complex nature of rosin.



In chemical nomenclature the terms "rosin" and "rosin acids and resin acids" are essentially synonymous. Abietic acid is generally the predominant resin acid in rosin and is often used to illustrate the typical structure of resin acids. The structure of abietic acid and some other common resin acids are shown under the next section. The ratio of the various resin acids in rosin varies depending upon the region from which it is obtained, the process used to isolate it, the species of tree from which it came and even in some cases, the climate is which the tree is grow. However, the chemistry is similar across the family.

The total acid content of rosin is typically 90-95% depending upon the source of the rosin and the manufacturing process. The remaining components are commonly called "neutrals" or "unsaponifiables" because these components do not have the carboxylic acid functionality and are generally less reactive. The "neutral fraction" is generally composed of diterpene hydrocarbons, alcohols, esters, or aldehydes. The neutral fraction is typically <10% and relatively unimportant relative to the resin acid components.

For commercial reasons the source of rosin is indicated by using trivial names: "gum rosin" is the term used for rosin that is derived from tapping live trees. "Tall oil rosin" is the term used for the rosin that is derived from tall oil, a product that is set free during the pulping of tree trunks for the paper industry. "Wood rosin" is rosin that is obtained from the extraction of tree stumps and root system that are left behind after the harvesting of pine trees for timber and paper making.

When EINECS was set up in the late 1970's and early 1980's, companies have submitted CASRN's to describe rosin. As the EINECS entries were submitted uncoordinated, it happened that 4 CASRN's were used to describe rosin: 8050-09-7 "rosin", 8052-10-6 "tall-oil-rosin", 73138-82-6 "resin-acids-and-Rosin-acids, tall-oil".

A detailed look at the composition of rosin and the source it is obtained from, i.e. live tree, pulping process or tree stump, it is obvious that there are slight differences in resin acid distribution. The table below, taken from the book *Naval Stores* [Zinkel and Russell], shows these details.

		Rosin	
Resin Acid	$Tall Oil^2$	Wood	Gum
Pimaric	4.4	7.1	4.5
Sandarcopimaric	3.9	2.0	1.3
Communic	1.0		3.1
Levopimaric			1.8
Paulstric	8.2	8.2	21.2
Isopimaric	11.4	15.5	17.4
Abietic	37.8	50.8	23.7
Dehydroabietic	18.2	7.9	5.3
Neobietic	3.3	4.7	19.1

#### Table 2. Typical Composition of the Common Resin Acids in Some U.S. Rosins<sup>1</sup>

<sup>1</sup>Per cent of acid fraction.

<sup>2</sup>Also contains fatty acids and other minor resin acids such as the secodehydroabietic acids.

One is tempted to regard these differences as significant. However, the resin acid distribution is much more dependent on species of the pine tree, geographical area, climate and season. The table below, taken from the same *Naval Stores*, shows a couple of things. Analysis of the resin acids in the oleoresin<sup>1</sup> shows significant variation in resin acid distribution, depending on the species of the tree: abietic acid ranges from 8.6 % in *Pinus taeda* to 37 % in *Pinus halepensis*, levopimaric and palustric acid ranges from 12 % in *Pinus peuce* to 64 % in *Pinus taeda*.

The table also shows the acid distribution in gum rosin from different geographical areas. Taking the same resin acids, abietic acid ranges from 22 % in American and Honduran rosin to 53.3 % in Mexican rosin. Levopimaric and palustric acid range from 9.8 % in Mexican rosin to 30 % in Portuguese rosin. These numbers illustrate very well that the resin acid distribution varies more due to tree species and geographical area than to the way the rosin was obtained, i.e. live tree, pulping process or tree stump.

<sup>&</sup>lt;sup>1</sup> Oleoresin is the resin that flows out of the living tree. Oleoresin is separated by distillation in a volatile fraction, consisting of terpenes like  $\alpha$ -pinene,  $\beta$ -pinene and d-limonene, and a non-volatile fraction: gum rosin.

				Levo-				
		Sandara-		pimaric/ Palus-	T		D. I. I.	
Samples	Pimaric	copimaric (	Communic		Iso- pimaric	Abietic	Dehydro- abietic	Neo- abietic
-	1 11111111	copinanie C			-		aotette	aoletic
Oleoresin			Per C	ent of Acid	in Acid Fr	action		
P. elliottii var. elliottii	5.1	1.8	3.1	37	21	9.7	3.7	16
P. elliottii var. densa	3.8	1.9	3.1	38	21	12	3.7	16
P. palustris	5.4	1.1	0	52	10	9.4	8.3	13
P. taeda	8.7	2.2	0	64	т	8.6	6.3	9.5
P. ponderosa	7.6	2.9	0	40	15	11	8.2	11
P. halepensis	0	1.2	0	39	10	37	1.5	9.7
P. brutia	0	1.2	0	44	10	32	2.5	10
P. pinaster	8.0	2.0	0	39	12	14	4.2	18
P. caribaea	4.2	2.2	0	49	8	10	8.6	16
P. peuce	1.8	1.0	0	12	32	35	0.8	14
Rosins								
American	5.1	1.8	2.8	25	17	22	5.7	20
American <sup>2,3</sup>	5.4	1.8	1.8	20.3(1.4)	14.2	27.9	7.1	16.3
$Brazilian^2$	4.7	1.7	3.2	11.4(.3)	18.2	36.3	5.4	
Burmese	7.9	3.0	0	44	8.3	30	6.0	2.2
Chinese	9.2	2.7	0	22	1.5	44	4.3	15
French	10	2.2	0.3	22	7.0	36	4.9	17
Greek	0	1.9	0	14	11	50	4.5	13
Honduran	9.6	2.2	0	21	17	22	12	15
Indian	9.2	1.5	0	11	20	38	2.0	18
Mexican <sup>2.4</sup>	6.8	1.2	0	9.8(0.3)	12.9	53.3	7.8	6.1
Portuguese	8.8	1.9	0.7	30	5.3	32	5.1	16
Portuguese <sup>2</sup>	8.3	1.4	0	20.4(11.7)	4.5	27.7	5.8	17.2
Russian	7.8	2.4	0	27	5.6	35	5.3	17
Spanish	8.7	1.5	0	27	0	36	1.9	24
Turkish	0	1.3	0	24	13	41	5.1	15

Table 3. Principal Resin Acids in Typical Pine Oleoresins and Some Commercial Gum Rosins<sup>1</sup>

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<sup>1</sup>Data from ref. 31. This table also appears in Chapter 4 as Table 1.

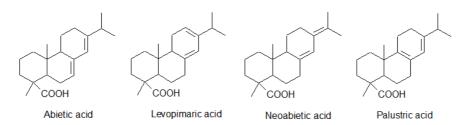
<sup>2</sup>D.F. Zinkel, Private communication. Palustric values given first; levopimaric values are in (). <sup>3</sup>Also contains small amounts of imbricataloic acid, as well as imbricatoloic and isocupressic acids and their acetates (32).

<sup>4</sup>A distilled rosin.

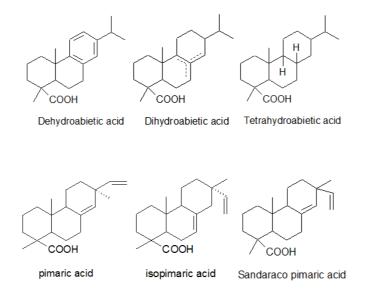
As variability of the composition of rosin is dominated by tree species and geographical area, it is reasonable to say that there are no significant differences between gum, wood and tall oil rosin. Therefore, as the three types of rosin are virtually the same, it is reasonable to say that there should be no distinction between the derivatives of the three types of rosin.

#### **Resin Acids in Rosin**

The four predominant and most important resin acids in rosin, commonly called the "abietic-type" resin acids, are shown below.



These resin acids are of importance because in addition to the carboxylic acid functionality, they also have conjugated double bonds. The importance of this will be discussed later under the section on "Reaction Chemistry". Depending upon source and method of manufacture, rosin typically contains 50-70% of these abietic-type resin acids. Additional structures for some of the less important resin acids are shown below.



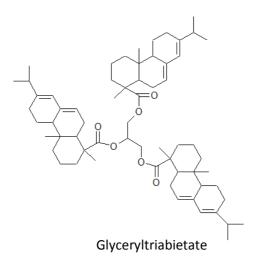
The most useful chemical and physical properties of rosin include: carboxylic acid functionality, unsaturation, thermoplastic, and low volatility. These two chemical properties make possible hundreds of various rosin derivatives that are used in a wide variety of end use applications such as adhesives, printing inks and coatings, paper sizing, lubricant additives, plasticizing agents, air entrainment aids and even food additives.

#### **Reaction Chemistry**

The carboxylic acid functionality and unsaturation of rosin (resin acids) makes it susceptible to various chemical reactions such as esterification, Diels-Alder addition, salt formation, phenol/formaldehyde addition, hydrogenation, and dehydrogenation/disproportionation isomerisation. These reactions result is literally hundreds of different rosin derivatives. The most important of these various reactions and derivatives are discussed below.

#### Esterification

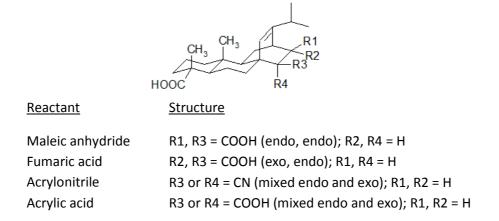
Rosin and hydrogenated rosin can undergo esterification with alcohols or polyols such as methanol, glycerol, pentaerythritol and triethylene glycol. The resulting esters are essentially the same because hydrogenation does not affect the carboxylic acid functionality. The diagram below shows a typical esterification reaction between rosin and glycerol to form the glycerol triester of rosin.



Esters can also be made with adducted rosin (see below under "Diels-Alder Addition"). Because rosin adduct is multifunctional, esterification with polyols such as such as glycerol, pentaerythritol and triethylene glycol can result in polyester formation and depending upon the ratio carboxylic (from the rosin) and hydroxyl (from the polyols), complex polymeric and cross linked structures are possible.

#### **Diels-Alder Addition**

Diels-Alder addition can be used to form what are commonly called "rosin adducts". This type of reaction is used to place additional functionality on the rosin molecule. Adduction reactions are typically done with heat and acid catalyst. Because Diels-Alder adduction occurs only to rosin molecules with a conjugated diene structure, only the abietic-type resin acids can be adducted in this fashion. Examples of some Diels-Alder reactants and their resulting structures are given below.



Formaldehyde can also react with rosin via Diels-Alder addition to create a methoxy bridge across the molecule where the conjugated double bonds were located. Under typical industrial conditions, this methoxy bridge will convert into a methyl group.

Hydrogenation rosin cannot undergo Diels-Alder adduction because the conjugated double bonds are eliminated by the hydrogenated process.

#### **Salt Formation**

Salts can be made from rosin, disproportionated rosin, hydrogenated rosin or adducted rosin. They can be split into 2 groups. The salts of monovalent cations (e.g.  $Na^+$ ,  $K^+$ ) usually called "soaps" on one hand and the salts of divalent cations (e.g.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ) usually called "resinates" on the other hand.  $Na^+$  and  $K^+$  salts of maleic or fumaric adducted rosin are commonly used as sizing agents in the manufacture of paper.  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Zn^{2+}$  resinates often find application in the ink and coating industry.

Whereas the salts of monovalent cations are partially soluble in water and stable at high pH (typically > 9), the salts of divalent cations are highly insoluble in water (Ca-salt: 43 mg/l, Mg-salt: 65 mg/l; Ca/Zn-salt: 18 mg/l) but relatively soluble in non-polar solvents and oils. Due to their difference in water solubility, the 2 types of salts will not have the same behaviour in the environmental compartment. The very low solubility of the salts of divalent cations is similar to the solubility of the resins they are synthesised from. For that reason, the behaviour of the starting resins and their divalent salts is expected to be the same. The higher solubility of the salts of monovalent cations make them available in the environmental compartment and then possibly more potent. They will be evaluated separately.

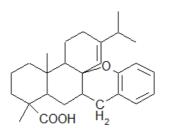
#### Hydrogenation

One of the less desirable properties is the potential for oxidation. The unsaturated bonds of resin acids which provide desirable reactive sites also make the molecule susceptible to oxidation. Those resin acids with conjugated double bonds are most prone to oxidation. Oxidation causes discoloration of the product and other undesirable changes in properties.

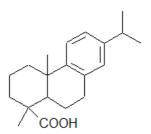
Hydrogenation is one way to reduce the active unsaturated sites thereby reducing the probability of oxidation. Those resin acids with conjugated double bonds are more easily oxidised that resin acids where the double bonds are not conjugated. Partial hydrogenation to saturate one of the conjugated double bonds is relatively easy to achieve. Full hydrogenation to saturate the second double bond is more difficult due to lower reactivity and stearic hindrance. Commercially available hydrogenated rosin has varying degrees of hydrogenation but is generally not fully hydrogenated. While hydrogenation significantly reduces the conjugated unsaturation in rosin and renders the rosin more resistant to oxidation, it does not significantly alter the structure and nor does it not affect the carboxylic acid functional group. Hydrogenation is often a useful "first step" and is used in applications requiring lighter color or higher oxidative stability of the finished rosin derivative.

#### Phenol/Formaldehyde Addition

The phenol/formaldehyde addition is another important modification that can occur with rosin. This modification has wide application in the printing ink industry. A representative structure is shown below.



Abietic acid reacted with phenol and formaldehyde



Dehydroabietic acid

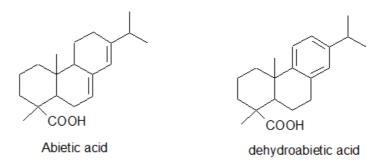
#### Dehydrogenation/Disproportionation Isomerisation

This process is sometimes used reduce the conjugated double bonds in some resin acids, thereby making the resulting disproportionated rosin less susceptible to oxidation. This process usually involved some type of catalyst. The reaction takes places between two identical dienes where one is hydrogenated and the other is dehydrogenated, thus altering the ratios from that of the original rosin. Disproportionated rosin may contain more than 50 weight-% of dehydroabietic acid (see structure figure).

### Justification for Grouping Rosin and Rosin Derivatives into Families

#### 1. Rosin, hydrogenated rosin and their salts

Rosin is described in EINECS under 2 types: rosin (EINECS Nr 232-475-7/CASRN 8050-09-7) and tall oil rosin (EINECS Nr 232-484-6/CASRN 8052-10-6). The GC-analyses of these types show that the distribution of the rosin components is very comparable. For general purposes of chemical inventory notifications, the similarity of the GC analyses is such that no toxicological differences between the various types of rosin are expected. For this reason, the US EPA has decided in 1992 that the distinction between rosin and tall oil rosin should be ignored. TSCA contains only one entry for rosin and tall oil rosin. Rosin and tall oil rosin are also listed in EINECS under EINECS Nr 277-299-1/CASRN 73138-82-6 as "Resin-acids-and-Rosin-acids" and EINECS Nr 302-657-1/CASRN 94114-23-5 as "Resin-acids-and-Rosin-acids,-tall-oil".

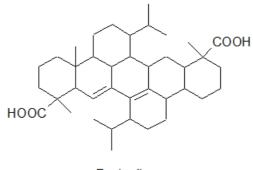


Rosin has 2 reactive sites: the carboxylic acid group and double bonds. In the hydrogenation process the double bonds are removed and thus the reactivity related to double bonds. As a matter of fact, hydrogenation is applied by industry to stabilise rosin against for example oxidation. Therefore, industry is convinced that the toxicology of rosin can be regarded as the worst case scenario for hydrogenated rosin. This is also the reasoning applied to the comparison of rosin derivatives and hydrogenated rosin derivatives, where the derivatisation, besides the reactant hydrogen, takes place with the same chemical. E.g., glycerol ester of rosin would be the worst case scenario for the glycerol ester of hydrogenated rosin.

The CASRN of rosin includes catalytically disproportionated rosin. A disproportionation reaction takes places between two identical dienes, leading to hydrogenation of one molecule and dehydrogenation of the other. Disproportionated rosin may contain more than 50 weight-% of dehydroabietic acid, an aromatic ring containing molecule (see figure below). Taking this into account, it is doubtful that disproportionated rosin would pass the sameness test with rosin. Question is whether it would be acceptable to cross read from rosin to disproportionated rosin. The presence of an aromatic ring may trigger (eco) toxicologists to closer investigate whether disproportionated rosin can be included in this family.

Rosin may react with itself at the double bonds in a [2+4]-Diels-Alder reaction to form a molecule carrying the trivial names "rosin dimer" and "polymerised rosin". In fact no polymerisation reaction is involved and thus the trivial names are incorrect, but there is no better name available. Rosin dimer is a  $C_{40}$ -terpene containing two double bonds and two carboxylic acid groups. It is believed that rosin dimer and its salts also belong to this family. The

dissociation constant of the carboxylic acid group is not believed to be influenced by the extension of the molecule. Due to the size of the molecule, it is believed that rosin dimer is less biologically available than rosin. Therefore, it is reasonable to expect that rosin dimer will be less biologically active than rosin.



Rosin dimer

Both the salts of monovalent cations (e.g.  $Na^+$ ,  $K^+$ ) and the salts of divalent cations (e.g.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ) are present in this family. Read-across between salts of divalent cations and their starting resins will be done and confirmed by testing key end-points. Due to much higher water solubility, the salts of monovalent cations will be treated separately for the ecotoxicological part. As water solubility is not a key parameter for toxicity, toxicologists will investigate whether the toxicological part can be read-across from the starting resins.

CASRN	name
001740-19-8	[1R-(1α,4aβ,10aα)]-1,2,3,4,4a,9,10,10a-octahydro-7-isopropyl-1,4a-
001740-19-8	dimethylphenanthren-1-carboxylic acid
	Rosin. A complex combination derived from wood, especially pine wood.
008050-09-7	Composed primarily of resin acids and modified resin acids such as dimers
008030-03-7	and decarboxylated resin acids. Includes rosin stabilized by catalytic
	disproportionation.
	Tall oil rosin. A complex combination derived from tall oil. Composed
008052-10-6	primarily of tricyclic monocarboxylic acids, mainly abietic and
000032 10 0	dehydroabietic acids. Includes tall-oil rosin stabilized by catalytic
	disproportionation.
009007-13-0	Resin acids and Rosin acids, calcium salts
009010-69-9	Resin acids and Rosin acids, zinc salts
061790-50-9	Resin acids and Rosin acids, potassium salts
061790-51-0	Resin acids and Rosin acids, sodium salts
065997-05-9	Rosin, oligomers
065997-06-0	Rosin, hydrogenated
068334-35-0	Resin acids and Rosin acids, calcium zinc salts
068648-50-0	Rosin, dimers, calcium salts
068990-01-2	Resin acids and Rosin acids, hydrogenated, potassium salts
068990-02-3	Resin acids and Rosin acids, hydrogenated, sodium salts
070879-76-4	Resin acids and rosin acids, calcium magnesium zinc salts
084776-85-2	Resin acids and Rosin acids, tall-oil, potassium salts
085409-26-3	Resin acids and Rosin acids, tall-oil, sodium salts

### 2. Rosin esters

In rosin esters, the carboxylic acid group has been esterified with alcohols of various types. For the rosin industry the following alcohols are the most important: methanol, di- and triethylene glycol, glycerol and pentaerythritol.

Any minimal hydrolysis that does occur would result is the rosin and the starting alcohol. Thus, under worse case scenarios, the toxicological and ecological effects the minimal hydrolysis products could assessed by looking at the effects of the starting materials: rosin and the alcohol. The simplest of the rosin esters is the methyl ester, the smallest ester possible. If there is any reaction possible at all, it would be hydrolysis into the free rosin acids and methanol. Considering the severity of the conditions needed to form the ester (long reaction time [hours], very high temperature [typically 200 °C]), it is clear that these esters are difficult to synthesise. Therefore, it is expected that the methyl ester of rosin is very stable under biotic conditions. This stability to hydrolysis could possibly be tested *in vitro*. If the methyl ester of rosin does not hydrolyse, it would be highly unlikely that other esters would show different behaviour.

The polyol esters, e.g. the glycerol and pentaerythritol esters, suffer from severe steric hindrance at the ester site. In combination with the poor water solubility, abiotic hydrolysis is not expected. In biological systems some hydrolysis may be expected of a "small" ester like the methyl ester. For the polyol esters, steric hindrance will strongly interfere with enzymatic hydrolysis.

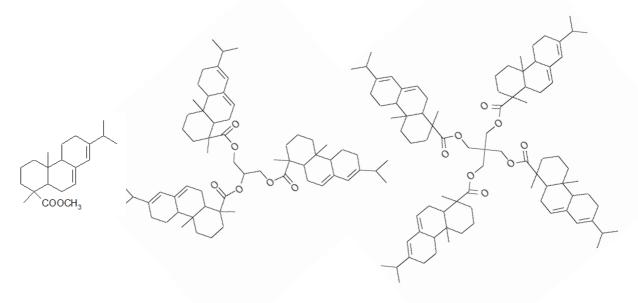
The same arguments as given above can be applied to esters of hydrogenated rosin. In addition, hydrogenation takes away the reactive centre at the double bond system. Hydrogenation leads to stabilization of the reactivity and will not otherwise affect the esterification of rosin.

Rosin dimer is grouped into the family of rosin, thus its esters belong in this group. These are even less soluble and less prone to hydrolysis than the straight esters of rosin due to even more severe steric hindrance. The structures below give an impression about the steric hindrance in various esters.

There is also the phthalic ester of hydroabietyl alcohol. For the starting material the carboxylic acid group in rosin was reduced to a methylol group. This group is esterified with phthalic acid. The resulting ester is just as sterically hindered as ester based on rosin. Therefore, the ester is expected to show the same behaviour as the other esters.

Based on the aforementioned arguments, the worst case scenario should be built on the methyl ester of rosin.

# H4R (Hydrocarbon Resin nd Rosin Resins REAC)



methylabietate

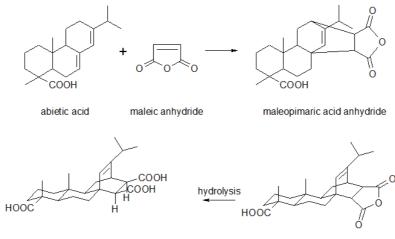
Glyceryltriabietate

pentaerythrityltetraabietate

CASRN	name
008050-15-5	Resin acids and Rosin acids, hydrogenated, Me esters
008050-25-7	Resin acids and Rosin acids, esters with triethylene glycol
008050-26-8	Resin acids and Rosin acids, esters with pentaerythritol
008050-31-5	Resin acids and Rosin acids, esters with glycerol
036388-36-0	Bis[[1,4a-dimethyl-7-(1- methylethyl)tetradecahydrophenanthryl]methyl] phthalate (phthalate ester of hydroabietyl alcohol)
064365-17-9	Resin acids and Rosin acids, hydrogenated, esters with pentaerythritol
065997-12-8	Resin acids and Rosin acids, polymerised, esters with pentaerythritol
065997-13-9	Resin acids and Rosin acids, hydrogenated, esters with glycerol
068153-38-8	Resin acids and Rosin acids, esters with diethylene glycol
068186-14-1	Resin acids and Rosin acids, Me esters
068475-37-6	Resin acids and Rosin acids, polymerised, esters with glycerol
068512-65-2	Resin acids and Rosin acids, esters with ethylene glycol
068515-02-6	Rosin, oligomeric reaction products with isophthalic acid and pentaerythritol
068648-53-3	Resin acids and Rosin acids, hydrogenated, esters with triethylene glycol
084776-83-0	Resin acids and Rosin acids, esters with trimethylolpropane
084776-84-1	Resin acids and Rosin acids, tall-oil, esters with triethylene glycol
085566-49-0	Resin acids and Rosin acids, tall-oil, esters with pentaerythritol
085711-66-6	Resin acids and Rosin acids, esters with glycerol and diethylene glycol
094581-15-4	Resin acids and Rosin acids, esters with glycerol

#### 3. Rosin adducts and rosin adduct salts

As has been said before, the double bond system in resins acids can be used in [2+4]-Diels-Alder reactions with maleic anhydride or fumaric acid. The reaction of abietic acid with maleic anhydride leads to the formation of maleopimaric acid anhydride that reacts with water to form a tricarboxylic acid molecule:



maleopimaric acid anhydride

Due to the fact that rosin adducts have three carboxylic acid groups, one may expect higher solubility into water and thus higher bioavailability, unlike rosin.

Both the salts of monovalent cations (e.g.  $Na^+$ ,  $K^+$ ) and the salts of divalent cations (e.g.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Zn^{2+}$ ) are present in this family. The same arguments as for rosin salts can be applied here.

It is noteworthy to mention that the Diels-Alder adduction occurs only on those resin acids which contain conjugated double bonds. The conjugated resin acid content of rosin typically varies from 50-70%, thus even under the best of react conditions, 30-50% of the resin acid molecules remain unadducted simply because they cannot undergo this reaction.

CASRN	name
008050-08-0	Maleated rosin
065997-04-8	Rosin, fumarated
068152-93-2	Tall oil, maleated
068201-59-2	Resin acids and Rosin acids, fumarated, sodium salt
068201-60-5	Resin acids and Rosin acids, maleated, sodium salts
068649-83-2	Resin acids and Rosin acids, fumarated, potassium salts
085409-27-4	Resin acids and Rosin acids, maleated, potassium salts
085409-30-9	Tall oil rosin, maleated
085631-69-2	Tall-oil rosin, fumarated
091722-01-9	Resin acids and Rosin acids, maleated, calcium salts
160901-14-4	Fatty acids, tall oil, oligomeric reaction products with maleic anhydride and
100501-14-4	rosin, calcium magnesium zinc salts

#### 4. Rosin adduct esters

In principle, rosin adducts may form polyesters when reacted to polyols. It should be checked whether these adduct esters meet the polymer definition as given in the REACH Regulation.

In practice, the intended reaction foresees only in a partial reaction of adduct with alcohol, leading to low and high acid number esters. "Acid number" is a measure of the unesterified hydroxyl content of rosin or rosin adducts. Actually, the acid number is the amount of potassium hydroxide (in mg) to neutralise 1 gramme of resin. Thus, a rosin or rosin adduct which is highly esterified will have a low acid number.

*Esters with a low acid number* could be read across with esters of (hydrogenated) rosin, since they could be considered as oligomeric rosin esters.

*Esters with a high acid number* could be grouped with unmodified rosin adducts since only a small portion of the hydroxyl functionality is esterified.

It is proposed to use a cut-off value of 100 for the acid number to distinguish between high and low acid number esters and thus the cut-off value for the grouping of the esters with either rosin esters (family 2) or with rosin adducts (family 3).

Compositions containing rosin, fumaric acid / maleic anhydride, and a polyol can have a broad range of physical properties. There are three classes of products with these compositions. One class is the "Alcohol solubles", which generally have acid values between 180 - 250 mg KOH/g, although there are grades which have acid values between 105 - 120 mg KOH/g. Obviously, these may contain very little polyol. All of these products, with an acid value greater than 120 mg KOH/g, can be regarded as "acid".

The second class of products tends to have acid values in the range of 30 - 70 mg KOH/g. The third class is called "alcohol insoluble" products, which have acid values below 25 mg KOH/g. From a chemist's perspective, these three classes behave differently primarily based on polarity, and thus water solubility. The latter two classes have similar properties.

Rolling those two paragraphs together, there seems to be a "cross-over" inflection point in properties related to an acid value somewhere between 70 - 120 mg KOH/g. An acid number of 100 mg KOH/g is approximately in the middle of the separation between "ester-type" and "acid-type".

CASRN	name
065997-11-7 Rosin, fumarated, oligomeric reaction products with pentaerythritol	
068038-41-4	rosin, maleated, polymer with glycerol
071243-68-0	Resin acids and Rosin acids, fumarated, decyl esters
091081-25-3	Resin acids and Rosin acids, maleated, mixed esters with diethylene glycol, glycerol and phthalic anhydride
092202-14-7	Rosin, fumarated, reaction products with glycerol and pentaerythritol
094581-15-4	Resin acids and Rosin acids, fumarated, esters with pentaerythritol
094581-16-5	Resin acids and Rosin acids, maleated, esters with glycerol
094581-17-6	Resin acids and Rosin acids, maleated, esters with pentaerythritol
094581-69-7	Rosin, maleated, polymer with pentaerythritol
097489-11-7	Resin acids and Rosin acids, fumarated, esters with glycerol
193293-72-0	Resin acids and Rosin acids, maleated, esters with diethylene glycol and triethylene glycol

#### 5. <u>Phenolic modified rosin and Phenolic modified rosin adducts</u>

The resins in this family are formed by the reaction of rosin, formaldehyde, phenol and alkyland/or arylphenols. These products may be esterified with polyols. Almost certain, these products are substances meeting the polymer definition of REACH and are thus exempt from registration under REACH.

REMARK: if it is determined that these substances are polymers, it is strongly advisable that the involved companies agree on the chemistry and determine the nature of the monomers. Note that an *in situ* formed monomer is exempted from REACH!

The same is true for rosin adduct modified with formaldehyde, phenol and alkyl- and/or arylphenols.

CASRN	name
067700-45-2	Rosin, polymer with formaldehyde and phenol
068140-03-4	Rosin, maleated, polymer with p-tert-butylphenol, formaldehyde, glycerol and
068152-62-5	pentaerythritol Rosin, maleated, polymer with formaldehyde, nonylphenol and pentaerythritol
068152-70-5	Rosin, polymer with bisphenol A, formaldehyde and glycerol
068309-61-5	Rosin, maleated, polymer with formaldehyde, pentaerythritol and phenol
068425-03-6	Rosin, maleated, polymer with formaldehyde, pentaerythritol and phenol
071243-71-5	Rosin, maleated, polymer with p-butylphenol, formaldehyde, glycerol and nonylphenol
091081-50-4	Rosin, maleated, reaction products with bisphenol A, formaldehyde and pentaerythritol
092202-16-9	Rosin, maleated, reaction products with p-ter-butylphenol, formaldehyde and pentaerythritol
092202-17-0	Rosin, maleated, reaction products with formaldehyde, pentaerythritol and 4-(1,1,3,3-tetramethylbutyl)phenol
129595-12-6	Rosin, maleated, polymer with bisphenol A, p-tert-butylphenol, formaldehyde, nonylphenol and pentaerythritol
132778-09-7	Rosin, polymer with p-tert-butylphenol, formaldehyde, maleic anhydride, pentaerythritol and soybean oil

#### 6. Decarboxylated rosin and rosin distillation overheads

Rosin distillation overheads consist of terpenes, as well as di- and tri-terpenes, hydrocarbons and neutrals from rosin.

#### Decarboxylated rosin

The removal of the carboxylic acid group can be complete or incomplete. The complete removal of the acid group leads to a cyclo-olefin, i.e. alkylated decahydrophenanthrene. This is a type of hydrocarbon that does not belong to the scope of substances covered by the consortium on rosin resins.

Incomplete removal of the carboxylic acid group leads to a complex mix of resin acids and alkylated decahydrophenanthrenes. The resin acid part is very comparable to unmodified rosin and should be cross-read with rosin. It should be investigated whether decahydrophenanthrene is a concern with regard to possible adverse effects.

CASRN	name
008002-16-2	Rosin oil
008050-18-8	Rosin, decarboxylated
068425-08-1 Rosin, distn, overheads	
068783-82-4	Rosin, low-boiling fraction . A complex combination obtained by the distillation of rosin. This low boiling fraction consists primarily of decarboxylated rosin, resin acids, decarboxylated resin acids, terpenes, and hydrocarbons derived from decarboxylated fatty acids.

#### 7. Fatty acids

Most likely these substances are exempted from REACH. Would that include the esters of fatty acids? It is the up to the pre-registrants of these substances to "negotiate" and agree whether a pre-registered fatty acid is exempted from registration or not.

CASRN	name	Possibly Annex V exempted?
60-33-3	linoleic acid	Yes?
61788-89-4	Fatty acids, C18-unsatd., dimers	No?
61790-11-2	Fatty acids, tall oil, zinc salts	No?
61790-44-1	Fatty acids, tall oil, potassium salts	Yes?
61790-45-2	Fatty acids, tall oil, sodium salts	Yes?
65997-03-7	Fatty acids, tall-oil, low boiling. The low boiling fraction obtained by the distillation of tall oil. Contains fatty acids such as palmitic, stearic, oleic and linoleic as well as neutral materials.	Most likely
68154-86-9	Fatty acids, tall oil, calcium salts	Yes?
68188-27-2	Fatty acids, tall-oil, esters with pentaerythritol	No?
68647-68-7	Soybean oil, ester with pentaerythritol	No?
91031-42-4	Fatty acids, C16-18, esters with triethylene glycol	No?
68955-98-6	Fatty acids, C16-18 and C18-unsatd., branched and linear	Yes?
68201-37-6	Octadecanoic-acid,-branched-and-linear	Yes?
30399-84-9	isooctadecanoic-acid	Yes?
61790-12-3	TOFA	Yes?
1592-23-0	Calcium distearate	No?
85586-17-0	Fatty acids, C18-unsatd., reaction products with acrylic acid	No?

## 8. <u>Tall oil</u>

Tall oil is derived from the acidulation of what is termed "black liquor soap" or BLS. BLS is a byproduct of the Kraft paper-making process and is a mixture consisting of tall oil, sodium salt, water, and sodium hydroxide. Some tall oil, potassium salt may also be present in the BLS if some of the sodium hydroxide used in the pulping process was replaced by potassium hydroxide. Tall oil is then distilled into 4 or 5 distillation fractions which, from lowest to highest boiling, are:

Fatty acid, tall oil, low boiling (65997-03-7)

Fatty acids, tall oil (61790-12-3)

Distilled tall oil (8002-26-4)

Tall oil rosin (8052-10-6)

Tall oil pitch (8016-81-7)

The fatty acids have been grouped in separate families and not discussed in this paragraph. Distilled tall oil, being an intermediate distillation fraction containing both tall oil fatty acids and tall oil rosin, maintains the same CASRN as the distillation feed. The high-boiling tall oil pitch is a constituent of the tall oil feed which does not belong in either the refined tall oil fatty acid group or the tall oil rosin group. The heavy pitch fraction has lower water solubility and less bioavailability that any of the other fractions of the tall oil feed and can therefore be grouped with the tall oil feed. The tall oil precursors 65997-01-5, 68647-71-2, the tall oil 8002-26-4, and the high boiling fraction pitch 8016-81-7 constitute a group with expected similar toxicology.

008002-26-4	Tall oil. A complex combination of tall oil rosin and fatty acids derived from acidulation of crude tall oil soap and including that which is further refined. Contains at least 10% rosin.
008016-81-7	Tall oil pitch. The residue from the distillation of tall oil. It contains primarily high-boiling esters of fatty acids and rosin. It may also contain neutral materials, free fatty acids and rosin acids.
065997-01-5	Tall oil, sodium salt
068647-71-2	Tall oil, potassium salt

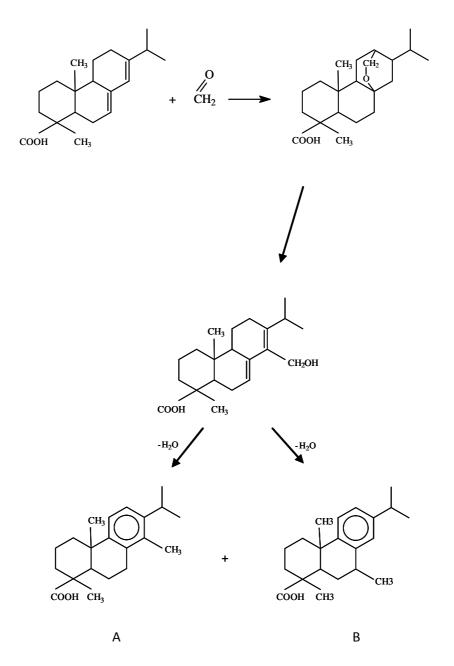
#### 9. Miscellaneous

These are the rosin derivatives that do not belong to any of the families. The resins listed here are orphans, standing on their own, not belonging to this consortium or can still be grouped into an existing family.

CACON			
CASRN	name	comment	
000083-46-5	Stigmast-5-en-3-β-ol	Looks like a steroid, not under the	
000003 40 3		scope of this consortium.	
		This is diethyleneglycol, a raw	
000111-46-6	2,2'-oxydiethanol	material, not under scope of this	
		consortium.	
	Tetradecahydro-7-isopropyl-1,4a-	On its own. Maybe in the distillations	
013393-93-6	dimethylphenanthrene-1-methanol	overheads group?	
	Bicyclo[3.1.1]hept-2-ene, 2,6,6- trimethyl-, polymer with 6,6- dimethyl-2- methylenebicyclo[3.1.1]heptane	This is a polyterpene of alpha- and	
031393-98-3 trir		beta-pinene. Exempted from REACH if	
		it is a real polymer. If not a polymer, it	
		is a terpene: EFFA takes care of	
		terpenes.	
004605.05.0	Formaldehyde, oligomeric reaction	Not under scope of this consortium.	
031605-35-3	products with 4-nonylphenol		
001700 05 0	Resin acids and Rosin acids, compds.	On its own. What is the chemistry? Is	
061790-65-6	with triethanolamine	it a salt or an ester? Or both?	
	Resin acids and Rosin acids, tall oil,		
091081-30-0	fumarated, compds. with	Polyester? Salt? Ester?	
	triethanolamine	,	
001672 20 2	Formaldehyde, reaction products		
091673-30-2	with butylphenol	Not under scope of this consortium	
094266-48-5	Pine extract	????	
100403-64-3	Rosin saponified	????	

#### Family group 9A – Formaldehyde reacted rosin and derivatives

The reaction between rosin and formaldehyde is primarily aimed at reducing the crystallization tendency of rosin. The reaction is also known as noxing and the product is often referred to as noxed rosin. The reaction takes place in a number of consecutive steps finally resulting under acidic conditions in the formation of methyl substituted (position 7 and 14) dehydroabietic acid, see below. The first step in the reaction (not given) is the transformation of abietic acid to levopimaric acid, which is the most reactive rosin acid for Diels-Alder reactions. The reaction and its mechanism have been described in the literature, see 1-4. The methyl substituted dehydroabietic acids will be referred to as A and B respectively further on in this text, see below.



The primary skeleton of rosin acids, being a decahydrophenanthrene ring system with a carboxylic acid group contains already two methyl groups and an isopropyl (abietic types) or ethyl, methyl group (pimaric types). The presence of one extra methyl group in A or B compared to rosin is not expected to have a major influence on the chemical and physical properties of A and B.

The methyl groups are positioned in such a way that an effect on the carboxylic group is not expected and hence the acidity of A and B is expected to be the same as for rosin or dehydroabietic acid. In the typical reactions of the carboxylic group like the esterification reaction or resination similar behavior is expected.

The effect of the methyl group on the solubility of A and B compared to rosin is expected to be very small and could make the product slightly more hydrophobic. As a result the water solubility is expected to be similar or slightly less than rosin and thus the bioavailability of A and B is similar or less than rosin.

The typical (conjugated) double bond systems in rosin are converted to an aromatic ring system in the formaldehyde reacted rosin. Since the (conjugated) double bond systems in rosin are prone to oxidation it can be safely stated that the methyl substituted dehydroabietic acids are more stable than most rosin acids and thus should undergo less oxidation.

It should also be remembered that tall oil rosin which is part of family 1 contains up to 20 - 25% of dehydroabietic acid. In case gum rosin is reacted with 2.5% formaldehyde the maximum amount of dehydroabietic acid is also about 25%. Since the percentages of formaldehyde treatment are generally between 0.5% and 4% by weight the dehydroabietic content in formaldehyde reacted rosin are very similar to those of Tall Oil Rosin.

The dissociation constant of the carboxylic group in A and B is very similar to the dissociation constant of rosin acids. This means that under normal physiological and environmental conditions the monovalent salts will return to their free form. The same arguments as for rosin salts can be applied here.

The members of family 9A are:

CASNR	EC number	
91081-53-7	293-659-0	Rosin, reaction products with formaldehyde
91081-28-6	293-631-8	Resin acids and Rosin acids, reaction products with formaldehyde, sodium salts
92129-53-8	295-855-1	Resin acids and Rosin acids, reaction products with formaldehyde, potassium salt

Literature

- 1. J. of Chromatographic Science, 1994, vol 32, 139-143
- 2. J. Org. Chem, 1986, vol 51, 2300-2303
- 3. J. Org. Chem, 1971, vol 36, 3271-3277
- 4. US patent 3,463,768, 1969



**Appendix 3** 

Justification for Considering Rosin as a Single Substance

# Justification for considering rosin as a single substance

This document has been prepared on behalf of the H4R-Rosin Resin producers Consortium. It is intended to justify why some SIEFS for rosin and rosin derivatives can be merged under the REACH Regulation (EC) no 1906/2007

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#### **Introduction**

When EINECS was set up in the late 1970s/early 1980s it was a major introduction as far as chemicals regulation was concerned. The UVCB (unknown or variable composition, complex reaction products or biological materials) designation was not well understood at the time. Companies took a cautious approach when submitting their substances to EINECSand substance submission lacked coordination. Thus there was potential for confusion and for multiple entries into EINECS. One clear case of this confusion concerns 'rosin'. Generally there are three recognized variants of rosin – gum, wood and tall oil. All three are composed largely of resin acids and rosin acids. When EINECS was set up in the late 1970's and early 1980's, companies submitted four CAS numbers to describe rosin, namely 8050-09-7 "rosin", 8052-10-6 "tall-oil-rosin", 73138-82-6 "resin-acids-and-rosin-acids" and 94114-23-5 "resin-acids-and-rosin-acids,-tall-oil". Rosin is defined as:

'A complex combination derived from wood, especially pine wood. Composed primarily of resin acids and modified resin acids such as dimers and decarboxylated resin acids. Includes rosin stabilized by catalytic disproportionation.'

This definition covers the three variants, i.e. gum rosin, wood rosin and tall-oil rosin. rosin.

As REACH requires one substance-one registration and encourages the formation of SIEFs, the opportunity has arisen for SIEFs (and groups of SIEFs – Consortia) to carefully examine the composition of their substances of interest and to realize that, in a number of cases, the same substance was originally registered under different names or that differentiation between, nominally, two essentially identical UVCB substances was not worthwhile.

Rosin and rosin products are often referred to as 'Naval Stores' – it is an inclusive term to denote pine oleoresins and their derivatives. Pine resin and pitch have been used for centuries, for example for caulking of sailing ships to make them watertight, hence the name 'Naval Stores'. Nowadays, these 'naval' uses are minor. The main source of information on 'Naval Stores' is Zinkel and Russel (1989).

#### <u>Sources</u>

Rosin is obtained from trees, typically pine trees. However, it is obtained from pine trees generally, not from a specific species. Typically, rosin is amber and glassy in appearance. See picture below.

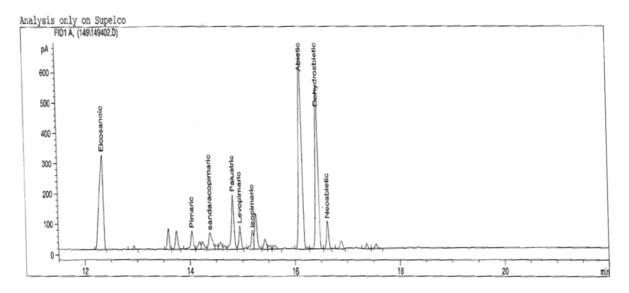


Justification for considering rosin as a single substance

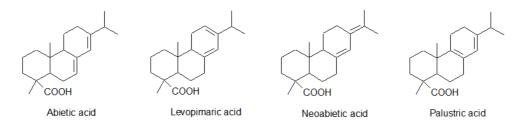
#### **Chemical composition**

Rosin is a complex naturally occurring mixture of diterpenic structures containing both saturated and unsaturated rings and carboxylic acid groups.

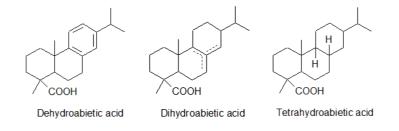
There are more than 20 different isomeric structures of resin acids, most of which have the general formula of  $C_{19}H_{29}COOH$ . Below is a typical chromatogram of rosin illustrating the complex nature of rosin.

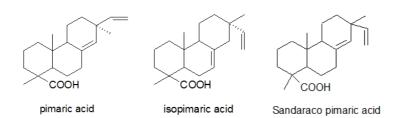


The four predominant and most important resin acids in rosin, commonly called the "abietic-type" resin acids, are shown below.



These resin acids are of importance because in addition to the carboxylic acid functionality, they have conjugated double bonds. Depending upon source and method of manufacture, rosin typically contains 50-70% of these abietic-type resin acids. Additional structures for some of the less important resin acids are shown below.





The total acid (i.e. in EU nomenclature terms resin acid and rosin acid) content of rosin is typically 90-95%. The remaining components are commonly called "neutrals" or "unsaponifiables" because these components do not have the carboxylic acid functionality and are generally less reactive. The "neutral fraction" is generally composed of diterpene hydrocarbons, alcohols, esters, or aldehydes. The neutral fraction is typically <10% and relatively unimportant relative to the resin acid components. For "rosin" these are defined as part of the substance, for "resin acids and rosin acids" (i.e., in practice, rosin) these are defined as impurities.

In practice the terms "rosin" and "resin acids and rosin acids" are synonymous. The distinction between rosin and resin acids and rosin acids is one of how the substance is defined, not one of what the substance consists of. Abietic acid is generally the predominant resin acid in rosin and is often used to illustrate the typical structure of resin acids.

#### **Species variation**

Rosin is not collected from a single species of pine tree. Rosin from a given geographical area is derived from a variable mixture of species. Often rosins from different geographical areas are mixed to obtain the desired physical properties. In taxonomic terms the description of a UVCB subtype 3, given in the ECHA Guidance, applies, but only at the family level. Chemically modified rosins are UVCB subtype 2

The resin acid distribution is dependent on species of the pine tree, geographical area, climate and season. The table below, taken from the book Naval Stores [Zinkel and Russell, 1989], indicates that analysis of the resin acids in the oleoresin<sup>1</sup> shows significant variation in resin acid distribution, depending on the species of the tree: abietic acid ranges from 8.6 % in *Pinus taeda* to 37 % in *Pinus halepensis*, levopimaric and palustric acid ranges from 12 % in *Pinus peuce* to 64 % in *Pinus taeda*.

The table also shows the acid distribution in gum rosin from different geographical areas. Taking the same resin acids, abietic acid ranges from 22 % in American and Honduran rosin to 53.3 % in Mexican rosin. Levopimaric and palustric acid range from 9.8 % in Mexican rosin to 30 % in Portuguese rosin. These numbers illustrate very well that the resin acid distribution varies more due

<sup>&</sup>lt;sup>1</sup> Oleoresin is the resin that flows out of the living tree. Oleoresin is separated by distillation in a volatile fraction, consisting of terpenes like  $\alpha$ -pinene,  $\beta$ -pinene and d-limonene, and a non-volatile fraction: gum rosin.

to tree species and geographical area than to the way the rosin was obtained, i.e. live tree, pulping process or tree stump.

				Levo- pimaric/				
		Sandara-		Palus-	Iso-		Dehydro-	Neo-
Samples	Pimaric	copimaric C	lommunic		pimaric	Abietic	abietic	abietic
OLEORESIN			Per C	Cent of Acid	in Acid Fr	action		
P. elliottii var. elliottii	5.1	1.8	3.1	37	21	9.7	3.7	16
P. elliottii var. densa	3.8	1.9	3.1	38.	21	12	3.7	16
P. palustris	5.4	1.1	0	52	10	9.4	8.3	13
P. taeda	8.7	2.2	0	64	т	8.6	6.3	9.5
P. ponderosa	7.6	2.9	0	40	15	11	8.2	11
P. halepensis	0	1.2	0	39	10	37	1.5	9.7
P. brutia	0	1.2	0	44	10	32	2.5	10
P. pinaster	8.0	2.0	0	39	12	14	4.2	18
P. caribaea	4.2	2.2	0	49	8	10	8.6	16
P. peuce	1.8	1.0	0	12	32	35	0.8	14
Rosins								
American	5.1	1.8	2.8	25	17	22	5.7	20
American <sup>2,3</sup>	5.4	1.8	1.8	20.3(1.4)	14.2	27.9	7.1	16.3
$Brazilian^2$	4.7	1.7	3.2	11.4(.3)	18.2	36.3	5.4	
Burmese	7.9	3.0	0	44	8.3	30	6.0	2.2
Chinese	9.2	2.7	0	22	1.5	44	4.3	15
French	10	2.2	0.3	22	7.0	36	4.9	17
Greek	0	1.9	0	14	11	50	4.5	13
Honduran	9.6	2.2	0	21	17	22	12	15
Indian	9.2	1.5	0	11	20	38	2.0	18
Mexican <sup>2,4</sup>	6.8	1.2	0	9.8(0.3)	12.9	53.3	7.8	6.1
Portuguese	8.8	1.9	0.7	30	5.3	32	5.1	16
Portuguese <sup>2</sup>	8.3	1.4	0	20.4(11.7)	4.5	27.7	5.8	17.2
Russian	7.8	2.4	0	27	5.6	35	5.3	17
Spanish	8.7	1.5	0	27	0	36	1.9	24
Turkish	0	1.3	0	24	13	41	5.1	15

<sup>1</sup>Data from ref. 31. This table also appears in Chapter 4 as Table 1.
 <sup>2</sup>D.F. Zinkel, Private communication. Palustric values given first; levopimaric values are in ().
 <sup>3</sup>Also contains small amounts of imbricataloic acid, as well as imbricatoloic and isocupressic acids and their acetates (32).
 <sup>4</sup>A distilled rosin.

An additional table, from the FAO document gives the predominant species in each region.

Table: Principal pine species by region.

Region	Main oleoresin pine species
United States	Pinus palustris, P. elliottii
France, Italy, Portugal, Spain	P. pinaster
Greece, Spain	P. halepensis

India, Pakistan	P. roxburghii		
China	P. massoniana, P. tabuliformis		
Malaysia	P. merkusii		
Central America	P. caribaea, P. oocarpa		
New Zealand	P. radiata		
From Iqbal, M 'International trade in non wood forest products: An overview' (FAO Corporate			
Document Repository, 1993).			

The principal pine species producing rosin in northern Europe is *P. sylvestris*.

As rosin is selected on the basis of physical properties, historically the material produced was not from a single species. The classification can only be on the basis that the rosin was derived from pine trees. This implies that, although >90% of rosin will consist of resin acids, there will be considerable variability on the proportion of the different resin acids present. In practical terms the distinction between resin acids and rosin acids and rosin is of very limited value; the former is defined as containing up to 10% of impurities. These same chemicals are present in similar quantities in the latter, but not distinguished out as impurities.

### Method of isolation

For commercial reasons the method of obtaining the rosin is indicated by using trivial names: "gum rosin" is the term used for rosin that is derived from tapping live trees. "Tall oil rosin" is the term used for the rosin that is derived from tall oil, a product that is set free during the pulping of tree trunks for the paper industry. "Wood rosin" is rosin that is obtained from the extraction of tree stumps that are left behind after the harvesting of pine trees for timber and paper making. All rosins are derived by distillation of the source material. Although the ECHA guidance indicates that the second main identifier is the processing of the substance (the extraction process), this criterion has not been adhered to in constructing EINECS and, while rosin can be divided into gum rosin, tall oil rosin, wood rosin , only tall oil rosin has been separated from the general definition "rosin".

On a detailed look at the composition of rosin obtained using the different sources, i.e. live tree, pulping process or tree stump, it is obvious that there are differences in resin acid distribution. The two tables below, taken from Naval Stores [Zinkel and Russell, 1989] and the EPA OPPT document entitled 'Screening level hazard characterisation on high production volume chemicals – Rosin and rosin salts' (Interim, October 2007), show these details.

		Rosin	
Resin Acid	$Tall \ Oil^2$	Wood	Gum
Pimaric	4.4	7.1	4.5
Sandarcopimaric	3.9	2.0	1.3
Communic	1.0		3.1
Levopimaric			1.8
Paulstric	8.2	8.2	21.2
Isopimaric	11.4	15.5	17.4
Abietic	37.8	50.8	23.7
Dehydroabietic	18.2	7.9	5.3
Neobietic	3.3	4.7	19.1

### Table 2. Typical Composition of the Common Resin Acids in Some U.S. Rosins<sup>1</sup>

<sup>1</sup>Per cent of acid fraction.

<sup>2</sup>Also contains fatty acids and other minor resin acids such as the secodehydroabietic acids.

EPA data comparing the chemical composition of gum, wood and tall oil rosin.

<u>Component</u>	<u>Tall oil<sup>1</sup></u>	Wood <sup>1</sup>	<u>Gum<sup>1</sup></u>
Abietic	35	45	20
Palustric	10	10	18
Isopimaric	7	11	18
Dehydroabietic	20	8	4
Neoabietic	4	7	18
Pimaric	3	3	2

<sup>1</sup> Percent composition

A further comparative set of samples for rosin used for testing for skin sensitization (Botham et al., 2008) had the composition:

<u>Component</u>	<u>Tall oil<sup>1</sup></u>	Wood <sup>1</sup>	<u>Gum<sup>1</sup></u>
Abietic acid	44.2	49.7	45.2
Dehydroabietic acid	18.1	8.5	3.3
Dihydroabietic acid	2.7	0.9	0.6
Isopimaric acid	6.6	13.5	3.6
8,5-Isopimaric acid	1.4	4.2	0.3
Levopimaric acid	2.5	0.2	0.4
Neoabietic acid	3.9	4.7	14.0
Palustric acid	7.8	8.6	19.2
Pimaric acid	3.7	5.9	7.4
Sandopimaric acid	2.5	1.9	1.5
Dimers	<0.1	4.2	1.0
Others	6.6	1.0	3.5
10/	1	1	l

Data from Botham et al (2008) comparing the compositions of gum, wood and tall oil rosins.

<sup>1</sup> % w/w

There is some variation in the compositions of dehydroabietic acid, neoabietic acid and palustric acid according to isolation method. However, the variation in the percentage of individual resin acids for the different isolation techniques has a similar range to the variation in species. As the comparison is on 'typical' materials, not on samples obtained from the same trees by the different methods, it is possible that these differences are, at least in part, artefactual.

### Available physical chemical, toxicological and ecotoxicological properties

Rosin is a glassy solid (supercooled liquids). The characterization of rosin for commercial purposes is based on physicochemical properties. These include acid number, iodine value, softening point and colour. Peroxide number can be used to determine the extent to which rosin has been oxidized.

Due to its complex nature, rosin does not have a well defined melting point and it can be described using a softening point. The softening points can cover a wide range, thus, while a softening point can be set for an individual sample, the substance as a whole does not have a specific softening point. Rosins thermally decomposes before boiling. Rosin is a solid at room temperature, thus vapour pressure for rosin is essentially zero at room temperature.

Rosin is essentially insoluble in water (water solubility: gum rosin 0.9 mg/L at  $20^{\circ}$ C) and the log Pow depends on pH, with values between 1.9 and 7.7 (several peaks being obtained).

A direct comparison of typical physical and chemical properties of rosin is given in the table below (from Zinkel and Russel, 1989, p581). The physical chemical parameters measured are those typically measured for rosins, not those required under REACH.

Rosin	<u>Tall oil</u>	<u>Wood</u>	<u>Gum</u>
Acid number	167	166	164
Saponification no	174	172	172
Unsaponifiable matter	7%	6%	8%
Fatty acids	<5%	-	-
Colour, US rosin grade	WG	WG	ww
Softening point (ASTM) ring and ball, °C	77	76	76
Refractive index	1.540	1.545	1.541
Density	1.07	1.07	1.07

The only available direct comparisons of results of toxicity and ecotoxicity testing from tall oil rosin and gum rosin are:

In a comparison study, gum rosin, wood rosin and tall oil rosin samples were negative in the guinea pig maximization test, but their oxidized analogues were positive (Botham et al, 2008).

In ecotoxicity testing direct comparisons for Daphnia toxicity, algal growth inhibition and ready biodegradability are available. These direct comparisons show no differences. The limited solubility and slow mixing makes comparisons where water accommodated fractions have been prepared using different protocols unsatisfactory.

### **Conclusions**

The following conclusions can be drawn from the above:

Rosin is >90% resin acids and, in practice, the distinction between rosin and "resin acids and rosin acids" is one of how the substance is defined, not one of what the substance consists of. The <10% 'other components' are part of the substance when it is called "rosin" and impurities when it is called "resin and rosin acids", but will be present in any case.

The ratio of the various resin acids in rosin varies depending upon the region from which it is obtained, the process used to isolate it, the species of tree from which it came and even in some cases, the climate is which the tree is grown. The variability of the composition of rosin is dominated by tree species and geographical area. The differences between the products obtained from different methods of preparation (i.e. between gum, wood and tall oil rosin) are less than those due species/geographical area variation and are largely contained within that variation.

As a result, there is only one substance, rosin, a substance of variable composition. Thus the statement about there being two substances (rosin and tall oil rosin) is inaccurate and the introduction of REACH is an opportunity to correct this inaccuracy. There are two entries for the same substance, one using a more specific definition (effectively distinguishing one form of rosin by incorporating the process of production into the definition, in contradistinction to the statement in the 'Manual of Decisions') than the other. This has been recognized by the US EPA who no longer distinguish between rosin and tall oil rosin (EPA, 1992 - Annex 1, confirmed in EPA, 2007). It would also appear to be the approach used by the US FDA when considering rosin and derivatives FDA, 2009). It is already accepted in the case of wood rosin, as it is not distinguished from gum rosin.

The consequence of these conclusions is that the SIEFs for rosin should be merged.

### **Consequences for rosin derivatives**

Generally, where there are two EINECS entries for the same chemical modification of rosin they differentiate between rosin and tall oil rosin.

Normally, when derivatising, rosin is not obtained from a single species. It is common for rosin resin producers to use rosin from different sources (e.g. to use gum rosin from China and Indonesia and tall oil rosin from a variety of sources), and combine them prior to derivatisation, such as ester production. If, as would happen on the basis of a series of definitions of rosin, with up to three definitions for each species (one for each production process) and a multiplicity of definitions to cover all the species from which rosin is collected, the product would have to be described as a complex reaction mass and the situation would be extremely complicated and without benefit. The simplest suitable approach is to treat these derivatives as derivatives of one substance of variable composition, rosin.

In some cases, chemical modification involving polyols such as glycerol or pentaerythritol, can lead to polymerisation. In a number of cases there are two definitions, one of which is a declared polymer and the other not so declared. In practice both are the same substance and the SIEFS can be merged. The SIEFS intended for merger are given in the appendix. This would be consistent with the EPA's approach for the TSCA Chemical Substance Inventory (see Annex 1).

#### **References**

Botham, P, A, Lees, D, Illing, H P A, Malmfors, T (2008). On the skin sensitization potential of rosin and oxidized rosin. Regulatory Toxicol Pharmacol 52, 257-263.

EPA (Oct 2007). Screening level hazard characterization of high production volume chemicals. Rosin and rosin salts.

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PCA (2001). Pine Chemicals Association: High production volume chemical challenge program. Test plan for rosin and rosin salts.

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### **APPENDIX:**

# Rosin and rosin derivatives: SIEFs intended for merger

### FAMILY 1

### Rosin

CAS	EU	Name
8050-09-7	232-475-7	Rosin
8052-10-6	232-484-6	Tall-oil rosin
73138-72-6	277-299-1	Resin acids and rosin acids
94114-23-5	302-657-1	Resin acids and rosin acids, tall-oil

### Rosin, potassium salt

CAS	EU	Name
61790-50-9	263-142-4	Resin acids and rosin acids, potassium salt
84776-85-2	284-011-8	Resin acids and rosin acids, tall-oil, potassium salt

### Rosin, sodium salt

CAS	EU	Name
61790-51-0	263-144-5	Resin acids and rosin acids, sodium salt
85409-26-3	287-093-3	Resin acids and rosin acids, tall-oil, sodium, salt

### FAMILY 2

### Rosin, triethylene glycol ester

CAS	EU	Name
8050-25-7	232-478-3	Resin acids and rosin acids, esters with triethylene glycol
84776-84-1	287-093-3	Resin acids and rosin acids, tall-oil, esters with triethylene glycol

### Rosin, pentaerythritol ester

CAS	EU	Name
8050-26-8	232-479-0	Resin acids and rosin acids, esters with pentaerythritol
85566-49-0	287-660-5	Resin acids and rosin acids, tall-oil, esters with pentaerythritol

### Rosin, glycerol ester

CAS	EU	Name
8050-31-5	232-479-0	Resin acids and rosin acids, esters with glycerol
85566-48-9	287-658-4	Resin acids and rosin acids, tall-oil, esters with glycerol

### FAMILY 3

## Note: The question whether rosin fumarated is the same as rosin, maleated has not been addressed in this document.

### Rosin, fumarated

CAS	EU	Name
65997-04-8	266-040-8	Rosin, fumarated
85631-69-2	288-017-1	Tall-oil rosin, fumarated

### Rosin, fumarated, potassium salt

CAS	EU	Name
68649-83-2	273-035-1	Resin acids and rosin acids, fumarated, potassium salt
84776-94-3	284-020-7	Resin acids and rosin acids, tall-oil, fumarated, potassium salts

### Rosin, fumarated, sodium salt

CAS	EU	Name
68201-59-2	269-227-2	Resin acids and rosin acids, fumarated, sodium salt
85736-81-8	288-493-0	Resin acids and rosin acids, tall-oil, fumarated, sodium salts

### Rosin, fumarated, compounds with triethanolamine

CAS	EU	Name
91081-22-0	293-625-5	Resin acids and rosin acids, fumarated,

		compounds with triethanolamine
91081-30-0	293-633-9	Resin acids and rosin acids, tall-oil, fumarated, compounds with triethanolamine

### Rosin, maleated

CAS	EU	Name
8050-28-0	232-480-4	Rosin, maleated
85409-30-9	287-098-0	Tall-oil rosin, maleated

### Rosin, maleated, reaction product with formaldehyde

CAS	EU	Name
98219-66-0	308-735-1	Rosin, maleated, reaction product with formaldehyde
94114-24-6	302-658-7	Resin acids and rosin acids, tall-oil, maleated, reaction products with formaldehyde

### Rosin, maleated, potassium salt

CAS	EU	Name
85409-27-4	287-094-9	Resin acids and rosin acids, maleated, potassium salt
91081-33-3	293-637-0	Resin acids and rosin acids, tall-oil, maleated, potassium salts

### Rosin, maleated, sodium salt

CAS	EU	Name

68201-60-5	269-228-8	Resin acids and rosin acids, maleated, sodium salts
85736-82-9	293-637-0	Resin acids and rosin acids, tall-oil, maleated, sodium salts

# Tall oil fatty acids, oligomeric products with maleic anhydride and rosin, calcium, magnesium, zinc salts

CAS	EU	Name
160901-14-4	500-451-8	Fatty acids, tall oil, oligomeric products with maleic anhydride and rosin, calcium magnesium zinc salts
160901-15-5	500-452-3	Fatty acids, tall oil, oligomeric products with maleic anhydride and tall- oil rosin, calcium magnesium zinc salts
160901-16-6	500-453-9	Fatty acids, tall oil, oligomeric products maleic anhydride, rosin and tall oil rosin, calcium magnesium zinc salts

### FAMILY 4

Note: The question whether rosin fumarated is the same as rosin, maleated, and hence whether the esters of rosin, fumarated are the same as the corresponding esters of rosin, maleated has not been addressed in this document.

### Rosin, fumarated, esters with pentaerythritol

CAS	EU	Name
65997-11-7	500-164-8	Rosin, fumarated, oligomeric products with pentaerythritol

94581-15-8	305-514-1	Resin acids and rosin acids, fumarated esters with pentaerythritol
161074-62-0	500-495-8	Rosin, tall-oil, fumarated, oligomeric reaction products with pentaerythritol

### Rosin, maleated, esters with glycerol

CAS	EU	Name
68038-41-5	Polymer	Rosin, maleated, polymer withy glycerol
94581-16-5	305-515-7	Resin and rosin acids, maleated, esters with glycerol

### Rosin, maleated, esters with pentaerythritol

CAS	EU	Name
68333-69-7	Polymer	Rosin, maleated, polymer with pentaerythritol
94581-17-6	305-516-2	Resin and rosin acids, maleated, esters with pentaerythritol

### Annex 1

22 February 2010



STATES ENVIRONMENTAL PROTECTION AGENCY

261157

MAR 1 3 1992

Dr. James Russell Special Consultant to the Pulp Chemicals Association, Inc. 2938 Jenks Avenue Panama City, Florida 32405

PESTICIDES AND TOXIC SUBSTANCES

CONTAINS NO CBI

Dear Dr. Russell:

It was a pleasure to meet with you and Dr. Frank Lambert on February 18, 1992. This letter confirms the Agency's intent to incorporate all Toxic Substances Control Act (TSCA) Chemical Substance Inventory references to tall-oil rosin (Chemical Abstracts Service Registry Number 8052-10-6) into rosin (CASRN 8050-09-7) as well as polymers and reaction products made from them.

The TSCA Chemical Substance Inventory currently lists both tall-oil rosin (CASRN 8052-10-6) and rosin (CASRN 8050-09-7), the names of which have been interchangeably used by manufacturers to describe rosins and their derivatives. The Pulp Chemicals Association (PCA) requested that the Agency consider CASRN 8052-10-6 (tall-oil rosin) and CASRN 8050-09-7 (rosin) equivalent for the purpose of the TSCA Chemical Substance Inventory, using CASRN 8050-09-7 (rosin) to describe both.

We have carefully studied the issue and decided that, for the purposes of the TSCA Inventory, rosin (CASRN 8050-09-7) will cover all types of rosin, irrespective of their method of production or the mixture of rosin used. We acknowledge that during the Initial Inventory reporting period EPA and industry might have agreed to use one CASRN 8050-09-7 (rosin) to cover all types of rosin. However, such agreement was never implemented when the TSCA Inventory was compiled. While we regret that PCA failed to bring this issue to our attention earlier, we now believe that the TSCA Inventory should no longer distinguish between rosin and tall-oil rosin.

Based on our discussion on February 18, the aforementioned change will be made retroactively so that all references to tall oil rosin will be removed from the TSCA Inventory upon completion of proper Inventory correction and delisting requirements. The tentative Inventory correction/delisting procedures that we intend to follow are summarized as follows:

The Agency will consolidate both tall-oil rosin (CASRN (1) 8052-10-6) and rosin (CASRN 8050-09-7) under one single definition for rosin which will still be identified by CASRN 8050-09-7.

- (2) The Pulp Chemicals Association will notify its member companies that rosin and tall-oil rosin are being treated equivalently, for the purposes of TSCA Inventory. Future Premanufacture Notifications (PMNS) for new substances based on rosin should use CASRN 8050-09-7 (rosin) only, irrespective of the type of rosins used.
- (3) The Pulp Chemicals Association will notify its member companies who reported substances containing tall-oil rosin during the Initial Inventory reporting period to submit TSCA Inventory correction request(s) to the Chemical Inventory Section (TS-790) of EPA. The member companies should in turn notify their customers who may have reported substances (including polymers, reaction products, and derivatives) based on tall-oil rosin to likewise submit correction requests, if necessary. Each correction request is to be made on a new Inventory Reporting Form C along with a copy of the original Inventory reporting form. The confidentiality claims, activity and production range information should be the same in both original Form C and new Form C. A cover letter should also be included to authorize the Agency to make the Inventory correction. The supporting documentation (such as commercial batch production records, customer invoices etc.) which is normally required to accompany an Inventory correction request will be waived for the aforementioned correction requests.
- (4) The PCA member companies and the downstream processors who reported tall-oil rosin containing substances (including polymers, reaction products, and derivatives) in PMNs should also submit correction requests to the Chemical Inventory Section (TS-790) of EPA for both commenced and uncommenced PMNs. The package of the correction request should include new page(s) of Section B (Chemical Identity Information) in Part I of the EPA PMN Form 7710-25, a copy of the corresponding original PMN page(s), and a cover letter to authorize the Agency to make the correction(s) from tall-oil rosin containing substance(s) to rosin containing substance(s). Again, the supporting documentation requirements as mentioned in (3) will be waived.
- (5) After the Agency approves the valid correction requests, the chemical name, "tall-oil rosin", would be changed to "rosin" in the affected substances in question. New CAS Registry Numbers will be assigned to the corrected substances and placed on the TSCA Chemical Substance Inventory.

(6) EPA will proceed to delist from the TSCA Inventory by formal Inventory delisting procedures those substances that were previously identified as tall-oil rosin derivatives.

Please be advised that our decision to consolidate the rosin and tall-oil rosin will impact other inventories, especially the Canadian Domestic Substances List (DSL) and Non-Domestic Substances List (NDSL), which is based on the 1985 Edition of the TSCA Inventory. Following the aforementioned TSCA Inventory Correction and delisting process, some corrected substances which are to be included in the TSCA Inventory may no longer be listed in the Canadian Inventory as a result of the change in chemical name. Likewise, the delisting of tall-oil rosin and its derivatives from the TSCA Inventory could create a compliance problem for persons who import those substances to Canada. Furthermore, the Chemical Abstracts Service (CAS) will continue to generate separate CAS Registry Numbers for substances containing rosin and tall-oil rosin, to support their routine abstracting, indexing, and Registry Services, which in turn supports other governmental organizations. Please note that EPA has no control over these CAS activities which are not related to the performance of the Agency's TSCA Inventory contract with CAS.

As I pointed out to Dr. Frank Lambert during a telephone conversation of March 12, 1992, the rosin industries perhaps should re-evaluate the ramifications of implementing the aforementioned correction/delisting procedures. If there are strong industry objections to the delisting of tall-oil rosin and derivatives from the TSCA Inventory, the Agency will not be able to proceed with the delisting and the Inventory would still contain both names. Consequently, the benefits that PCA anticipates from this correction will not be realized, while the confusion surrounding the use of the two names will become even more significant. I understand that Dr. Lambert will bring this matter to the attention of PCA member companies in the forthcoming PCA meeting. PCA will then advise EPA whether we need to re-examine our position regarding this issue.

In closing, we thank you again for your patience and cooperation in resolving this complex matter.

Sincerely,

Henry P. Law/ Chief Chemical Inventory Section

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