

433C d-Limonene—Industrial Strength MG Chemicals UK Limited

Version No: A-2.00

Safety data sheet according to REACH Regulation (EC) No 1907/2006, as amended by UK REACH Regulations SI 2019/758

Issue Date: 02/11/2021 Revision Date: 01/02/2022 L.REACH.GB.EN

SECTION 1 Identification of the substance / mixture and of the company / undertaking

1.1. Product Identifier

Product name	433C				
Synonyms	SDS Code: 433C-Liquid; 433C-1L, 433C-4L UFI:V5C0-P0CS-200E-DH6T				
Other means of identification	d-Limonene—Industrial Strength				

1.2. Relevant identified uses of the substance or mixture and uses advised against

Relevant identified uses	Solvent
Uses advised against	Not Applicable

1.3. Details of the supplier of the safety data sheet

Registered company name	MG Chemicals UK Limited	MG Chemicals (Head office)	
Address	Heame House, 23 Bilston Street, Sedgely Dudley DY3 1JA United Kingdom	9347 - 193 Street Surrey V4N 4E7 British Columbia Canada	
Telephone	+(44) 1663 362888	+(1) 800-201-8822	
Fax	Not Available	+(1) 800-708-9888	
Website	Not Available	www.mgchemicals.com	
Email	sales@mgchemicals.com	Info@mgchemicals.com	

1.4. Emergency telephone number

Association / Organisation	Verisk 3E (Access code: 335388)
Emergency telephone numbers	+(44) 20 35147487
Other emergency telephone numbers	+(0) 800 680 0425

SECTION 2 Hazards identification

2.1. Classification of the substance or mixture

Classified according to GB-CLP Regulation, UK SI 2019/720 and UK SI 2020/1567 [1]	H226 - Flammable Liquids Category 3, H315 - Skin Corrosion/Irritation Category 2, H317 - Sensitisation (Skin) Category 1, H410 - Hazardous to the Aquatic Environment Long-Term Hazard Category 1, H304 - Aspiration Hazard Category 1
Legend:	1. Classified by Chemwatch; 2. Classification drawn from GB-CLP Regulation, UK SI 2019/720 and UK SI 2020/1567

2.2. Label elements

Hazard pictogram(s)









Signal word

Danger

Hazard statement(s)

H226	Flammable liquid and vapour.
H315	Causes skin irritation.
H317	May cause an allergic skin reaction.
H410	Very toxic to aquatic life with long lasting effects.
H304	May be fatal if swallowed and enters airways.

Not Applicable

Precautionary statement(s) Prevention

P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P233	Keep container tightly closed.
P280	Wear protective gloves and protective clothing.
P240	Ground and bond container and receiving equipment.
P241	Use explosion-proof electrical/ventilating/lighting/intrinsically safe equipment.
P242	Use non-sparking tools.
P243	Take action to prevent static discharges.
P261	Avoid breathing mist/vapours/spray.
P273	Avoid release to the environment.
P264	Wash all exposed external body areas thoroughly after handling.
P272	Contaminated work clothing should not be allowed out of the workplace.

Precautionary statement(s) Response

P301+P310	IF SWALLOWED: Immediately call a POISON CENTER/doctor/physician/first aider.
P331	Do NOT induce vomiting.
P370+P378	In case of fire: Use alcohol resistant foam or normal protein foam to extinguish.
P302+P352	IF ON SKIN: Wash with plenty of water.
P333+P313	If skin irritation or rash occurs: Get medical advice/attention.
P362+P364	Take off contaminated clothing and wash it before reuse.
P391	Collect spillage.
P303+P361+P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water [or shower].

Precautionary statement(s) Storage

P403+P235	Store in a well-ventilated place. Keep cool.
P405	Store locked up.

Precautionary statement(s) Disposal

P501 Dispose of contents/container to authorised hazardous or special waste	te collection point in accordance with any local regulation.
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2.3. Other hazards

Inhalation, skin contact and/or ingestion may produce health damage*.

Cumulative effects may result following exposure $\!\!\!^\star.$

Limited evidence of a carcinogenic effect*.

SECTION 3 Composition / information on ingredients

3.1.Substances

See 'Composition on ingredients' in Section 3.2

3.2.Mixtures

1.CAS No 2.EC No 3.Index No 4.REACH No	%[weight]	Name	Classified according to GB-CLP Regulation, UK SI 2019/720 and UK SI 2020/1567	SCL / M-Factor	Nanoform Particle Characteristics
1.5989-27-5 2.227-813-5 3.601-029-00-7 4.Not Available	74	d-limonene	Flammable Liquids Category 3, Skin Corrosion/Irritation Category 2, Sensitisation (Skin) Category 1, Hazardous to the Aquatic Environment Acute Hazard Category 1, Hazardous to the Aquatic Environment Long-Term Hazard Category 1; H226, H315, H317, H400, H410 [2]	Not Available	Not Available
1.99-85-4 2.202-794-6 3.Not Available 4.Not Available	9	gamma- terpinene	Flammable Liquids Category 3, Skin Corrosion/Irritation Category 2, Serious Eye Damage/Eye Irritation Category 2, Sensitisation (Skin) Category 1, Specific Target Organ Toxicity - Single Exposure (Respiratory Tract Irritation) Category 3, Specific Target Organ Toxicity - Single Exposure (Narcotic Effects) Category 3, Hazardous to the Aquatic Environment Long-Term Hazard Category 2; H226, H315, H319, H317, H335, H336, H411 [1]	Not Available	Not Available
1.127-91-3 2.204-872-5 3.Not Available 4.Not Available	5	beta-pinene	Flammable Liquids Category 3, Acute Toxicity (Oral, Dermal and Inhalation) Category 4, Skin Corrosion/Irritation Category 2, Serious Eye Damage/Eye Irritation Category 2, Sensitisation (Skin) Category 1, Specific Target Organ Toxicity - Single Exposure (Respiratory Tract Irritation) Category 3, Specific Target Organ Toxicity - Single Exposure (Narcotic Effects) Category 3, Hazardous to the Aquatic Environment Long-Term Hazard Category 1; H226, H302+H312+H332, H315, H319, H317, H335, H336, H410 [1]	Not Available	Not Available

1.CAS No 2.EC No 3.Index No 4.REACH No		%[weight]	Name	Classified according to GB-CLP Regulation, UK SI 2019/720 and UK SI 2020/1567	SCL / M-Factor	Nanoform Particle Characteristics
1.586-62-9 2.209-578-0 3.Not Available 4.Not Available		4	terpinolene	Flammable Liquids Category 3, Sensitisation (Skin) Category 1, Specific Target Organ Toxicity - Single Exposure (Narcotic Effects) Category 3, Aspiration Hazard Category 1, Hazardous to the Aquatic Environment Long-Term Hazard Category 1; H226, H317, H336, H304, H410 [1]	Not Available	Not Available
1.123-35-3 2.204-622-5 3.Not Available 4.Not Available		4	myrcene	Flammable Liquids Category 3, Skin Corrosion/Irritation Category 2, Serious Eye Damage/Eye Irritation Category 2, Sensitisation (Skin) Category 1, Reproductive Toxicity Category 2, Specific Target Organ Toxicity - Single Exposure (Respiratory Tract Irritation) Category 3, Specific Target Organ Toxicity - Single Exposure (Narcotic Effects) Category 3, Hazardous to the Aquatic Environment Long-Term Hazard Category 1; H226, H315, H319, H317, H361f, H335, H336, H410 [1]	Not Available	Not Available
1.80-56-8 2.201-291-9 3.Not Available 4.Not Available		3	alpha- pinene	Flammable Liquids Category 3, Skin Corrosion/Irritation Category 2, Serious Eye Damage/Eye Irritation Category 2, Sensitisation (Skin) Category 1, Specific Target Organ Toxicity - Single Exposure (Respiratory Tract Irritation) Category 3, Specific Target Organ Toxicity - Single Exposure (Narcotic Effects) Category 3, Hazardous to the Aquatic Environment Long-Term Hazard Category 1; H226, H315, H319, H317, H335, H336, H410 [1]	Not Available	Not Available
1.99-86-5 2.202-795-1 3.Not Available 4.Not Available		1	alpha- terpinene	Flammable Liquids Category 3, Acute Toxicity (Oral) Category 4, Sensitisation (Skin) Category 1, Specific Target Organ Toxicity - Single Exposure (Narcotic Effects) Category 3, Hazardous to the Aquatic Environment Long-Term Hazard Category 1; H226, H302, H317, H336, H410 [1]	Not Available	Not Available
	Legend:	1. Classified by Chemwatch; 2. Classification drawn from GB-CLP Regulation, UK SI 2019/720 and UK SI 2020/1567; 3. Classification drawn from C&L * EU IOELVs available; [e] Substance identified as having endocrine disrupting properties				

SECTION 4 First aid measures

4.1. Description of first aid measures

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Eye Contact	If this product comes in contact with the eyes: Wash out immediately with fresh running water. Ensure complete irrigation of the eye by keeping eyelids apart and away from eye and moving the eyelids by occasionally lifting the upper and lower lids. Seek medical attention without delay; if pain persists or recurs seek medical attention. Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.
Skin Contact	If skin contact occurs: Immediately remove all contaminated clothing, including footwear. Flush skin and hair with running water (and soap if available). Seek medical attention in event of irritation.
Inhalation	 If fumes, aerosols or combustion products are inhaled remove from contaminated area. Other measures are usually unnecessary.
Ingestion	 If swallowed do NOT induce vomiting. If vomiting occurs, lean patient forward or place on left side (head-down position, if possible) to maintain open airway and prevent aspiration. Observe the patient carefully. Never give liquid to a person showing signs of being sleepy or with reduced awareness; i.e. becoming unconscious. Give water to rinse out mouth, then provide liquid slowly and as much as casualty can comfortably drink. Seek medical advice.

4.2 Most important symptoms and effects, both acute and delayed

See Section 11

4.3. Indication of any immediate medical attention and special treatment needed

Treat symptomatically.

SECTION 5 Firefighting measures

5.1. Extinguishing media

5.2. Special hazards arising from the substrate or mixture

Fire Incompatibility	Avoid contamination with oxidising agents i.e. nitrates, oxidising acids, chlorine bleaches, pool chlorine etc. as ignition may result

5.3. Advice for firefighters

5.3. Advice for firefighters	
Fire Fighting	
Fire/Explosion Hazard	 Liquid and vapour are flammable. Moderate fire hazard when exposed to heat or flame. Vapour forms an explosive mixture with air. Moderate explosion hazard when exposed to heat or flame. Vapour may travel a considerable distance to source of ignition. Heating may cause expansion or decomposition leading to violent rupture of containers.

▶ On combustion, may emit toxic fumes of carbon monoxide (CO).

Combustion products include:

carbon monoxide (CO)

carbon dioxide (CO2)

other pyrolysis products typical of burning organic material.

WARNING: Long standing in contact with air and light may result in the formation of potentially explosive peroxides

SECTION 6 Accidental release measures

6.1. Personal precautions, protective equipment and emergency procedures

See section 8

6.2. Environmental precautions

See section 12

6.3. Methods and material for containment and cleaning up

Environmental hazard - contain spillage. ▶ Remove all ignition sources

Minor Spills

- Clean up all spills immediately. Avoid breathing vapours and contact with skin and eyes
- Control personal contact with the substance, by using protective equipment.
- Contain and absorb small quantities with vermiculite or other absorbent material.
- Wipe up.
- Collect residues in a flammable waste container.

Environmental hazard - contain spillage.

- ▶ Clear area of personnel and move upwind.
- Alert Fire Brigade and tell them location and nature of hazard.
- Wear breathing apparatus plus protective gloves.
- Prevent, by any means available, spillage from entering drains or water course.
- ▶ Stop leak if safe to do so.
- Contain spill with sand, earth or vermiculite.
- **Major Spills**
 - ▶ Collect recoverable product into labelled containers for recycling.
 - ▶ Neutralise/decontaminate residue (see Section 13 for specific agent).
 - Collect solid residues and seal in labelled drums for disposal.
 - ▶ Wash area and prevent runoff into drains
 - After clean up operations, decontaminate and launder all protective clothing and equipment before storing and re-using.
 - If contamination of drains or waterways occurs, advise emergency services

CARE: Absorbent materials wetted with occluded oil must be moistened with water as they may auto-oxidize, become self heating and ignite. Some oils slowly oxidise when spread in a film and oil on cloths, mops, absorbents may autoxidise and generate heat, smoulder, ignite and burn. In the workplace oily rags should be collected and immersed in water.

6.4. Reference to other sections

Personal Protective Equipment advice is contained in Section 8 of the SDS.

SECTION 7 Handling and storage

Safe handling

7.1. Precautions for safe handling

- Containers, even those that have been emptied, may contain explosive vapours.
- Do NOT cut, drill, grind, weld or perform similar operations on or near containers.
- Avoid all personal contact, including inhalation.
- Wear protective clothing when risk of overexposure occurs.
- Use in a well-ventilated area.
- Prevent concentration in hollows and sumps.
- DO NOT enter confined spaces until atmosphere has been checked.
- Avoid smoking, naked lights or ignition sources.
- Avoid generation of static electricity.
- DO NOT use plastic buckets
- Earth all lines and equipment.
- Use spark-free tools when handling. Avoid contact with incompatible materials.
- When handling, DO NOT eat, drink or smoke
- Keep containers securely sealed when not in use.
- Avoid physical damage to containers.
- Always wash hands with soap and water after handling.
- Work clothes should be laundered separately.
- Use good occupational work practice.
- Observe manufacturer's storage and handling recommendations contained within this SDS.
- Atmosphere should be regularly checked against established exposure standards to ensure safe working conditions.
- ▶ DO NOT allow clothing wet with material to stay in contact with skin

Fire and explosion protection

See section 5

Consider storage under inert gas.

Store in original containers in approved flammable liquid storage area.

▶ Store away from incompatible materials in a cool, dry, well-ventilated area. **DO NOT** store in pits, depressions, basements or areas where vapours may be trapped.

- Other information
 - ▶ No smoking, naked lights, heat or ignition sources. Storage areas should be clearly identified, well illuminated, clear of obstruction and accessible only to trained and authorised personnel adequate security must be provided so that unauthorised personnel do not have access.

- Store according to applicable regulations for flammable materials for storage tanks, containers, piping, buildings, rooms, cabinets, allowable quantities and minimum storage distances.
- b Use non-sparking ventilation systems, approved explosion proof equipment and intrinsically safe electrical systems.
- Have appropriate extinguishing capability in storage area (e.g. portable fire extinguishers dry chemical, foam or carbon dioxide) and flammable gas detectors.
- Keep adsorbents for leaks and spills readily available.
- ▶ Protect containers against physical damage and check regularly for leaks.
- Observe manufacturer's storage and handling recommendations contained within this SDS.

In addition, for tank storages (where appropriate):

- Store in grounded, properly designed and approved vessels and away from incompatible materials.
- For bulk storages, consider use of floating roof or nitrogen blanketed vessels; where venting to atmosphere is possible, equip storage tank vents with flame arrestors; inspect tank vents during winter conditions for vapour/ ice build-up.
- ▶ Storage tanks should be above ground and diked to hold entire contents.

7.2. Conditions for safe storage, including any incompatibilities

- Packing as supplied by manufacturer.
- Plastic containers may only be used if approved for flammable liquid.
- Check that containers are clearly labelled and free from leaks.
- For low viscosity materials (i): Drums and jerry cans must be of the non-removable head type. (ii): Where a can is to be used as an inner package, the can must have a screwed enclosure.
- For materials with a viscosity of at least 2680 cSt. (23 deg. C)

Suitable container

- For manufactured product having a viscosity of at least 250 cSt. (23 deg. C)
- Manufactured product that requires stirring before use and having a viscosity of at least 20 cSt (25 deg. C): (i) Removable head packaging; (ii) Cans with friction closures and (iii) low pressure tubes and cartridges may be used.
- Where combination packages are used, and the inner packages are of glass, there must be sufficient inert cushioning material in contact with inner and outer packages
- In addition, where inner packagings are glass and contain liquids of packing group I there must be sufficient inert absorbent to absorb any spillage, unless the outer packaging is a close fitting moulded plastic box and the substances are not incompatible with the plastic.

d-Limonene

- ▶ forms unstable peroxides in storage, unless inhibited; may polymerise
- reacts with strong oxidisers and may explode or combust
- F is incompatible with strong acids, including acidic clays, peroxides, halogens, vinyl chloride and iodine pentafluoride
- If flow or agitation may generate electrostatic charges due to low conductivity
- ▶ The various oxides of nitrogen and peroxyacids may be dangerously reactive in the presence of alkenes. BRETHERICK L.: Handbook of Reactive Chemical Hazards
- Avoid reaction with strong Lewis or mineral acids.
- Reaction with halogens requires carefully controlled conditions.
- Free radical initiators should be avoided.

HAZARD:

- Although anti-oxidants may be present, in the original formulation, these may deplete over time as they come into contact with air.
- Rags wet / soaked with unsaturated hydrocarbons / drying oils may auto-oxidise; generate heat and, in-time, smoulder and ignite. This is especially the case where oil-soaked materials are folded, bunched, compressed, or piled together this allows the heat to accumulate or even accelerate the reaction
- Oily cleaning rags should be collected regularly and immersed in water, or spread to dry in safe-place away from direct sunlight.or stored, immersed, in solvents in suitably closed containers.

Terpenoids and terpenes, are generally unsaturated, are thermolabile, are often volatile and may be easily oxidised or hydrolysed depending on their respective structure.

Terpenoids are subject to autoxidation. Autoxidation is any oxidation that occurs in open air or in presence of oxygen (and sometimes UV radiation) and forms peroxides and hydroperoxides.

Though autoxidation has been particularly investigated in the field of fatty oils, it also plays a most crucial part for terpenoid deterioration. Although virtually all types of organic materials can undergo air oxidation, certain types are particularly prone to autoxidation, including unsaturated compounds that have allylic or benzylic hydrogen atoms (C6H5CH2-); these materials are converted to hydroperoxides by autoxidation. Promoted by heat, catalytic quantities of redox-reactive metals, and exposure to light, autoxidation may result in the formation of explosive peroxides which may become explosive upon concentration.

explosive peroxides which may become explosive upon concentration.

As a rule, however, primary autoxidation products such as hydroperoxides eventually break down during advanced stages of oxidation depending on their individual stability. Thereby they give rise to a range of stable oxidised secondary products such as mono- to polyvalent alcohols, aldehydes, ketones, epoxides, peroxides, or acids as well as highly viscous, often oxygen-bearing polymers. Light, heat, or increasing acidity often promote this breakdown.

Compounds rich in allylic hydrogen atoms (2HC=CHCH2-R), found in most terpenoids, make up the most probable targets for autoxidation. Several terpenoids (typically oxygen containing derivatives) are saturated and do not react in a similar fashion to their unsaturated congeners. Thermolabile terpenoids, especially mere terpenes and aldehydes, are susceptible to rearrangement processes at elevated temperatures. Terpenic conversion reactions, upon heating, have been reported both for isolated compounds as well as for essential oils.(which tend to be rich in mono-, and sesqui-terpenes.

Mono-, bi-, or tricyclic mono- terpenoids (those containing two isoprene units, dienes) and sesquiterpenoids (with three isoprene units, trienes) of different chemical classes, such as hydrocarbons, ketones, alcohols, oxides, aldehydes, phenols, or esters, make up the major part in essential oils.

Electron-donating groups and increasing alkyl substitution contribute to a stronger carbon-peroxide bond through a hyperconjugative effect, thus leading to more stable and subsequently built-up hydroperoxides.

Some oxygen-bearing terpenoids such as menthol, eucalyptol (1,8-cineol), and menthone do not form hydroperoxides upon oxidation but are directly converted into ketones, acids, and aldehydes. None of these are unsaturated compounds.

Due to their low volatility, diterpenes (with four isoprenes, tetraenes) are barely encountered in genuine essential oils obtained by distillation, while tri- and higher terpenoids such as sterols or carotenoids are only present in the nonvolatile fractions such as plant resins or gums and will remain in the residue

Aging processes generally come along with a more or less pronounced quality loss In addition to the frequent development of unpleasant and often pungent flavours, shifting colors such as the formation of a yellow staining or changes in consistency up to resinification have been reported both upon degradation of single terpenoids as well as of essential oils.

- The interaction of alkenes and alkynes with nitrogen oxides and oxygen may produce explosive addition products; these may form at very low temperatures and explode on heating to higher temperatures (the addition products from 1,3-butadiene and cyclopentadiene form rapidly at -150 C and ignite or explode on warming to -35 to -15 C). These derivatives ('pseudo- nitrosites') were formerly used to characterise terpene hydrocarbons.
- Exposure to air must be kept to a minimum so as to limit the build-up of peroxides which will concentrate in bottoms if the product is distilled. The product must not be distilled to dryness if the peroxide concentration is substantially above 10 ppm (as active oxygen) since explosive decomposition may occur. Distillate must be immediately inhibited to prevent peroxide formation. The effectiveness of the antioxidant is limited once the peroxide levels exceed 10 ppm as active oxygen. Addition of more inhibitor at this point is generally ineffective. Prior to distillation it is

Storage incompatibility

recommended that the product should be washed with aqueous ferrous ammonium sulfate to destroy peroxides; the washed product should be immediately re-inhibited.

- · A range of exothermic decomposition energies for double bonds is given as 40-90 kJ/mol. The relationship between energy of decomposition and processing hazards has been the subject of discussion; it is suggested that values of energy released per unit of mass, rather than on a molar basis (J/g) be used in the assessment. For example, in 'open vessel processes' (with man-hole size openings, in an industrial setting), substances with exothermic decomposition energies below 500 J/g are unlikely to present a danger, whilst those in 'closed vessel processes' (opening is a safety valve or bursting disk) present some danger where the decomposition energy exceeds 150 J/g. BRETHERICK: Handbook of Reactive Chemical Hazards, 4th Edition
- · The reaction of ozone with alkenes is believed to proceed *via* the formation of a vibrationally excited Primary Ozonide (POZ) which falls apart to give a vibrationally excited Criegee Intermediate (CI) The CI can decompose to give OH radicals, or be stabilised. This may be of relevance in atmospheric chemistry.
- · Violent explosions at low temperatures in ammonia synthesis gas units have been traced to the addition products of dienes and nitrogen dioxide
- Avoid reaction with oxidising agents

7.3. Specific end use(s)

See section 1.2

SECTION 8 Exposure controls / personal protection

8.1. Control parameters

Ingredient	DNELs Exposure Pattern Worker	PNECs Compartment
d-limonene	Dermal 9.5 mg/kg bw/day (Systemic, Chronic) Inhalation 66.7 mg/m³ (Systemic, Chronic) Dermal 4.8 mg/kg bw/day (Systemic, Chronic) * Inhalation 16.6 mg/m³ (Systemic, Chronic) * Oral 4.8 mg/kg bw/day (Systemic, Chronic) *	14 µg/L (Water (Fresh)) 1.4 µg/L (Water - Intermittent release) 3.85 mg/kg sediment dw (Sediment (Fresh Water)) 0.385 mg/kg sediment dw (Sediment (Marine)) 0.763 mg/kg soil dw (Soil) 1.8 mg/L (STP) 133 mg/kg food (Oral)
gamma-terpinene	Dermal 0.833 mg/kg bw/day (Systemic, Chronic) Inhalation 2.939 mg/m³ (Systemic, Chronic) Dermal 0.417 mg/kg bw/day (Systemic, Chronic) * Inhalation 0.725 mg/m³ (Systemic, Chronic) * Oral 0.417 mg/kg bw/day (Systemic, Chronic) *	0.003 mg/L (Water (Fresh)) 0 mg/L (Water - Intermittent release) 0.49 mg/kg sediment dw (Sediment (Fresh Water)) 0.049 mg/kg sediment dw (Sediment (Marine)) 0.423 mg/kg soil dw (Soil) 10 mg/L (STP)
beta-pinene	Dermal 0.8 mg/kg bw/day (Systemic, Chronic) Inhalation 5.69 mg/m³ (Systemic, Chronic) Dermal 54 µg/cm² (Local, Chronic) Dermal 0.3 mg/kg bw/day (Systemic, Chronic) * Inhalation 1 mg/m³ (Systemic, Chronic) * Oral 0.3 mg/kg bw/day (Systemic, Chronic) * Dermal 27 µg/cm² (Local, Chronic) *	1.004 µg/L (Water (Fresh)) 0.1 µg/L (Water - Intermittent release) 5.02 (Water (Marine)) 0.337 mg/kg sediment dw (Sediment (Fresh Water)) 0.034 mg/kg sediment dw (Sediment (Marine)) 0.067 mg/kg soil dw (Soil) 3.26 mg/L (STP) 13.1 mg/kg food (Oral)
terpinolene	Dermal 0.52 mg/kg bw/day (Systemic, Chronic) Inhalation 3.6 mg/m³ (Systemic, Chronic) Dermal 44 µg/cm² (Local, Chronic) Dermal 0.26 mg/kg bw/day (Systemic, Chronic) * Inhalation 0.9 mg/m³ (Systemic, Chronic) * Oral 0.26 mg/kg bw/day (Systemic, Chronic) *	0.001 mg/L (Water (Fresh)) 0 mg/L (Water - Intermittent release) 0.013 mg/L (Water (Marine)) 0.145 mg/kg sediment dw (Sediment (Fresh Water)) 0.015 mg/kg sediment dw (Sediment (Marine)) 0.016 mg/kg soil dw (Soil) 0.2 mg/L (STP) 10.31 mg/kg food (Oral)
alpha-pinene	Dermal 0.132 mg/kg bw/day (Systemic, Chronic) Inhalation 0.933 mg/m³ (Systemic, Chronic) Dermal 161 µg/cm² (Local, Chronic) Dermal 0.134 mg/kg bw/day (Systemic, Chronic) * Inhalation 0.467 mg/m³ (Systemic, Chronic) * Oral 0.134 mg/kg bw/day (Systemic, Chronic) *	0 mg/L (Water (Fresh)) 0 mg/L (Water - Intermittent release) 0.003 mg/L (Water (Marine)) 0.03 mg/kg sediment dw (Sediment (Fresh Water)) 0.003 mg/kg sediment dw (Sediment (Marine)) 0.003 mg/kg soil dw (Soil) 0.2 mg/L (STP) 8.76 mg/kg food (Oral)
alpha-terpinene	Dermal 0.833 mg/kg bw/day (Systemic, Chronic) Inhalation 2.939 mg/m³ (Systemic, Chronic) Dermal 0.417 mg/kg bw/day (Systemic, Chronic) * Inhalation 0.725 mg/m³ (Systemic, Chronic) * Oral 0.417 mg/kg bw/day (Systemic, Chronic) *	0.002 mg/L (Water (Fresh)) 0 mg/L (Water - Intermittent release) 0.017 mg/L (Water (Marine)) 0.196 mg/kg sediment dw (Sediment (Fresh Water)) 0.02 mg/kg sediment dw (Sediment (Marine)) 0.023 mg/kg soil dw (Soil) 0.1 mg/L (STP) 8.333 mg/kg food (Oral)

^{*} Values for General Population

Occupational Exposure Limits (OEL)

INGREDIENT DATA

Source	Ingredient	Material name	TWA	STEL	Peak	Notes
Not Available						

Not Applicable

Emergency Limits

Ingredient	TEEL-1	TEEL-2	TEEL-3
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Ingredient	TEEL-1	TEEL-2	TEEL-3
d-limonene	15 ppm	67 ppm	170 ppm
alpha-pinene	60 ppm	120 ppm	1,500 ppm

Ingredient	Original IDLH	Revised IDLH
d-limonene	Not Available	Not Available
gamma-terpinene	Not Available	Not Available
beta-pinene	Not Available	Not Available
terpinolene	Not Available	Not Available
myrcene	Not Available	Not Available
alpha-pinene	Not Available	Not Available
alpha-terpinene	Not Available	Not Available

Occupational Exposure Banding

Ingredient	Occupational Exposure Band Rating	Occupational Exposure Band Limit
d-limonene	E	≤ 0.1 ppm
gamma-terpinene	E	≤ 0.1 ppm
beta-pinene	E	≤ 0.1 ppm
terpinolene	D	> 0.1 to ≤ 1 ppm
myrcene	E	≤ 0.1 ppm
alpha-pinene	E	≤ 0.1 ppm
alpha-terpinene	E	≤ 0.1 ppm
Notes:	Occupational exposure banding is a process of assigning chemicals into specific categories or bands based on a chemical's potency and the adverse health outcomes associated with exposure. The output of this process is an occupational exposure band (OEB), which corresponds to a range of exposure concentrations that are expected to protect worker health.	

MATERIAL DATA

Fragrance substance with is an established contact allergen in humans.

Scientific Committee on Consumer Safety SCCS OPINION on Fragrance allergens in cosmetic products 2012

IFRA Restricted Fragrance Substance

The International Fragrance Association (IFRA) Standards form the basis for the globally accepted and recognized risk management system for the safe use of fragrance ingredients and are part of the IFRA Code of Practice. This is the self-regulating system of the industry, based on risk assessments carried out by an independent Expert Panel. for d-Limonene:

CEL TWA: 30 ppm, 165.6 mg/m3 (compare WEEL-TWA*)

(CEL = Chemwatch Exposure Limit)

A Workplace Environmental Exposure Level* has been established by AIHA (American Industrial Hygiene Association) who have produced the following rationale:

d-Limonene is not acutely toxic. In its pure form it is not a sensitiser but is irritating to the skin. Although there is clear evidence of carcinogenicity in male rats, the effect has been attributed to an alpha-2u-globin (a2u-G) renal toxicity which is both species and gender specific. Humans do not synthesise a2u-G, and metabolism studies indicate that 75% to 95% of d-limonene is excreted in 2-3 days with different metabolites identified between humans and rats. In a 2-year study, liver effects were noted in male mice at 500 mg/kg and reduced survival was noted in female rats at 600 mg/kg. The no observable effect levels (NOELs) were 250 and 300 mg/kg, respectively. A WEEL of 30 ppm is recommended to protect against these effects.

8.2. Exposure controls

Care: Atmospheres in bulk storages and even apparently empty tanks may be hazardous by oxygen depletion. Atmosphere must be checked before entry.

Requirements of State Authorities concerning conditions for tank entry must be met. Particularly with regard to training of crews for tank entry; work permits; sampling of atmosphere; provision of rescue harness and protective gear as needed

Engineering controls are used to remove a hazard or place a barrier between the worker and the hazard. Well-designed engineering controls can be highly effective in protecting workers and will typically be independent of worker interactions to provide this high level of protection. The basic types of engineering controls are:

Process controls which involve changing the way a job activity or process is done to reduce the risk.

Enclosure and/or isolation of emission source which keeps a selected hazard 'physically' away from the worker and ventilation that strategically 'adds' and 'removes' air in the work environment. Ventilation can remove or dilute an air contaminant if designed properly. The design of a ventilation system must match the particular process and chemical or contaminant in use.

Employers may need to use multiple types of controls to prevent employee overexposure.

8.2.1. Appropriate engineering controls

For flammable liquids and flammable gases, local exhaust ventilation or a process enclosure ventilation system may be required. Ventilation equipment should be explosion-resistant.

Air contaminants generated in the workplace possess varying 'escape' velocities which, in turn, determine the 'capture velocities' of fresh circulating air required to effectively remove the contaminant.

Type of Contaminant:	Air Speed:
solvent, vapours, degreasing etc., evaporating from tank (in still air).	0.25-0.5 m/s (50-100 f/min.)
aerosols, fumes from pouring operations, intermittent container filling, low speed conveyer transfers, welding, spray drift, plating acid fumes, pickling (released at low velocity into zone of active generation)	0.5-1 m/s (100-200 f/min.)
direct spray, spray painting in shallow booths, drum filling, conveyer loading, crusher dusts, gas discharge (active generation into zone of rapid air motion)	1-2.5 m/s (200-500 f/min.)

Within each range the appropriate value depends on:

Lower end of the range	Upper end of the range
1: Room air currents minimal or favourable to capture	1: Disturbing room air currents
2: Contaminants of low toxicity or of nuisance value only.	2: Contaminants of high toxicity
3: Intermittent, low production.	3: High production, heavy use
4: Large hood or large air mass in motion	4: Small hood-local control only

Simple theory shows that air velocity falls rapidly with distance away from the opening of a simple extraction pipe. Velocity generally decreases with the square of distance from the extraction point (in simple cases). Therefore the air speed at the extraction point should be adjusted, accordingly, after reference to distance from the contaminating source. The air velocity at the extraction fan, for example, should be a minimum of 1-2 m/s (200-400 f/min.) for extraction of solvents generated in a tank 2 meters distant from the extraction point. Other mechanical considerations, producing performance deficits within the extraction apparatus, make it essential that theoretical air velocities are multiplied by factors of 10 or more when extraction systems are installed or used.

8.2.2. Personal protection











Eve and face protection

Safety glasses with side shields.

Chemical goggles.

Contact lenses may pose a special hazard; soft contact lenses may absorb and concentrate irritants. A written policy document, describing the wearing of lenses or restrictions on use, should be created for each workplace or task. This should include a review of lens absorption and adsorption for the class of chemicals in use and an account of injury experience. Medical and first-aid personnel should be trained in their removal and suitable equipment should be readily available. In the event of chemical exposure, begin eye irrigation immediately and remove contact lens as soon as practicable. Lens should be removed at the first signs of eye redness or irritation - lens should be removed in a clean environment only after workers have washed hands thoroughly. [CDC NIOSH Current Intelligence Bulletin 59], [AS/NZS 1336 or national equivalent]

Skin protection

Hands/feet protection

See Hand protection below

- ▶ Wear chemical protective gloves, e.g. PVC.
- ▶ Wear safety footwear or safety gumboots, e.g. Rubber

NOTE:

- The material may produce skin sensitisation in predisposed individuals. Care must be taken, when removing gloves and other protective equipment, to avoid all possible skin contact.
- Contaminated leather items, such as shoes, belts and watch-bands should be removed and destroyed.

The selection of suitable gloves does not only depend on the material, but also on further marks of quality which vary from manufacturer to manufacturer. Where the chemical is a preparation of several substances, the resistance of the glove material can not be calculated in advance and has therefore to be checked prior to the application.

The exact break through time for substances has to be obtained from the manufacturer of the protective gloves and has to be observed when making a final choice.

Personal hygiene is a key element of effective hand care. Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly. Application of a non-perfumed moisturiser is recommended.

Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include:

- · frequency and duration of contact,
- $\boldsymbol{\cdot}$ chemical resistance of glove material,
- · glove thickness and
- · dexterity

Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739, AS/NZS 2161.1 or national equivalent).

- When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374, AS/NZS 2161.10.1 or national equivalent) is recommended.
 When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN
- 374, AS/NZS 2161.10.1 or national equivalent) is recommended.

 Some glove polymer types are less affected by movement and this should be taken into account when considering gloves for long-term use.
 - · Contaminated gloves should be replaced.
 - As defined in ASTM F-739-96 in any application, gloves are rated as:
 - Excellent when breakthrough time > 480 min Good when breakthrough time > 20 min
 - Fair when breakthrough time < 20 min
 - · Poor when glove material degrades

For general applications, gloves with a thickness typically greater than 0.35 mm, are recommended.

It should be emphasised that glove thickness is not necessarily a good predictor of glove resistance to a specific chemical, as the permeation efficiency of the glove will be dependent on the exact composition of the glove material. Therefore, glove selection should also be based on consideration of the task requirements and knowledge of breakthrough times.

Glove thickness may also vary depending on the glove manufacturer, the glove type and the glove model. Therefore, the manufacturers technical data should always be taken into account to ensure selection of the most appropriate glove for the task.

Note: Depending on the activity being conducted, gloves of varying thickness may be required for specific tasks. For example:

- Thinner gloves (down to 0.1 mm or less) may be required where a high degree of manual dexterity is needed. However, these gloves are only likely to give short duration protection and would normally be just for single use applications, then disposed of.
- · Thicker gloves (up to 3 mm or more) may be required where there is a mechanical (as well as a chemical) risk i.e. where there is abrasion or puncture potential

Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly. Application of a non-perfumed moisturiser is recommended.

Body protection

Other protection

See Other protection below

Overalls.

- ► PVC Apron.
- PVC protective suit may be required if exposure severe.

Eyewash unit.

- ▶ Ensure there is ready access to a safety shower
 - Some plastic personal protective equipment (PPE) (e.g. gloves, aprons, overshoes) are not recommended as they may produce static electricity.
- For large scale or continuous use wear tight-weave non-static clothing (no metallic fasteners, cuffs or pockets).
- Non sparking safety or conductive footwear should be considered. Conductive footwear describes a boot or shoe with a sole made from a

Continued...

conductive compound chemically bound to the bottom components, for permanent control to electrically ground the foot an shall dissipate static electricity from the body to reduce the possibility of ignition of volatile compounds. Electrical resistance must range between 0 to 500,000 ohms. Conductive shoes should be stored in lockers close to the room in which they are worn. Personnel who have been issued conductive footwear should not wear them from their place of work to their homes and return.

Recommended material(s)

GLOVE SELECTION INDEX

Glove selection is based on a modified presentation of the:

'Forsberg Clothing Performance Index'.

The effect(s) of the following substance(s) are taken into account in the *computer-generated* selection:

433C d-Limonene-Industrial Strength

Material	СРІ
NITRILE	Α
PVA	Α
VITON	Α

^{*} CPI - Chemwatch Performance Index

A: Best Selection

- B: Satisfactory; may degrade after 4 hours continuous immersion
- C: Poor to Dangerous Choice for other than short term immersion

NOTE: As a series of factors will influence the actual performance of the glove, a final selection must be based on detailed observation. -

* Where the glove is to be used on a short term, casual or infrequent basis, factors such as 'feel' or convenience (e.g. disposability), may dictate a choice of gloves which might otherwise be unsuitable following long-term or frequent use. A qualified practitioner should be consulted.

Respiratory protection

Type A Filter of sufficient capacity. (AS/NZS 1716 & 1715, EN 143:2000 & 149:2001, ANSI Z88 or national equivalent)

Selection of the Class and Type of respirator will depend upon the level of breathing zone contaminant and the chemical nature of the contaminant. Protection Factors (defined as the ratio of contaminant outside and inside the mask) may also be important.

Required Maximum gas/vapour concentration present in air p.p.m. (by volume)		Half-face Respirator	Full-Face Respirator
up to 10	1000	A-AUS / Class1	-
up to 50	1000	-	A-AUS / Class 1
up to 50	5000	Airline *	-
up to 100	5000	-	A-2
up to 100	10000	-	A-3
100+			Airline**

- * Continuous Flow ** Continuous-flow or positive pressure demand A(All classes) = Organic vapours, B AUS or B1 = Acid gasses, B2 = Acid gas or hydrogen cyanide(HCN), B3 = Acid gas or hydrogen cyanide(HCN), E = Sulfur dioxide(SO2), G = Agricultural chemicals, K = Ammonia(NH3), Hg = Mercury, NO = Oxides of nitrogen, MB = Methyl bromide, AX = Low boiling point organic compounds(below 65 degC)
- Cartridge respirators should never be used for emergency ingress or in areas of unknown vapour concentrations or oxygen content.
- The wearer must be warned to leave the contaminated area immediately on detecting any odours through the respirator. The odour may indicate that the mask is not functioning properly, that the vapour concentration is too high, or that the mask is not properly fitted. Because of these limitations, only restricted use of cartridge respirators is considered appropriate.
- Cartridge performance is affected by humidity. Cartridges should be changed after 2 hr of continuous use unless it is determined that the humidity is less than 75%, in which case, cartridges can be used for 4 hr. Used cartridges should be discarded daily, regardless of the length of time used

8.2.3. Environmental exposure controls

See section 12

SECTION 9 Physical and chemical properties

9.1. Information on basic physical and chemical properties

Appearance	Colorless		
Physical state	Liquid	Relative density (Water = 1)	0.85
Odour	Not Available	Partition coefficient n-octanol / water	4.23
Odour threshold	Not Available	Auto-ignition temperature (°C)	237
pH (as supplied)	Not Available	Decomposition temperature	Not Available
Melting point / freezing point (°C)	Not Available	Viscosity (cSt)	<20.50
Initial boiling point and boiling range (°C)	>155	Molecular weight (g/mol)	Not Available
Flash point (°C)	31	Taste	Not Available
Evaporation rate	Not Available BuAC = 1	Explosive properties	Not Available
Flammability	Flammable.	Oxidising properties	Not Available
Upper Explosive Limit (%)	Not Available	Surface Tension (dyn/cm or mN/m)	Not Available
Lower Explosive Limit (%)	Not Available	Volatile Component (%vol)	100
Vapour pressure (kPa)	0.20	Gas group	Not Available

Solubility in water	Partly miscible	pH as a solution (Not Available%)	Not Available
Vapour density (Air = 1)	4.7	VOC g/L	846
Nanoform Solubility	Not Available	Nanoform Particle Characteristics	Not Available
Particle Size	Not Available		

9.2. Other information

Not Available

SECTION 10 Stability and reactivity

10.1.Reactivity	See section 7.2
10.2. Chemical stability	 Unstable in the presence of incompatible materials. Product is considered stable. Hazardous polymerisation will not occur.
10.3. Possibility of hazardous reactions	See section 7.2
10.4. Conditions to avoid	See section 7.2
10.5. Incompatible materials	See section 7.2
10.6. Hazardous decomposition products	See section 5.3

SECTION 11 Toxicological information

11.1. Information on toxicological	
Inhaled	The material is not thought to produce either adverse health effects or irritation of the respiratory tract following inhalation (as classified by EC Directives using animal models). Nevertheless, adverse systemic effects have been produced following exposure of animals by at least one other route and good hygiene practice requires that exposure be kept to a minimum and that suitable control measures be used in an occupational setting. Inhalation of vapours may cause drowsiness and dizziness. This may be accompanied by narcosis, reduced alertness, loss of reflexes, lack of coordination and vertigo. Acute effects from inhalation of high concentrations of vapour are pulmonary irritation, including coughing, with nausea; central nervous system depression - characterised by headache and dizziness, increased reaction time, fatigue and loss of co-ordination
Ingestion	Accidental ingestion of the material may be damaging to the health of the individual. Terpenes and their oxygen-containing counterparts, the terpenoids, produce a variety of physiological effects. Pine oil monoterpenes, for example, produce a haemorrhagic gastritis characterised by stomach pain and bleeding and vomiting. Systemic effects of pine oils include weakness and central nervous depression, excitement, loss of balance, headache, with hypothermia and respiratory failure. Central nervous system (CNS) depression may include nonspecific discomfort, symptoms of giddiness, headache, dizziness, nausea, anaesthetic effects, slowed reaction time, slurred speech and may progress to unconsciousness. Serious poisonings may result in respiratory depression and may be fatal. Five healthy male volunteers receiving a single oral dose of 20 grams d-limonene all developed transient proteinuria, a non-bloody diarrhoea and tenesmus. The results of other functional tests of the liver, kidney and pancreas were normal flaimi, et al, 1976i. d-Limonene causes abnormal
	bone formation following oral administration in animals. A human fatality has been reported following ingestion of a dose estimated to be 35 to 350 gm/kg d-limonene. Evidence exists, or practical experience predicts, that the material either produces inflammation of the skin in a substantial number of individuals following direct contact, and/or produces significant inflammation when applied to the healthy intact skin of animals, for up to four hours, such
	inflammation being present twenty-four hours or more after the end of the exposure period. Skin irritation may also be present after prolonged or repeated exposure; this may result in a form of contact dermatitis (nonallergic). The dermatitis is often characterised by skin redness (erythema) and swelling (oedema) which may progress to blistering (vesiculation), scaling and thickening of the epidermis. At the microscopic level there may be intercellular oedema of the spongy layer of the skin (spongiosis) and intracellular oedema of the epidermis. The material may accentuate any pre-existing dermatitis condition

Skin Contact

Skin contact with the material may damage the health of the individual; systemic effects may result following absorption.

It is likely that older pine oils become irritants from the build up of peroxides of delta- 3-carene and limonene etc.

Open cuts, abraded or irritated skin should not be exposed to this material

Entry into the blood-stream through, for example, cuts, abrasions, puncture wounds or lesions, may produce systemic injury with harmful effects. Examine the skin prior to the use of the material and ensure that any external damage is suitably protected.

Application of d-limonene produced moderate irritation to both intact and abraded skin. High purity d-limonene does not cause significant allergic reaction in guinea pigs; d-limonene, exposed to air for 2-months, sensitised the animals and it is surmised that allergenic compounds are formed after prolonged air contact. In human patch testing, weak or moderate reactions (erythema, swelling) have been observed. Positive eczematous responses to purified limonene were observed in 5 of 16 previously sensitised to oil of turpentine. In one study, a 39-year old male immersed one hand in a jar of solvent, ensuring that inhalation exposure was minimal. After only few minutes of exposure, the subject experienced painful itching and burning. Itching decreased after the exposure but burning continued for 10 minutes. Swelling disappeared after 100 minutes. Six hours post-exposure, a purpuric eruption was observed; this persisted for several weeks. Blood concentrations during skin exposure were low compared to those during inhalation exposure.

Eye

Although the liquid is not thought to be an irritant (as classified by EC Directives), direct contact with the eye may produce transient discomfort characterised by tearing or conjunctival redness (as with windburn).

Repeated or long-term occupational exposure is likely to produce cumulative health effects involving organs or biochemical systems.

On the basis, primarily, of animal experiments, concern has been expressed that the material may produce carcinogenic or mutagenic effects; in respect of the available information, however, there presently exists inadequate data for making a satisfactory assessment.

Practical evidence shows that inhalation of the material is capable of inducing a sensitisation reaction in a substantial number of individuals at a greater frequency than would be expected from the response of a normal population.

Pulmonary sensitisation, resulting in hyperactive airway dysfunction and pulmonary allergy may be accompanied by fatigue, malaise and aching. Significant symptoms of exposure may persist for extended periods, even after exposure ceases. Symptoms can be activated by a variety of nonspecific environmental stimuli such as automobile exhaust, perfumes and passive smoking.

Practical experience shows that skin contact with the material is capable either of inducing a sensitisation reaction in a substantial number of individuals, and/or of producing a positive response in experimental animals.

Substances that can cause occupational asthma (also known as asthmagens and respiratory sensitisers) can induce a state of specific airway hyper-responsiveness via an immunological, irritant or other mechanism. Once the airways have become hyper-responsive, further exposure to the substance, sometimes even to tiny quantities, may cause respiratory symptoms. These symptoms can range in severity from a runny nose to asthma. Not all workers who are exposed to a sensitiser will become hyper-responsive and it is impossible to identify in advance who are likely to become hyper-responsive.

Substances than can cuase occupational asthma should be distinguished from substances which may trigger the symptoms of asthma in people with pre-existing air-way hyper-responsiveness. The latter substances are not classified as asthmagens or respiratory sensitisers. Wherever it is reasonably practicable, exposure to substances that can cuase occupational asthma should be prevented. Where this is not possible the primary aim is to apply adequate standards of control to prevent workers from becoming hyper-responsive.

Activities giving rise to short-term peak concentrations should receive particular attention when risk management is being considered. Health surveillance is appropriate for all employees exposed or liable to be exposed to a substance which may cause occupational asthma and there should be appropriate consultation with an occupational health professional over the degree of risk and level of surveillance.

There is sufficient evidence to provide a strong presumption that human exposure to the material may result in impaired fertility on the basis of: clear evidence in animal studies of impaired fertility in the absence of toxic effects, or evidence of impaired fertility occurring at around the same dose levels as other toxic effects but which is not a secondary non-specific consequence of other toxic effects.

Essential oils and isolates derived from the Pinacea family, including Pinus and Abies genera, should only be used when the level of peroxides is kept to the lowest practicable level, for instance by adding antioxidants at the time of production. Such products should have a peroxide value of less than 10 millimoles peroxide per liter. Based on the published literature mentioning sensitising properties when containing peroxides (Food and Chemical Toxicology 11,1053(1973); 16,843(1978); 16,853(1978).

Pine needles and their extracts may contain isocupressic acids. Isocupressic acids have been described as causing toxicity problems in beef cattle. It has been found that a substantial amount of isocupressic acid remains in the extracts

It has surprisingly been found that isocupressic acids can be removed from pine needle extracts to form an extract which still exhibits therapeutic activity (such as the ability to lower blood pressure).

In the presence of air, a number of common flavour and fragrance chemicals can form peroxides surprisingly fast. Antioxidants can in most cases minimise the oxidation.

Chronic

Fragrance terpenes are generally easily oxidised in air. Non-oxidised limonene, linalool and caryophyllene turned out to be very weak sensitizers, however after oxidation limonene hydroperoxide and linalool hydroperoxide are strong sensitizers. Of the patients tested 2.6% showed positive reaction to oxidised limonene, 1.3% to oxidised linalool, 1.1% to linalool hydroperoxide, 0.5% to oxidised caryophyllene, while testing with caryophyllene oxide and oxidised myrcene resulted in few positive patch tests. 2/3 of the patients reacting positive to oxidised terpenes had fragrance related contact allergy and/or positive history for adverse reactions to fragrances.

As well as the hydroperoxides produced by linalol, limonene and delta-3-carene other oxidation and resinification effects progressively causes other fairly major changes in essential oil quality over time. Autoxidation of fragrance terpenes contributes greatly to fragrance allergy, which emphasizes the need of testing with compounds that patients are actually exposed to and not only with the ingredients originally applied in

Hydroperoxides of d-limonene are potent contact allergens when studied in guinea pigs. They may result when d-limonene is unstabilised against oxidation, or upon prolonged standing at room temperature and/ or upon exposure to light, or when stabiliser levels diminish. The two major hydroperoxides in auto-oxidised d-limonene, are cis- and trans- limonene-2-hydroperoxide (2-hydroperoxy-p-mentha-6,8-diene). In photo-oxidised d-limonene, they represent a minor fraction. Hydroperoxides may bind to proteins of the skin to make antigens either via a radical mechanism or after reactions to give epoxides. The cross-reactivity between the epoxide limonene-1,2-oxide, a potent contact allergen, and the hydroperoxides is NOT significant, indicating different mechanisms of sensitisation.

d-Limonene was considered to be weakly carcinogenic for the mouse fore-stomach epithelium, but not tumour producing. In 13-week and 2-year gavage-studies, male rats showed a range of compound-related kidney lesions including exacerbation of age-related nephropathy, mineralisation in the renal medulla, hyperplasia of the transitional epithelium overlying the renal papilla and proliferation of the renal tubular epithelium. Neoplasms were believed to be caused by progression to tubular cell hyperplasia to tubular cell adenomas and, with increasing size, to adenocarcinomas or carcinomas. The similarity of the nephrotoxicity caused by trichloroethylene and N-(4'-fluor-4-biphenyl)acetamide, tris(2,3-dibromopropyl)phosphate in rats and the species specific nature of the response suggests that degeneration and necrosis of convoluted tubules may be associated with the accumulation of alpha-2u-globin (a2u-G). Since a2u-G is a species and gender-specific protein that is causal for both the cytotoxic and carcinogenic response in male rats, extrapolation of d-limonene carcinogenicity data from rat studies to other species (including humans) is probably not warranted. Humans do not synthesise a2u-G; they do however produce other related low molecular weight proteins capable of binding chemicals that cause a2u-G nephropathy in rats but this does not necessarily connote human risk. The Risk Assessment Forum of the USA EPA concluded;

- Male renal rat tumours arising as a result of a process involving a2u-G accumulation do not contribute to the qualitative weight-of-evidence that the chemical poses a human carcinogenic hazard. Such tumours are included in dose-response extrapolations for the estimation of human carcinogenic risk.
- If the chemical induces a2u-G accumulation in male rats, the associated nephropathy is not to be used as an end-point for determining non-carcinogenic hazard.

433C d-Limonene—Industrial Strength

TOXICITY	IRRITATION
Not Available	Not Available

d-limonene

TOXICITY	IRRITATION
Dermal (rabbit) LD50: >5000 mg/kg ^[2]	Eye: no adverse effect observed (not irritating) ^[1]
Oral (Rat) LD50; >2000 mg/kg ^[1]	Skin (rabbit): 500mg/24h moderate
	Skin: no adverse effect observed (not irritating) ^[1]

	TOXICITY		IRRITATION		
gamma-terpinene	dermal (rat) LD50: >2000 mg/kg ^[1]		Skin (rabbit): 500 mg/2	4h mod.	
gamma-terpmene	Oral (Rat) LD50; >2000 mg/kg ^[1]		Olim (rabbit). 000 mg/2	ATT THOU.	
	Oral (Nat) 2000, >2000 mg/kg				
	TOXICITY	IRRITA	TION		
hata mimana	Oral (Rabbit) LD50; 4700 mg/kg ^[2]	adverse effect observed (not in	ot irritating) ^[1]		
beta-pinene	Skin (rabbit):500 mg/24h-moderate				
		Skin: n	o adverse effect observed (not i	rritating) ^[1]	
	TOXICITY			IRRITATION	
terpinolene	dermal (rat) LD50: >2000 mg/kg ^[1]			Not Available	
·	Oral (Rat) LD50; >2000 mg/kg ^[1]				
	TOXICITY		IRRITATION		
	Dermal (rabbit) LD50: >5000 mg/kg ^[2]		Eye: adverse effect observed	(irritating) ^[1]	
myrcene	Oral (Rat) LD50; >5000 mg/kg ^[2]		Skin (rabbit): 500 mg/24h - mc	od	
			Skin: adverse effect observed	(irritating) ^[1]	
	TOXICITY	IRRITA	TION		
	dermal (rat) LD50: >2000 mg/kg ^[1]	Eye: n	adverse effect observed (not i	rritating) ^[1]	
alpha-pinene	Oral (Rat) LD50; >500 mg/kg ^[1]		nan): 100% - SEVERE		
			abbit): 500 mg/24h - mod	.M1	
		Skin: a	dverse effect observed (irritating	g)r.i	
	TOXICITY	IF	RITATION		
alpha-terpinene	dermal (rat) LD50: >2000 mg/kg ^[1] Eye: adverse effect observed (irritating Oral (Rat) LD50; 1680 mg/kg ^[2] Skin: adverse effect observed (irritating		tating) ^[1]		
l ogand:	Value obtained from Europe ECHA Registered	Substances - Acut	a tovicity 2 * Value obtained from	n manufacturar's SDS - Unlass otherwise	
Legend:	specified data extracted from RTECS - Register of			ir manufacturer's SDS. Offiess outerwise	
433C d-Limonene—Industrial Strength	Allergic reactions which develop in the respiratory allergen with specific antibodies of the IgE class a allergen-specific potential for causing respiratory disposition of the exposed person are likely to be person to allergy. They may be genetically determ Immunologically the low molecular weight substar (haptens) or after metabolism (prohaptens). Particular attention is drawn to so-called atopic dia asthma and atopic eczema (neurodermatitis) whice Exogenous allergic alveolitis is induced essentially lymphocytes) may be involved. Such allergy is of Epoxidation of double bonds is a common bioactic capacity in vivo and in vitro and to chemically reactivate are prohaptens, whereas related alkenes contain compounds. This difference in sensitizing capacity to the high reactivity and sensitizing capacity of the Allergic Contact Dermatitis—Formation, Structura Ann-Therese Karlberg et al: Chem. Res. Toxicol. 2 http://ftp.cdc.gov/pub/Documents/OEL/06.%20Do	and belong in their resensitisation, the ardecisive. Factors whined or acquired, forces become compathesis which is chach is associated with y by allergen specifithe delayed type whation pathway for active towards a comenic alkenes demong isolated double of conjugated dien eallylic epoxides in al Requirements, and 2008, 21, pp 53–69	eaction rates to the manifestation ount of the allergen, the exposibility of exposibility of the exposibil	on of the immediate type. In addition to the ure period and the genetically determined he mucosa may play a role in predisposing a exposure to irritant substances. Ither by binding to peptides or proteins ceptibility to allergic rhinitis, allergic bronchial of type; cell-mediated reactions (Ting exposure. Formed, were found to possess sensitising e most common nucleophilic amino acids. In or in conjunction with a six-membered ring diene were weak or nonsensitizing isolated double bonds was found to be due	
D-LIMONENE	Tumorigenic by RTECS criteria The substance is classified by IARC as Group 3: NOT classifiable as to its carcinogenicity to humal Evidence of carcinogenicity may be inadequate or	r limited in animal te	-		
TERPINOLENE	Terpinolene was not irritating to human skin when petrolatum for 48 hours under a closed patch in 2- maximization test. However, in a case report and forearms using a machine cleaner containing terp Terpinolene was not irritating in rabbits when appl	4 volunteers, and it was reported that a inolene. Upon patc	was not a sensitiser in the 49-year old woman developed a testing, terpinolene gave a po	sitive reaction.	
MYRCENE	NOTE: beta-Myrcene above 0.25 g/kg was found during pregnancy by gavage	to be detrimental to	the fertility and progeny number	er and development in the rat when given	
	The material may produce severe skin irritation af form of dermatitis is often characterised by skin re			uce a contact dermatitis (nonallergic). This	

433C d-Limonene—Industrial Strength & D-LIMONENE & GAMMA-TERPINENE & BETA-PINENE & TERPINOLENE & MLPHA-PINENE & ALPHA-TERPINENE

The following information refers to contact allergens as a group and may not be specific to this product.

Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's oedema. The pathogenesis of contact eczema involves a cell-mediated (T lymphocytes) immune reaction of the delayed type. Other allergic skin reactions, e.g. contact urticaria, involve antibody-mediated immune reactions. The significance of the contact allergen is not simply determined by its sensitisation potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitising substance which is widely distributed can be a more important allergen than one with stronger sensitising potential with which few individuals come into contact. From a clinical point of view, substances are noteworthy if they produce an allergic test reaction in more than 1% of the persons tested.

Adverse reactions to fragrances in perfumes and in fragranced cosmetic products include allergic contact dermatitis, irritant contact dermatitis, photosensitivity, immediate contact reactions (contact urticaria), and pigmented contact dermatitis. Airborne and connubial contact dermatitis occur.

Intolerance to perfumes, by inhalation, may occur if the perfume contains a sensitising principal. Symptoms may vary from general illness, coughing, phlegm, wheezing, chest-tightness, headache, exertional dyspnoea, acute respiratory illness, hayfever, and other respiratory diseases (including asthma). Perfumes can induce hyper-reactivity of the respiratory tract without producing an IgE-mediated allergy or demonstrable respiratory obstruction. This was shown by placebo-controlled challenges of nine patients to 'perfume mix'. The same patients were also subject to perfume provocation, with or without a carbon filter mask, to ascertain whether breathing through a filter with active carbon would prevent symptoms. The patients breathed through the mouth, during the provocations, as a nose clamp was used to prevent nasal inhalation. The patient's earlier symptoms were verified; breathing through the carbon filter had no protective effect. The symptoms were not transmitted via the olfactory nerve but they may have been induced by trigeminal reflex via the respiratory tract or by the eyes.

Cases of occupational asthma induced by perfume substances such as isoamyl acetate, limonene, cinnamaldehyde and benzaldehyde, tend to give persistent symptoms even though the exposure is below occupational exposure limits.

Inhalation intolerance has also been produced in animals. The emissions of five fragrance products, for one hour, produced various combinations of sensory irritation, pulmonary irritation, decreases in expiratory airflow velocity as well as alterations of the functional observational battery indicative of neurotoxicity in mice. Neurotoxicity was found to be more severe after mice were repeatedly exposed to the fragrance products, being four brands of cologne and one brand of toilet water.

Contact allergy to fragrances is relatively common, affecting 1 to 3% of the general population, based on limited testing with eight common fragrance allergens and about 16 % of patients patch tested for suspected allergic contact dermatitis.

Contact allergy to fragrance ingredients occurs when an individual has been exposed, on the skin, to a suffcient degree of fragrance contact allergens. Contact allergy is a life-long, specifically altered reactivity in the immune system. This means that once contact allergy is developed, cells in the immune system will be present which can recognise and react towards the allergen. As a consequence, symptoms, i.e. allergic contact dermatitis, may occur upon re-exposure to the fragrance allergen(s) in question. Allergic contact dermatitis is an inflammatory skin disease characterised by erythema, swelling and vesicles in the acute phase. If exposure continues it may develop into a chronic condition with scaling and painful fissures of the skin. Allergic contact dermatitis to fragrance ingredients is most often caused by cosmetic products and usually involves the face and/or hands. It may affect fitness for work and the quality of life of the individual. Fragrance contact allergy has long been recognised as a frequent and potentially disabling problem. Prevention is possible as it is an environmental disease and if the environment is modified (e.g. by reduced use concentrations of allergens), the disease frequency and severity will decrease Fragrance contact allergy is mostly non-occupational and related to the personal use of cosmetic products. Allergic contact dermatitis can be severe and widespread, with a significant impairment of quality of life and potential consequences for fitness for work. Thus, prevention of contact sensitisation to fragrances, both in terms of primary prevention (avoiding sensitisation) and secondary prevention (avoiding relapses of allergic contact dermatitis in those already sensitised), is an important objective of public health risk management measure.

Hands: Contact sensitisation may be the primary cause of hand eczema, or may be a complication of irritant or atopic hand eczema. The number of positive patch tests has been reported to correlate with the duration of hand eczema, indicating that long-standing hand eczema may often be complicated by sensitisation. Fragrance allergy may be a relevant problem in patients with hand eczema; perfumes are present in consumer products to which their hands are exposed. A significant relationship between hand eczema and fragrance contact allergy has been found in some studies based on patients investigated for contact allergy. However, hand eczema is a multi-factorial disease and the clinical significance of fragrance contact allergy in (severe) chronic hand eczema may not be clear.

fragrance contact allergy in (severe) chronic hand eczema may not be clear. **Axillae Bilateral axillary** (underarm) dermatitis may be caused by perfume in deodorants and, if the reaction is severe, it may spread down the arms and to other areas of the body. In individuals who consulted a dermatologist, a history of such first-time symptoms was significantly related to the later diagnosis of perfume allergy.

Face Facial eczema is an important manifestation of fragrance allergy from the use of cosmetic products (16). In men, after-shave products can cause an eczematous eruption of the beard area and the adjacent part of the neck and men using wet shaving as opposed to dry have been shown to have an increased risk of of being fragrance allergic.

Irritant reactions (including contact urticaria): Irritant effects of some individual fragrance ingredients, e.g. citral are known. Irritant contact dermatitis from perfumes is believed to be common, but there are no existing investigations to substantiate this, Many more people complain about intolerance or rashes to perfumes/perfumed products than are shown to be allergic by testing. This may be due to irritant effects or inadequate diagnostic procedures. Fragrances may cause a dose-related contact urticaria of the non-immunological type (irritant contact urticaria). Cinnamal, cinnamic alcohol, and Myroxylon pereirae are well recognised causes of contact urticaria, but others, including menthol, vanillin and benzaldehyde have also been reported. The reactions to Myroxylon pereirae may be due to cinnamates. A relationship to delayed contact hypersensitivity was suggested, but no significant difference was found between a fragrance-allergic group and a control group in the frequency of immediate reactions to fragrance ingredients in keeping with a nonimmunological basis for the reactions seen.

Pigmentary anomalies: The term "pigmented cosmetic dermatitis" was introduced in 1973 for what had previously been known as melanosis faciei feminae when the mechanism (type IV allergy) and causative allergens were clarified... It refers to increased pigmentation, usually on the face/neck, often following sub-clinical contact dermatitis. Many cosmetic ingredients were patch tested at non-irritant concentrations and statistical evaluation showed that a number of fragrance ingredients were associated: jasmine absolute, ylang-ylang oil, cananga oil, benzyl salicylate, hydroxycitronellal, sandalwood oil, geraniol, geranium oil.

Photo-reactions Musk ambrette produced a considerable number of allergic photocontact reactions (in which UV-light is required) in the 1970s and was later banned from use in the EU. Nowadays, photoallergic contact dermatitis is uncommon. Furocoumarins (psoralens) in some plant-derived fragrance ingredients caused phototoxic reactions with erythema followed by hyperpigmentation resulting in Berloque dermatitis. There are now limits for the amount of furocoumarins in fragrance products. Phototoxic reactions still occur but are rare.

General/respiratory: Fragrances are volatile and therefore, in addition to skin exposure, a perfume also exposes the eyes and naso-respiratory tract. It is estimated that 2-4% of the adult population is affected by respiratory or eye symptoms by such an exposure. It is known that exposure to fragrances may exacerbate pre-existing asthma. Asthma-like symptoms can be provoked by sensory mechanisms. In an epidemiological investigation, a significant association was found between respiratory complaints related to fragrances and contact allergy to fragrance ingredients, in addition to hand eczema, which were independent risk factors in a multivariate analysis.

Fragrance allergens act as haptens, i.e. low molecular weight chemicals that are immunogenic only when attached to a carrier protein. However, not all sensitising fragrance chemicals are directly reactive, but require previous activation. A **prehapten** is a chemical that itself is non- or low-sensitising, but that is transformed into a hapten outside the skin by simple chemical transformation (air oxidation, photoactivation) and without the requirement of specific enzymatic systems.

In the case of prehaptens, it is possible to prevent activation outside the body to a certain extent by different measures, e.g. prevention of air exposure during handling and storage of the ingredients and the final product, and by the addition of suitable antioxidants. When antioxidants are used, care should be taken that they will not be activated themselves and thereby form new sensitisers.

Prehaptens

Most terpenes with oxidisable allylic positions can be expected to autoxidise on air exposure due to their inherent properties. Depending on the stability of the oxidation products that are formed, a difference in the sensitisation potency of the oxidised terpenes can be seen Autoxidation is a free radical chain reaction in which hydrogen atom abstraction in combination with addition of oxygen forms peroxyl radicals. The reaction shows selectivity for positions where stable radicals can be formed. So far, all fragrance substances that have been investigated with regard to the influence of autoxidation on the allergenic potential, including identification of formed oxidation products, have oxidisable allylic positions that are able to form hydroperoxides and/or hydrogen peroxide as primary oxidation products upon air exposure. Once the

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hydroperoxides have been formed outside the skin they form specific antigens and act as skin sensitisers. Secondary oxidation products such as aldehydes and epoxides can also be allergenic, thus further increasing the sensitisation potency of the autoxidation mixture. The process of photoactivation may also play a role, but further research is required to establish whether this activation route is currently underestimated in importance due to insufficient knowledge of the true haptens in this context.

It should be noted that activation of substances via air oxidation results in various haptens that might be the same or cross-reacting with other haptens (allergens). The main allergens after air oxidation of linalool and linalyl acetate are the hydroperoxides. If linalyl acetate is chemically hydrolysed outside the skin it can thereafter be oxidised to the same haptens as seen for linalool. A corresponding example is citronellol and citronellyl acetate. In clincal studies, concomitant reactions to oxidised linalool and oxidised linalyl acetate have been observed. Whether these reactions depend on cross-reactivity or are due to exposure to both fragrance substances cannot be elucidated as both have an allergenic effect themselves. Linalool and linalyl acetate are the main components of lavender oil. They autoxidise on air exposure also when present in the essential oil, and form the same oxidation products found in previous studies of the pure synthetic terpenes. Experimental sensitisation studies showed that air exposure of lavender oil increased the sensitisation potency. Patch test results in dermatitis patients showed a connection between positive reactions to oxidised linalool. linalyl acetate and lavender oil.

Prohaptens

Compounds that are bioactivated in the skin and thereby form haptens are referred to as prohaptens.

In the case of prohaptens, the possibility to become activated is inherent to the molecule and activation cannot be avoided by extrinsic measures. Activation processes increase the risk for cross-reactivity between fragrance substances. Crossreactivity has been shown for certain alcohols and their corresponding aldehydes, i.e. between geraniol and geranial (citral) and between cinnamyl alcohol and cinnamal.

The human skin expresses enzyme systems that are able to metabolise xenobiotics, modifying their chemical structure to increase hydrophilicity and allow elimination from the body. Xenobiotic metabolism can be divided into two phases: phase I and phase II. Phase I transformations are known as activation or functionalisation reactions, which normally introduce or unmask hydrophilic functional groups. If the metabolites are sufficiently polar at this point they will be eliminated. However, many phase I products have to undergo subsequent phase II transformations, i.e. conjugation to make them sufficiently water soluble to be eliminated. Although the purpose of xenobiotic metabolism is detoxification, it can also convert relatively harmless compounds into reactive species. Cutaneous enzymes that catalyse phase I transformations include the cytochrome P450 mixed-function oxidase system, alcohol and aldehyde dehydrogenases, monoamine oxidases, flavin-containing monooxygenases and hydrolytic enzymes. Acyltransferases, glutathione S-transferases, UDP-glucuronosyltransferases and sulfotransferases are examples of phase II enzymes that have been shown to be present in human skin. These enzymes are known to catalyse both activating and deactivating biotransformations, but the influence of the reactions on the allergenic activity of skin sensitisers has not been studied in detail. Skin sensitising prohaptens can be recognised and grouped into chemical classes based on knowledge of xenobiotic bioactivation reactions, clinical observations and/or in vivo and in vitro studies of sensitisation potential and chemical reactivity.

QSAR prediction: The relationships between molecular structure and reactivity that form the basis for structural alerts are based on well established principles of mechanistic organic chemistry. Examples of structural alerts are aliphatic aldehydes (alerting to the possibility of sensitisation via a Schiff base reaction with protein amino groups), and alpha,beta-unsaturated carbonyl groups, C=C-CO- (alerting to the possibility of sensitisation via Michael addition of protein thiol groups). Prediction of the sensitisation potential of compounds that can act via abiotic or metabolic activation (pre- or prohaptens) is more complex compared to that of compounds that act as direct haptens without any activation. The autoxidation patterns can differ due to differences in the stability of the intermediates formed, e.g. it has been shown that autoxidation of the structural isomers linalool and geraniol results in different major haptens/allergens. Moreover, the complexity of the prediction increases further for those compounds that can act both as pre- and prohaptens. In such cases, the impact on the sensitisation potency depends on the degree of abiotic activation (e.g. autoxidation) in relation to the metabolic activation.

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d-Limonene is readily absorbed by inhalation and ingestion. Dermal absorption is reported to be lower than by the inhalation route. d-Limonene is rapidly distributed to different tissues in the body, readily metabolised and eliminated primarily through the urine.

Limonene exhibits low acute toxicity by all three routes in animals. Limonene is a skin irritant in both experimental animals and humans. Limited data are available on the potential to cause eye and respiratory irritation. Autooxidised products of d-limonene have the potential to be skin sensitisers. Limited data are available in humans on the potential to cause respiratory sensitisation. Autooxidation of limonene occurs readily in the presence of light and air forming a variety of oxygenated monocyclic terpenes. Risk of skin sensitisation is high in situations where contact with oxidation products of limonene occurs.

Renal turnours induced by limonene in male rats is though to be sex and species specific and are not considered relevant to humans. Repeated exposure affects the amount and activity of liver enzymes, liver weight, blood cholesterol levels and bile flow in animals. Increase in liver weight is considered a physiological adaption as no toxic effects on the liver have been reported. From available data it is not possible to identify an NOAEL for these effects. Limonene is neither genotoxic or teratogenic nor toxic to the reproductive system.

Monomethyltin chloride, thioglycolate esters, and tall oil ester reaction product:

Monomethyltin trichloride (MMTC, CAS RN: 993-16-8), monomethyltin tris[2-ethylhexylmercaptoacetate (MMT (EHTG; MMT (2-EHMA), CAS RN: 57583-34-3), monomethyltin tris[isooctylmercaptoacetate (MMT(IOTG), CAS RN: 54849-38-6) and methyltin reverse ester tallate reaction product (TERP, CAS RNs: 201687-58-3, 201687-57-2, 68442-12-6, 151436-98-5) are considered one category of compounds for mammalian studies via the oral route. The justification for this category is based on structural similarities and the demonstrated rapid conversion of all of the esters to the MMTC when placed in simulated mammalian gastric contents [0.07M HCI] under physiological conditions. For the MMT(EHTG) >90% conversion to MMTC occurred within 0.5 hours. For TERP, 68% of the monomethyltin portion of the compound was converted to MMTC within 1 hour. Thus, MMTC is the appropriate surrogate for mammalian toxicology studies via the oral route.

TERP is a reaction product of MMTC and dimethyltin dichloride (DMTC), Na2S, and tall oil fatty acid [a mixture of carboxylic acids, predominantly C-18]. The reaction product is a mixture of carboxylic esters and includes short oligomers of mono/dimethyltins bridged by sulfide groups. Although the tall oil component of TERP is not structurally similar to EHTG, TERP s conversion to MMTC justifies its inclusion. While the contribution of the various ligands to the overall toxicity may vary, the contribution is expected to be small relative to that of the MMTC. Further, the EHTG ligand from MMT(EHTG) is likely to be more toxic than the oleic or linoleic acid from TERP so inclusion of TERP in the category is a rather conservative approach. The other possible degradate of tall oil and EHTG is 2-mercaptoethanol (2-ME), and it is common to both ligands. Data for MMT(EHTG) and MMT(IOTG) are used interchangeably because they are isomers differing only slightly in the structure of the C-8 alcohol of the mercaptoester ligand. In addition, the breakdown products of MMT(EHTG) and MMT(IOTG) are the thioglycolate esters (EHTG and IOTG), which have the common degradates, thioglycolic acid and C-8 alcohols (either 2-ethylhexanol or isooctanol). EHTG and IOTG also have similar physicochemical and toxicological properties.

D-LIMONENE & GAMMA-TERPINENE & BETA-PINENE & TERPINOLENE & MYRCENE & ALPHA-PINENE & ALPHA-TERPINENE

The chemistry of the alkyl organotins has been well studied. For organotins, like MMT(EHTG), the alkyl groups are strongly bound to tin and remain bound to tin under most reaction conditions. However, other ligands, such as carboxylates or sulfur based ligands (EHTG), are more labile and are readily replaced under mild reaction conditions. To assess the reactivity of MMT(EHTG) under physiological conditions simulating the mammalian stomach, an in-vitro hydrolysis test was performed. This in vitro test provides chemical information that strongly suggests both the probable in vivo metabolic pathway and the toxicokinetics of the MMT(EHTG) substance. This result verifies that under physiological conditions MMT(EHTG) is rapidly and essentially completely converted to the corresponding monomethyltin chloride, MMTC. Acute toxicity:

The majority of toxicology studies were conducted with commercial mixtures having high monoalkyltin to dialkyltin ratios.

Gastric hydrolysis studies were conducted with TERP and MMT(EHTG) in which simulated gastric fluid [0.07M HCl under physiological conditions] converted these substances to methyltin chloride and the respective organic acids. Based on data for DMTC and DMT esters the dermal penetration of MMTC and its esters is expected to be low.

Oral:

Acute oral LD50 values for MMTC, MMT(EHTG), MMT(IOTG), and TERP indicated low to moderate toxicity; the most reliable data place the LD50s in the range of 1000 mg/kg.

The acute oral LD50 of MMT(2-EHMA) was 880 mg/kg in rats. Clinical observations included depression, comatose, piloerection, eye squinting, hunched posture, laboured breathing, ataxia, faecal/urine stains, and masticatory movement. No gross pathological changes were reported in surviving animals.

Dermal

Acute dermal LD50 values were =1000 mg/kg bw, and inhalation LC50 was >200 mg/L. MMTC was corrosive to skin and assumed corrosive to

eyes.

The acute dermal LD50 of MMT(2-EHMA) in rabbits was 1000 (460 to 2020) mg/kg for females and 2150 (1000 to 4620) mg/kg for males. There were no deaths at 215 and 464 mg/kg, 0/2 males and 1/2 females died at 1000 mg/kg and 1/2 males and 2/2 females died at 2150 mg/kg. All animals died at 4640 and 10 000 mg/kg. A variety of clinical abnormalities were observed and disappeared in surviving animals by the end of the exposure period. Clinical signs included death, uncoordinated movements, shaking, and hypersensitivity to external stimuli.

Gross necropsy results for animals that died during the study included irritated intestines; blanched stomach; reddened lungs; pale or congested kidneys; and oral, ocular and/or nasal discharges

Inhalation:

The acute inhalation LC50 of MMT(2-EHMA) was 240 mg/L.

The study reported an acute inhalation LC50 of 240 (212 to 271) mg/L in a 1-hr aerosol exposure to male and female rats. The mortality rate was 2/10, 6/10, 9/10 and 10/10 animals at dose levels of 200, 250, 300 and 250 mg/L/hr, respectively. Gross findings included blood in lungs, dark spleen, pale kidneys, fluid in the chest cavity, and heart failure. The slope of the dose-response curve was 1.22 (1.04 to 1.43). Irritation:

MMT(IOTG)/(EHTG) are irritating to skin, but not to eyes.

Sensitisation:

No data on sensitization are available on MMT(EHTG/(IOTG), but the hydrolysis products EHTG or IOTG are sensitizers. No primary irritation data were available for TERP, but it was a sensitizer in the mouse Local Lymph Node Assay.

Topical application with 5, 25 and 50 % v/v MMT(2-EHMA) elicited a stimulation index (SI) of 2.13, 7.25 and 9.05, respectively in a local lymph node assay (OECD 429), thus the material is a sensitiser.

Repeat dose toxicity:

There are no repeated-dose studies for the category members via the dermal or inhalation routes.

In a 90-day repeated dose oral study of MMTC, treatment-related changes were limited to the high dose group (750 ppm in diet; 50 mg/kg bw/d with some gender-related variation). Organ weight changes (adrenal, kidney, thymus, spleen, brain, epididymides), haematology, clinical chemistry, and urinalysis changes were noted, but histopathology only confirmed effects in the thymus and brain. The critical toxic effects were neurotoxicity and thymic atrophy. Both sexes had decreased cortex/medulla ratios in the thymus. In the brain there was loss of perikarya of neuronal cells in the pyramidal layer of the Hippocampus CA1/2 in both sexes, and in males there was loss of perikarya in the piriform cortex. The NOAEL was 150 ppm (10 mg/kg bw/d). Another 90-day dietary study using MMTC showed increased relative kidney weights and slight to moderate epithelial hyperplasia of the bladder in females at the lowest dose (NOAEL <20 ppm in diet [<1-3.6 mg/kg bw/d]) and additional effects including increased relative thymus weights in females and urinalysis results in both sexes at higher doses.

A 90-day dietary study with dose levels of 30, 100, 300, and 1000 ppm TERP in the diet resulted in slightly decreased food intake, body and organ weight changes, and decreased specific gravity of the urine at the highest dose. The NOAEL was 300 ppm in diet (equivalent to 15 mg/kg bw/d). A 28-day gavage study using TERP showed changes in clinical chemistry and slight differences in haematology at 150 mg/kg bw/d and higher. The NOAEL was 50 mg/kg bw/d.

The effects of MMT(IOTG) were evaluated in a 90-day dietary study using doses of 100, 500, and 1500 ppm (decreased from 2500 ppm) in the diet. Based on clinical chemistry effects at 500 ppm and other effects at higher doses, the NOAEL was 100 ppm in diet (approximately 6-21 mg/kg bw/d).

Neurotoxicity:

In a guideline 90-day subchronic dietary study conducted in Wistar rats, effects occurred at the high dose of 750 ppm MMT(2-EHMA, (equivalent to 49.7 mg/kg bw/day in males and 53.6 mg/kg bw/day in females), which consisted of changes in neurobehavioral parameters and associated brain histopathology. The NOAEL was the next lower dose of 150 ppm (equivalent to 9.8 mg/kg bw/day in males and 10.2 mg/kg bw/day in females

Immunotoxicity:

Immune function was assessed in male Sprague-Dawley rats exposed to the mixture of organotins used in PVC pipe production. Adult male rats were given drinking water for 28 d containing a mixture of dibutyltin dichloride (DBTC), dimethyltin dichloride (DMTC), monobutyltin trichloride (MBT), and monomethyltin trichloride (MMT) in a 2:2:1:1 ratio, respectively, at 3 different concentrations (5:5:2.5:2.5, 10:10:5:5, or 20:20:10:10 mg organotin/L). Rats were also exposed to MMT alone (20 or 40 mg MMT/L) or plain water as a control. Delayed-type hypersensitivity, antibody synthesis, and natural killer cell cytotoxicity were evaluated in separate endpoint groups immediately after exposure ended.

The evaluated immune functions were not affected by the mixture or by MMT alone. The data suggest that immunotoxicity is unlikely to result from the concentration of organotins present in drinking water delivered via PVC pipes, as the concentrations used were several orders of magnitude higher than those expected to leach from PVC pipes

Genotoxicity:

In a guideline 90-day subchronic dietary study in rats, with MMT(2-EHMA), based on the changes in neurobehavioral parameters and associated brain histopathology that occurred at the high dose of 750 ppm (equivalent to 49.7 mg/kg bw/day in males and 53.6 mg/kg bw/day in females), as well as changes in haematology, clinical chemistry, urinalysis, organ weights, and pathology of the thymus at the same dose, the NOAEL was the next lower dose of 150 ppm (equivalent to 9.8 mg/kg bw/day in males and 10.2 mg/kg bw/day in females).

The monomethyltin compounds as a class are not mutagenic in the Ames test. TERP was positive in a human lymphocyte assay. MMTC was equivocal for induction of micronucleated polychromatic erythrocytes (MPEs) in an in vivo rat micronucleus test (OECD 474). In this study a statistically significant increase in MPE was observed only at 24 h and not at 48 h after treatment and there was no dose-response. Based on these observations the overall conclusion is that MMTC does not have genotoxic potential.

From the results obtained in a micronucleus test with MMT(2-EHMA), it was demonstrated that the substance was weakly genotoxic to bone marrow cells of rats and that the substance has the potential to induce damage to the mitotic spindle apparatus of the bone marrow target cells. Carcinogenicity:

In a limited carcinogenicity study, MMT(EHTG) produced no compound-related macroscopic or microscopic changes in rats fed 100 ppm in the diet for two years.

Toxicity to reproduction:

In the reproductive satellite portion of the 90-day study using MMTC (with dose levels of 30, 150, and 750 ppm in the diet), post-implantation loss, decreased litter size and increased neonatal mortality occurred at 750 ppm (26-46 mg/kg bw/d for females). Maternal gestational body weights were transiently suppressed and other maternal toxicity was inferred from the repeated dose results at this dose. There were no malformations observed at any dose. The NOAEL for maternal toxicity, and reproductive, and foetotoxic effects was 150 ppm in the diet (6-12 mg/kg bw/d). SIDS Initial Assessment Profile (SIAM 23 2006)

ECHA Registration Dossier for MMT(2-EHMA) (ethylhexyl 10-ethyl-4-[[2-[(2-ethylhexyl)oxy]-2-oxoethyl]thio]-4-methyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate)

GAMMA-TERPINENE & BETA-PINENE & TERPINOLENE & MYRCENE & ALPHA-PINENE

Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound. Key criteria for the diagnosis of RADS include the absence of preceding respiratory disease, in a non-atopic individual, with abrupt onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. A reversible airflow pattern, on spirometry, with the presence of moderate to severe bronchial hyperreactivity on methacholine challenge testing and the lack of minimal lymphocytic inflammation, without eosinophilia, have also been included in the criteria for diagnosis of RADS. RADS (or asthma) following an irritating inhalation is an infrequent disorder with rates related to the concentration of and duration of exposure to the irritating substance. Industrial bronchitis, on the other hand, is a disorder that occurs as result of exposure due to high concentrations of irritating substance (often particulate in nature) and is completely reversible after exposure ceases. The disorder is characterised by dyspnea, cough and mucus production.

GAMMA-TERPINENE & TERPINOLENE & MYRCENE & ALPHA-TERPINENE

For monoterpenes:

The chemical category designated terpenoid hydrocarbons includes three simple C10 isomeric monocyclic terpene hydrocarbons (*d*-limonene, *dl*-limonene, and terpinolene) two simple C10 acyclic terpene hydrocarbons (*beta*-myrcene and dihydromyrcene) and mixtures composed

primarily of d-limonene, dl-limonene (dipentene), terpinolene, myrcene, and alphaand beta-pinene

Monoterpene hydrocarbons are mainly released by coniferous woodland such as pine trees, cedars, redwood and firs. To a lesser extent, they are also produced and released by deciduous plants. They are common components of traditional foods occurring in essentially all fruits and vegetables

Members of this chemical category are of very low acute toxicity

Studies of terpene hydrocarbons indicate that they are rapidly absorbed, distributed, metabolised and excreted. The principal metabolic pathway involves side chain oxidation to yield monocyclic terpene alcohols and carboxylic acids. These metabolites are mainly conjugated with glucuronic acid and excreted in the urine, or to a lesser extent in the feces. A secondary pathway involves epoxidation of either the exocyclic or endocyclic double bond yielding an epoxide that is subsequently detoxicated via formation of the corresponding diol or conjugation with glutathione. Although some species- and sex-specific differences exist, studies for d-limonene and beta-myrcene indicate that the monoterpene hydrocarbons in this chemical category will participate in common pathways of absorption, distribution, metabolism and excretion.

Genotoxicity: Based on the results of this in vivo genotoxicity assay and the numerous in vitro genotoxicity assays, it is unlikely that any of these materials would exhibit a significant genotoxic potential in vivo.

Carcinogenicity: Under the conditions of 2-year gavage studies, conducted by NTP, there was clear evidence of carcinogenic activity of d-limonene for male F344/N rats as shown by increased incidences in tubular cell hyperplasia, adenomas, and adenocarcinomas of the kidney. There was no evidence of carcinogenic activity of d-limonene for female rats receiving 300 or 600 mg/kg bw/d. It has been demonstrated that renal lesions, which were observed in the NTP study, resulted from the accumulation of aggregates of alpha-2 microglobulin (a low molecularweight protein synthesised in the liver) and limonene-1,2-epoxide in the P2 segment of the renal proximal tubule. While humans produce low molecular weight serum proteins, which are reabsorbed by the kidney, there is no evidence that a similar alpha-2 microglobulin is produced. The kidney changes seen in male rats administered limonene have been well characterized, and are known to be specific to the male rat and of no significance in human risk assessment.

Reproductive toxicity: Substances within this chemical category exhibit low reproductive toxicity potential. This is based on the results of three reproductive toxicity assays, using sweet orange peel oil predominantly composed of d-limonene and beta-myrcene

Developmental toxicity: Given the results of six developmental toxicity assays using limonene, sweet orange oil and beta-myrcene, it may be concluded that the substances within this chemical category exhibit low developmental toxicity potential

GAMMA-TERPINENE & MYRCENE

The material may cause skin irritation after prolonged or repeated exposure and may produce a contact dermatitis (nonallergic). This form of dermatitis is often characterised by skin redness (erythema) and swelling the epidermis. Histologically there may be intercellular oedema of the spongy layer (spongiosis) and intracellular oedema of the epidermis.

Acute toxicity: The literature abounds with clinical reports of accidental and intentional acute poisoning with pinene-based turpentine. Rat oral LD50 values are available for alpha-pinene, beta-pinene, camphene and turpentine oil and indicate these materials to be very low in oral acute toxicity with LD50 values in the range from 3388 mg/kg to greater than 5000 mg/kg. Rabbit dermal LD50 values similarly indicate very low toxicities with values greater than the limit doses of 2000 or 5000 mg/kg.

Acute inhalation toxicity has been measure in different animal species. The acute LC50 was reported to be 13,500 mg/m3 in rats, 13,500 mg/m3 in guinea pigs, and 9000 mg/m3 in mice. The acute inhalation LC50 of commercial grade turpentine in Wistar rats is reported to be in the range of 12,000-20,000 mg/m3 for 1 to 6 hour exposures and the LC50 for a 2-hour exposure in Swiss-Webster mice is 29,000 mg/m3. Based on these results the acute oral, dermal, and inhalation toxicities of bicyclic terpene hydrocarbons is concluded to be low.

Repeat dose toxicity: A 28-day repeat dose study has been performed with camphene according to an OECD Guideline 407 in both sexes of Wistar rats. Animals of both sexes at the 1000 mg/kg bw/day dose exhibited vacuolization of hepatocytes and increase liver weights. Male rats also exhibited alpha-2-microglobulin-type nephrotoxicity at all dose levels.

Subsequent investigations have shown that the alpha-2-microglobulin nephropathy found in the F344/N male rat does not develop in mammals that do not express the hepatic form of alpha-2-microglobulin (e.g. other strains of rats, mice, dogs, humans). Therefore, the nephrotoxicity observed in the camphene study in male F344 rats is not relevant to the human health risk assessment. Based on liver toxicity, the NOAEL for this study is concluded to be 250 mg/kg bw/day

BETA-PINENE & ALPHA-PINENE

Reproductive toxicity: In the a-animal species study, no reproductive effects were observed when dose levels of up to 260 to 600 mg/kg bw of an essential oil predominantly composed of bicyclic terpene hydrocarbons (alpha-pinene, beta-pinene, and sabinene) was administered daily to mice, rats, or hamsters during gestation. When this data is combined with the fact that no adverse effects were observed to the reproductive organs in a 28-day study with camphene at dose levels up to 250 mg/kg bw/day, it is concluded that bicyclic terpene hydrocarbons including alpha-pinene and beta-pinene are not reproductive toxicants

Two ninety day inhalation studies have been performed for alpha-pinene in which a full complement of male and female sex organs and tissues were subjected to histopathological examination. Both studies reported no microscopic changes that could be associated with exposure to the test substance. Taking into account the lack of any effects to females in a earlier teratology study, the absence of any maternal or developmental effects in a reproductive/developmental study of a pinene-based oil and for a structurally related monoterpene hydrocarbon, myrcene, it can be concluded that the members of this category show no significant reproductive or developmental toxicity

Developmental toxicity: Based on the NOAELs for maternal and developmental toxicity in studies with camphene (250 and 1000 mg/kg bw/day) and a terpene hydrocarbon mixture containing alpha- and beta-pinene and camphene (688 mg/kg bw/day), and the lack of any signs of maternal or developmental toxicity in a mice,

rats, or hamsters given 260 to 600 mg/kg bw/day of a mixture composed primarily (>80%) of alpha- and beta-pinene and sabinene, it is concluded that bicyclic terpene hydrocarbons are not maternal or developmental toxicants.

Genotoxicity:

In vitro: In vitro genotoxicity assays available for alpha-pinene, beta-pinene and camphene demonstrate that these substances have a little, if any, genotoxic potential. In standard Ames assays of alpha-pinene, beta-pinene and camphene, Salmonella typhimurium strains TA97, TA98, TA100, TA1535, TA1537, and TA1538 provided no evidence of mutagenicity at any dose tested.

In vivo: Based on the lack of any evidence of genotoxicity in numerous in vitro assays with and without metabolic activation, it is unlikely that any of these bicyclic terpenes would exhibit a significant genotoxic potential in vivo.

Acute Toxicity	×	Carcinogenicity	×
Skin Irritation/Corrosion	✓	Reproductivity	×
Serious Eye Damage/Irritation	×	STOT - Single Exposure	×
Respiratory or Skin sensitisation	✓	STOT - Repeated Exposure	×
Mutagenicity	×	Aspiration Hazard	✓

Leaend:

X - Data either not available or does not fill the criteria for classification

– Data available to make classification

11.2.1. Endocrine Disruption Properties

Not Available

SECTION 12 Ecological information

C d-Limonene—Industrial	Endpoint		Test Duration (hr)		Species Value			Source		ırce
Strength	Not Available Not Available		Not Available		Not Availab	ole	Not Available	е	Not	Available
	Endpoint	Te	st Duration (hr)		Species				/alue	Source
	NOEC(ECx)	50			Crustacea			(0.05mg/l	2
d-limonene	LC50	96			ish).46mg/l	2
	EC50	72	<u> </u>		Algae or other a	quatic plants).214mg/l	2
	EC50	48	1		Crustacea				0.307mg/l	2
	Endpoint		Duration (hr)	-	cies			Value		Source
gamma-terpinene	EC50(ECx)	96h		Fish)			2.792	mg/l	2
3	EC50	72h		Alga	ae or other aqua	tic plants		>10.8	2mg/l	2
	EC50	48h		Cru	stacea			2.99-4	4.07mg/l	4
	Endpoint	Tes	Duration (hr)	s	pecies			V	/alue	Source
	EC10(ECx)	48h	, ,		lgae or other aq	uatic plants).378mg/l	2
beta-pinene	EC50	72h			lgae or other aq).7mg/l	2
	LC50	96h			ish	aato pianto).557mg/l	2
	EC50	48h			rustacea				.09mg/l	2
	1									
	Endpoint	Tes	: Duration (hr)	S	pecies			V	/alue	Source
	EC10(ECx)	72h		А	lgae or other aq	uatic plants		0).054mg/l	2
terpinolene	LC50	96h		F	ish			0).805mg/l	2
·	EC50	72h		А	lgae or other aq	uatic plants		0).302mg/l	2
	EC50	48h		С	rustacea	•		0).634mg/l	2
	Endpoint	Tes	t Duration (hr)		Species				Value	Source
	EC50(ECx)	72h			Algae or other ac	quatic plants			0.31mg/l	2
myrcene	EC50	72h			Algae or other ac	quatic plants			0.31mg/l	2
	EC50	48h		(Crustacea				1.47mg/l	2
	Endpoint	Te	st Duration (hr)		Species				/alue	Source
	NOEC(ECx)	48			Algae or other a	nuatic plante).131mg/l	2
alpha-pinene	LC50	96			Fish	4 datio pianto			0.303mg/l	2
	EC50	48			Crustacea				0.475mg/l	2
	2000	10	•		Jidolaooa				7. 17 Omg/1	
	Endpoint		Test Duration (hr)			Species	,	/alue		Source
alpha-terpinene	EC50(ECx)		48h		Crustacea			1.7mg/l		2
	EC50		48h			Crustacea		I.7mg/	1	2
Legend:			oxicity Data 2. Europe Toxicity Data 5. ECET							

Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Do NOT allow product to come in contact with surface waters or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment wash-waters.

Wastes resulting from use of the product must be disposed of on site or at approved waste sites.

Monomethyltin chloride, thioglycolate esters, and tall oil ester reaction product

Monomethyltin trichloride (MMTC, CAS RN: 993-16-8), monomethyltin tris[2-ethylhexylmercaptoacetate (MMT (EHTG; MMT (2-EHMA)), CAS RN: 57583-34-3), monomethyltin tris[isooctylmercaptoacetate (MMT(IOTG), CAS RN: 57583-34-3) and methyltin reverse ester tallate reaction product (TERP, CAS RNs: 201687-58-3, 201687-57-2, 68442-12-6, 151436-98-5) are considered as a single category of compounds for the purpose of an environmental assessment.

All share a MMTC as a building block.

Environmental fate:

MMT(IOTG), MMT(EHTG), and TERP are sparingly soluble in water (0.6-10.7 mg/L). In water, these monomethyltin compounds undergo rapid degradation by hydrolysis. Although there is no stability data for MMT(EHTG)/(IOTG) or TERP, data for other organotins [DOTC, DBTL and DBT(EHTG)] indicate that the monomethyltin compounds are expected to hydrolyze within minutes to hours in water. The thioester ligands on MMT(EHTG)/(IOTG) will be rapidly displaced to form mono-methyltin hydroxide which eventually precipitates as the oxide. It is also possible that the labile ligands can be displaced by other anions in the medium. The displaced thioester ligands, EHTG/IOTG, can also undergo further hydrolysis of the ester linkage to form thioglycolic acid and ethylhexanol or isooctanol, respectively.

MMTC is a solid at room temperature and melts at 43 deg C, boils at 171 deg C, has a calculated vapour pressure of 1.7 hPa at 25 deg C, and is soluble in water (1038 g/L at 20 deg C). The measured log Kow is -0.9 and MMTC is not readily biodegradable. Atmospheric degradation occurs by photochemical induced hydroxyl radicals, with a half-life of 15.7 days. A Henry s Law constant of 3.83 x 10-7 atm-m3/mol predicts MMTC will volatilize from surface water (t1/2 = 99 days and 3 years for model river and lake, respectively). If released to the environment, MMTC is expected to partition primarily into water (54%) and soil (43%).

In water, MMTC undergoes rapid degradation by hydrolysis and is expected to hydrolyze within minutes. It is expected that the chlorines in MMTC will be displaced to form

mono-methyltin hydroxide which eventually precipitates as the oxide (the alkyltin moiety (MMT) was hydrolytically stable at pH 4, 7, and 9 (t1/2 > 1 year at 25 deg C)). TERP is a liquid at room temperature, boils at 216 deg C, and has a calculated vapour pressure of 0.2 hPa at 25 deg C. TERP is slightly soluble in water (4.4 mg/L), highly hydrophobic (log Kow = 25.5), has low potential for bioaccumulation (log BCF = 2.0), and is readily biodegradable. It is degraded atmospherically by hydroxyl radicals and ozone, with a half-life of 0.5 hours. If released to the environment, TERP is predicted to partition primarily to sediment (99%).

MMT(EHTG) is a liquid at room temperature and has a freezing point of -85 to -65 deg C, decomposes at 260 deg C has a derived vapour pressure of 0.02 hPa at 25 deg C, a calculated log Kow of 10.98, is slightly soluble in water (1.8-6 mg/L), and is readily biodegradable. MMT(EHTG) is also degraded atmospherically, with a half-life of 6.3 hours. A Henry s Law constant of 3.18×10+4 atm-m3/mol predicts MMT(EHTG) will volatilize from surface water (t1/2 = 8 hours and 11 days for a model river and lake, respectively). If released to the environment, MMT(EHTG) is expected to partition primarily into sediment (71%) and soil (25%). Bioavailability:

The considerable difference in the structures of the labile ligands causes differences in water solubility between the alkyltin chloride and thioesters affecting their respective bioavailabilities and distribution in the environment. Furthermore, MMT(EHTG) and MMT(IOTG) will degrade in aqueous solution such that organisms will be exposed to the parent material and their different degradation products. MMTC is not an appropriate surrogate for the thioesters or TERP for the ecotoxicity and environmental fate endpoints. **Ecotoxicity**

In the ecotoxicity tests the organisms were most likely exposed to parent substance as well as hydrolysis/degradation products.

 $MMTC \ was \ not \ acutely \ toxic \ to \ zebra \ fish \ (Brachydanio \ rerio) \ (96-h \ LC50 > 102 \ mg/L) \ or \ Daphnia \ magna \ (48-h \ EC50 > 101 \ mg/L). \ MMTC \ inhibited \ the \ growth \ (72-h \ EC50 = 0.03 \ mg/L) \ or \ Daphnia \ magna \ (48-h \ EC50 > 101 \ mg/L).$ mg/L) and biomass (72-h EC50 = 0.02 mg/L) of the green alga Scenedesmus subspicatus (NOEC = 0.007 mg/L). MMTC was not acutely toxic to earthworms at nominal concentrations up to 1000 mg/kg.

TERP was not acutely toxic to rainbow trout (Oncorhynchus mykiss) (96-hr LC50 >4.4 mg/L), inhibited D. magna survival and mobility (48-h EC50 = 0.27 mg/L), and inhibited growth of the freshwater green alga Pseudokirchneriella subcapitata was (72-h EC50 = 0.64 mg/L; NOEC = 0.28 mg/L).

MMT(EHTG) was not acutely toxic to B. rerio (LC50 > 6 mg/L; NOEC = 3.6 mg/L) and did not inhibit the growth of S. subspicatus (72-h EC50 > 1.84 mg/L; NOEC = 0.6 mg/L). The 21-d EC50 for reproduction in a chronic Daphnia magna study was > 0.134 mg/L (NOEC = 0.134 mg/L).

Substances containing unsaturated carbons are ubiquitous in indoor environments. They result from many sources (see below). Most are reactive with environmental ozone and many produce stable products which are thought to adversely affect human health. The potential for surfaces in an enclosed space to facilitate reactions should be considered. Source of unsaturated substances Unsaturated substances (Reactive Emissions)

personal care products)

houseplants

Carpets and carpet backing Linoleum and paints/polishes containing linseed oil Latex paint

Certain cleaning products, polishes waxes, air fresheners

Natural rubber adhesive

Photocopier toner, printed paper, styrene polymers

Environmental tobacco smoke

Soiled clothing, fabrics, bedding

Soiled particle filters

Ventilation ducts and duct liners

'Urban grime Perfumes, colognes, essential oils

(e.g. lavender, eucalyptus, tea tree) terpinene-4-ol, gamma-terpinene

Overall home emissions

Isoprene, nitric oxide, squalene, unsaturated sterols, oxidation products

Soft woods, wood flooring, including Isoprene, limonene, alpha-pinene, other terpenes and

4-Phenylcyclohexene, 4-vinylcyclohexene, styrene, 2-ethylhexyl acrylate, unsaturated fatty acids and esters

Linoleic acid. linolenic acid

Residual monomers Limonene, alpha-pinene, terpinolene, alpha-terpineol,

and other sesquiterpenes Isoprene, terpenes

Styrene

Styrene, acrolein, nicotine

Squalene, unsaturated sterols, oleic acid and other saturated fatty acids

Unsaturated fatty acids from plant waxes, leaf litter, and

other vegetative debris; soot; diesel particles Unsaturated fatty acids and esters, unsaturated oils,

Polycyclic aromatic hydrocarbons

Limonene, alpha-pinene, linalool, linalyl acetate,

Limonene, alpha-pinene, styrene

Major Stable Products produced following reaction with ozone. Methacrolein, methyl vinyl ketone, nitrogen dioxide, acetone, 6MHQ, geranyl acetone. Occupants (exhaled breath, ski oils, oleic acid and other unsaturated fatty acids, unsaturated 40PA, formaldehyde, nonanol, decanal, 9-oxo-nonanoic acid, azelaic acid, nonanoic

> Formaldehyde, 4-AMC, pinoaldehyde, pinic acid, pinonic acid, formic acid, methacrolein, methyl vinyl ketone, SOAs including ultrafine particles

Formaldehyde, acetaldehyde, benzaldehyde, hexanal, nonanal, 2-nonenal

Propanal, hexanal, nonanal, 2-heptenal, 2-nonenal, 2-decenal, 1-pentene-3-one, propionic acid, n-butyric acid

Formaldehyde

Formaldehyde, acetaldehyde, glycoaldehyde, formic acid, acetic acid, hydrogen and linalool, linalyl acetate and other terpenoids, longifolene organic peroxides, acetone, benzaldehyde, 4-hydroxy-4-methyl-5-hexen-1-al, 5-ethenyldihydro-5-methyl-2(3H)-furanone, 4-AMC, SOAs including ultrafine particles Formaldehyde, methacrolein, methyl vinyl ketone

Formaldehyde, benzaldehyde

Formaldehyde, benzaldehyde, hexanal, glyoxal, N-methylformamide, nicotinaldehyde, cotinine

Acetone, geranyl acetone, 6MHO, 40PA, formaldehyde, nonanal, decanal, 9-oxo-

nonanoic acid, azelaic acid, nonanoic acid Formaldehyde, nonanal, and other aldehydes; azelaic acid; nonanoic acid; 9-oxo-

nonanoic acid and other oxo-acids; compounds with mixed functional groups (=O, -OH, and -COOH)

C5 to C10 aldehydes

Oxidized polycyclic aromatic hydrocarbons

Formaldehyde, 4-AMC, acetone, 4-hydroxy-4-methyl-5-hexen-1-al, 5-ethenyl-dihydro-5-methyl-2(3H) furanone, SOAs including ultrafine particles

Formaldehyde, 4-AMC, pinonaldehyde, acetone, pinic acid, pinonic acid, formic acid, benzaldehyde, SOAs including ultrafine particles

Abbreviations: 4-AMC, 4-acetyl-1-methylcyclohexene; 6MHQ, 6-methyl-5-heptene-2-one, 4OPA, 4-oxopentanal, SOA, Secondary Organic Aerosols

Reference: Charles J Weschler; Environmental Helath Perspectives, Vol 114, October 2006

Atmospheric fate: Due to the high volatility of limonene the atmosphere is expected to be the major environmental sink for this chemical where it is expected to undergo gas-phase reactions with photochemically produced hydroxyl radicals, ozone and nitrate radicals. Calculated lifetimes for the reaction of d-limonene with photochemically produced hydroxyl radicals range from 0.3-2 h based on experimentally determined rate constants. The oxidation of limonene may contribute to aerosol and photochemical smog formation. Calculated lifetimes for the night-time reaction of d-limonene with nitrate radicals range form 0.9 to 9 minutes. The daytime atmospheric lifetime of d-limonene is estimated to range from 12 to 48 min. depending upon local hydroxyl rate and ozone concentrations. Products produced from hydroxy radical reaction with limonene are 4-acetyl-1-methylcyclohexene, a keto-aldehyde, formaldehyde, 3-oxobutanal, glyoxal and a C10 dicarbonyl. The same carbonyls, along with formic acid and C8 and C9 carboxylic acids, may form in reactions with ozone. Ozonolysis of limonene may also lead to the formation of hydrogen peroxide and organic peroxides, which have various toxic effects on plant cells and may damage forests Products of ozonolysis include bis(hydroxmethyl)peroxide, a precursor to hydroxymethyl hydroperoxide and hydrogen peroxide. The reaction of d-limonene with ozone in the dark results in the formation of 4-acetyl-1-methylcyclohexene and formaldehyde. Reactions with nitrogen oxides produce aerosol formation as well as lower molecular weight products such as formaldehyde, acetaldehyde, formic acid, acetone and peroxyacetyl nitrate.

Terrestrial fate: When released to the ground limonene is expected to have low to very low mobility in soil based on its physicochemical properties. The soil adsorption coefficient (Koc) calculated on the basis of solubility (13.8 mg/l, 25 C) and the log octanol/ water partition coefficient (4.23) ranges from 1030 and 4780. The Henry's law constant indicates that limonene will rapidly volatilise from both dry and moist soil; however its absorption to soil may slow the process.

Aquatic fate: In the aquatic environment, limonene is expected to evaporate to a significant extent owing to its high volatility. The estimated half-life for volatilisation of limonene from a model river (1 m deep, flow 1 m/s and wind speed 3 m/s) is 3.4 h. Some limonene is expected to absorb to sediment and suspended organic matter.

Biodegradation and bioaccumulation: Limonene does not have functional groups for hydrolysis and its cyclohexene ring and ethylene group are known to resist hydrolysis. Therefore, hydrolysis of limonene is not expected in terrestrial or in aquatic environments. The hydrolytic half-life of d-limonene is estimated to be >1000 days. Biotic degradation of limonene has been shown with some species of microorganisms such as Penicillium digitatum, Corynespora cassiicola, Diplodia gossyppina and a soil strain of Pseudomonans sp (SL strain). Limonene is readily biodegradable (41-98% degradation by biological oxygen demand in 14 d) under aerobic conditions in a standard test (OECD 301 C 'Modified MITI Test (1)', OECD, 1981a; MITI, 1992). Also in a test simulating aerobic sewage treatment (OECD 303 A 'Simulation Test - Aerobic Sewage Treatment: Coupled Units Test'; OECD, 1981b), limonene disappeared almost completely (>93.8%) during 14 days of incubation.

Biodegradation has been assessed under anaerobic conditions; there was no indication of any metabolisms, possibly because of the toxicity to micro-organisms. The bioconcentration factor, calculated on the basis of water solubility and the log octanol/ water partition coefficient (log Kow) is 246-262, suggesting that limonene may bioaccumulate in fish and other aquatic species.

Ecotoxicity: Technical limonene is practically nontoxic to birds on a subacute dietary basis, and is slightly toxic to freshwater fish and invertebrates on an acute basis.

LD50 Colinus virginianus (Bobwhite quail, 16 weeks old) oral >2000 mg/kg

LC50 Colinus virginianus (Bobwhite quail, 10 day old) dietary >5620 ppm/8 days

LC50 Colinus virginianus (Bobwhite quail, 14 day old) dietary >5000 ppm/8 days

LC50 Anas platyrhynchos (Mallard duck, 14 day old) dietary >5000 ppm/8 days

LC50 Oncorhynchus mykiss (Rainbow trout) 80 ppm/96 hr (95% confidence limit: 71.4-88.7 ppm); static /92% Al formulated product

LC50 Oncorhynchus mykiss (Rainbow trout) 568 ppm/96 hr (95% confidence limit: 437-852 ppm); static /4.0% Al formulated product

EC50 Daphnia magna (Water flea, <24 hr old; intoxication, immobilization) 17 ppm/48 hr (95% confidence limit: 11-33 ppm); static /4.0% Al formulated product

LC50 Pimephales promelas (Fathead minnow) 966 ppm/96 hr (95% confidence limit: 740-1652 ppm); static /4.0% Al formulated product

LC50 Pimephales promelas (Fathead minnow) 38.5 mg/L/96 hr; flow through /from table/ LC50

Leuciscus idus (Golden orfe) 32 mg/L/48 hr /Conditions of bioassay not specified in source examined

The acute toxicity of d-limonene ranges from slight to high for aquatic organisms. The lowest acute toxicity values (EC50 or LC50) identified were approximately 0.4 mg/litre for Daphnia (US EPA, 1990b) and 0.7 mg/litre for fish (US EPA, 1990a,b). The no-observed-effect concentration (NOEC) for

green algae is approximately 4 mg/litre (US EPA, 1990a). The acute toxicity (EC50 or LC50) of dipentene to Daphnia and fish is about 50-70 times lower than that for d-limonene (US EPA, 1990b). No studies were identified on the chronic toxicity of limonene to aquatic organisms.

DO NOT discharge into sewer or waterways.

12.2. Persistence and degradability

Ingredient	Persistence: Water/Soil	Persistence: Air
d-limonene	HIGH	HIGH
gamma-terpinene	HIGH	HIGH
beta-pinene	HIGH	HIGH
terpinolene	HIGH	HIGH
myrcene	HIGH	HIGH
alpha-pinene	HIGH	HIGH
alpha-terpinene	HIGH	HIGH

12.3. Bioaccumulative potential

Ingredient	Bioaccumulation
d-limonene	HIGH (LogKOW = 4.8275)
gamma-terpinene	MEDIUM (LogKOW = 4.5)
beta-pinene	MEDIUM (LogKOW = 4.16)
terpinolene	MEDIUM (LogKOW = 4.47)
myrcene	MEDIUM (LogKOW = 4.17)
alpha-pinene	MEDIUM (LogKOW = 4.44)
alpha-terpinene	MEDIUM (LogKOW = 4.25)

12.4. Mobility in soil

Ingredient	Mobility
d-limonene	LOW (KOC = 1324)
gamma-terpinene	LOW (KOC = 1324)
beta-pinene	LOW (KOC = 1204)
terpinolene	LOW (KOC = 1324)
myrcene	LOW (KOC = 1269)
alpha-pinene	LOW (KOC = 1204)
alpha-terpinene	LOW (KOC = 1324)

12.5. Results of PBT and vPvB assessment

	Р	В	Т
Relevant available data	Not Available	Not Available	Not Available
PBT	×	×	×
vPvB	×	X	×
PBT Criteria fulfilled?			
vPvB			No

12.6. Endocrine Disruption Properties

Not Available

12.7. Other adverse effects

One or more ingredients within this SDS has the potential of causing ozone depletion and/or photochemical ozone creation.

SECTION 13 Disposal considerations

13.1. Waste treatment methods

Product / Packaging disposal

- Containers may still present a chemical hazard/ danger when empty.
- ▶ Return to supplier for reuse/ recycling if possible.

Otherwise:

- If container can not be cleaned sufficiently well to ensure that residuals do not remain or if the container cannot be used to store the same product, then puncture containers, to prevent re-use, and bury at an authorised landfill.
- Where possible retain label warnings and SDS and observe all notices pertaining to the product.

Legislation addressing waste disposal requirements may differ by country, state and/ or territory. Each user must refer to laws operating in their area. In some areas, certain wastes must be tracked.

A Hierarchy of Controls seems to be common - the user should investigate:

- Reduction
- ► Reuse
- ► Recycling
- Disposal (if all else fails)

This material may be recycled if unused, or if it has not been contaminated so as to make it unsuitable for its intended use. If it has been contaminated, it may be possible to reclaim the product by filtration, distillation or some other means. Shelf life considerations should also be applied in making decisions of this type. Note that properties of a material may change in use, and recycling or reuse may not always be appropriate.

- ▶ DO NOT allow wash water from cleaning or process equipment to enter drains.
- It may be necessary to collect all wash water for treatment before disposal.
- ▶ In all cases disposal to sewer may be subject to local laws and regulations and these should be considered first.
- ▶ Where in doubt contact the responsible authority.
- ► Recycle wherever possible.
- Consult manufacturer for recycling options or consult local or regional waste management authority for disposal if no suitable treatment or disposal facility can be identified.
- Dispose of by: burial in a land-fill specifically licensed to accept chemical and / or pharmaceutical wastes or Incineration in a licensed apparatus (after admixture with suitable combustible material).
- Decontaminate empty containers. Observe all label safeguards until containers are cleaned and destroyed.

Waste treatment options

Not Available

Sewage disposal options

Not Available

SECTION 14 Transport information

Labels Required



Limited quantity: 433C-1L, 433C-4L

Land transport (ADR-RID)

,	1	
14.1. UN number	2319	
14.2. UN proper shipping name	TERPENE HYDROCARBONS, N.O.S. (contains d-limonene)	
14.3. Transport hazard class(es)	Class 3	
	Subrisk Not Applicable	
14.4. Packing group	III	
14.5. Environmental hazard	Environmentally hazardous	
	Hazard identification (Kemler)	30
	Classification code	F1
14.6. Special precautions for	Hazard Label	3
user	Special provisions	Not Applicable
	Limited quantity	5 L
	Tunnel Restriction Code	3 (D/E)

Air transport (ICAO-IATA / DGR)

· ·	•			
14.1. UN number	2319			
14.2. UN proper shipping name	Terpene hydrocarbons, n.o.s. (contains d-limonene)			
	ICAO/IATA Class 3			
14.3. Transport hazard class(es)	ICAO / IATA Subrisk	brisk Not Applicable		
ciass(cs)	ERG Code 3L			
14.4. Packing group	III			
14.5. Environmental hazard	Environmentally hazardo	ous		
	Special provisions		Not Applicable	
	Cargo Only Packing Instructions		366	
	Cargo Only Maximum Qty / Pack		220 L	
14.6. Special precautions for user	Passenger and Cargo Packing Instructions		355	
	Passenger and Cargo Maximum Qty / Pack		60 L	
	Passenger and Cargo Limited Quantity Packing Instructions		Y344	
	Passenger and Cargo Limited Maximum Qty / Pack		10 L	
	i assenger and Cargo Elimited Maximum Qty / Fack			

Sea transport (IMDG-Code / GGVSee)

14.1. UN number	2319	
14.2. UN proper shipping name	TERPENE HYDROCARBONS, N.O.S. (contains d-limonene)	
14.3. Transport hazard class(es)	IMDG Class 3 IMDG Subrisk Not Applicable	
14.4. Packing group		
14.5. Environmental hazard	Marine Pollutant	
14.6. Special precautions for user	EMS Number F-E , S-D Special provisions Not Applicable Limited Quantities 5 L	

Inland waterways transport (ADN)

14.1. UN number	2319	
14.2. UN proper shipping name	TERPENE HYDROCARBONS, N.O.S. (contains d-limonene)	
14.3. Transport hazard class(es)	3 Not Applicable	
14.4. Packing group		
14.5. Environmental hazard	Environmentally hazardous	
	Classification code	F1
	Special provisions	Not Applicable
14.6. Special precautions for user	Limited quantity	5 L
4001	Equipment required	PP, EX, A
	Fire cones number	0
	<u> </u>	•

14.7. Transport in bulk according to Annex II of MARPOL and the IBC code

Not Applicable

14.8. Transport in bulk in accordance with MARPOL Annex V and the IMSBC Code

Product name	Group
d-limonene	Not Available
gamma-terpinene	Not Available
beta-pinene	Not Available
terpinolene	Not Available
myrcene	Not Available
alpha-pinene	Not Available
alpha-terpinene	Not Available

14.9. Transport in bulk in accordance with the ICG Code

Product name	Ship Type	
d-limonene	Not Available	
gamma-terpinene	Not Available	
beta-pinene	Not Available	
terpinolene	Not Available	
myrcene	Not Available	
alpha-pinene	Not Available	
alpha-terpinene	Not Available	

SECTION 15 Regulatory information

15.1. Safety, health and environmental regulations / legislation specific for the substance or mixture

d-limonene is found on the following regulatory lists

EU REACH Regulation (EC) No 1907/2006 - Annex XVII - Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles

Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (EINECS)

European Union (EU) Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of Substances and Mixtures - Annex VI International Agency for Research on Cancer (IARC) - Agents Classified by the IARC Monographs

gamma-terpinene is found on the following regulatory lists

Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (EINECS)

beta-pinene is found on the following regulatory lists

EU European Chemicals Agency (ECHA) Community Rolling Action Plan (CoRAP) List of Substances

Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (EINECS)

terpinolene is found on the following regulatory lists

Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (EINECS)

myrcene is found on the following regulatory lists

Chemical Footprint Project - Chemicals of High Concern List Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (EINECS)

International Agency for Research on Cancer (IARC) - Agents Classified by the IARC Monographs

International Agency for Research on Cancer (IARC) - Agents Classified by the IARC Monographs - Group 2B: Possibly carcinogenic to humans

alpha-pinene is found on the following regulatory lists

Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (EINECS)

alpha-terpinene is found on the following regulatory lists

Europe EC Inventory

European Union - European Inventory of Existing Commercial Chemical Substances (FINECS)

This safety data sheet is in compliance with the following EU legislation and its adaptations - as far as applicable - : Directives 98/24/EC, - 92/85/EEC, - 94/33/EC, - 2008/98/EC, - 2010/75/EU; Commission Regulation (EU) 2020/878; Regulation (EC) No 1272/2008 as updated through ATPs.

15.2. Chemical safety assessment

No Chemical Safety Assessment has been carried out for this substance/mixture by the supplier.

National Inventory Status

National Inventory	Status
Australia - AIIC / Australia Non-Industrial Use	Yes
Canada - DSL	Yes
Canada - NDSL	No (d-limonene; gamma-terpinene; beta-pinene; terpinolene; myrcene; alpha-terpinene)
China - IECSC	Yes
Europe - EINEC / ELINCS / NLP	Yes
Japan - ENCS	Yes
Korea - KECI	Yes
New Zealand - NZIoC	Yes
Philippines - PICCS	Yes
USA - TSCA	Yes
Taiwan - TCSI	Yes
Mexico - INSQ	No (alpha-terpinene)
Vietnam - NCI	Yes
Russia - FBEPH	Yes
Legend:	Yes = All CAS declared ingredients are on the inventory No = One or more of the CAS listed ingredients are not on the inventory. These ingredients may be exempt or will require registration.

SECTION 16 Other information

Revision Date	02/11/2021
Initial Date	30/10/2017

Full text Risk and Hazard codes

H302	Harmful if swallowed.	
H302+H312+H332	Harmful if swallowed, in contact with skin or if inhaled.	
H319	Causes serious eye irritation.	
H335	May cause respiratory irritation.	
H336	May cause drowsiness or dizziness.	
H361f	Suspected of damaging fertility.	
H400	Very toxic to aquatic life.	
H411	Toxic to aquatic life with long lasting effects.	

Other information

Classification of the preparation and its individual components has drawn on official and authoritative sources as well as independent review by the Chemwatch Classification committee using available literature references.

The SDS is a Hazard Communication tool and should be used to assist in the Risk Assessment. Many factors determine whether the reported Hazards are Risks in the workplace or other settings. Risks may be determined by reference to Exposures Scenarios. Scale of use, frequency of use and current or available engineering controls must be considered. For detailed advice on Personal Protective Equipment, refer to the following EU CEN Standards:

EN 166 Personal eye-protection

EN 340 Protective clothing

EN 374 Protective gloves against chemicals and micro-organisms

EN 13832 Footwear protecting against chemicals

EN 133 Respiratory protective devices

Definitions and abbreviations

PC-TWA: Permissible Concentration-Time Weighted Average PC-STEL: Permissible Concentration-Short Term Exposure Limit

IARC: International Agency for Research on Cancer

ACGIH: American Conference of Governmental Industrial Hygienists

STEL: Short Term Exposure Limit

TEEL: Temporary Emergency Exposure Limit。

IDLH: Immediately Dangerous to Life or Health Concentrations

ES: Exposure Standard OSF: Odour Safety Factor

NOAEL :No Observed Adverse Effect Level

LOAEL: Lowest Observed Adverse Effect Level

TLV: Threshold Limit Value LOD: Limit Of Detection

OTV: Odour Threshold Value

BCF: BioConcentration Factors

BEI: Biological Exposure Index

AIIC: Australian Inventory of Industrial Chemicals

DSL: Domestic Substances List NDSL: Non-Domestic Substances List

IECSC: Inventory of Existing Chemical Substance in China

EINECS: European INventory of Existing Commercial chemical Substances

ELINCS: European List of Notified Chemical Substances

NLP: No-Longer Polymers

ENCS: Existing and New Chemical Substances Inventory

KECI: Korea Existing Chemicals Inventory NZIoC: New Zealand Inventory of Chemicals

PICCS: Philippine Inventory of Chemicals and Chemical Substances

TSCA: Toxic Substances Control Act

TCSI: Taiwan Chemical Substance Inventory

INSQ: Inventario Nacional de Sustancias Químicas

NCI: National Chemical Inventory

FBEPH: Russian Register of Potentially Hazardous Chemical and Biological Substances

Reason For Change

A-2.00 - Added UFI number and changes to the format on the saafety data sheet.