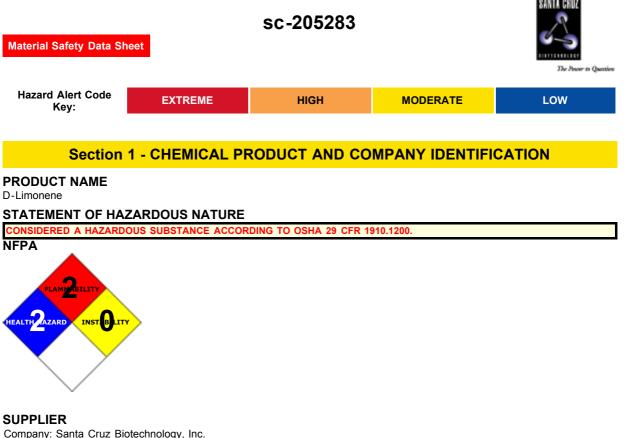
# **D-Limonene**



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# PRODUCT USE

Flavouring, fragrance and perfume materials. Used as solvent in cleaners and degreasers; solvent for resins, polymers, waxes; wetting agent. Manufacture of specialist resins. Sulfurised derivatives in lube oils. Fragrance

# SYNONYMS

C10H16, limonene, (+)-4-isopropenyl-1-methylcyclohexene, (+)-4-isopropenyl-1-methylcyclohexene, D-(+)-limonene, D-(+)-limonene, (+)-R-limonene, "d-p-mentha-1, 8-diene", "d-p-mentha-1, 8-diene", "p-mentha-1, 8-diene", "4-isopropyl-1-methyl cyclohexene", "1, 8, (9)-menthadiene", "cyclohexene", "1-methyl-4-(1-methylethenyl)-, (R)-", "1-methyl-4-(1-methylethenyl)-, (R)-", "(R)-(+)-limonene (CAS RN: 5989-27-5)", "(+)-p-Mentha-1, 8-diene", "(+)-p-Mentha-1, 8-diene", (+)-Carvene, (R)-4-lsopropenyl-1-methyl-1-cyclohexene, (R)-4-lsopropenyl-1-methyl-1-cyclohexene, "aromatic cyclic", "terpene hydrocarbon", Refchole, Cinene, Cajeputene, Histoclear, Histolene, "orange skin extract", "citrus orange terpenes", menthadiene

# **Section 2 - HAZARDS IDENTIFICATION**

## CANADIAN WHMIS SYMBOLS



# EMERGENCY OVERVIEW

Explosive when dry. Irritating to skin. May cause SENSITIZATION by skin contact. HARMFUL - May cause lung damage if swallowed.

# POTENTIAL HEALTH EFFECTS

# ACUTE HEALTH EFFECTS

#### SWALLOWED

Swallowing of the liquid may cause aspiration into the lungs with the risk of chemical pneumonitis; serious consequences may result. (ICSC13733).

Accidental ingestion of the material may be damaging to the health of the individual.

■ d-limonene, if ingested, causes a non-bloody diarrhea and abnormalities in bone formation. A strong urge to pass bowel may occur with little or no stools actually passed. In massive doses death may occur.

EYE

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

#### SKIN

This material can cause inflammation of the skin oncontact in some persons.

- The material may accentuate any pre-existing dermatitis condition.
- Skin contact with the material may damage the health of the individual; systemic effects may result following absorption.
- Open cuts, abraded or irritated skin should not be exposed to this material.

• Entry into the blood-stream, through, for example, cuts, abrasions 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.

 d-limonene causes moderate irritation to skin including redness and swelling. Sometimes there are delayed hemorrhagic lesions.

## INHALED

■ Inhalation of vapours may cause drowsiness and dizziness. This may be accompanied by narcosis, reduced alertness, loss of reflexes, lack of coordination and vertigo.

■ Inhalation of vapors or aerosols (mists, fumes), generated by the material during the course of normal handling, may be damaging to the health of the individual.

• There is some evidence to suggest that the material can cause respiratory irritation in some persons. The body's response to such irritation can cause further lung damage.

■ Inhalation of high concentrations of gas/vapor causes lung irritation with coughing and nausea, central nervous depression with headache and dizziness, slowing of reflexes, fatigue and inco-ordination.

■ Central nervous system (CNS) depression may include general 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.

# CHRONIC HEALTH EFFECTS

Skin contact with the material is more likely to cause a sensitization reaction in some persons compared to the general population.

There has been some concern that this material can cause cancer or mutations but there is not enough data to make an assessment.

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.

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 commercial formulations.

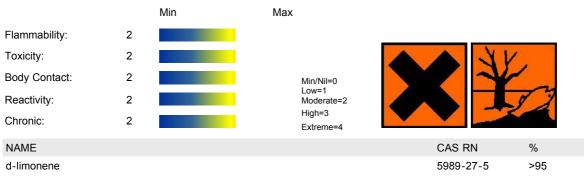
d-Limonene may cause damage to and growths in the kidney. These growths can progress to cancer.

Peroxidisable terpenes and terpenoids 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. This requirement is based on the published literature mentioning sensitising properties when containing peroxides.

Sensitization may result in allergic dermatitis responses includingrash, itching, hives or swelling of extremities.

# Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

# HAZARD RATINGS



# SWALLOWED

- - 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
- If spontaneous vomiting appears imminent or occurs, hold patient's head down, lower than their hips to help avoid possible aspiration of vomitus.

# EYE

- 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.
- If pain persists or recurs seek medical attention.
- Removal of contact lenses after an eye injury should only be undertaken by skilled personnel.

#### SKIN

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.

# INHALED

- If fumes or combustion products are inhaled remove from contaminated area.
- Lay patient down. Keep warm and rested.
- Prostheses such as false teeth, which may block airway, should be removed, where possible, prior to initiating first aid procedures.
- Apply artificial respiration if not breathing, preferably with a demand valve resuscitator, bag-valve mask device, or pocket mask as trained. Perform CPR if necessary.
- Transport to hospital, or doctor.

## NOTES TO PHYSICIAN

Any material aspirated during vomiting may produce lung injury. Therefore emesis should not be induced mechanically or pharmacologically. Mechanical means should be used if it is considered necessary to evacuate the stomach contents; these include gastric lavage after endotracheal intubation. If spontaneous vomiting has occurred after ingestion, the patient should be monitored for difficult breathing, as adverse effects of aspiration into the lungs may be delayed up to 48 hours.

# Section 5 - FIRE FIGHTING MEASURES

Vapor Pressure (mmHg):	0.975 @ 14 deg.C
Upper Explosive Limit (%):	6.1 @ 150C.
Specific Gravity (water=1):	0.84
Lower Explosive Limit (%):	0.7 @ 150C.

# **EXTINGUISHING MEDIA**

- Foam
- ٠
- Dry chemical powder. BCF (where regulations permit).
- Carbon dioxide.
- Water spray or fog Large fires only. •

# **FIRE FIGHTING**

- Alert Emergency Responders and tell them location and nature of hazard.
- May be violently or explosively reactive.
- Wear breathing apparatus plus protective gloves.
- Prevent, by any means available, spillage from entering drains or water course.
- If safe, switch off electrical equipment until vapor fire hazard removed.
- Use water delivered as a fine spray to control fire and cool adjacent area.
- Avoid spraying water onto liquid pools.
- DO NOT approach containers suspected to be hot.
- Cool fire exposed containers with water spray from a protected location.
- If safe to do so, remove containers from path of fire.

# **GENERAL FIRE HAZARDS/HAZARDOUS COMBUSTIBLE PRODUCTS**

- Liquid and vapor are flammable.
- Moderate fire hazard when exposed to heat or flame.
- Vapor forms an explosive mixture with air.
- Moderate explosion hazard when exposed to heat or flame.
- Vapor 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. FIRE INCOMPATIBILITY

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

# PERSONAL PROTECTION

Glasses Chemical goggles. Gloves 1.NITRILE 2.VITON 3.PVA Respirator: Type A Filter of sufficient capacity

# Section 6 - ACCIDENTAL RELEASE MEASURES

MINOR SPILLS

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

MAJOR SPILLS

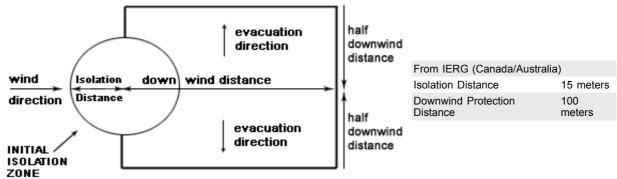
CARE: Absorbent material wet with occluded oil must be wet with water as they may auto-oxidize, become self heating and ianite.

Some oils slowly oxidize when spread in a film and oil on cloths, mops, absorbents may auto-oxidize and generate heat, smoulder, ignite and burn. In the workplace oily rags should be collected and immersed in water.

- Clear area of personnel and move upwind.
- Alert Emergency Responders and tell them location and nature of hazard.
- May be violently or explosively reactive.
- Wear breathing apparatus plus protective gloves. ٠
- Prevent, by any means available, spillage from entering drains or water course.
- No smoking, naked lights or ignition sources. Increase ventilation.
- Stop leak if safe to do so.
- Water spray or fog may be used to disperse / absorb vapor.
- Contain spill with sand, earth or vermiculite.
- Use only spark-free shovels and explosion proof equipment.
- Collect recoverable product into labeled containers for recycling.
- Absorb remaining product with sand, earth or vermiculite.
- Collect solid residues and seal in labeled drums for disposal.
- Wash area and prevent runoff into drains.
- If contamination of drains or waterways occurs, advise emergency services.

# PROTECTIVE ACTIONS FOR SPILL

#### PROTECTIVE ACTION ZONE



# FOOTNOTES

1 PROTECTIVE ACTION ZONE is defined as the area in which people are at risk of harmful exposure. This zone assumes that random changes in wind direction confines the vapour plume to an area within 30 degrees on either side of the predominant wind direction, resulting in a crosswind protective action

distance equal to the downwind protective action distance. 2 PROTECTIVE ACTIONS should be initiated to the extent possible, beginning with those closest to the spill and working away from the site in the downwind direction. Within the protective action zone a level of vapour concentration may exist resulting in nearly all unprotected persons becoming incapacitated and unable to take protective action and/or incurring serious or irreversible health effects. 3 INITIAL ISOLATION ZONE is determined as an area, including upwind of the incident, within which a high probability of localised wind reversal may expose

3 INITIAL ISOLATION ZONE is determined as an area, including upwind of the incluent, within which a high probability of localised wind reversal may expose nearly all persons without appropriate protection to life-threatening concentrations of the material.
4 SMALL SPILLS involve a leaking package of 200 litres (55 US gallons) or less, such as a drum (jerrican or box with inner containers). Larger packages leaking less than 200 litres and compressed gas leaking from a small cylinder are also considered "small spills". LARGE SPILLS involve many small leaking packages or a leaking package of greater than 200 litres, such as a cargo tank, portable tank or a "one-tonne" compressed gas cylinder.
5 Guide 128 is taken from the US DOT emergency response guide book.
6 IERG information is derived from CANUTEC - Transport Canada.

# ACUTE EXPOSURE GUIDELINE LEVELS (AEGL) (in ppm)

AEGL 1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL 2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

# **Section 7 - HANDLING AND STORAGE**

# PROCEDURE FOR HANDLING

- Containers, even those that have been emptied, may contain explosive vapors.

• Do NOT cut, drill, grind, weld or perform similar operations on or near containers.

• DO NOT allow clothing wet with material to stay in contact with skin

The substance accumulates peroxides which may become hazardous only if it evaporates or is distilled or otherwise treated to concentrate the peroxides. The substance may concentrate around the container opening for example.

Purchases of peroxidizable chemicals should be restricted to ensure that the chemical is used completely before it can become peroxidized.

- A responsible person should maintain an inventory of peroxidizable chemicals or annotate the general chemical inventory to indicate which chemicals are subject to peroxidation. An expiration date should be determined. The chemical should either be treated to remove peroxides or disposed of before this date.
- The person or laboratory receiving the chemical should record a receipt date on the bottle. The individual opening the container should add an opening date.
- Unopened containers received from the supplier should be safe to store for 18 months.
- Opened containers should not be stored for more than 12 months.
- 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 storing and handling recommendations.
- Atmosphere should be regularly checked against established exposure standards to ensure safe working conditions.
- · Electrostatic discharge may be generated during pumping this may result in fire.
- Ensure electrical continuity by bonding and grounding (earthing) all equipment.
- Restrict line velocity during pumping in order to avoid generation of electrostatic discharge (<=1 m/sec until fill pipe submerged to twice its diameter, then <= 7 m/sec).</li>
- Avoid splash filling.
- Do NOT use compressed air for filling discharging or handling operations.

#### **RECOMMENDED STORAGE METHODS**

■ Packing as supplied by manufacturer. Plastic containers may only be used if approved for flammable liquid. Check that containers are clearly labeled and free from leaks.

- For low viscosity materials (i): Drums and jerricans 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)
- 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 (23 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 molded plastic box and the substances are not incompatible with the plastic.

# STORAGE REQUIREMENTS

- Store in original containers in approved flammable liquid storage area.
- DO NOT store in pits, depressions, basements or areas where vapors may be trapped.
- No smoking, naked lights, heat or ignition sources.
- · Keep containers securely sealed.

- Store away from incompatible materials in a cool, dry, well-ventilated area.
- Protect containers against physical damage and check regularly for leaks.
- Observe manufacturer's storing and handling recommendations.

# SAFE STORAGE WITH OTHER CLASSIFIED CHEMICALS



X: Must not be stored together

O: May be stored together with specific preventions

+: May be stored together

# Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

# EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m³	STEL ppm	STEL mg/m³	Peak ppm	Peak mg/m³	TWA F/CC	Notes
US AIHA Workplace Environmental Exposure Levels (WEELs)	d-limonene (d-Limonene)	30							
Canada - Alberta Occupational Exposure Limits	d-limonene (Turpentine and selected monoterpenes)	20	111						
Canada - Saskatchewan Occupational Health and Safety Regulations - Contamination Limits	d-limonene (Turpentine and selected monoterpenes)	20		30					SEN
Canada - British Columbia Occupational Exposure Limits	d-limonene (Diesel fuel, as total hydrocarbons, Inhalable)		100 (V)						Skin

# MATERIAL DATA

D-LIMONENE:

for d-Limonene:

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

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.

# PERSONAL PROTECTION



Consult your EHS staff for recommendations **EYE** 

#### .

- · Safety glasses with side shields.
- Chemical goggles.
- Contact lenses pose a special hazard; soft lenses may absorb irritants and all lenses concentrate them. DO NOT wear contact lenses.

#### HANDS/FEET

■ Wear chemical protective gloves, eg. PVC.

Wear safety footwear or safety gumboots, eg. Rubber.

NOTE: The material may produce skin sensitization in predisposed individuals. Care must be taken, when removing gloves and other protective equipment, to avoid all possible skin contact.

Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include: such as: • frequency and duration of contact,

- chemical resistance of glove material,
- glove thickness and
- dexterity
- Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739).
- · 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) 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) is recommended.
- Contaminated gloves should be replaced.

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.

#### OTHER

- 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 footwear.

# 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: d-limonene

Protective Material CPI *.	
NITRILE	A
VITON	Α
PVA	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.

#### RESPIRATOR

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.

Breathing Zone Level ppm (volume)	Maximum Protection Factor	Half-face Respirator	Full-Face Respirator
1000	10	A-1	-
1000	50	-	A-1
5000	50	Airline*	-
5000	100	-	A-2
10000	100	-	A-3
	100+		Airline* *

\* - Continuous Flow \*\* - Continuous-flow or positive pressure demand.

The local concentration of material, quantity and conditions of use determine the type of personal protective equipment required.

Use appropriate NIOSH-certified respirator based on informed professional judgement. In conditions where no reasonable estimate of exposure can be made, assume the exposure is in a concentration IDLH and use NIOSH-certified full face pressure demand SCBA with a minimum service life of 30 minutes, or a combination full facepiece pressure demand SAR with auxiliary self-contained air supply. Respirators provided only for escape from IDLH atmospheres shall be NIOSH-certified for escape from the atmosphere in which they will be used.

#### **ENGINEERING 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.

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.

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Type of Contaminant:	Air Speed:
solvent, vapors, 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	1-2.5 m/s (200-500 f/min.)

generation into zone of rapid air motion) Within each range the appropriate value depends on: Lower end of the range

1: Room air currents minimal or favorable 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

Upper end of the range

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.

# Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

# PHYSICAL PROPERTIES

Liquid. Does not mix with water. Floats on water.			
State	Liquid	Molecular Weight	136.23
Melting Range (°F)	-144.4	Viscosity	Not Available
Boiling Range (°F)	348.8	Solubility in water (g/L)	Immiscible
Flash Point (°F)	114.8	pH (1% solution)	Not applicable
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not applicable
Autoignition Temp (°F)	458.6	Vapor Pressure (mmHg)	0.975 @ 14 deg.C
Upper Explosive Limit (%)	6.1 @ 150C.	Specific Gravity (water=1)	0.84
Lower Explosive Limit (%)	0.7 @ 150C.	Relative Vapor Density (air=1)	4.66
Volatile Component (%vol)	Not available	Evaporation Rate	< 1 BuAc=1
VOC(regulatory)	lb/gall	VOC(actual)	lb/gall

# APPEARANCE

Colourless to very pale yellow flammable liquid; floats on water. Pleasant lemon-like odour. Mixes with alcohol and ether. An unsaturated aromatic terpene hydrocarbon which oxidises in air. Occurs in nature as a component of Lemon, Orange, Bergamot and other oils.

# Section 10 - CHEMICAL STABILITY

# CONDITIONS CONTRIBUTING TO INSTABILITY

- Presence of incompatible materials. Product is considered stable.
- Hazardous polymerization will not occur.

#### STORAGE INCOMPATIBILITY

- d-Limonene.
- · forms unstable peroxides in storage, unless uninhibited; may polymerise
- · reacts with strong oxidisers and may explode or combust
- · is incompatible with strong acids, including acidic clays, peroxides, halogens, vinyl chloride and iodine pentafluoride
- 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.

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 ("pseudonitrosites") were formerly used to characterize 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 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.

HAZARD: Rags wet / soaked with unsaturated hydrocarbons / drying oils auto oxidize; may generate heat and in-time smoulder and ignite. Oily cleaning rags should be collected regularly and immersed in water. Avoid reaction with oxidizing agents.

For incompatible materials - refer to Section 7 - Handling and Storage.

# Section 11 - TOXICOLOGICAL INFORMATION

#### d-limonene

#### TOXICITY AND IRRITATION

unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Oral (rat) LD50: 4400 mg/kg	Nil Reported
Inhalation (rat) LC50: 90860 mg/m <sup>3</sup>	Skin (rabbit): 500mg/24h Moderate

Oral (Rat) LD50: 5300 mg/kg

Dermal (Rabbit) LD50: >5000 mg/kg

• Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's edema. 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 sensitization potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitizing substance which is widely distributed can be a more important allergen than one with stronger sensitizing 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.

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 tumours 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.

#### The substance is classified by IARC as Group 3:

NOT classifiable as to its carcinogenicity to humans.

Evidence of carcinogenicity may be inadequate or limited in animal testing.

Tumorigenic by RTECS criteria

# CARCINOGEN

· · ·	B: Overall evaluation downgraded from 2B to ng evidence from other relevant data)	International Agency for Research on Cane - Agents Reviewed by the IARC Monograp		Group 3
SKIN				
d-limonene	Canada - British Columbia Occupational Exp	oosure Limits - Skin	Notation	Skin

# Section 12 - ECOLOGICAL INFORMATION

Refer to data for ingredients, which follows:

D-LIMONENE:

■ 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.

For limonenes

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.

for d-limonene:

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% AI 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.

Terpenes such as limonene and isoprene contribute to aerosol and photochemical smog formation. Emissions of biogenic hydrocarbons, such as the terpenes, to the atmosphere may either decrease ozone concentrations when oxides of nitrogen are low or, if emissions take place in polluted air (i.e containing high concentrations of nitrogen oxides), leads to an increase in ozone concentrations. Lower terpenoids can react with unstable reactive gases and may act as precursors of photochemical smog therefore indirectly influencing community and ecosystem properties.

Complex chlorinated terpenes such as toxaphene (a persistent, mobile and toxic insecticide) and its degradation products, were produced by photoinitiated reactions in an aqueous system, initially containing limonene and other monoterpenes, simulating pulp bleach conditions

The reactions of ozone with larger unsaturated compounds, such as the terpenes can give rise to oxygenated species with low vapour pressures that subsequently condense to form secondary organic aerosol.

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.

Unsaturated substances (Reactive Emissions)	Major Stable Products produced following reaction with ozone.
Isoprene, nitric oxide, squalene, unsaturated sterols, oleic acid and other unsaturated fatty acids, unsaturated oxidation products	Methacrolein, methyl vinyl ketone, nitrogen dioxide, acetone, 6MHQ, geranyl acetone, 4OPA, formaldehyde, nonanol, decanal, 9-oxo-nonanoic acid, azelaic acid, nonanoic acid.
Isoprene, limonene, alpha-pinene, other terpenes and sesquiterpenes	Formaldehyde, 4-AMC, pinoaldehyde, pinic acid, pinonic acid, formic acid, methacrolein, methyl vinyl ketone, SOAs including ultrafine particles
4-Phenylcyclohexene, 4- vinylcyclohexene, styrene, 2-ethylhexyl acrylate, unsaturated fatty acids and esters	Formaldehyde, acetaldehyde, benzaldehyde, hexanal, nonanal, 2- nonenal
Linoleic acid, linolenic acid	Propanal, hexanal, nonanal, 2-heptenal, 2-nonenal, 2-decenal, 1-pentene-3-one, propionic acid, n-butyric acid
Residual monomers	Formaldehyde
Limonene, alpha-pinene, terpinolene, alpha-terpineol, linalool, linalyl acetate and other terpenoids, longifolene and other sesquiterpenes	Formaldehyde, acetaldehyde, glycoaldehyde, formic acid, acetic acid, hydrogen and organic peroxides, acetone, benzaldehyde, 4-hydroxy-4-methyl-5- hexen-1-al, 5-ethenyl-dihydro-5-methyl- 2(3H)-furanone, 4-AMC, SOAs including ultrafine particles
Isoprene, terpenes	Formaldehyde, methacrolein, methyl vinyl ketone
Styrene	Formaldehyde, benzaldehyde
Styrene, acrolein, nicotine	Formaldehyde, benzaldehyde, hexanal, glyoxal, N-methylformamide, nicotinaldehyde, cotinine
Squalene, unsaturated sterols, oleic acid and other saturated fatty acids	Acetone, geranyl acetone, 6MHO, 40PA, formaldehyde, nonanal, decanal, 9-oxo- nonanoic acid, azelaic acid, nonanoic
	<ul> <li>Emissions)</li> <li>Isoprene, nitric oxide, squalene, unsaturated sterols, oleic acid and other unsaturated fatty acids, unsaturated oxidation products</li> <li>Isoprene, limonene, alpha-pinene, other terpenes and sesquiterpenes</li> <li>4-Phenylcyclohexene, 4- vinylcyclohexene, styrene, 2-ethylhexyl acrylate, unsaturated fatty acids and esters</li> <li>Linoleic acid, linolenic acid</li> <li>Residual monomers</li> <li>Limonene, alpha-pinene, terpinolene, alpha-terpineol, linalool, linalyl acetate and other terpenoids, longifolene and other sesquiterpenes</li> <li>Styrene</li> <li>Styrene, acrolein, nicotine</li> <li>Squalene, unsaturated sterols, oleic acid</li> </ul>

		acid		
Soiled particle filters	Unsaturated fatty acids from plant waxes, leaf litter, and other vegetative debris; soot; diesel particles	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)		
Ventilation ducts and duct liners	Unsaturated fatty acids and esters, unsaturated oils, neoprene	C5 to C10 aldehydes		
"Urban grime"	Polycyclic aromatic hydrocarbons	Oxidized polycyclic aromatic hydrocarbons		
Perfumes, colognes, essential oils (e.g. lavender, eucalyptus, tea tree)	Limonene, alpha-pinene, linalool, linalyl acetate, terpinene-4-ol, gamma-terpinene	Formaldehyde, 4-AMC, acetone, 4- hydroxy-4-methyl-5-hexen-1-al, 5- e ethenyl-dihydro-5-methyl-2(3H) furanone, SOAs including ultrafine particles		
Overall home emissions	Limonene, alpha-pinene, styrene	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.

DO NOT discharge into sewer or waterways.

## Ecotoxicity

LOOLOXICIty				
Ingredient	Persistence: Water/Soil	Persistence: Air	Bioaccumulation	Mobility
d-limonene	HIGH		LOW	MED

# **Section 13 - DISPOSAL CONSIDERATIONS**

# **US EPA Waste Number & Descriptions**

A. General Product Information

Ignitability characteristic: use EPA hazardous waste number D001 (waste code I)

# **Disposal Instructions**

All waste must be handled in accordance with local, state and federal regulations.

Puncture containers to prevent re-use and bury at an authorized landfill.

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 equipment to enter drains. Collect all wash water for treatment before disposal.

- Recycle wherever possible.
- Consult manufacturer for recycling options or consult Waste Management Authority for disposal if no suitable treatment or disposal facility can be identified.
- Dispose of by: Burial in a licensed land-fill 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.

# **Section 14 - TRANSPORTATION INFORMATION**



001.			
Symbols:	None	Hazard class or Division:	3
Identification Numbers:	UN2319	PG:	III
Label Codes:	3	Special provisions:	B1, IB3, T4, TP1, TP29
Packaging: Exceptions:	150	Packaging: Non-bulk:	203
Packaging: Exceptions:	150	Quantity limitations: Passenger aircraft/rail:	60 L
Quantity Limitations: Cargo aircraft only:	220 L	Vessel stowage: Location:	A
Vessel stowage: Other:	None	S.M.P.:	YES
COMBUSTIBLE LIQUID			

A flammable liquid with a flash point at or above 38 deg.C (100 deg.F) that does not meet the definition of any other hazard

class may be

UN Number:

reclassed as a combustible liquid. This provision does not apply to transportation by vessel or aircraft, except where other means of

transportation is impracticable. An elevated temperature material that meets the definition of a Class 3 material because it is intentionally heated and offered for transportation or transported at or above its flash point may not be reclassed as a combustible liquid.

Refer to 49 CFR 173.120(b)(2)

	Air Transport IATA:	Transport IATA:					
	ICAO/IATA Class:	3	ICAO/IATA Subrisk:	None			
	UN/ID Number:	2319	Packing Group:	III			
	Special provisions:	None					
Shipping Name: TERPENE HYDROCARBONS, N.O.S.(CONTAINS D-LIMONENE) Maritime Transport IMDG:							
	IMDG Class:	3	IMDG Subrisk:	None			

EMS Number: F-E,S-D

Limited Quantities: 5 L

Shipping Name: TERPENE HYDROCARBONS, N.O.S.(contains d-limonene)

2319

# **Section 15 - REGULATORY INFORMATION**

Packing Group:

Special provisions:

Ш

944

# d-limonene (CAS: 5989-27-5,138-86-3) is found on the following regulatory lists;

"Canada Domestic Substances List (DSL)", "Canada Ingredient Disclosure List (SOR/88-64)", "Canada National Pollutant Release Inventory (NPRI)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "Canada Toxicological Index Service - Workplace Hazardous Materials Information System - WHMIS (English)", "International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs", "OECD Representative List of High Production Volume (HPV) Chemicals", "OSPAR List of Substances of Possible Concern", "US - Maine Chemicals of High Concern List", "US DOE Temporary Emergency Exposure Limits (TEELs)", "US EPA High Production Volume Program Chemical List", "US Food Additive Database", "US NFPA 30B Manufacture and Storage of Aerosol Products - Chemical Heat of Combustion", "US Toxic Substances Control Act (TSCA) - Inventory"

# **Section 16 - OTHER INFORMATION**

# LIMITED EVIDENCE

- Contact with air may produce sufficient heat to ignite combustible materials.\*.
- Potentially explosive peroxides may form on standing.\*.
- Inhalation skin contact and/or ingestion may produce health damage\*.
- May produce discomfort of the respiratory system\*.
- Limited evidence of a carcinogenic effect\*.
- \* (limited evidence).

# Ingredients with multiple CAS Nos

Ingredient Name d-limonene

CAS 5989-27-5, 138-86-3

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Classification of the mixture 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. A list of reference resources used to assist the committee may be found at: www.chemwatch.net/references.

• The (M)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.

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