

## Industrial Uses of Eucalyptus Oil

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### Summary

The large-scale planting of *Eucalyptus* oil mallees to rehabilitate water-logged and salt-affected agricultural land will permit the use of high-cineole leaf oils to replace environmentally unacceptable industrial solvents such as the ozone-depleting trichloroethane. At the same time this process will provide a renewable fuel biomass and a carbon sequestration mechanism.

### Eucalyptus Oil

A few *Eucalyptus* species, mainly mallees, produce a leaf oil for which there is an existing limited world trade as a pharmaceutical product and a large potential market as an industrial solvent. These oils are composed of mixtures of volatile organic compounds including hydrocarbons, alcohols, aldehydes, ketones, acids, ethers and esters. Most are monoterpenes and sesquiterpenes which consist of two or more isoprene (C<sub>5</sub>H<sub>8</sub>) units. They are products of photosynthesis, with functions for the plants that are still poorly understood. At present the most important of these is 1,8-cineole (Figure 1).

Eucalyptus oil has numerous traditional uses, especially in non-prescription pharmaceuticals, but the market is small. Currently somewhere between three and five thousand tonnes are traded each year on international markets, with only two or three hundred tonnes being produced by Australia. Eucalyptus oil based products have been used as a traditional non-ingestive treatment for coughs and colds (Opdyke, 1975), a topically applied medication for relief of muscular pain (Hong and Shellock, 1991), and as a solvent/sealer in root canal dentistry (Leung, 1980).

It has uses as a fragrance in soaps, detergents and perfumes and as a flavouring in food (Furia and Bellanca, 1971). Household uses include spot and stain remover and a wool wash component. It has also been used as a flotation agent in the mining industry (Clarke and Moore, 1931).

### 1,8-Cineole

1,8-Cineole (often just "cineole") is the pharmaceutically active component of eucalyptus oil. It occurs in complex mixtures with numerous other terpenoid compounds in the leaf oils of many eucalypts, but to differing extents - usually 60 to 70% in the case of bluegums and up to 95% in some oil mallees. Cineole (Figure 1) is a cyclic ether with empirical formula C<sub>10</sub>H<sub>18</sub>O and systematic name 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane. It is sometimes traded commercially as "eucalyptol". The carbon atoms linked to the ether oxygen are fully substituted and this fact, together with the chemical saturation (no carbon-carbon double bonds) endow cineole with stability and low chemical reactivity. These properties include resistance to oxidation, polymerisation and thermal decomposition, in contrast to most other terpenoid compounds.

It is a colourless liquid over the temperature range 0°C to 177°C with a vapour pressure of 69 mmHg at 20°C and a strong characteristic odour. Its flash point is reasonably high (48°C). It is slightly less dense than water (0.927 g mL<sup>-1</sup> at 20°C). Cineole's ether oxygen atom is moderately polar, making it either fully or partly miscible in a wide range of other liquids from hydrocarbons to polar organics. Cineole has a limited solubility in water (0.4% by weight at 20°C).

Carboxylation and hydroxylation of cineole have been described by various processes, including enzymatic, biological and metabolic routes. It has an odour which at low concentration is considered pleasant by most people and is used in aromatherapy applications as well as for deodorising waste sludges. Cineole therefore has a future as an industrial and commercial solvent as well as the potential to control insects and weeds in an environmentally acceptable manner, in addition to its existing use in pharmaceuticals. In particular, in many situations cineole may well replace 1, 1, 1 -trichloroethane, previously widely used for metal degreasing and other cleaning operations.

## **Bioactivity of Cineole**

Cineole and other components of eucalyptus oil are readily biodegradable, unreactive and relatively non-toxic (Webb and Pitt, 1993; Haley, 1982; Patel and Wiggins, 1980; Opdyke, 1975; Stoner et al., 1973; Roe and Field, 1965; MacPherson, 1925). Eucalyptus oil carries the US Food and Drug Authority classification GRAS (Generally Regarded as Safe) and is approved for incorporation into foods such as chewing gum and throat lozenges at low concentrations.

Cineole can readily penetrate tissue, one of the reasons for its efficacy in various decongestants and pain relief products (Levison et al., 1994; Yamane et al., 1995). It also has mild bactericidal properties and has been used in herbicidal, insecticidal and allelopathic applications. All these properties are presumably associated with its unique compact chemical form, with the cyclic ether linkage spanning a structure based on cyclohexane (Figure 1).

Essential oils containing cineole demonstrate antimicrobial (Gundidza et al., 1993) and nematocidal (Sangwan et al., 1990) properties. High-cineole eucalyptus oil has been reported to display pesticide qualities, including effects demonstrated by cineole on its own as well as synergistic effects when cineole is used as a carrier solvent for pesticides. Edwards *et al.* (1993) reported that *Eucalyptus* trees with a high cineole content showed less susceptibility to herbivore by Christmas beetles. Calderone and Spivak (1995) found that treating the western honey bee for the parasitic mite *Varroa jacobsonii* with a terpene based solution containing cineole gave a mite mortality of 96.7% against a 4.4% mortality in the control colonies. Scriven and Meloan (1984) have reported that cineole is a natural repellent to the American cockroach and results of tests reported by Corbet *et al.* (1995) for the use of eucalyptus oil and cineole as a mosquito larvicide also indicate it has insecticidal potential. Cineole has been investigated as a fumigant against stored-product insects (Shaaya et al., 1991). It inhibits the enzyme acetylcholinesterase (Ryan, 1988), it interferes with sonic communication and mating in leafhoppers (Saxena and Kumar, 1984) and it is a mosquito feeding and ovipositional repellent (Klocke et al., 1987). Work by Srivastava et al. (1995) has shown that exposure of nymphs of *Dysdercus koenigii* to eucalyptus oil vapours during rearing affected their mortality in the course of their development. A shortening of postembryonic development time was observed for certain exposure times and for both male and female nymphs reaching adulthood there was appreciable loss in fresh weight; a reduction in adult fecundity and hatchability of eggs was also observed in certain nymphal treatments. Schafer et al. (1983) have reported on the effect of cineole on birds.

All these observations suggest that cineole has a potentially large-scale use as a benign agricultural bioagent.

## **Industrial Solvents**

Cineole's combination of cleaning properties and pleasant odour have resulted in its incorporation into a wide range of household cleaning products.

To put this in the context of the future of this compound as a substitute industrial solvent, it is necessary to consider briefly the background of the solvent trichloroethane and of wider environmental issues.

The vapour of the chlorohydrocarbon 1,1,1-trichloroethane ( $\text{CCl}_3\text{CH}_3$ ) is now known to be both an ozone-damaging and a "greenhouse" gas and this solvent has been effectively phased out for all but essential purposes. Worldwide annual production has fallen dramatically from its peak in the early 1990's. Trichloroethane has a relatively low ozone depletion potential (ODP) of approximately 0.11 (Rowland, 1991). (The ODP, which was first suggested by Wuebbles (1983), is the ratio of the impact due to the release of a particular molecule on global ozone loss compared to the impact of a molecule of CFC-11, CFC13.) However trichloroethane's stability in the lower atmosphere (atmospheric lifetime of  $5.7 \pm 0.7$  years: Derwent et al., 1989) and widespread use as a degreaser and general all purpose solvent since the late 1950's means that it is a significant contributor to ozone layer depletion. Despite its adverse environmental record and poor occupational health standing (Baker, 1994; House et al., 1994; Tay et al., 1995), trichloroethane was the degreasing solvent of choice, with annual international sales of the order of a million tonnes in 1993.

High-cineole eucalyptus oil has a combination of chemical and physical properties that makes it suitable for several solvent applications. It is a good solvent for a wide range of materials

- chemically stable, not deteriorating on storage or heating
- liquid over a wide range of temperatures with a moderate vapour pressure at ambient temperature

- slightly soluble in water and has the ability to steam distil
- relatively safe, with minimal environmental and occupational health implications
- a "familiar" but unexploited product worldwide.

Several market sectors have been identified:

- solvent degreasing: low price and high volume. Although there is significant competition from petroleum-based solvents, there is a growing popular demand for "natural" solvents, and high-cineole eucalyptus oil has advantages over other natural solvents like pinene and limonene. Both have development and production constraints as by-products of other industries (wood products and orange juice, respectively), and cineole has an inherent chemical stability compared with the unsaturated terpenoids such as pinene and limonene.
- carrier solvent: medium price and moderate volume. Synergistic efficiency improvement and more controlled application of pesticides have been demonstrated but not yet fully explored.
- extraction solvent: medium to high price and moderate volume. Cineole has been investigated for a few specific applications, but again there is considerable scope for investigation.

There is a significant market opportunity for eucalyptus oil in industrial degreasing and solvent applications. Best practice is changing rapidly in response to the phasing out of trichloroethane under international conventions (the Montreal Accord) to arrest ozone depletion. Solvent systems have been replaced by

- solvent-free systems
- aqueous detergent systems
- natural products which have other industrial ecological advantages over petrochemical products.

### **Measurements of Degreasing Ability**

An important development has been the successful practical trial of high-cineole eucalyptus oil as a workshop degreaser combined with Murdoch University laboratory simulation of practical workshop procedures. Following the trials, eucalyptus oil is used routinely as a degreaser in the Kwinana workshops of Alcoa Australia. Blends are also in use, with reports indicating improved degreasing and a favourable response from workers to their less pronounced eucalyptus door. The other components in the blends are also botanically derived (Barton, 1995; Barton and Knight, 1997).

Although it is unlikely that any one solvent will replace trichloroethane in its full range of applications, cineole has great potential to replace it as a degreaser. Biodegradability and ease of recovery from grease-contaminated solvent through steam distillation are also desirable properties in this solvent. The size of this potential market is 300 times the size of the existing world eucalyptus oil market, so replacing even a small proportion of the degreasing solvent market would dramatically change the situation for eucalyptus oil.

I have been able to demonstrate that high-cineole eucalyptus oil formulations have solvent capabilities comparable to those of trichloroethane. While solvent properties can be assessed by a variety of theoretical and semi-empirical methods, it is desirable to be able to measure degreasing ability directly, but there were no established standard methods.

A typical method for testing the effectiveness of grease removal by a solvent is the Australian Defence Standard 5631 (Method 503/86). In this method a specified surface area of a standard metal panel is coated with a wedge of grease and then immersed in the solvent, or the solvent is brushed onto the grease. The percentage area of the grease removed is estimated visually by viewing the greased surface through a glass panel divided longitudinally into ten equal parts. These methods estimate degreasing ability by assessing surface residue contamination or ultimate surface cleanness after application of the solvent and do not give readily a measure of the rate of grease removal by a solvent. Therefore in the context of degreasers it was considered desirable to develop a more quantitative and reproducible means to measure the effectiveness of a solvent.

For this purpose we developed a method for measuring dissolution characteristics of semi-solid materials in 3 non-aqueous solvents and applied it to the dissolution of several industrial greases. Our method utilises the

rotating disc concept popular in dissolution and electrochemical reaction studies (Riddiford, 1966; Gregory and Riddiford, 1956).

A theoretically ideal rotating disc system consists of an infinite, planar, horizontal surface rotating about a vertical axis with constant angular velocity in a fluid of infinite volume. In practice, a disc of finite radius will conform to the theoretical requirement of an infinite diameter if its radius is much larger than the thickness of the fluid boundary layer which is dragged with the disc. Generally, in practical situations the theoretical requirements are met when the thickness of the boundary layer is less by at least a decade order of magnitude than the disc radius and when the distance from the disc to vessel surfaces is greater by an order of magnitude than the thickness of the boundary layer.

The removal of grease from the surface involves transport of the solvent to the surface, interaction at the interface between the solvent and solute and transport of products away from the interface. In the rotating disc system the most significant transport method is forced convection, but the rate of dissolution is also a function of the diffusion rate through a thin stationary layer, the Nernst diffusion layer, of liquid at the interface. The thickness of this diffusion layer is determined by the speed of rotation in the rotating disc system. Under conditions described that provide laminar flow of a solvent over the surface of a rotating disc, the thickness of the diffusion layer is well defined and reproducible.

An inverted circular brass "cup" is used to accommodate the grease. The upper face of the disc has a centrally mounted vertical spindle for connection to the rotating shaft. The cup is filled with grease and its surface smoothed to allow laminar flow of the solvent over the grease surface. The disc is lowered into the solvent which is in a water jacketed container that has water at constant temperature circulating around it. The solvent volume and the speed of disc rotation are such that laminar flow is approximated. Solvency properties are determined by measuring the mass of grease lost as a function of time during rotation of the cup in the solvent.

The rotating cup method of assessing the degreasing ability of solvents provides a number of advantages over previously used techniques for determining solvency power. These include

- a direct measure of the mass of grease lost from a surface as a function of time; other methods not giving this type of quantitative measure of degreasing power;
- measurement of the degreasing endurance of solvents over a range of concentrations;
- the replacement of immersion in the solvent or brushing with the solvent (as in the Australian Defence Standard Method) with hydrodynamic control during the dissolution process;
- the replacement of visual inspection (Australian Defence Standard Method) with weighing;
- improved reproducibility of results; and
- the ability to be used with all solvent types rather than being restricted to hydrocarbons as is the case for the aniline point (ASTM D611) and the Kauri-Butanol number (ASTM D1133).

Thus the rotating cup method can provide a means for a more rigorous comparison of the degreasing ability of solvents which can facilitate the development and selection of solvents for particular degreasing situations.

Three greases were used. Mobilith SHC 220 is described as a lithium complex grease with over 75% naphthenic and petroleum hydrocarbons. Mobilgrease BP is a high pressure grease with greater than 85% refined mineral oil. Other ingredients include nonanedioic acid dilithium salt (<10%) and lithium-soap thickener (<10%) Molub-alloy 860/220 grease has a high content of petroleum hydrocarbons.

Figure 2 shows results for dissolution studies for the industrial grease Mobilgrease SHC 220. Trichloroethane is the most effective solvent and the commercial hydrocarbon solvent, containing more than 60% naphthenic hydrocarbons, is the least effective of those tested. The degreasing endurance of trichloroethane was lower than for the other solvents. Blend 1 showed no decline in degreasing endurance over the range tested whilst results for cineole were generally constant.

The intercepts of these lines yield the S-codes reported in Table 1 (based on a benchmark value of 100 for 1,1,1-trichloroethane). The low values for ethyl lactate and N-methyl-2-pyrrolidone, sometimes advocated as trichloroethane substitutes, are significant.

The results for the dissolution of the greases presented here for the range of solvents tested show that

- \* it is unlikely that a single replacement solvent with a wide range of applications similar to that of 1,1,1-trichloroethane will be found. It is more probable that solvent blends will be developed for specific applications;
- \* cineole is as elective a degreaser as the hydrocarbons solvents being used as replacements for trichloroethane (except perhaps with greases like Molub-alloy); and
- \* the blending of cineole with suitable liquids can result in a solvent with degreasing ability close to that of trichloroethane and other substitute degreasers currently being (again, perhaps not the case for Molub-alloy).

Hydrocarbons and chlorinated hydrocarbons derived from petroleum have been widely used as degreasing solvents, paint removers and all purpose solvents. Toxicity and environmental concerns over these compounds, particularly 1, 1, 1 -trichloroethane, have resulted in a search for substitute solvents. Studies in these laboratories have assessed the suitability of high-cineole eucalyptus oils for these purposes.

### **Solvent Ability and Solvent Selection**

Some methods make an empirical assessment of solvency power. The aniline point of hydrocarbon solvents (ASTM D611) is the minimum equilibrium temperature for complete miscibility of equal volumes of aniline and the solvent. The Kauri-Butanol number (ASTM D1133) measures the volume of a standard solution of kauri resin in 1-butanol needed to give a cloud point in the solvent. These and similar methods were developed for hydrocarbon solvents and are not necessarily suitable for oxygenated liquids like cineole.

Alternatively, the ability of a liquid to dissolve a substance can be assessed by a comparison of the "cohesion parameter" (or "solubility parameter") values (Table 1) of the solvent and solute. Each compound can be characterised by a cohesion parameter value, which depends upon its structure. The closer their cohesion parameter values, the more likely materials are to be miscible (Barton, 1991; Hoy, 1985; Hansen and Beerbower, 1971). Terpenoid liquids like cineole form one class of compounds for which cohesion parameters are not yet readily available.

The interactions of solvents and solutes are functions of their internal energy, and molecules with the same internal pressure (the energy needed to vaporise unit volume of a substance) are most effective in attracting and interacting with each other because the resultant heat of mixing will equal zero. The cohesion parameter is defined as the square root of the cohesive energy density, which is the ratio of the molar cohesive energy (vaporisation enthalpy) to the molar volume. Cohesion parameter values were determined for cineole using these and related methods, and also estimated in our laboratories from its solubilising effect on a range of polymers.

A vaporisation enthalpy reported for cineole is 44.2 kJ/mol, giving a Hildebrand parameter of 15.8 MPa<sup>1/2</sup> (at 25°C). Enthalpy and density values have not been reported for most terpenoids, so it is necessary to use indirect methods to estimate cohesion parameters. The enthalpy of vaporisation can be calculated from empirical temperature and pressure data and the Clausius-Clapeyron equation. Cohesion parameter values determined for cineole using this and related methods range from 13.4 to 17.6 MPa<sup>1/2</sup>.

The concept of group contributions can be used to estimate cohesion parameters. This assumes that the cohesion parameter for a liquid can be calculated by summing contributions from atoms or structural groups of atoms, and that the properties of materials change in regular manners as the chain length increases. Group contributions to vaporisation energies and group molar attraction constants gave values of 17.0 (subsequently revised to 16.2) and 17.7 MPa<sup>1/2</sup>, respectively (Barton and Knight, 1996).

The cohesion parameter for cineole has also been estimated in our laboratories from its solubilising effect on a range of polymers (Table 2) (Barton and Tjandra, 1993). Polymers were classified into groups: soluble, strongly swollen (>100%), slightly swollen (<101/o) and inert. (Degree of swelling was determined from the difference in specific volume of the polymer before and after a 4-month immersion in cineole. It is also important to determine the compatibility of solvents with polymers so that they can be safely contained and also for cleaning components having polymeric seals or fittings.) A comparison of the cohesion parameters for the polymers with their solubility or swelling in cineole indicates a cohesion parameter for cineole in the range 15.5 to 21 MPa<sup>1/2</sup>. These observations and the calculations discussed above suggest a cohesion parameter for cineole of 16.2 MPa<sup>1/2</sup>.

The suitability of cineole and its blends as degreasers will also require investigation of other properties like flashpoints, as well as the costs of the recovery of the oil and the other liquids. Table 1 provides a comparison of various liquids as potential substitutes for 1,1,1-trichloroethane: the cohesion parameter values should be comparable, the S-codes and the flash points both as high as possible. The flash point of cineole compares favourably with those of most of the hydrocarbon solvents shown here. The blending of small amounts of other sustainably produced liquids reduces the flash point, but not to those of the xylenes and the other aromatic hydrocarbons.

### **Other Components of Eucalyptus Oil**

So far we have concentrated on 1,8-cineole, but even in high-cineole eucalyptus oil there are small quantities of other compounds which have existing or potential specialised uses. Once this oil is produced in high volumes, it will be economic to extract the high-value minor components for particular purposes without reducing the value of the remaining solvent-grade oil.

In addition, we have identified other varieties of mallees which contain higher than usual levels of very interesting chemical, such as natural food flavourings. These can be planted in appropriate areas and harvested separately while still retaining the economies of scale in equipment use.

Both of these opportunities await the development of large-scale eucalyptus oil production and marketing.

### **Renewable Biomass Fuel and Carbon Sequestration**

Eucalyptus oil has been demonstrated to have potential as a fuel component (Takeda and Hoki, 1982) and cineole used as an additive in ethanol-gasoline fuel blends ("gasohol") prevents phase separation in the presence of water (Barton and Tjandra, 1988, 1989). This is another potentially large application, likely to attract interest after world petroleum production peaks, which is predicted to occur in the first decade of the twenty first century. However, there are related uses which may well become significant much sooner.

Australian initiatives to reduce global atmospheric carbon dioxide levels include mandatory generation of a proportion of energy production from renewable rather than fossil sources. These legislative requirements match practical issues in Western Australia, which has communities remote from the existing electricity grid. The woody residue from eucalyptus oil production as a feedstock for steam and electricity production could provide a component of this requirement.

Adequately long time scales for carbon sequestration in plantation vegetation are still the subject of debate, with a range from a few years for woody fuel production to thousands of years for some timber trees. Oil mallees can contribute at both extremes:

Leaf oil (and associated biomass fuel) harvesting cycles are typically two years, providing a rapid renewable biomass fuel cycle.

At the same time the lignotuber or mallee root continues to grow in the ground. Areas near Bendigo in Victoria have been producing oil from the same lignotubers for over a hundred years and some of these lignotubers were probably hundreds of years old when the process started. These carbon sinks will meet even the most stringent definitions of permanent carbon sequestration.

The Oil Mallee Association (1998) estimates an annual carbon sink of 3 or 4 tonnes of carbon per kilometre of "hedge". (A standard oil mallee hedge is a double planting row 2 metres apart with 1.5 metres between trees in each row

## Conclusion

The planting of eucalypts for leaf oil has the potential to simultaneously provide

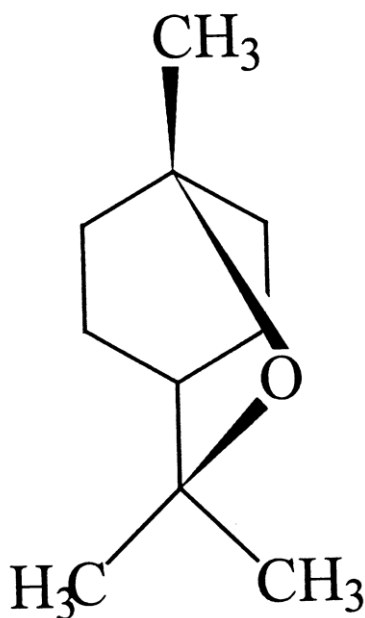
- a commercial incentive for restoring original vegetation,
- a sustainable method of controlling groundwater and salinity,
- an environmentally benign substitute for a widely used solvent damaging to the ozone layer,
- a source of specially chemical products,
- a source of biomass fuels, and
- a carbon sequestration mechanism.

With integrated tree crop systems and improved harvesting and processing technologies, the Western Australian wheatbelt could produce large volumes of high-cineole eucalyptus oil from mallee eucalypts, reliably and well below current market prices. With new industrial markets a scale of planting could be achieved that would result in substantial landcare benefits.

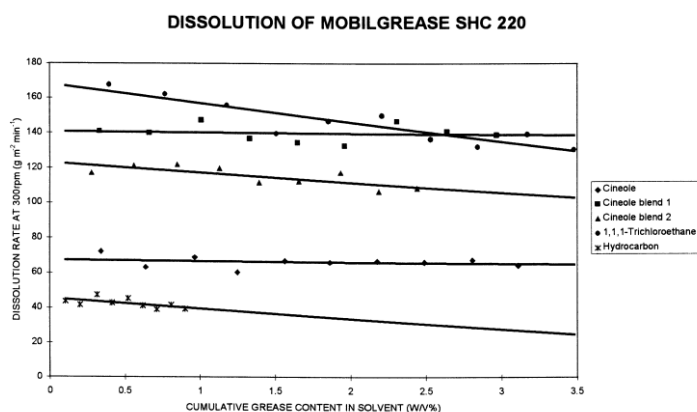
Industrial solvent markets are large and currently in transition following recent withdrawal of 1,1,1-trichloroethane as a result of international measures to control ozone depletion. There is a strong preference in these markets for "natural" replacement products. Although large-scale penetration of these markets would need prices about half those prevailing in traditional eucalyptus oil markets, this goal should be achievable with the potential for economies of scale, genetic advances, and improved harvesting and processing technologies.

The risk of commercial investment in oil mallees can be reduced by diversifying: pursuing an integrated venture yielding high-cineole solvents, high-value specially chemicals, biomass for energy, activated carbon, and lignotubers as carbon sinks as well as natural and sustainable pumps for groundwater control.

**Figure 1.** Molecular structure of 1,8-cineole, showing the system of "fused rings": the cyclohexane ring with 6 carbon atoms and two cyclic ether rings of 5 carbon atoms and an oxygen atom.



**Figure 2.** Rotating cup dissolution studies for the industrial grease Mobilgrease SHC 220 at the standard rotation speed (300 rpm) as a function of the removal of the solvent. The degreasing ability of 1,1,1-trichloroethane is exceeded by Cineole Blend 2 when the solvent becomes contaminated by grease. For this grease, even pure cineole is a better degreaser than the hydrocarbon solvent. Zero-grease intercepts of these lines yield the S-code values.



**Table 1.** Cohesion parameters, S-codes and flash points for 1, 8-cineole, 1, 1, 1 -trichloroethane and a variety of other potential solvents.

Substance	Cohesion parameter MPa <sup>1/2</sup>	----- S-Code -----				
		Mobilith	SHC	Mobilgrease HP	Molub-alloy	Flash Point, °C
1,8-Cineole	16.2	27	65	34	48	
Limonene	16.5	38	104	29	48	
Blend 1	17.4	66	81	32	-	
Blend 2	16.9	7.1	61	-	-	
Hydrocarbon degreaser	-	27	<0.1	-	-	84
1, 1, 1 -Trichloroethane	17.7	100	100	100	-	Nonflammable
p-Xylene	18.1	-	-	-	-	27
Ethylbenzene	18.1	-	-	-	-	15
Ethyl acetate	18.2	716	114	-	-	-3
Toluene	18.2	-	-	-	-	4
m-Xylene	18.2	-	-	-	-	27
o-Xylene	18.5	-	-	-	-	17
Ethyl lactate	21.6	1	17	-	-	48
N-Methyl-2-pyrrolidone	23.7	0.6	<0.1	-	-	86



**Table 2.** The effect of 4 months' continuous exposure to cineole at ambient temperature on a number of polymers.

**Polymers Soluble in Cineole**

Natural rubber ( <i>cis</i> -isoprene)	
Polystyrene	
Styrene-butadiene elastomer	Kemcor; SBR M%te (Austrapol 1220) SBR Yellow (Austrapol 9705) SBR Brown (Austrapol 9712EP)

**Polymers Strongly Swollen by Cineole (more than 100%)**

Polychloroprene	Neoprene
Polyurethane rubber	
Silicone rubber	

**Polymers Slightly Swollen by Cineole (less than 10%)**

Acrylic-styrene-acrylonitrile	Luran VLZ, BASF
Polyester-urethane	Elastollan C78 A15, BASF
Polyether-urethane	Elastollan 1175 IOW, BASF
Polycarbonate/acrylic-styrene-acrylonitrile	Terblend S, BASF
Fluoroelastomer (exhibited shrinkage)	Fluororubber FC 2230, 3M

**Polymers Resistant to Cineole**

Acrylonitrile-butadiene-styrene	Terluran VLC, BASF
Acetal, polyoxyethylene	Ultraforin, BASF
Polycaprolactam, Nylon 6	Ultramid, BASF
Polyhexamethylene adipamide, Nylon 6,6	BASF
Polyethylene	Dotmar and BASF
Polybutylene terephthalate	BASF
Polyethylene terephthalate	BASF
Polymethyl methacrylate	Plexiglas, Rohm; and Lucryl, BASF
Polypropylene	BASF
Polycarbonate	BASF
Polytetrafluoroethylene (Teflon)	
Polyvinyl chloride	

## References

- Ammon, D. G., A. F. M. Barton, D. A. Clarke and J. Tjandra. 1985a. "Rapid and Accurate Chemical Determination of the Water Content of Plants Containing Volatile Oils." *Analyst*. 110: 917-920.
- Ammon, D. G., A. F. M. Barton, D. A. Clarke and J. Tjandra. 1985b. "Rapid and Accurate Determination of Terpenes in Leaves of Eucalyptus Species." *Analyst*. 110: 921-924.
- Baker, E. L. 1994. "A Review of Recent Research on Health Effects of Human Occupational Exposure to Organic Solvents". *Journal of Occupational Medicine*. 36(10):1079-1092.
- Bartle, J. R. 1993. "Commercial Tree Crops: Concepts and Practice". In *Proceedings, Landcare 93 - A Conference for Landcare*, edited by D. A. Hills and J. S. Dug. Perth: Western Australian Department of Agriculture (Misc. Pub. 20/94).
- Barton, A. F. M. 1991. *Handbook of Solubility Parameters and Other Cohesion Parameters*. 2nd Edition. Boca Raton, Florida: CRC Press,
- Barton, A. F. M. 1995. "High Cineole Eucalyptus Oil - A Natural Industrial Solvent." In *Cleaner Production Symposium, Royal Australian Chemical Institute 10th National Congress*. Adelaide.
- Barton, A. F. M. and A. R. Knight. 1996. "Determination of Cohesion Parameters for Terpenoids such as 1,8-Cineole using Semi-Empirical Methods and Calculations Based on Group Contributions." *Journal of the Chemical Society, Faraday Transactions*. 92: 753-755.
- Barton, A. F. M. and A. R. Knight. 1997. "High Cineole Eucalyptus Oils in Degreasing Applications." *Chemistry in Australia*. 64(1): 4-6.
- Barton, A. F. M. and J. Tjandra. 1988. "Ternary Phase Equilibrium Studies of the Water/Ethanol/1,8-Cineole System." *Fluid Phase Equilibria*. 44: 117-123.
- Barton, A. F. M. and J. Tjandra. 1989. "Eucalyptus Oil as a Cosolvent in Water - Ethanol - Gasoline Mixtures." *Fuel*. 68: 11-17.
- Barton, A. F. M. and J. Tjandra. 1993. *Cineole as a Degreasing Solvent* Research Report. Perth: Murdoch University.
- Barton, A. F. M., J. Tjandra and P. G. Nicholas. 1989. "Chemical Evaluation of Volatile Oils in Eucalypts." *Journal of agricultural and Food Chemistry*. 37: 1253-1257.
- Barton, A. F. M., P. P. Cotterill, and M. I. H. Brooker. 1991. "Heritability of Cineole Yield in *Eucalyptus kochii*." *Silvae Genetica*. 40: 37-38.
- Boland, D. J., J. J. Brophy and A. P. N. House. 1991. *Eucalyptus Leaf Oils: Use, Chemistry, Distillation and Marketing* (ACAIWCSIRO). Melbourne: Inkata Press.
- Brooker, M. I. H., A. F. M. Barton, B. A. Rockel and J. Tjandra. 1988. "The Cineole Content and Taxonomy of *Eucalyptus kochii* Maiden and Blakely and *E. plenissima* (Gardner) Brooker." *Australian Journal of Botany*. 36: 119-129.
- Brooker, M. I. H. and D. A. Kleinig. 1990. *Field Guide to Eucalypts. South-western and Southern Australia*. Melbourne: Inkata Press.
- Calderone, N. W. and M. Spivak. 1995. "Plant Extracts for Control of the Parasitic Mite *Varroa jacobsonii* (Acari: Varroidae) in Colonies of the Western Honey Bee (Hymenoptera: Apidea)" *Journal of Economic Entomology*. 88(5):1211-1215.
- Clarke, W. G. and B. H. Moore. 1931. *Reports on Investigations conducted in the Metallurgical Laboratory*. (Bulletin 6, School of Mines). Kalgoorlie: Dept. of Mines.
- Corbet, S. A., G. W. Danahar, V. King, C. L. Chalmers and C. F. Tiley. 1995. "Surfactant-Enhanced Essential Oils as Mosquito Larvicides". *Entomologia Experimentalis et Applicata*. 75(3):229-236.
- Derwent, R. G., A. M. Volz-Thomas and M. J. Prather. 1989. "Scientific Assessment of Stratospheric Ozone." (Report No. 20). *World Meteorological Organization Global Ozone Research and Monitoring Projects*. 2:124.

- Eastham, J., P. R. Scott, R. A. Steckis, A. F. M. Barton, L. J. Hunter and R. J. Sudineyer. 1993. "Survival, 10 Growth and Productivity of Tree Species Under Evaluation for Agroforestry to Control Salinity in the Western Australian Wheatbelt." *Agroforestry Systems*. 21:223-237.
- Edwards, P. B., W. J. Wanjura and W. V. Brown. 1993. "Selective Herbivory by Christmas Beetles in Response to Intraspecific Variation in *Eucalyptus Terpenoids*." *Oecologia*. 95(4): 551-557.
- Furia, T. E, and N. Bellanca, (editors). 1971. *Fenaroli's Handbook of Flavor Ingredients*. Cleveland, Ohio: Chemical Research Co.
- Gregory, D. P. and A. C. Riddiford. 1956. "Transport to the Surface of a Rotating Disc". *Journal of the Chemical Society*. 1956:3756-3764.
- Gundidza, M., S. G. Deans, A. I. Kennedy, S. Mavi, P. G. Waten-nan and A. I. Gray. 1993. "The Essential Oil from *Heteropyxis natalensis* Harv: Its Antimicrobial Activities and Phytoconstituents." *Journal of the Science of Food and Agriculture*. 63:361-364.
- Haley, T. J. 1982. "Cineole(1,8-Cineole)". *Dangerous Properties of Industrial Materials Report*. 2(4):10-14.
- Hansen, C. M. and A. Beerbower. 1971. *Kirk-Othmer Encyclopedia of Chemical Technology*, 2<sup>nd</sup> ed., A, Standen (editor). New York: Interscience. Suppl. Volume:889.
- Hong, C.-Z. and F. G. Shellock. 1991. "Effects of a Topically Applied Counterirritant (Eucalyptaniin) on Cutaneous Blood Flow and on Skin and Muscle Temperatures. A Placebo-Controlled Study." *American Journal of Physica] Medicine and Rehabilitation*. 70(1):29-33.
- House, R. A., G. M. Liss and M. C. Wills. 1994. "Peripheral Sensory Neuropathy Associated with 1,1,1-Trichloroethane." *Archives of Environmental Health*. 49(3):196-199.
- Hoy, K. L. 1985. *The Hoy Table of Solubility Parameters*. South Charleston ": Union Carbide Corporation, Solvents and Coatings Materials Division.
- Klocke, J. A., M. V. Darlington and M. F. Balandrin. 1987. "1, 8-Cineole (Eucalyptol), a Mosquito Feeding and Ovipositional Repellent from Volatile Oil of *Hemizonia fitchii* (Asteraceae)". *Journal of Chemical Ecology*. 13(12):2131-2141.
- Lefroy, E. C. and P. R. Scott. 1994. "Alley Farming: a New Vision for Western Australian Farmland". *Journal of Agriculture*. 35(4):119-126.
- Leung, Y. 1980. "Eucalyptus". *Encyclopaedia of Common Natural Ingredients Used in Food, Drugs and Cosmetics*. New York: Wiley.
- Levison, K. K., K. Takayama, K. Isowa, K. Okabe and T. Nagai. 1994. "Formulation Optimization of Indomethacin Gels Containing a Combination of Three Kinds of Cyclic Monoterpenes as Percutaneous Penetration Enhancers." *Journal of Pharmaceutical Sciences*. 83(9):1367-1372.
- MacPherson, J. 1925. "The Toxicology of Eucalyptus Oil." *The Medical Journal of Australia*. 1925(July 25):108-110.
- Nfilthorpe, P. L., J. M. Hillan, and H. I. Nicol. 1994. "The Effect of Time of Harvest, Fertiliser and Irrigation on Dry Matter and Oil Production of Blue Mallee". *Industrial Crops and Products*. 3 (3):165-173.
- Oil Mallee Association of Western Australia (Inc) (1 998), Quarterly Newsletter, *The Dinkum Oil*, (10) .. 1-2.
- Opdyke, D. L. J. 1975. Monographs on Fragrance Raw Materials." *Food and Cosmetics Toxicology*. 13(1):91 – 112. ("Eucalyptoill, 105-106 and "Eucalyptus Oil", 107-108.)
- Patel S. and J. Wiggins. 1980. "Eucalyptus Oil Poisoning." *Archives of diseases in Children*. 1980:405-406.
- Riddiford, A. C. 1966. "The Rotating Disc System". *Advances in Electrochemistry and Electrochemical Engineering*, P. Delahay(editor). New York: Interscience. 4: 447.
- Roe, F. J. C. and W. E. H. Field. 1965. "Chronic Toxicity of Essential Oils and Certain Other Products of Natural Origin." *Food and Cosmetics Toxicology*. 3:311-324.

- Rowland, F. S. 1991. "Stratospheric Ozone Depletion." *Annual Review of Physical Chemistry*. 42:73 1.
- Ryan, M. F. and O. Byrne. 1988. "Plant-Insect Coevolution and Inhibition of Acetylcholinesterase". *Journal of Chemical Ecology*. 14(10):1965-1975.
- Sangwan, N. K., B. S. Verma, K. K. Verma and K. S. Dhindsa. 1990. "Nematicidal Activity of Some Essential Plant Oils." *Pesticide Science*. 28:331-335.
- Saxena, K. N. and H. Kumar. 1984. "Interference of Sonic Communication and Mating in Leafhopper *Amrasca devastans* (Distant) by Certain Volatiles." *Journal of Chemical Ecology*. 10(10): 1521-153 1.
- Schfaer, E. W., Jr., W. A. Bowles, Jr. and J. Hurlbutt. 1983. "The Acute Oral Toxicity, Repellency, and Hazard Potential of 998 Chemicals to One or More Species of Wild and Domestic Birds." *Archives of Environmental Contamination and Toxicology*. 12:355-382.
- Scriven R. and C. E. Meloan. 1984. "Determining the Active Component in 1,3,3-Trimethyl-2-oxabicyclo[2,2,2]octane (Cineole) that repels the American Cockroach, *Periplaneta americana*." *Ohio Journal of Science*., 84(3):85-88.
- Shaaya, E., U. Ravid, N. Paster, B. Juven, U. Zisman and V. Pissarev. 1991. "Fumigant Toxicity of Essential Oils Against Four Major Stored-Product Insects." *Journal of Chemical Ecology*. 17(3):499-504.
- Shiel, D. 1985. *Eucalyptus - Essence of Australia*, Cariton, Victoria: Queensberry Hill Press,.
- Srivastava, R. K., G. Gurusubramanian and S. S. Krishna. 1995. "Postembryonic Development and Reproduction in *Dysdercus Koenigii* (F) (Heteroptera, Pyrrhocoridae) on Exposure to Eucalyptus Oil Volatiles." *Biological Agriculture and Horticulture*. 12(1): 81-88.
- Stoner, G. D., M. B. Shimkin, A. J. Kniazee, J. H. Weisburger, E. K. Weisburger and G. B. Gori. 1973. "Test for Carcinogenicity of Food Additives and Chemotherapeutic Agents by the Pulmonary Tumor Response in Strain A Mice." *Cancer Research*. 33: 3069-3085.
- Takeda, S. and M. Hoki. 1982. "Study of Eucalyptus Oil and its Application to Spark Ignition Engines". *Mie Daigaku Nogakubu Gakujutsu Hokoku*. 64:5 5.
- Tay, P., J. Pinnagoda, C. T. Sam, S. F. Ho, K. T. Tan. and C. N. Ong. 1995. "Environmental and Biological Monitoring of Occupational Exposure to 1,1,1-Trichloroethane." *Occupational Medicine-Oxford*. 45(3):147-150,
- Webb, N. J. A. and W. R. Pitt. 1993. "Eucalyptus Oil Poisoning in Childhood: 41 Cases in South-East Queensland." *Journal of Paediatrics and Child Health*. 29:368-37 1.
- Wuebbles, D. J. 1983. "Chlorocarbon Emission Scenarios: Potential Impact on Stratospheric Ozone." *Journal of Geophysical Research*. 88:1433-1443.
- Yamane, M. A., A. C. Williams and B. W. Barry. 1995. "Effects of Terpenes and Oleic Acid as Skin Penetration Enhancers towards 5-Fluorouracil as Assessed with Time; Permeation, Partitioning and Differential Scanning Calorimetry". *International Journal of Pharmaceutics*. 116:237-25 1.