Stability of pure Australian Tea Tree Oil

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Introduction

The Australian Tea Tree Industry Association (ATTIA Ltd) is an Australian-based not-for-profit organization formed in 1986 as the peak body to promote and represent the interests of the Australian tea tree industry. From the grower/producers to the manufacturers of off-the-shelf products for public use, ATTIA supports and promotes the responsible use of 100% pure Australian tea tree oil (TTO).

ATTIA's aim is to develop a stable, cohesive, environmentally friendly, and internationally competitive TTO industry producing quality assured 100% pure Australian TTO that meets or exceeds international standards. ATTIA promotes the safe effective use of 100% pure Australian TTO for a wide range of applications.

ATTIA members include growers, processors, exporters and product manufacturers. We have an international associate membership of importers and manufacturers. We are active in maintaining an Australian and International Standard for tea tree oil, and promote an industry-wide Code of Practice. Our membership accounts for around 95% of the Australian TTO crop.

This document provides a synopsis of research conducted on the stability of 100% pure Australian TTO and expresses ATTIA's opinion, based on research and experience, for optimal storage times (use-by, best-before or retest dates) and packaging choices for pure Australian TTO in Code of Practice (COP) approved containers for transport and storage as well as in glass or aluminium containers used for retail sale of the product.

Summary

Much discussion has occurred over many years on the stability and therefore the 'use by', 'retest' or 'best before' date for 100% pure Australian TTO. A body of research data is available on the subject.

Although tea tree oil has demonstrated excellent stability for periods in excess of 2 years at temperatures of 40°C in ATTIA approved packaging **ATTIA recommends that wherever possible TTO should be stored under stable conditions, preferably at or below 25°C.**

The answer to an often posed question on the 'use-by' date of tea tree oil depends entirely on level and frequency of exposure to oxygen from the air. Thus how it is stored, handled and transported from immediately post-distillation to final consumption is critical. For this reason ATTIA's COP Quality Manual goes into extensive detail regarding the proper storage, handling and transportation of TTO to ensure it maintain its purity and consistency.

Tea tree oil, particularly in the presence of light, air (oxygen) and elevated temperature degrades over time. The decrease in levels of α-terpinene and γ-terpinene over time and the increase of ρ-cymene and peroxide levels are prime indicators of this ageing (degradation) process. [1].

> **ATTIA recommends that the use-by (best before or expiry) date for pure Australian tea tree oil sold in commercially available small (up to 100 ml) dark glass bottles stored at ambient temperature be set at 12 months (1 year) from when first opened or 24 months (2 years) in unopened bottles.**

For TTO storage ATTIA's Code of Practice [2] requires producers to use only stainless steel bulk storage vessels. Stainless steel, uncoated aluminium flasks with PTFE wadding, level 5 fluorinated HDPE containers and caps as well as specific Schütz IBC's are approved as transport vessels and to store the oil in cool

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(ambient), dark conditions with no exposure to air (oxygen). When stored correctly pure Australian TTO can retain its quality for periods of up to 10 years [3] although this is not recommended.

> **ATTIA recommends that the use-by (best before or retest) date for pure Australian tea tree oil sold in correctly filled, purged (Nitrogen or Argon) and tightly sealed COP approved vessels stored at ambient temperature be set at 36 months (3 years) from the filling and sealing date.**

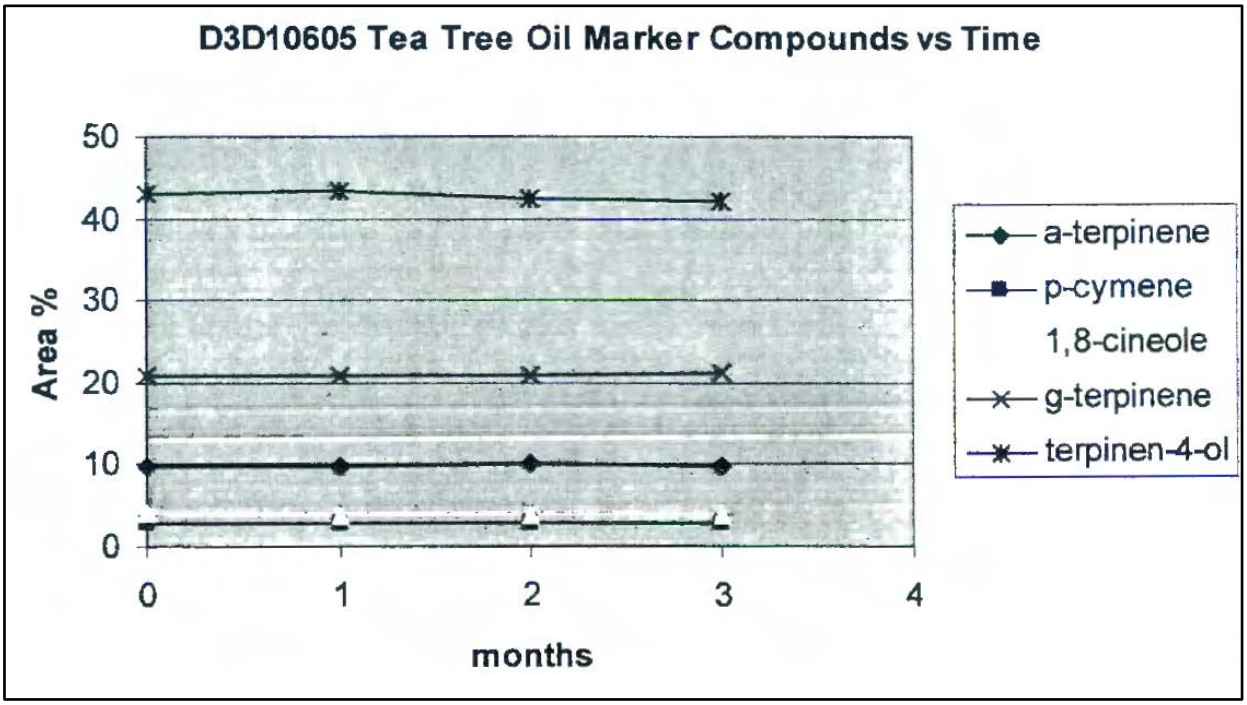
If there is any doubt about the quality of pure Australian TTO, a sample should be tested or retested according to international standard **ISO 4730: 2017 Essential oil of *Melaleuca*, terpinen-4-ol type (Tea Tree oil)** or its successors. The levels of terpinen-4-ol, ρ-cymene, α-terpinene, γ-terpinene and terpinolene can then be used to determine potential levels of oxidation. This is particularly useful when compared with the original Certificate of Analysis (CofA) issued when the batch was first created. If there is still doubt then the peroxide value of the oil may also be determined using appropriate analytical standards.

ATTIA recommends that peroxide levels should be no higher than 9.0 milli-eq. O_2/Kg.

Amber Glass bottles stored in a cool (ambient), dark environment

The Australian **Poisons Standard** requires the use of suitably marked and/or labelled dark amber glass bottles for any product classed as an S6 poison; TTO falls into this class. The use of dark or amber glass bottles may not be a legislative requirement in other jurisdictions. The degradation of TTO usually only occurs when it is in direct contact with air (oxygen) allowing oxidative degradation of some constituents.

Data available to ATTIA for oil stability in accelerated (40°C) and real time retail-shelf conditions, including exposure to fluorescent light, demonstrates no discernible difference in the TTO quality based on constituent values in either amber or clear glass bottles at the end of a three month trial – see Figure below.



A small increase in peroxide level from 0.6 to 4.6 after 3 months was observed in one of the samples. This slight upward trend in the peroxide level is minor when compared with degraded TTO which typically has peroxide levels greater than 10.0 Milli-Eq. O_2/Kg. While peroxide levels increased for both batches the total levels observed in both amber and clear glass remained well below 9.0 milli-eq. 0_2/Kg.

In 2007 a jointly commissioned ATTIA/RIRDC study [3] asked researchers to investigate the stability of 100% pure Australian TTO. The objective of this study was to determine the changes in tea tree oil composition

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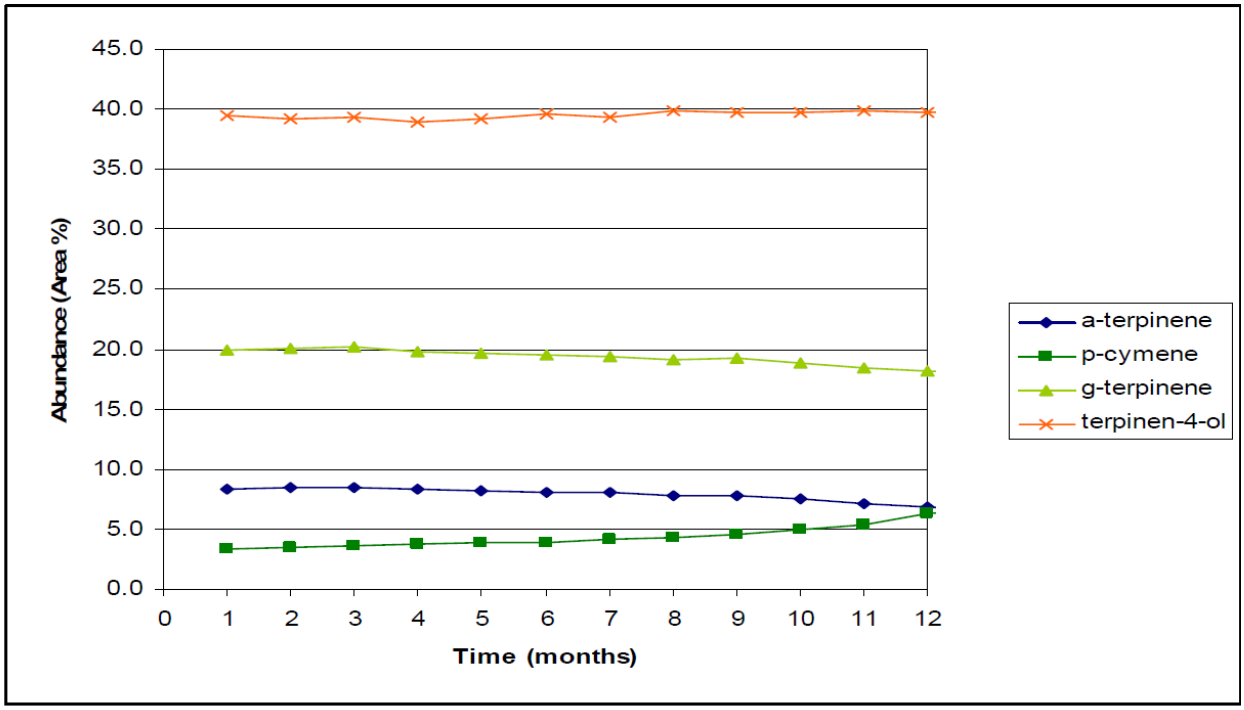
and peroxide value over 12 months under simulated in-use conditions using 100 ml round amber glass bottles stored in controlled conditions at 25 °C.

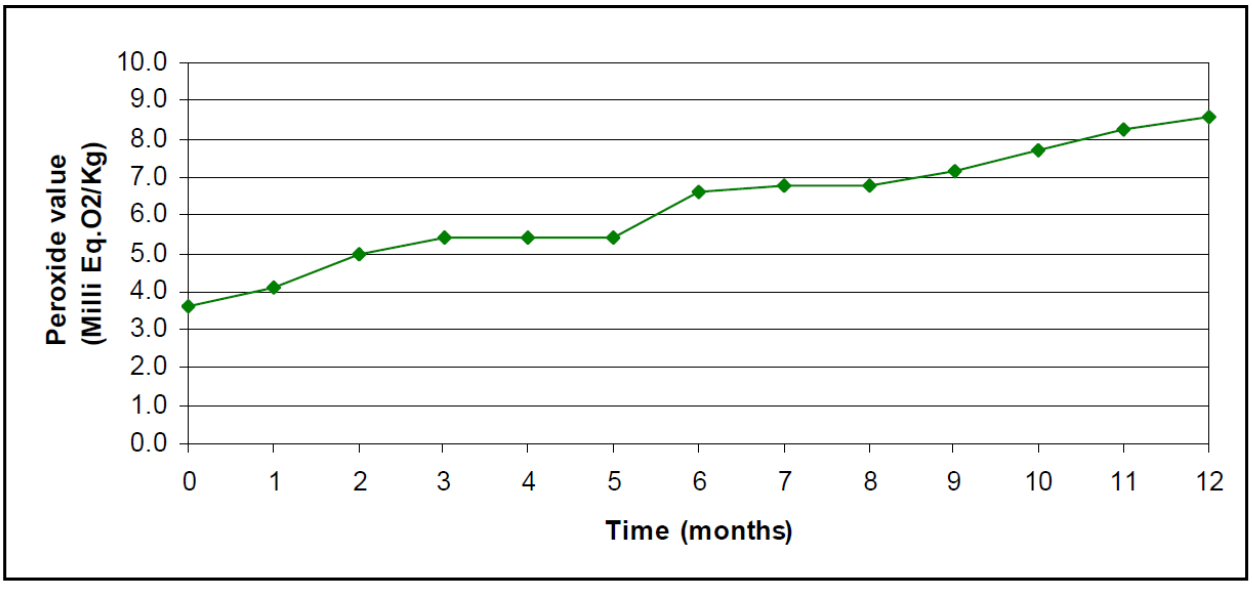
The results indicate that duplicate samples of the two tea tree oil batches tested remained relatively stable over the test period. No significant change was observed in the level of terpinen-4-ol. In both batches after 6 months there is a noticeable downward trend in α-terpinene and γ-terpinene with a similar upward trend in ρ-cymene. See Figure 1 on page 2.

Figure 1. Batch 60175 – Abundance of Major Tea Tree Oil Components over Time



The peroxide level in both batches rose gradually over the test period. See Figure 3 below.

Figure 3. Batch 60175 – Peroxide level over Time



Researchers concluded that 100% pure Australian tea tree oil monitored over 12 months at 25°C using a standard in-use protocol confirmed that the oils used in this study were stable and safe for use over that period.

On the basis of these results ATTIA Ltd recommends that a use-by (best before) date for pure Australian tea tree oil sold in dark glass bottles in a cool (ambient) dark environment be set at 12 months (1 year) from when first opened or 24 months (2 years) in unopened bottles.

Bulk stainless steel or other non-reactive containers

For bulk storage ATTIA's Code of Practice [2] requires producers to use only stainless steel bulk storage vessels. Stainless steel, uncoated aluminium flasks with PTFE wadding, level 5 fluorinated HDPE containers and caps as well as specific Schütz IBC's as well as specific Schütz IBC's are approved as transport vessels and to store the oil in cool (ambient), dark conditions with no exposure to air (oxygen). Producers are also encouraged to sparge the headspace of any storage containers with Nitrogen or Argon to exclude air. Incorrect storage and handling procedures can cause oil quality to deteriorate rapidly through oxidation. Quality may alter to the point where it is not saleable or poses a contamination risk to other oil it may be batched with. It is particularly important to manage air exposure in partially filled containers, preferably by sparging with an inert gas.

Although tea tree oil has demonstrated excellent stability for periods in excess of 2 years at temperatures of 40°C in ATTIA approved packaging **ATTIA recommends that wherever possible TTO should be stored under stable conditions, preferably at or below 25°C.**

Southwell [1] reported that laboratories were surveyed for tea tree oil and product analyses where both peroxide value and ρ-cymene proportion were determined. Peroxide values for 139 tea tree oils were found. For 77 of these the ρ-cymene proportion had also been determined. Records also showed aged oils remain stable for from 3-10 years if stored correctly.

Brophy et al [3] reported that the variability of the composition of aged oils suggests that oil will retain original quality for 10 years or more if stored in tightly sealed non-reactive vessels under cool (ambient), dark, and dry conditions. The extrinsic factors that accelerate oxidation has shown that in the presence of air and sunlight for 7 months ρ-cymene concentration can increase 2-fold while α-terpinene, γ-terpinene and terpinolene concentrations are halved.

Brophy et al went on to say: *In an attempt to determine whether this oxidation was brought about by aging or by extrinsic factors such as moisture, light, or oxygen, several samples of different ages and storage conditions were analysed and compositions compared. Deterioration rates were variable, with occasional samples oxidizing rapidly and failing to meet the requirements of the ISO Standard. After periods as brief as 21 months, some samples contain 20-40% ρ-cymene and are almost devoid of α-terpinene, γ-terpinene and terpinolene, all of which oxidize to ρ-cymene.*

Some of the data extracted from Table 3 in the paper from Brophy et al: 1986 is shown in Table 1 below which demonstrates the change in levels of ρ-cymene, α-terpinene, γ-terpinene, and terpinolene over time depending on the relative deterioration rate. The presence of oxidative degradation compounds, particularly ρ-cymene and peroxides appears to accelerate degradation exacerbated by increasingly higher levels. This reinforces the need to continuously optimise storage conditions for 100% pure Australian TTO immediately after distillation is completed.

Table 1: Data extracted from Brophy et al (1986) demonstrating change in component % in differing environments

Sample No	**1**	**2**	**3**	**4**	**5**
Age (Years)	**10**	**10**	**5**	**2**	**1**
Relative deterioration rate	**Slow**	**Rapid**	**Rapid**	**Rapid**	**Moderate**
Component %					
terpinen-4-ol	41.6%	31.5%	45.9%	23.8%	37.3%
ρ-cymene	4.3%	32.0%	21.7%	35.3%	8.0%
α-terpinene	5.8%	0.0%	N/A	0.1%	6.6%
γ-terpinene	15.0%	trace	trace	trace	17.6%
terpinolene	2.7%	trace	trace	trace	3.1%

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Based on these data ATTIA recommends that the use-by (best before or retest) date for 100% pure Australian TTO sold in correctly filled, purged (Nitrogen or Argon) and tightly sealed COP approved vessels stored at a cool (ambient) temperature be set at 36 months (3 years) from the filling date.

References

1. Southwell IA (2006) ρ-Cymene and Peroxides, indicators of oxidation in tea tree oil, RIRDC Publication No 06/112 available from URL https://www.agrifutures.com.au/wp-content/uploads/publications/06-112.pdf
2. Entwistle P(2005) *Australian Tea Tree Industry Code of Practice*, available from URL http://www.attia.org.au/teatree_about_quality.php
3. Brophy JJ, Davies NW, Southwell IA, Stiff IA, Williams LR (1989) *Gas chromatographic quality control for oil of Melaleuca Terpinen-4-ol type (Australia Tea Tree).* Journal of Agricultural & Food Chemistry 37: 1330-5 available from URL https://pubs.acs.org/doi/abs/10.1021/jf00089a027
4. Southwell IA (2007) *Tea Tree Oil Stability and Evaporation Rate*, RIRDC Publication No 06/112 addendum available from URL https://www.agrifutures.com.au/wp-content/uploads/2020/03/06-112_addendum.pdf

Date	Version No.	Changes	Author
01 May 2012	1.0	Original document – superseded by ver. 1.1 on 11 May 2020	Tony Larkman
11 May 2020	1.1	Significant changes made – read the entire document.	Tony Larkman

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