Second fiddle: a review of lesser-known volatile binding media in conservation

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While cyclododecane (CDD) is well known to conservators as a versatile material for temporary treatments, other volatile binding media have also been tested for use in conservation. Camphene, tricyclene and menthol have all been suggested as alternatives, each having slightly different properties that can make them more suitable for some applications. This paper reviews the literature about these materials and summarises what is known about their characteristics. Concern about possible health effects from CDD has led to recent interest in the alternatives, particularly menthol. Menthol is inexpensive, has good working properties and forms a fine-grained film. It has potential uses particularly for moulding and on archaeological sites, where it may even perform better than CDD in slightly damp conditions. These benefits need to be offset against its strongly irritant vapour. Camphene and tricyclene sublime rapidly and once seemed promising materials for very short term treatments. However, camphene is unstable and requires an antioxidant additive, which may leave residues after sublimation. It is also now recognised as more hazardous than previously thought. Recent research suggests that menthyl lactate and cyclododecanone also have potential as alternatives to CDD, though more work is needed to understand these materials fully.

1 Introduction

Over the last 20 years, cyclododecane (CDD) has been by far the most widely used volatile binding medium (VBM), with a very broad range of applications reported by conservators and preparators (Rowe and Rozeik 2008). However, there are alternative volatile binders that may also be used in conservation. Menthol, tricyclene and camphene have been much less popular, and much less has been written about how they are used. More recently, menthyl lactate and cyclododecanone have been explored as alternatives to CDD. Less than 10% of publications about VBM deal with these materials, and until recently only German conservators reported using them (Rozeik 2018).

Recent concern about the effects of CDD on human health and the environment, and also some dissatisfaction with its working properties, have in the last five years led conservators outside Germany to reconsider the other volatile compounds (Han et al. 2014; Langdon 2012). There are now a number of examples of conservators choosing these compounds in preference to CDD. As they are still comparatively little known, this paper offers a review of their use in conservation to date.

2 The history of alternative volatile binders

The idea for using volatile binders in conservation was born when Hans Hangleiter used xylene frozen with liquid nitrogen as a temporary adhesive (Hangleiter and Saltzmann 2015). Once the xylene thawed it could flow away and evaporate, leaving no trace. The principle behind this method was obviously very attractive. However, the need to freeze the solvent was a limitation, in that many artefacts would not be able to withstand extreme local cooling. It was also somewhat awkward to do in practice. Hangleiter contacted the chemists Elisabeth and Erhard Jägers, and together they investigated whether subliming compounds existed that could be used in a more suitable temperature range for treating historic artefacts.

Once they started looking for alternative volatile binders, Jägers, Jägers and Hangleiter found that there were actually quite a few subliming compounds that they could choose from. However, several of these had to be excluded because they were too toxic or environmentally damaging for conservation use – for example naphthalene (used in mothballs), camphor (a very well known, strong-smelling compound with ancient medicinal and food uses) and $p$-dichlorobenzene (used as a pest...
fumigant and deodorant in urinals) (Hangleiter et al. 1995). The substances that are known in conservation today were selected because they are hydrophobic, are all soluble in standard non-polar solvents and have a low enough melting point that they can be applied to objects at fairly low temperatures (Jägers 1999).

3 Camphene and tricyclene

Camphene and tricyclene are chemically closely related and are often used in mixtures in conservation, so will be considered together.

The camphene molecule is shown in Figure 1. Camphene (C₁₀H₁₆, CAS no. 79-92-5) occurs naturally in essential oils from various pine species, and it is also produced industrially as an intermediate in the synthesis of compounds found in perfumes, lacquers, cleaning products, insecticides etc (US National Library of Medicine 2015). The synthetic version of camphene is a racemic mixture (in other words it contains mirror image isomers of the same molecule) (Hangleiter et al. 1995). It is a waxy white solid that melts at 48–52°C (Sigma Aldrich 2018). The camphene molecule includes a double bond, making it rather sensitive to oxidation. In practice, camphene breaks down quite readily and needs to be stabilised with an antioxidant.

Camphene is readily soluble in non-polar solvents and fairly soluble in polar solvents apart from water. It can therefore protect surfaces from water but is unsuitable as a barrier against any other solvents. Camphene is always applied as a melt, because if it is applied in solution it actually fails to form a film. When it is dissolved it forms an azeotropic mixture with the solvent, where the melting point of the camphene is lowered to the point that it is no longer solid at room temperature (Hangleiter no date). This means it cannot form a solid film when the solution is painted onto an object.

It is important to note that camphene and tricyclene both have low flash points (35°C and 26°C respectively), and are easily ignited. In fact camphene was used as a lamp fuel in the nineteenth century and was notorious for being explosive and dangerous (for example, see the comments by R.V. de Guinon in his patent for a non-explosive camphene lamp (de Guinon 1852)). It is important to keep both substances away from naked flames, especially as they are mostly used in molten form.

Tricyclene (C₁₀H₁₄, CAS no 508-32-7) is also a component of essential oils from conifers; the molecule is shown in Figure 2. However, the molecule is saturated and so it is more stable than camphene. In fact, tricyclene is produced as an intermediate in the synthesis of camphene and even in so-called ‘pure’ camphene, there may be 10–20% tricyclene present. Tricyclene melts at 64°C (Sigma Aldrich 2006).

During the manufacture of camphene there is a stage at which camphene and tricyclene are both present about equally. This is referred to in the literature as the ‘technical mixture’ of camphene and tricyclene, and historically it has been readily available to conservators in small quantities from Kremer Pigmente in Germany (purer versions of camphene or tricyclene have to be obtained from chemical suppliers if required). The melting point of this mixture is slightly lower than for camphene or tricyclene alone (35°C), and it is slightly more volatile. The mixture still needs a small amount of stabilisation with an antioxidant – namely 25 ppm butylhydroquinone (Kremer Pigmente 2015a). In 1995, Jägers, Jägers and Hangleiter reported that this gave good
stability (Hangleiter et al. 1995). However, Hangleiter subsequently experienced problems with the stability of large quantities of the stored mixture and therefore stopped using it (Hangleiter 2015).

Although it was previously possible to buy the technical mixture of camphene and tricyclene from Kremer Pigmente, in 2013 it was discontinued because the material was reclassified as more and more hazardous, making it difficult for Kremer to store. For a while, it was possible to buy the mixture from Kremer in 170kg units (Kremer Pigmente 2015b) but it is now no longer obtainable.

In the literature it is very rare to find any mention of the use of camphene or the camphene–tricyclene mixture for actual treatments: Hangleiter published a couple of examples (Hangleiter 1998b, 2000) and it has recently been tested by Sadek et al for protecting ceramics during desalination (Sadek et al. 2018). The addition of an antioxidant may well put conservators off using it, as they assume that once the camphene itself has sublimed the antioxidant will remain on the surface of the object. This assumption is apparently supported by two recent and separate conservation research projects, which found unidentified residues on glass slides after complete sublimation of the camphene–tricyclene mixture supplied by Kremer (Aalto 2010; Langdon 2012).

In the 1990s, camphene was considered to have low oral and dermal toxicity, though it was known to cause irritation if it got in direct contact with the eyes (Hangleiter et al. 1995). However, more recently camphene has been identified as a substance of very high concern (SVHC) on the Trade Union Priority List for REACH Authorisation published by the European Trade Union Institute, the aim of which is to contribute to the practical implementation of the European REACH legislation on chemical use. The Substitutions Support Portal SUBSPORT is a free website that offers less toxic alternatives to hazardous chemicals, and here it is recommended that conservators should use tricyclene instead (SUBSPORT no date).

Pure tricyclene seems theoretically preferable to camphene, since it is has similar properties but is much more stable. In 1995 when VBMss were first introduced to conservators, pure tricyclene was hard to come by and very expensive. This may be why there are no published accounts of it ever being used in conservation. Unfortunately, tricyclene has recently become effectively unobtainable so one can now only speculate about its potential. The only company selling it as a solid in small quantities, Sigma Aldrich, discontinued sales in 2014, for unknown reasons. In July 2015, tricyclene was only obtainable from the Wuhan 3B Scientific Corporation in China, who would supply 1 kilogram for $15,800 (excluding post and packing) (Wuhan 3B Scientific Corporation 2015). This price puts tricyclene out of the reach of most conservators.

Camphene and tricyclene are both highly toxic to aquatic life and so if they ever are used, they must be disposed of legally and responsibly (Sigma Aldrich 2006, 2018).

4 Menthol

The molecule of menthol is shown in Figure 3. Menthol is the main constituent of peppermint oil, and is very well known as a flavouring and natural decongestant. It is available as a naturally derived product (L-menthol) and a synthetic compound (DL-menthol). These two versions of menthol have different CAS numbers, namely 2216-51-5 (L-menthol) and 89-78-1 (DL-menthol). As with camphene, synthetic DL-menthol is a racemic mixture containing mirror image isomers of the same molecule, whereas L-menthol is not racemic. There are some differences in the properties of the two materials, since L-menthol has a higher melting point (42–45°C) than DL menthol (31–35°C). L-menthol also has a higher flash point (93°C as opposed to 80°C for DL-menthol). However, both have much lower melting points than cyclooctadecane, which melts at 58–60°C. A useful comparative table of data is given in Langdon (2012).
The menthol sold by Kremer Pigmente is L-menthol. This is not stated explicitly in the product data sheets, but it can be deduced from the CAS number on the MSDS (Kremer Pigmente 2013), and the fact that the melting point is given as 41–44°C (Kremer 2015). DL-menthol and L-menthol are both also available from chemical suppliers, for a similar price. As yet there is no published information about whether the two forms of menthol behave significantly differently in conservation applications.

Like camphene, menthol is not a saturated hydrocarbon. It has an OH (hydroxyl) group on the third carbon, so it is fairly soluble in polar solvents like alcohols and ethers, as well as readily soluble in non-polar solvents. The solubility in polar solvents also means that menthol is less hydrophobic than the other VBMs. It is therefore not suitable for treatments where a very effective seal against water is needed.

The presence of the OH group also means that, in theory, menthol could react with materials in an artefact, as it has the potential to oxidise or react in other ways under acidic conditions. Some conservators have expressed concern about this. For example, Historic Scotland evaluated menthol for use in the temporary facing of fragile renaissance painted wooden ceilings (Thuer 2011). It was thought that the acidity of the wooden substrate might facilitate a reaction with menthol, and that the product (menthone) could fail to sublime completely and remain on the surface.

However, a Chinese group recently investigated menthol as a temporary consolidant for polychrome negative prints from Qin Shihuang’s terracotta army, and they reached a different conclusion (Han et al. 2014). They state that menthol requires more aggressive conditions to activate this sort of reaction, and that in ambient or cool conditions it is most unlikely to react with an ancient surface. For their purposes, therefore, they consider menthol inert. It is interesting in this context to quote from Atkinson and Yoshida, who wrote about their experiences trying to oxidise menthol to menthone in 1882. They reported that ‘Weak chromic acid liquor has very little action upon menthol at 100 °’ (Atkinson and Yoshida 1882: 50). It was necessary to heat menthol for 10 hours at 120 °C in acid bichromate solution to make it react to form menthone. Other experiments to convert menthol into other substances required similarly aggressive heating or treatment with highly reactive chemicals like nitric acid (Atkinson and Yoshida 1882; Moriya 1881). These accounts support the supposition that menthol is fairly unreactive in ambient conditions. However, if a conservation treatment involving menthol with reactive materials, heating or electrolysis is proposed it would be wise to consult a chemist about possible interactions beforehand, as well as testing samples.

Menthol is attractive to conservators because it is easy to use, especially when using the pure melted wax. CDD has a much higher melting point and when applied by brush it often solidifies before it even touches the object. This is especially problematic on archaeological sites where the temperature is cool (Han et al. 2014). Menthol has a much lower melting point than CDD so brush application is significantly easier. Menthol also forms a dense even film which is useful for mould-making. It can be used to seal an original surface to protect it from silicone oils in moulding compounds, while retaining fine surface detail (Breyer et al. 1999; Hangleiter 1998b). It is more difficult to achieve this detail with CDD because of the awkward working properties when using it in molten form.

Menthol is reported to have the best adhesive properties of all the volatile binders (Hangleiter et al. 1995; Jägers 1999; Han et al. 2014) and this is attributed to the OH group on the molecule making it the most polar of these substances. The Chinese researchers also found that despite being more viscous than CDD, it penetrated terracotta samples to a similar depth; again, the OH group was thought to help penetration because the samples themselves have some water content (Han et al. 2014). Another potentially useful feature is that menthol adheres better to damp surfaces than CDD and so may offer a useful alternative for block lifting archaeological material in damp conditions.

Little research has been done into potential residues left by menthol. Han et al. (2014) found that it sublimed completely from glass slides and after 70 days there were no traces detectable by GC–MS (which has a detection limit of 5 ppb). Langdon also tested for residues after sublimation of menthol and did find some, but this may have...
been due to experimental anomalies (Langdon 2012). As with all volatile binders, it is important to ensure that the products used in conservation are of high purity, and if in doubt to test any batch on a glass slide before use.

Menthol is strongly irritating to mucous membranes and so not suitable for large scale use. The vapour is very smelly (Hangleiter 1998a; Thuer 2011), and large quantities of it could be overwhelming. Menthol is also toxic to aquatic life forms and so must be disposed of in accordance with local regulations and not with normal domestic waste (Kremer Pigmente 2013).

5 Sublimation

One of the major ways that the VBMs differ from each other is in their sublimation rate. This is an important concern for conservators in planning treatments. Camphene and tricyclene have higher vapour pressure and sublume about ten times faster than CDD and menthol, which, despite their different melting points, have quite similar sublimation times (Jägers 1999). Camphene and tricyclene sublume so quickly that they are only present on surfaces for a few hours. This means they are only useful for very short term applications – examples include stabilising crumbling surfaces while samples are taken or crusts are removed from wall paintings (Hangleiter 1998b), and holding fragments in place or sealing paint surfaces during adhesive treatment from behind (Hangleiter 2000). If tricyclene or camphene are needed for longer they have to be applied very thickly, which is not necessarily economic (Hangleiter 1998a).

CDD often sublimes more slowly than people expect, and studies of the sublimation rate from different surfaces show that there are many variables, like temperature, airflow and porosity of the substrate, that all influence how fast it evaporates (Stein et al. 2000; Hiby 1997; Bruhin 2010). The same factors presumably affect the sublimation of all the VBMs, although no studies have been published except for CDD.

The sublimation of menthol and CDD were compared in detail by Han et al. (2014), who looked at sublimation rates from glass slides and terracotta samples. Interestingly they found that menthol sublimed more slowly than CDD from a glass slide, but this was completely reversed on terracotta samples, where CDD sublimed more slowly than menthol. This result was the opposite of what Hangleiter, Jägers and Jägers predicted in 1995 (Hangleiter et al. 1995). Basing their hypothesis on CF Hansen’s solvent theory, they proposed that non-polar substances would be released from porous substrates more quickly than polar substances, because most substrates are polar and so tend to retain polar solvents. But as shown above, menthol is more polar than CDD, yet Han et al. found it evaporated more quickly from the terracotta samples. This suggests that the sublimation rate of menthol is speeded up on terracotta because there is more surface area for sublimation within the structure of the pores and this effect is more important than the polar nature of menthol.

Han et al. also found that the sublimation rate of menthol was proportional to the weight of the sample, so that the menthol sublimed more quickly when there was more of it.

6 Mixtures

In principle it might be possible to mix combinations of volatile binders to achieve an optimised sublimation time. Hangleiter and Langdon have both experimented with mixing the fast-subliming technical mixture of camphene–tricyclene with the slower-subliming CDD. Unfortunately, this produces an azeotropic mixture, just as camphene does with solvents. This means that the melting point of the solids is lowered in the mixture to the point that the substances become liquid at room temperature and can no longer function properly as sealing or hydrophobic layers (Hangleiter 1998a; Langdon 2012). Langdon has also tested CDD with small additions of menthol (5 or 10%) to reduce the sublimation time, with some success (Langdon et al. 2018). However, if the proportion of menthol is too high the mixture becomes too soft at room temperature to be useful as a temporary support (Langdon 2012).

It is also possible to slow sublimation by adding 1% naphthalene to CDD, which retards the sublimation time and creates a harder film (Hangleiter 1998a). There is no published account of this being
used in an actual treatment. As it is possible to slow sublimation down by physical means, like sealing the object in polyethylene film, there is probably little need for adding a more toxic substance to CDD.

7 Conclusion

At the time of the Subliming Surfaces conference in 2015, there were three volatile binders that could be considered as alternatives to cyclododecane: camphene, tricyclene and menthol. Of these, only menthol was stable, available and affordable, and none of the alternatives could rival the range of applications where CDD has been tried and tested.

However market forces and recent research mean that the situation has changed quite rapidly, and at the time of writing this update (autumn 2018), there is new interest in alternatives to CDD. The price of cyclododecane has more than doubled since 2015 (Kremer Pigmente 2018) and some conservators report difficulty in getting hold of it (Pieri 1999). There is also still concern about the safety of CDD, which is another factor stimulating interest in alternatives (Koss Schrager et al. 2017). New substances have also been proposed for use in conservation since 2015, so the potential for alternative VBMs can be summarised rather differently today.

95% pure camphene is currently available from chemical suppliers Sigma-Aldrich and is slightly cheaper than CDD (Sigma Aldrich 2018). Camphene is problematic because it needs to be stabilised with an antioxidant and it has also been identified as a substance of very high concern for health. However, it has recently been tested for use in protecting ceramics during desalination (Sadek et al. 2018). The fast sublimation rate of camphene could make it preferable to CDD for some applications, for example as a hydrophobic mask during grouting or flake-laying, or to stabilise fragile areas during sampling. However, this feature may not be enough to compensate for the significant health and stability issues. Tricyclene is apparently a much more stable material with the same benefits as camphene, but unfortunately it is still unavailable commercially in Europe.

Menthol is currently the best understood alternative to cyclododecane. Despite having fairly similar sublimation rates to CDD, menthol does have other distinct advantages. It has better working properties when applied by brush, can adhere much better to damp surfaces and easily forms a very even, dense film. For mould-making and in some archaeological situations, these properties may make menthol preferable to CDD. In her presentation at the ‘Subliming Surfaces’ conference, Dr Bianca Jackson discussed how CDD can act as a contrast enhancer in terahertz imaging, and noted that CDD films that are cooled very fast and have small crystals give the best results (Jackson et al. 2015; see also Bowen et al. 2015). Menthol creates a finer-grained film than CDD in ambient conditions and so may also have potential in this field.

In November 2018, the author met Dr Han Xiangna, from the University of Science and Technology in Beijing. She reported that menthol is now extensively used as a temporary support and consolidant on archaeological sites in China, because CDD is unobtainable there. Dr Han and colleagues have conducted much more research since their paper published in Archaeometry in 2014 (Han et al. 2014), including studying human exposure levels from typical application scenarios in the field. This research is not yet widely known outside China, but menthol deserves greater attention so that its potential for different applications can be more thoroughly explored.

The strongly irritant nature of menthol vapour has also prompted Han to investigate other menthol related compounds which could be used in a similar way, and she reports that methyl lactate is a promising odourless alternative. Meanwhile, in the US, Sadek et al. have identified another alternative VBM, cyclodecanone (Sadek et al. 2018). This material sublimes much more slowly than CDD but can be used as a temporary consolidant during desalination of ceramics.

For over 20 years cyclododecane was the undisputed king of volatile binding media. However, changing market forces and revised assessments of health and environmental risks mean that alternative volatile binders may eventually overtake it for some uses. Menthol and its less irritant relative methyl lactate are easily obtained and much less expensive than CDD, but so far have only been studied for use on archaeological sites. Potential for cyclodecanone in conservation has very recently been identified, while tricyclene could be...
developed further if it ever becomes commercially available in future. Much more work is needed to develop the full potential of these materials as alternatives to CDD, and this offers some exciting opportunities in conservation.

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Biography

Sophie Rowe read Anglo-Saxon, Norse & Celtic and History of Art at the University of Cambridge and then trained as a conservator at the Institute of Archaeology, University College London. She specialised in the conservation of organic artefacts while working at the British Museum, and developed a sub-specialty in conserving Egyptian polychrome objects, particularly cartonnage. She is especially interested in creative mounting methods for fragile objects. She has been conservator at the Polar Museum, Cambridge since 2012. In early 2017 she spent a field season on Horseshoe Island in Antarctica, cataloguing artefacts in a historic 1950s base managed by the United Kingdom Antarctic Heritage Trust.

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