

Table 2: Effect of molecular weight on shrinkage temperature

| Class            | Molecular weight (g/mol) | Shrinkage temperature (°C) |
|------------------|--------------------------|----------------------------|
| Highly condensed | 6600                     | 70                         |
| Medium condensed | 1943                     | 64                         |
| Monomer          | 108                      | 47                         |

aqueous conditions. But, in terms of hydrothermal stability the benzylidene spacer proved to impart the highest shrinkage temperatures. However, based on physico-chemical properties such as solubility in water or accessibility of chemical synthesis, the methylene and sulphonate groups remain the best suited. An interesting point is that the benzylidene group gives the 'syntan' a higher molecular weight, which suggests that molecular weight may be important.

#### Impact of molecular weight

Natural tannins frequently contain higher oxidised moieties based on catechol or

pyragallol building blocks. Condensing these and phenol with urea and formaldehyde to obtain a water soluble product, may lead to a better understanding of the effect of molecular weight. Three products of differing molecular weights were synthesised in table 2.

It seems that the molecular weight of the moiety does play a significant role in determining the tanning effect. The monomer, which was sodium sulphonate, seems to have produced a 'negative tannage', which may be due to the negative thermodynamic effects of the monomer on the solvent.

#### References

- [1] Holmes J, 'Reactive Chelators in metal tanning', IULTCS Congress 1995, Paper 15.
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- [3] Baekeland LH, Ind. Eng Chem 1909, 1 (3), 149-161
- [4] Stiasny E, J Anal Chem 1920, 59 (2-3), 97-99 and Lauffmann, Colloid & Polymer Science 1916. 19 (1), 36-46
- [5] Tu, ST and Lollar, RM, J Amer Leather Chem Assn 1950 (45), 324-328

Generally, it can be seen that the different structure-property or structure activity relationships do exist in synthetic organic tanning agents, which could be further exploited to develop optimised syntans for specific needs. ■

# Increasing pressure of formaldehyde limits

Within recent years there has been a renewed focus on chemical safety in all consumer products. Leather is far from immune from this drive and the global supply chain has been under growing pressure to provide guarantees of safe product supply.



By BLC Leather Technology Centre

One such chemical increasingly under the spotlight is formaldehyde, the limits that in leather have been driven progressively downwards in recent years with many brands and retailers now pushing for levels of formaldehyde which are essentially non-detectable by the currently accepted analytical methods for leather.

#### Formaldehyde

Formaldehyde is a colourless, strong smelling chemical compound (also known as methanal) widely used in many industries. It is the simplest aldehyde chemically with the formula  $\text{CH}_2\text{O}$ . Formaldehyde is a gas at room

temperature but it is also readily soluble in water (and is often sold as an aqueous solution).

Formaldehyde is often found in everyday products such as handbags, footwear, accessories, garments, beauty and cosmetic products and areas of application include adhesives, textile processing and as a preservative in some paints, coating products and also in some cosmetics. Formaldehyde is also used in the production of some polymers. When combined with phenol, urea or melamine, formaldehyde produces a hard thermoset resin. It is also used during the embalming processes to preserve corpses. Legislation/guidelines exist that limit the



levels of formaldehyde in products to protect consumers and ensure that products are safe for the consumer.

Potential exposure routes for formaldehyde are as wide ranging as smog, cigarettes and tobacco smoke, and some household sources such as fibreglass, carpets, foam in cushions, permanent press fabrics, paper products, household cleaners, shampoo, medicines and disinfectants.

### Why is it restricted?

The use of formaldehyde in many construction materials means that it is a common indoor air pollutant. At concentrations above 0.1 mg/kg in air, inhaled formaldehyde can irritate the eyes and mucous membranes, potentially resulting in watery eyes, headache, a burning sensation in the throat and difficulty breathing. Formaldehyde is also classified as a carcinogen.

### How is it relevant to leather?

Historically, formaldehyde has been used as a tanning agent due to its ability to crosslink proteins such as collagen. In addition, it has been used (again historically) to crosslink protein finishes such as casein.

In modern processing, formaldehyde can be used in the manufacture of certain polymeric-based synthetic tanning agents. Its presence in leather may be as a result of the condensation residue from some synthetic tanning agents. Some biocides are also formaldehyde generators.

Theoretically, formaldehyde should be fixed to the collagen during processing (considering that formalin is used as a preservative because of its reactivity with protein). However, some of the reactions used in the preparation of syntans are reversible (eg production of melamine

formaldehyde resins). This means that, under certain conditions, it is possible that it is liberated. Also oxidation of oils/fats can result in formaldehyde formation.

### What is the legislation?

Restricted substance legislation is highly variable depending upon:

- Final application of the leather in the product
- Target user
- The country where the leather or product is manufactured or sold

Formaldehyde is commonly restricted according to the end consumer (ie adult or child) with the acceptable limits for children being significantly lower than those for adults. Formaldehyde is one of the key examples of how variable the restrictions can be.

Within Europe there is no general legislation that limits the presence of formaldehyde in leather. Some individual countries have restrictions on its presence in consumer products. Various eco-labels require that levels of formaldehyde are determined and the automotive industry tends to have strict limits on formaldehyde release from car interior materials.

Brands and retailers have recently imposed restrictions that go beyond compliance, setting limits in the region of 20-30ppm. With modern tanning techniques and reputable chemical supply it is possible to manufacture leather with such low levels of formaldehyde, however this can be challenging to the tanner.

### Methods of analysis

There are two main methods used in the leather industry for the analysis of formaldehyde. Their application depends on the final use of the product.

The most commonly used methods for analysis are described in BS EN ISO 17226. There are two parts to this method, with part 1 relying on the use of high performance liquid chromatography (HPLC) being the preferred and favoured method. This has two parts: an HPLC method and a colorimetric method (part 2), which can be used in some instances.

HPLC method: (part 1) This method is based on determination of the extractable formaldehyde using high performance liquid chromatography. The formaldehyde is extracted at 40°C, after which the extract is reacted with 2,4-

dinitrophenylhydrazine (DNPH). The resulting extract is then separated using HPLC, with UV detection at 350nm.

Colorimetric method: (part 2) This method involves a colorimetric determination of the extractable formaldehyde. The leather is extracted at 40°C, after which the extract is treated with acetyl acetone. A yellow compound (3,5-diacetyl-1,4-dihydroxylutin) is formed in the presence of formaldehyde, which is quantified photometrically at 412nm. Within this method there is a check to determine the presence of other compounds that may result in a coloured compound when reacted with acetylacetone. This involves addition of Dimedone to the extract prior to addition of the acetylacetone. If the resulting solution has an absorbance in excess of 0.025 (for a 1cm cell) there is the possibility of a false-positive result being obtained.

In addition, the automotive industry uses a separate analysis based on a headspace extraction technique. Within this method the sample is suspended in a sealed container over a defined amount of water. After heating, any formaldehyde liberated by the leather should be dissolved in the water. This resulting solution is then analysed colorimetrically. Acceptable limits for automotive leather as analysed by this method are typically in the very low ppm range.

### Conclusions

There can be no doubt that the global leather industry is facing more stringent restrictions on the use of chemicals. Formaldehyde is currently topical and limits are being lowered. While challenging, with modern manufacturing techniques and appropriate methodology for measuring formaldehyde levels in leathers, manufacturers can produce leathers, which are compliant to such low limits. ■

BLC is able to offer support and advice about the presence of formaldehyde in leathers and offers a range of testing services and failure analysis for formaldehyde and for other restricted substances. For further information/advice on formaldehyde, formaldehyde testing or other chemical testing needs, please contact [info@blcleathertech.com](mailto:info@blcleathertech.com) or visit [www.blcleathertech.com](http://www.blcleathertech.com)