



Slow vegetable tannage in pits.

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VEG OR NON-VEG?

In the previous article, we reported on the presentation made by Dr Dietrich Tegtmeier, vice-president of product development and product application for specialty chemicals provider Lanxess at this year's Beast to Beauty conference. His comments on the use of chrome tanning agents will be welcomed by the leather industry in general. Indeed, tanners have become increasingly frustrated in the way that the use of chrome has been presented to the public in general. It is high time that its continued usage or replacement by vegetable tanning agents was examined in a less hysterical and alarmist manner.

The debate over chrome versus vegetable tanning and the risk of chrome VI (hexavalent chromium) being present in footwear particularly children's made from chrome upper leather, has been rumbling on for many years. It received

fresh impetus as the result of a survey on the level of chromium VI present in children's shoes carried out in 2007 by a German consumer affairs magazine called marktXL which concluded that all was not well. It based this view on a sample of just 20 pairs of shoes from 16 different manufacturers and brands.

Chromium, a metal salt that has become synonymous with tanning leather, is harmless in itself and in compounds involving chromium III, the commonly used tanning agent. Double the valency, however, to chromium VI compounds and toxicity becomes a real potential health-risk. Having said that, we have been wearing shoes made using chrome tanned leather for 100 years seemingly without any problems. Why has it suddenly become a potential health hazard?



Chrome tanning is a fast mechanised process – drum line at ISA TanTec, Guanzhou. CREDIT: WTP

A LIMITED STUDY

The study focused on children's and baby shoes as anything affecting children's health makes has the biggest impact on the buying public. Five pairs were in fact found to be over the limit (by an additional 0.15mg per kilo or 1,000,000mg) and, as a result, consumers were said to be 'horrified' to learn that inadmissible levels of such a strongly allergenic substance could be present in shoes, with the potential to cause skin lesions on the wearer's foot and, according to the suspicions of some experts, even cancer.

All this in turn led to much high-level technical discussion and the German federal government to impose strict controls on the levels of chrome VI permissible in leather, leather shoes (adults' as well as children's) and other leathersgoods to three milligrams per kilo. While everyone involved agreed the problem needed addressing, was it and is it fact as serious as some would have us believe?

NOT SO EASY

One thing is clear: eliminating chrome from the tanning of upper leathers is easier said than done. An estimated 80% of all leather produced globally at the moment uses chrome tanning. Tanners and shoemakers have worked hard to eliminate the formation of chrome VI. Salts containing this form of the metal have almost entirely disappeared from the tanning industry, even though the metal—in its safe form—remains at the heart of the production process. If this is indeed the case, how could the marktXL random study have possibly produced its negative results?

There are several possibilities, the most obvious being that the source of the shoes and/or the leather they were

made from, may have been countries or companies that have been less than rigorous in eradicating chrome VI. On the other hand, it has been suggested that either exposure to air, heat and light during the footwear manufacturing process or the aqueous-based adhesives that are involved may be transforming chromium III into its (allegedly) carcinogenic form. Footwear manufacturers for their part have pointed the finger at some of the fatliquoring that takes place in the tanning process as another possible cause.

A further complication lies in the fact that there appears to be a genuine possibility of chrome VI suddenly appearing in leather that has already been tested and approved. Despite much head-scratching, no one has is quite sure how this comes about. In addition, tests on the same material carried out at different testing centres can show different results. There is simply no consistency to this problem. The complex supply network of the footwear industry also makes it a global concern that calls for a global solution if it is to be totally eradicated.

WHY USE CHROME TANNAGE?

Leather was traditionally processed in pits and vats using traditional vegetable tanning agents and natural oils. It was essentially a rule of thumb craft procedure which produced extremely variable results. While shoemaking remained essentially a hand process, this could be accommodated.

The mechanisation of the industry towards the end of the 19th century, however, called for more uniform materials in order to produce shoes of consistent quality. Fortunately, it also coincided with the emergence of the modern chemical industry which soon discovered how to convert chrome ore into a tanning agent produced more consistent upper leather



Most leather is now tanned to the wet blue state and then sold on as a commodity to be finished to specific needs.

CREDIT: WTP

at a faster rate and a lower price. It has been the staple tannage for upper leather ever since.

Chrome also provides flexibility in manufacture. Most skins and hides are now chrome-tanned to the wet blue state and sold on as a commodity material from which specialist tanners produce specialist leathers for the full range of end applications. This is not possible with vegetable tanning where the process has to be continuous from raw hide to finished leather.

Chrome tanning is also a much faster method which takes as little as 24 hours compared to the six weeks needed for traditional pit methods and, although vegetable tanning in drums is faster, it still remains slower than chrome. It also consumes up to three times the amount of tanning agents so, taking these two factors together, it is more expensive.

Although only chrome III is used in tanning, it can change into chrome VI through oxidization due to some fatliquors such as sulfited fish, lard and vegetable oils containing a degree of oxidizing agent. These have been shown to act as 'starters' for the change to chrome VI. There is, however, no need for any of these oils to be used when producing upper leather. Furthermore, if chrome III should for whatever reason change into chrome VI, it will start to reverse itself after a three week period.

TOP OF FORM

Chromium is itself a transition metal that can exist in a number of different oxidation states each of which have distinct properties:

Metallic chromium is a steel grey, hard metal found as chromite ore (it does not occur in the metallic state naturally). It is used to harden steel, manufacture stainless steel, to form alloys and produce corrosion resistant plated surfaces.

Trivalent chromium or chrome III compounds occur naturally in rocks, soil, plants and volcanic

emissions. Chromium salts are also present in foodstuffs and form a key role in the metabolism of fats and sugars in the human body. Nutritional supplements are currently on sale containing chromium picolinate and chrome III is considered safe for use in leather manufacture.

Hexavalent chromium or chrome VI is the hazardous form of this element. It can be formed when trivalent chromium is oxidised. This usually occurs in the presence of oxygen

combined with other factors such as extremes in pH (hydrogen ions). The salts have a characteristic yellow colour, are classified as carcinogens and chrome VI is therefore not used in the tanning of leather.

WHY NOT USE VEGETABLE TANNAGE?

As stated earlier, before the development of chrome salts as a tanning agent, all types of leather were produced using vegetable tanning agents. These agents were derived from a variety of trees and plants and exhibited a broad range of properties that dictated the type of leather that could be produced. Today, the main one used is mimosa, followed by quebracho and then chestnut.

Used as the main tanning agent, they produce firm leathers that vary in base colour from the pinky-beige of mimosa to the dark nut brown of chestnut. They all tend to be light-sensitive and redden or darken further on exposure to natural light. While they are eminently suitable for the manufacture of leathers, belting and saddlery, they are less so for footwear uppers other than traditional products such as clogs.

Mimosa is however playing an increasingly important role in the retanning of chrome leather as the swing to more 'natural' leathers continues to grow, particularly for automotive seating. Used in this way, it would more easily find a place in footwear manufacture provided of course enough could be produced.

It is extracted from the bark of the Black Wattle tree which is found in the cool, mist-belt regions of Southern and Central Africa at altitudes in excess of 1,100m above sea level which limits where it can be grown commercially. There are about 130,000 hectares of commercial plantations in South Africa grown by around 2,700 farmers. In Kenya there are no commercial plantations and bark is sourced from small rural growers and wood-lots while in Zimbabwe there is just one commercial grower with some 11,000 hectares. Supply is therefore limited whereas chrome is plentiful and widely spread.

“...as a matter of interest...”

Any one who has travelled on Indian State Railways will be familiar with the question “Veg or non-veg sir?” coming from the carriage steward at mealtimes. In a country where diet is dictated

by a mixture of religion, caste and personal preference, one is always offered the two alternatives. Unlike veg or non-veg tanning agents, it is a simple choice.

ARE THERE ANY VEGETABLE ALTERNATIVES?

The short answer is yes. Spruce and birch can be used as a veg tanning agent and indeed the Russians were famous for it. A ship called the Metta Catherina sank off the Cornish coast of Britain in 1786. Its cargo of leather produced from reindeer hides has been brought up to the surface in recent years that, once dried, was found to be in perfect condition and has been used to make exclusive shoes for Prince Charles among others. It also still smells of birch.

Spruce also provides an extremely effective tanning agent so why not use it instead of mimosa? One problem is that up to five times more spruce agent is needed than with mimosa to achieve the same level of tannage. Scandinavia and Russia have vast spruce and birch forests that could be used as raw material. Unfortunately, the forestry industry in general has yet to be convinced that there is a sufficiently large and profitable demand for the product to justify the investment that would be necessary.

There are further disadvantages. Firstly, requiring five times the amount of spruce or birch tanning agent compared to mimosa, has a corresponding additional cost. This makes it an even less commercially viable proposition for mainstream tanners: vegetable tanning of all types also leaves a residue or ‘sludge’ that, unlike chrome salts, cannot be so readily recycled. While this does not create a serious problem in the quantities currently involved, it certainly would if it became a major player. And, finally, there is the matter of logistics. A major proportion of tanneries today are located in Asia and China, which is a long way from either South Africa or Scandinavia in terms of additional freight costs.

Having said all this, there are some specialist tanners using spruce or birch extracts and footwear manufacturers using their leather. It is very small scale however and aimed at the top end of the market where price is less important. It is a classic chicken and egg situation where uncertainty over demand prevents the forestry industry from investing and no guarantee of supply stops tanners from looking at the possibility of changing from chrome. It therefore currently looks extremely unlikely that vegetable tanned leathers will increase market share to any marked degree, let alone widespread usage for shoe upper leather.

THE FUTURE

Since no one seems to agree on the remaining global reserves of chromium, except that we will run out of oil long before then, we can only speculate about the future of its use as a tanning agent. Unless regulatory authorities impose unattainable consent limits for discharges, it will certainly continue in use for the foreseeable future. Furthermore, it has been conclusively shown that chrome tanning is environmentally sound and creates little environmental impact if the process is controlled. Nevertheless, further improvements can still be made. This is something the industry is keenly aware of and is making every effort to achieve.

It is also aware that it faces a problem beyond the environmental impact of manufacturing: what to do with leather at the end of its useful life? It used to be thought it was enough to address environmental impact ‘from cradle to grave’ with the final destination typically landfill. Perhaps the thinking should progress to ‘from cradle to cradle’, such that some further value can be extracted from waste leather and its products.

Technologies to separate chromium and protein are well established. Biogas can be generated from leather although it is surprising to find that chrome tanned leather is better than vegetable in this respect, which calls into question the widely held perception of the ‘greenness’ of traditional tanning methods. This is because chromium salts are inactivated by the tanning process, whereas plant polyphenols remain unaffected by reversing the tanning reaction and can deactivate the bacteria responsible for converting protein into methane. In both cases, treatment of the leather starts with a denaturation step using heat or alkali or both. A further positive step would be to make leather predisposed to break down completely in landfill or in any other end treatment situation.

It therefore seems that while the use of vegetable agents for tanning purposes would appear on the surface to have much to commend it, the reality is less certain. Furthermore, there is clearly insufficient material available to supply a global tanning industry. Chrome III has been shown to be safe and will continue to be readily available, so that there would appear to be no alternative for the immediate future, unless we all made to walk barefoot. 🍄