



The formation of volatile organic compounds (VOC) and hexavalent chrome in chrome tanned leather

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Following a remarkable number of recent customer enquiries regarding the mechanism of the formation of VOCs, as determined by head space analyses, it was decided recently to re-examine this important subject in connection with hexavalent chrome formation.

The basic cause of the problem had been observed in 1998 in connection with hexavalent chrome formation and consequently a solution was found involving the use of lipid-soluble antioxidants^(Legend 1), which lead to a patent⁽¹⁾. Nevertheless, at the recent Eco Trends in Leather conference (Hong Kong, March 2010) it was stated that 18% of leathers submitted for grading in the Leather Working Group scheme failed due to the presence of Cr (VI) after the ageing test⁽²⁾. This shows the importance placed on the matter by the leather industry.

The problem originates in the oxidation of fatliquor components, which is falsely called auto-oxidation. This oxidation of long chain polyunsaturated fatty acids is not an “auto” reaction but is a free radical induced oxidation. Free radicals, such as superoxide anion and hydroxyl radical, are initially created by the effect of sunlight (U/V photo-oxidation) on, for example, incompletely burnt hydrocarbons in the air.

These highly reactive free radicals (•) initiate the primary oxidation of the unsaturated fatty acids creating a chain reaction that cleaves the double bonds by removing a hydrogen atom from the fatty acid. This creates a lipid radical (L•) which reacts with atmospheric oxygen (O₂) to form a peroxy radical (LOO•). The peroxy radical removes a hydrogen atom from another fatty acid molecule to form a lipid hydroperoxide molecule (LOOH) which then in the secondary oxidation breaks down to form an alkoxy radical (LO•) and the hydroxyl radical (HO•).

The lipid hydroperoxide molecule creation is the most important occurrence, and this highly reactive and unstable reagent is oxidised in the secondary oxidation stage. It is a type of catalysed reaction whereby a heavy metal will act as the catalyst or starter, and then the reaction is self-propagating.

In simple terms, the long chain polyunsaturated fatty acids are split into progressively shorter chain length fatty acids. This eventually destroys the fat or oil completely, creating degradation products encompassing alcohols, ketones, and aldehydes. Considerable amounts of aldehydes are formed alongside the usual aldehydes arising from the specific type of oil which is oxidised - propanal from fish, hexanal from linoleic, and nonanal from oleic acid. These are all VOCs.

The catalytic interaction between lipid hydroperoxide and heavy metals, with its accompanying valency change, is well known and documented in the field of degradation of edible oils, and in nutritional and medical sciences.

The investigation

To confirm the catalytic effect of chrome on the first and/or secondary oxidation step of long chain polyunsaturated fatty acids, it was decided to carry out the oxidation of a fish oil in the

same way as used for the preparation of oxidised fish oil, which is a step before sulfiting the oil. In industrial practice, a raw cod oil, together with the starter, is heated under stirring up to 100°C, and stirred holding the temperature at 100°C for three hours during which a stream of air, containing atmospheric oxygen, is passed through it.

Normally a metal soap is used, for example, cobalt oleate as a catalyst or “starter” for the oxidation. In this experiment we substituted the cobalt oleate with chrome sulfate, and also with a chrome soap.

The aim of the oxidation process here is to form lipid hydroperoxides and a lipid hydroperoxide variant with the so called oxirane ring, which is the reaction point for the sulfitation process. The progress of the oxidation can be measured by the peroxide value, which is the sum of the oxidative capacity present.

In our experiment the terminal peroxide value in the case of the cobalt oleate was 12.4 O₂/g, i.e. the normal expected level. In the case of chrome sulphate it was 73.8 O₂/g and in the case of the chrome soap 31.8 O₂/g. These values denote an enormous increase in the oxidative capacity within the oil, confirming that chrome is an extremely effective catalyst in the presence of lipid hydroperoxide.

The reversal of hexavalent chromium to the trivalent state

Attempts to extract chrome from the oil were unsuccessful and we found that as hexavalent chrome is oil-soluble the chrome was, indeed, dissolved in the oil.

After two weeks came the “Eureka” effect: at the bottom of the flask containing the oxidized oil was a fine layer of green sediment. Subsequent analysis revealed that the whole of the offered chrome was present and in the oil-insoluble trivalent form.

We believe that immediately after the oxidation of the fish oil all the chrome was present as hexavalent chrome dissolved in the oil and contributed partly to the very high peroxide value. The reaction belongs to the REDOX type so that a reductive product results (an aldehyde in this case) which reduced the hexavalent chrome back to trivalent chrome. The very high peroxide value was reduced to half, much more than could be due to dimerisation of the oxirane groups.

The Cr (VI) phenomenon was demonstrated recently in new research by Ling Zhang and Congzheng Yu⁽³⁾. It was shown that a representative lipid hydroperoxide (tert-butyl hydroperoxide) reacts readily at room temperature with trivalent chrome sulphate or chrome chloride in aqueous solution oxidising some trivalent chrome to hexavalent chrome. It was furthermore demonstrated that the same representative hydroperoxide in solution with a hexavalent chromate was able to reduce the chrome to the trivalent state but at a much slower rate.

In view of the slower rate of the reduction process described

To try to show the reversibility of the chrome oxidation reaction we carried out a series of experiments on leather fatliquored with 8% of a lecithin based fatliquor after a simple sodium bicarbonate/ sodium formate neutralisation. Dyestuffs and retanning agents were not included as studies by the Lederinstitut Gerberschule Reutlingen⁽⁵⁾ in 1998 showed that the use of retanning agents and strongly masking sodium sulfite reduced the extent of the oxidation of chrome, and we wanted to take this effect out of the equation. The findings from this investigation are given in *Panel 1*.

Treatment	Sample A	Sample B	Sample C
1. Leather after drying and 24 hours at 20°C	15	15	15
2. as Row 1 followed by the ageing test 24hrs at 80°C	30	No test	30
3. as Row 1 but after 3 weeks, then ageing test 24 hrs at 80°C	No test	9	15
4. End control 3 weeks plus one day	11	9	15

Row 1: Samples A, B and C show that the initial oxidation has taken place during the normal drying process.

Row 2: Samples A and C experienced a doubling of the hexavalent chrome after the ageing test (24 hr at 80°C).

Row 3: Sample C, after ageing at standard moisture/temperature for three weeks, then subjected to the ageing test (24 hr at 80°C), showed that the hexavalent chrome did not increase from the original values (given in Row 1)

Row 4: Sample B, after ageing at standard moisture/temperature for three weeks + one day, shows a significant reduction in the hexavalent chrome when compared to the original value (given in Row 1).

For producers of emission-free or automotive leathers, the importance of the self-propagating oxidation of the polyunsaturated long chain fatty acids cannot be underestimated, as all the degradation products will show up in the headspace test.

With reference to the prevention of the induced oxidation of the fatty acids and the transient, hexavalent chrome formation in leather, a diagram⁽⁶⁾ is shown as *Panel 2* which represents the reaction mechanism and the points (A) at which oil soluble antioxidants must be positioned to prevent the oxidation from even beginning.

The diagram illustrates the metabolic pathways of a lipid. It starts with a 'Lipid' box at the top. An arrow labeled 'Peroxidase' leads to a circle labeled 'A', which then leads to a 'Lipid peroxide' box. From 'Lipid peroxide', an arrow labeled 'Hydroperoxide' leads to another circle labeled 'A', which then leads to a 'Lipid hydroperoxide' box. From 'Lipid hydroperoxide', there are several pathways: 1) An arrow labeled 'Alcohol' leads to a 'Lipid hydroxyl' box. 2) An arrow labeled 'Diol' leads to a 'Lipid diol' box. 3) An arrow labeled 'Hydroxyl radical' leads to a 'Lipid hydroxyl radical' box. 4) An arrow labeled 'Hydroxylated' leads to a 'Lipid hydroxylated' box. From 'Lipid hydroxyl radical', an arrow labeled 'Hydroxylated' leads to a 'Lipid hydroxylated' box. From 'Lipid hydroxylated', an arrow labeled 'Ketone' leads to a 'Lipid hydroxylated ketone' box, and an arrow labeled 'Carboxylic acid' leads to a 'Lipid hydroxylated carboxylic acid' box. The diagram also shows a 'Lipid hydroperoxide' box with an arrow labeled 'Hydroperoxide' leading to a 'Lipid hydroperoxide' box, and a 'Lipid hydroperoxide' box with an arrow labeled 'Hydroperoxide' leading to a 'Lipid hydroperoxide' box. The diagram is a complex network of reactions and intermediates, with many arrows and boxes, and it is a detailed representation of the metabolic pathways of a lipid.

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- Automotive leather tanners and producers of low emission leathers should be aware that chrome is not the only heavy metal with the “starter” characteristic. The selection of dyestuff is also critical as metal complex dyes particularly those with copper and iron in the complex can cause catastrophic increases of VOC emissions.
- Due to the significant presence of breakdown products from the oxidation part of the sulfitation process, sulfited fish oils, sulfited lard oils and sulfited vegetable oils are unsuitable for the production of low emission leathers even if they were to be treated with antioxidants.
- Chrome-free leather producers must also take particular care in dyestuff selection. The amounts needed to act as a secondary oxidation “starter” are in the case of copper as low as 0.01 ppm and for iron 0.03 ppm. 

- (1) *Patent Number 198 60 610 Method to inhibit the chrome (VI) formation in chrome tanned leather.*
- (2) *Presentation: Dr. V. Addy, BLC, UK, March 2010.*
- (3) *“Exploration on Mechanism of the Transformation from Chrome (III) into Chrome (VI) by Hydroperoxide”. 2009 Ling Zhang and Congzheng Yu, Shaanxi University of Science and Technology, Xian 710021*
- (4) *“Hochdruckinduzierte Veraenderungen von Lebensmittelinhalstoffe” 2007 Katharina Irena Krzikalla, Berlin*
- (5) *“Untersuchung zur Entstehung und Vermeidung von Chromat im Leder” C. Hauber, H-P Germann 1998*
- (6) *“The use of antioxidants to stabilize fish and soya oil.” Dr Heiko Stoeckmann, Kiel and Dr. Antje Holthausen, Cuxhaven. Lohman Information 4/2005.*