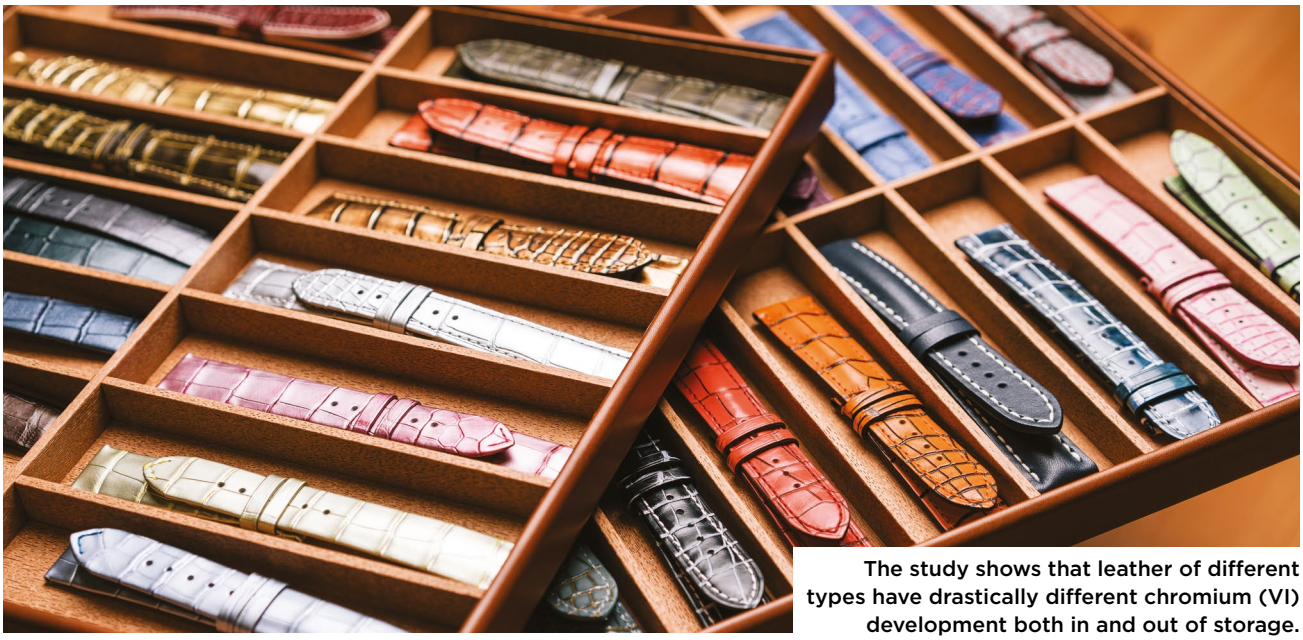
Cr(VI) storage stability for leather watch bracelets



The study shows that leather of different types have drastically different chromium (VI) development both in and out of storage.

Deputy Editor **Tom Hogarth** speaks to Sébastien Bagot, Technical & Quality Manager at the Association for Quality Assurance of Leather Bracelets Manufacturers (AQC), to find out more about the organisation's five-year storage study.

Towards the end of 2021, the AQC, a Swiss-based International Association of Leather Bracelet Manufacturers for the watch industry, released its preliminary results of a five-year study to explore a storage solution for preventing the development of chromium (VI) (hexavalent chromium) in leather bracelets.

Bagot explains that the stability study was initiated by the organisation in May 2017 in response to an industry need to address the lack of any standard for ideal storage of leather and leather bracelets.

He elaborated that, according to the EU Safety Portal for Hazardous Non-Food Products (formerly RAPEX), chromium (VI) non-compliance in leather remains a major problem for the industry. However, AQC members are reportedly avoiding the issue thanks to effective quality policies on chromium (VI) testing and prevention, with no cases of non-compliant bracelets reported since the AQC policies were implemented.

With the addition of fully established storage guidelines after the completion of this study, the AQC will represent an ideal standard for the prevention of chromium (VI) development in leather goods.

Bagot added: "It is important to point out that the optimal storage conditions we have defined with the study are not the only solution; it is only one element in the supply chain to achieve compliance. The most effective way to avoid chromium (VI) remains the implementation of tanning best practices during leather production."

He added that, for some years now, chrome-free tanned leathers have been used in the manufacture of leather bracelets with many AQC members making this option available to their customers. At the end of the day, he says, it's up to customers to decide what type of leather they want. Furthermore, he said: "From the point of view of

Above: **Sébastien Bagot (left), pictured here with Quality Assurance & Quality Control Officer David Astier, who also worked on the study.**

sustainability, we do not yet have clear and recognised references that chrome-free tanning methods could have an environmental advantage from a holistic point of view."

Ideal conditions

However, AQC members, whose customers were raising questions about optimal storage conditions and solutions for the prevention of chromium (VI) development, chromium (VI) reversion and pH and formaldehyde stability, needed the problem solved and so the AQC set out to determine concise storage recommendations for leather and leather bracelets.

Not an easy task to undertake with all of the variables in play and so the organisation planned out a five-year study to ensure that the full scope of the issues could be investigated and solved as far as possible. Bagot added: "There are two main reasons for [the length of the study]. Firstly, we decided to carry out a real-time stability study, to represent the actual storage conditions of leather at our members, i.e. without accelerated ageing. Secondly, we believe that five years is representative of the length of time most leathers are stored by our members."

No existing standard

With the absence of any real standard for the storage of leather and leather watch bracelets that would meet the needs of its members, the AQC drew on inspiration from other fields to begin solving the problem. Looking to the international pharmaceutical standards of the World Health Organisation, the AQC settled on stability conditions for temperature levels at 20.25°C and humidity levels at 60% ± 5% of relative humidity.

When it came to light exposure, the association acknowledged that it is not always feasible for manufacturers to store leather in total darkness, although this would be the ideal conditions. Therefore, the study applied UV-free LED lighting at a dose of 300-500 lux per day in order to simulate expected storage conditions in the real world, based on the usual lighting of a working environment.

Bagot elaborated on the scope of the study and the potential for further investigation down the line beyond the variables explored in this research: "The parameters selected for this study were focused on chemical compliance (chromium (VI), formaldehyde, pH). The study of other physical parameters, such as colour, finish resistance and appearance, would be interesting to assess the quality of the leather and the leather bracelets over the years of storage."

With the storage conditions settled on for the study, the right samples had to be chosen to produce the most comprehensive and appropriate results across the length of the study. Bagot explains that the panel of leathers selected represents, as much as possible, the types of leather demanded by the haute horlogerie.

Therefore, the association chose 16 alligator leather samples with different colours and finishes (glazed, safari or high shiny) as well as 16 bovine leather samples used as the top layer or lining layer of a bracelet. The AQC also included a less used leather, ostrich, to complete the study. In order to also assess the behaviour of leathers with non-compliant levels of chromium (VI), the association also selected some leather materials that were rejected for chromium (VI) content above the EU-restricted level of 3mg/kg.

Leather samples in the ideal storage conditions for the study.

Results over time

After four of the five years prescribed for the study, Bagot says that the results show a clear benefit of the storage conditions when it comes to the prevention of chromium (VI) development. All of the 16 bovine leather samples used in the study had levels of <3mg/kg of chromium (VI) when entered into the study and remained below this level throughout the storage time.

The 10 alligator leather samples with <3mg/kg chromium (VI) followed a similar result, and the six samples with non-compliant levels of chromium (VI) actually decreased to below 3mg/kg after three to six months of storage, which the association puts down to the humidity conditions.

A further comparison was undertaken on four alligator leather samples, where those in the storage conditions became/remained at <3mg/kg levels of chromium (VI), while those kept in ambient conditions developed higher levels of chromium (VI) formation. In fact, one sample was kept in storage and maintained its sub 3mg/kg level before jumping to levels of chromium (VI) as high as 30-40mg/kg after removal from storage, and then reducing to <3mg/kg after returning to storage.

"Our study on non-conforming leather stored under appropriate conditions shows that the removal of chromium (VI) from alligator leather takes several months (three to six months) to reach a level below the limit of 3mg/kg."

An outlier, the sole sample of ostrich leather continued to develop higher than allowed levels of chromium (VI) even in storage. The association concluded this may be down to tanning methods from its country of origin – South Africa.

Bagot said: "Our study on non-conforming leather stored under appropriate conditions shows that the removal of chromium (VI) from alligator leather takes several months (three to six months) to reach a level below the limit of 3mg/kg. However, if returned to uncontrolled (dry) conditions, chromium (VI) reappears.

"For formaldehyde, we are pleased to show a decrease in formaldehyde release over time. This observation allows us to put to rest old beliefs about the release of formaldehyde from leather stored for several years. Finally, the pH of the leather, which is a crucial physical-chemical parameter for skin contact, remains stable over the years of this study."

After the study

He explained that, once the study is completed in 2023, the obtained data will be sufficient for publication in a scientific journal and will be established as AQC guidelines or standards for the leather industry.

When it comes to real-world environments, Bagot affirms that the recommendations given by the AQC are useful for all stakeholders from tanners to watch brands, or any other company, when creating or revamping a storage facility for leather. Furthermore, members of the AQC have invested in this study under open-source principles and will share their knowledge with all concerned and interested stakeholders in the leather industry.

Discussing the European restrictions on chromium (VI) levels in leather goods themselves, Bagot said: "We believe that the current global limit of 3mg/kg is the correct limit for chromium (VI) compliance. The European Chemicals Agency, through a proposal to restrict allergens in leather in contact with the skin, wants to lower this limit to 1mg/kg.

"Given the instability of chromium (VI) and the lack of a testing standardised method to obtain such a low limit, we do think that lowering the limit further and further without the technical capabilities is not the appropriate way to prevent customers from contact with chromium (VI).

"To fully respect the current limit of 3mg/kg, the international leather industry should strengthen quality control and open its testing programmes to predictive tests, such as heat ageing, UV ageing or natural ageing. As well as implement concrete actions in its tanning process to achieve good practices for chromium (VI) prevention."