WG6 WAS ESTABLISHED AT CEN 289: STANDARDIZATION OF METHODS FOR CHEMICALS FOR TANNERY

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ABSTRACT
With increasing regulatory restrictions on some chemicals for tanneries, brands have developed Restricted Substance Lists (PRSLs), which generally go beyond legal restrictions and limit values. However, to avoid the presence or excess of certain chemicals in the leather – the product- but also in the final waste, Manufacturing Restricted Substance Lists (MRSL) have been developed to check the chemicals.
REACH is monitoring and limiting more and more substances and some aspects have become more insidious, for example the allergenic potential instead of a specific analyte, trace substances, contaminations. The goal, therefore, is to add standardized methods to the leather supply chain in response to the increasingly frequent incoming regulatory requests.
The UNI CT013 / GL01 commission has decided to start a systematic process of standardization of methods for chemical products for tannery, an activity later requested by CEN289 WG1, temporarily managed by the Ad Hoc Group and, finally, from October 2021, the purpose of the new Group (WG6: "Test methods for tannery chemicals"). This standardization starts from the problems already faced in the transitional phase (eg Bisphenols, APEO) and redefined by the numerous experts of the WG6, according to the evolution of the regulations.
The goal of WG6 is also to link up with IULTCS to have EN ISO methods for the international market. The WG6 represents a potential glue for the supply chain having consolidated experts, representatives of associations and experts up to now new in that sector, with innovative objectives that go beyond the development of standardized analytical methods.

Keywords: "standardized methods", "chemicals", CEN/TC289/WG6

1. Introduction

On 14 October 2020, the European Commission published its Chemicals Strategy for Sustainability, one of the cornerstones of the European Green Deal. Its aim is to boost innovation for safe and sustainable chemicals and increase the protection of human health and the environment against hazardous chemicals.

This is only the last step of the EU's last long-term vision on chemical products. Indeed, the first approach to a global vision of needing for management of chemical substances dates back to the White Book adopted twenty years ago, which spawned the REACH and CLP regulations governing the marketing of chemical substances in Europe.

The European REACh and other global regulations on hazardous chemicals (Prop 65, CPSIA, etc.) have increased

awareness of safer products and this has led to the need for standardized analytical methods for the determination of unwanted chemicals.

The use of standards helps guarantee access to global markets, fosters interoperability of products, and enhances international competitiveness. Indeed, in a world interconnected such as we have today, the availability of international standards is fundamental to support regulatory convergence at the international level because they are the result of a process that guarantees all interested parties.

Indeed, the ISO ((International Standardisation Organisation) key principles in standard development are:

i. Respond to a need in the market
ii. Developed through a multistakeholder process
iii. Based on global expert opinion
iv. Based on consensus

The tanning sector has always been sensitive to the need to have shared methods: the first international conference of leather chemists was held in London in 1897, with the primary aim of finding a consensus on some standard methods, first of all, the determination of tanning content of natural tannins, the most relevant tanning agents at the time.

That meeting was the first step in the standardization process in the leather sector and led, a few years later, to the publication of the first systematic collection of "Official Analysis Methods" (methods of sampling and testing of leathers and materials associated with leather manufacture) of The International Association of Leather Trades Chemists, later became IULTCS (International Union of Leather Technologists and Chemists Societies).

Clearly, the purpose of this collection was to have a recognized standard to characterize the leather and the chemical products used in the transformation from hide and skin to leather from the point of view of quality control and compliance with the specifications.

With the partnership set up in 1990, ISO recognized the IULTCS as an international standardizing body, reflecting the fact that the IULTCS has an established consultation process in its sector that resembles that of ISO in its ability to obtain a consensus opinion in a democratic manner. Remarkable that IULTCS is one of only six other external bodies developing standards or guides recognised by ISO (versus 258 ISO technical committees).

With the advent of the European Community, the European standardization committee was created; for the leather sector, the Technical Committee was established as CEN/TC 289 “Leather” with experts nominated by the national standard bodies (UNI, ENE, AFNOR, DIN, etc), in the national mirror committees. In 1991 an agreement on technical cooperation (Vienna Agreement) was defined between ISO and CEN developed with the aim of optimizing the use of available resources and expertise for the benefit of the interested parties of both organizations, and, from it, the meetings CEN-ISO (IULTCS) are held together.

Over the past 20-30 years, eco-labels (such as OEKO-TEX, Blue Angel, SG Mark and Ecolabel) have been developed introducing the concept of product certification, followed in the last 10-15 years by the customer-developed PRSL "Product Restricted Substances List" (fashion brands, automotive

industries). This type of list reports both substances inherently Reach (Annex XIV and XVII) with lower admitted content or substances not covered by the legislation.

This has resulted in many standard (over 40) methods being developed by CEN/TC 289 to control the unwanted presence of these chemicals in the leather.

More recently “Manufacturing Restricted Substances List” has been introduced on the market by clients. Therefore, tanneries are constantly required to check these substances in the chemicals they use. For the number of tanneries involved, the most important MRSL comes from ZDHC (Zero Discharge of Hazardous Chemicals). ZDHC was born in 2011 from a few signatories brand with the goal of eliminating hazardous substances to human health and pollutants from processing cycles by acting at all levels of the supply chain of the textile, apparel, and footwear industries, and, after a rapidly grow it's become now the most important reference for the sector.

In 2014 ZDHC publishes the MRSL 1.0, followed by version 2.0 in 2020.

The ZDHC MRSL establishes restrictions on trace concentrations for prohibited chemicals that are not intentionally used, but that can be found as unintended contaminants within a commercial chemical formulation.

Thus, the chemical manufacturing companies must demonstrate compliance with the MRSL of more than 200 different analytes: the problem is that for these matrices, in almost all cases, standardized methods have not yet been developed, because the need had not yet emerged. In fact, a generic "Principle of the method" is indicated in the MRSL, leaving it to the arbitrariness and experience of the laboratories on how to perform the determination. This can generate a lack of clarity on the information produced along the value chain, also because laboratories often don't know the characteristics of the matrix that they have to analyse.

The major risk associated with this is that different analytical approaches can lead to different analytical results.

From this, therefore, the need to fill this gap emerged, gathering around the standardization tables the experts of both the matrix, coming from the chemical manufacturing companies, and the experts of the analysis laboratories.

The Italian Commission for Standardization UNI CT/013, after the enrolment of experts coming from Italian chemical suppliers, 2017 has set up a dedicated working group (GL01, presented to the CEN/TC 289 meeting in 2018) to deal with the lack of methods for chemical products.

This systematic work led, in October 2021, to the creation of a new working group of the European Commission CEN/TC 289: WG6 "Test methods for tannery chemicals".

2. Material and Methods

When the GL01 dedicated to the development of methods for chemical products for tannery of the Italian commission CT013 "Leather, leather and leather goods", was set up in 2017, it prepared its work plan:

i. a selection of all existing methods for the analysis of undesirable substances in chemicals
ii. the verification, with real matrices, of the repeatability and reproducibility of the methods in point (i)
iii. the creation of a priority list of analytes that require a method, a list constructed on the basis of the results of points (i) and (ii), but which remains dynamically linked with the needs that may emerge from the regulatory sector, or to deal with inconsistent results obtained with internal methods from laboratories, or from new needs of clients in the PRSL or MRSL.

The results of this approach (detailed in the "Results and Discussion" section) confirmed the need to systematically and internationally address the lack of specific methods for chemicals. So, as a natural development, UNI has proposed in 2020 to create a new Working Group of CEN/TC 289 focused on chemical products for the tannery in order to:

i. enrol new international experts with deep knowledge of chemicals
ii. elaborate methods focusing on the most variable and problematic part: the extraction
iii. speed up standardization processes as the standardization rules permits, avoiding overloading of "WG1 chemical test method" already charged with methods for leather

The CEN/TC 289 on 2020-10-07 decided (decision N. 22/2020) to establish an Ad Hoc Goup within WG 1, with the following Scope:

i. enroll additional specific expertise on chemicals.
ii. define connection with IULTCS for taking advantage of the Vienna Agreement, in case a specific WG is created
iii. define a distinct scope, responsibilities and work program of methods to be elaborated on chemicals for the tanning industry

reporting back at the next CEN/TC 289 plenary meeting for the eventual creation of a new Working Group.

After one year of preparatory work of Ad Hoc Group (see "Results and Discussion" section), with the decision N. 9/2021 the CEN/TC 289 on 2021-10-06 decided to create the new WG 6 "Test methods for tannery chemicals" with the scope of to develop analytical methods for chemicals used in the tanning industry.

3. Results and Discussion

The results obtained following the work plan of UNI CT013-GL01 dedicated to the development of methods for chemical products for tannery have been:

i. the selection of available methods for the analysis of chemicals for tannery, lead to identifier six methods developed by CEN/TC 289 appliable to chemicals for tannery:

- two regarding quality of chemicals, so not relevant in relationship with unwanted substances: "ISO 14088 Quantitative analysis of tanning agents by filter method" and "ISO 17489 Determination of tan content in synthetic tanning agents"
- two regarding restricted substances in leather also suitable for chemicals: "ISO 18218-1 (Direct method) and ISO 18218-2 (Indirect method) - Determination of ethoxylated alkylphenols"
- two regarding restricted substances in chemicals: "ISO 19071:2016 Determination of chromium (VI) and the reductive potential for chromium tanning agents" and ISO 27587 Determination of free formaldehyde in process auxiliaries"

ii. so, the verification, with real matrices of chemicals, of the repeatability and reproducibility of the methods ISO 18218-1 and -2, to determine APEO: in fact, both methods indicate that can be used for determining that analytes in the chemical product. The round robin test that has been done has demonstrated that only the standard ISO 18218-2 gives good reliability for all the matrices tested, meanwhile ISO 18218-1 underestimates the content of APEO in some matrices.

iii. The initial priority list of standard methods to be create established by GL01, was composed, at the beginning of APEO/AP, SCCP and MCCP, Phthalates, Azo colourants, PFC, some metals (As, Cd, Pb, Hg) is changed several because the market requests change rapidly, and new regulatory rules coming from REACH as well. Therefore, in the meantime the list was enriched (also priority has been revised) and become:

1. APEO/AP
2. SCCP and MCCP
3. Bisphenols (A, S, F, AF)
4. Tanning metals
5. Titanium dioxide
6. Phtalates
7. PFC
8. Azo colorants
9. Polysiloxanes

Consequently, the second round robin test has regarded SCCP and MCCP, in order to verify if the standard for the leather (ISO 18219-1 for SCCP and ISO 18219-2 for MCCP) was suitable for chemicals, testing samples of chemical with different amount of:

- Short Chain Chlorinated Paraffins
- Medium Chain Chlorinated Paraffins
- Medium Chain Sulphochlorinated Paraffins

The preliminary results, which need more tests, show that it is necessary to define the purpose of analyses because those substances are classified relating the amount of Cl loaded (over 50% Cl MCCP are POP, not readily biodegradable), instead, to check the chemical to verify the commercial content of MCCP we have to use a standard solution with 42% Cl (that are readily biodegradable) shall be used.

All these results confirmed the need to systematically and internationally address the lack of specific methods for

chemicals. So, as a natural development, UNI has proposed in 2020 to create a new Working Group of CEN/TC 289 focused on chemical products for the tannery in order to:

i. Engage international experts with in-depth product knowledge
ii. Develop analytical methods, focusing attention on the problematic part, the extraction, while the instrumental part could be easily adapted to the existing method on the leather in most cases
iii. In view of the large number of methods that are missing, a dedicated Group could take care of the standardization of numerous methods at the same time

The CEN/TC 289 plenary meeting decided (decision N. 22/2020) to establish an Ad Hoc Group within WG 1, with the Scope reported in the section "2. Standard and Methods". In the year of activity, the Ad Hoc Group has:

iv. Regarding the enroll additional specific expertise on chemicals: seven new Experts have been involved. Most of these Experts represent Italian and European producers of chemicals for leather and some European Associations. Moreover, some Experts already present in CEN/TC 289 declared their interest in participating in the work on chemicals.
v. Regarding the connection with IULTCS for taking advantage of the Vienna Agreement, in case a specific WG is created, the Ad Hoc Group has proposed a connection with the IUC commission
vi. Regarding a distinct scope, responsibilities and work program of methods to be elaborated on chemicals for the tanning industry:

a. the scope of the Working Group is to elaborate the analytical methods for tannery chemicals (leather chemicals), both to determine traces of unwanted substances and to characterize the chemical, with the priority on unwanted substance

b. Responsibilities:

i. Establish the priority: identify the methods considered priority according to the criticalities that have emerged (dynamically linked to Reach restrictions or market requests),

ii. To develop the methods following the priorities taking advantage of the presence of both the experts of the chemical matrix and the experts of the instrumental part,

c. Work program:

i. Establish a priority list

ii. Develop an analytical strategy for the treatment of the different matrices; where the leather method is already present, try to keep the instrumental part already present and work on the development of the extraction part

iii. Organize RRTs to verify the correctness of the proposed method

d. Priority list of analytes (an open list that can be changed if new needs arise) that need a standard method:

• APEO (reliability for the chemicals in the Scope of EN ISO 18218-1 and 2 has already been elaborated by UNI mirror group)
• SCCP and MCCP (already been elaborated by UNI mirror group)
• Bisphenols (UNI mirror group and CEN/TC 289)
• metals in dyes and pigments
• TiO_2
• phthalates
• azo dyes
• PFC
• polysiloxanes
• glutaraldehyde
• sensitisers

vii. Standardisation activity of Ad Hoc Group: determination of bisphenols in leather and chemicals

The call for restriction announced in 2020 from Germany to ECHA for bisphenol A and structurally related bisphenols (including derivatives) requiring a limit of 200 mg/kg in substances used in the non-automatized processes has generated worries along the supply chain, so an RRT about this analytes was planned in the Italian standardization commission UNI CT 013 / GL01 and extended to ad Hoc Group involving a total of 13 laboratories that have determined Bisphenols A, F and S in 4 specially formulated chemicals (absent, presence of S and F alone, a mixture of S and F) and in 4 wet-blue leather retanned according to a standard procedure with 4 chemicals. A total of 8 samples were analyzed with 8 different analytical approaches, covering both the analytical approaches already on the market and other new proposals. This, allowed us to evaluate the correlation between the chemicals and the leather, the different methods of preparation and the different instrumental techniques: that information (more than 1500 analytical results) led to outlining the structure of the method for the leather and giving important suggestions on which to make further investigations for the chemicals.

Finally, the plenary meeting of CEN/TC 289 on 2021-10-06 decided, positively evaluating the work done by the Ad Hoc Group, to create the new WG 6 “Test methods for tannery chemicals" with the scope of developing analytical methods for chemicals used in the tanning industry.

The call for experts has engaged numerous people: the WG6 is composed of 24 members, coming from European industry, laboratories, and research centres. The first topic managed by WG6 is the development of the standard for bisphenols in chemicals for the total and the extractable content in order to obtain two reliable methods which are strongly asked by the supply chain.

4. Conclusion

The REACh regulation, the PRSL and finally, the MRSL, have increased exponentially the analytes to be determined on the leather matrix and chemicals used in the tanning process. Having standardized methods available for their determination is the key to having a correct evaluation of their content, and it is to fill the lack of these methods that the CEN / TC WG6 was created at an international level, from input from the Italian supply chain, that thanks to the significant presence on its territory of both tanneries and companies of chemical product formulators, is at the forefront in grasping the needs of the supply chain.

In an increasingly interconnected world, WG6 has the further objective of becoming a direct, or indirect interlocutor through trade organizations, of the regulatory bodies. This with the aim of avoiding being faced with new restrictions without having standardised methods to quantify the analytes subjected to restriction, in order to work harmoniously between all the interested parties.

Note