Problematic SVHCs in leather: boron compounds

Caracciolo D., Naviglio B., Calvanese G.

Stazione Sperimentale Industria Pelli (SSIP), Via Nuova Poggioreale 39, Naples, Italy,
Phone: +39-081-5979101, Fax: +39-081-265574, e-mail: ssip@ssip.it

1. Introduction

REACH is the European Community Regulation on chemicals and their safe use (EC 1907/2006). It deals with the Registration, Evaluation, Authorisation and Restriction of Chemical substances.

The main aim of REACH Regulation is to ensure a high level of protection of human health and the environment from the risks that can be posed by chemicals.

The REACH foresees an authorisation system aiming to ensure that the risks from substances of very high concern are properly controlled, and those substances are progressively replaced by suitable alternative substances or technologies where these are economically and technically viable. Where risks cannot be adequately controlled, the use of those substances may only be authorised where there is an overall benefit for society of using the substance and there are no suitable alternatives.

In this regard, not all substances that could be danger to humans and the environment ("hazardous substances") are considered "substances of very high concern" (SVHC).

SVHC are defined in Article 57 of Regulation and include substances which are:

- Carcinogenic, Mutagenic or toxic to Reproduction (CMR), meeting the criteria for classification in category 1 or 2 in accordance with Directive 67/548/EEC. This directive was replaced by the new EU regulation (EC) No 1272/2008 on classification, labelling and packaging of chemical substances and mixtures, the so-called CLP Regulation.
- Persistent, Bioaccumulative and Toxic (PBT) or very Persistent and very Bioaccumulative (vPvB) according to the criteria in Annex XIII of the REACH Regulation,
- Identified, on a case-by-case basis, from scientific evidence as causing probable serious effects to human health or the environment of an equivalent level of concern as those above (e.g. endocrine disrupters)
-

A substance, once identified as SVHC by European Chemicals Agency – ECHA -, is included in the "Candidate List" o for Authorisation" (Annex XIV of Regulation).

The Canditate List is published and updated on the ECHA website as soon as a decision about inclusion of a substance was taken. The number of substances of very high concern currently contained in the Candidate List is 138 (last update 19/12/12).

The identification of a substance as Substance of Very High Concern and its inclusion in the Candidate List is the first step of the authorisation procedure.
Companies that manufacture, import or use of these substances in the European Union (EU) or the European Economic Area (EEA), may have immediate legal obligations following such inclusion which are linked to the listed substance:

- on its own
- as components in preparations
- as components of articles

Article 33(1) states that producers, importers and other suppliers of articles containing substances of very high concern (SVHC), which are on the candidate list for authorization with a threshold above 0.1% (w/w), have to provide information available to them about the substances to the recipients (does not include consumers) of the articles. This information has to be provided in the Safety Data Sheet (SDS)

The supplier of a mixture, not classified as hazardous, but containing a substance on the Candidate List in a concentration greater than or equal to 0.1% must be provided to recipients, if requested, the safety data sheet.

Any producer or importer of articles containing a SVHC substance shall notify the Agency, if both the following conditions are met:

(a) the substance is present in those articles in quantities totalling over 1 tonne per producer or importer per year;
(b) the substance is present in those articles above a concentration of 0,1 % weight by weight (w/w).

Pursuant to the Adaptations to Technical Progress (ATPs) to Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures, the following boron derivatives:

- Diboron trioxide CAS N. 1303-86-2
- Tetraboron disodium heptaoxide, hydrate CAS N. 12267-73-1
- Boric acid CAS N. 10043-35-3 and 11113-50-1
- Disodium tetraborate, anhydrous CAS N. 1303-96-4, 1330-43-4, 12179-04-3

have been classified as toxic to reproduction category 2, R60-61 (May impair fertility. May cause harm to the unborn child).

Due to this classification, the substances meets the criteria for classification as toxic for reproduction in accordance with Article 57 (c) of REACH, and so they have been included in the Canditate List of SVHC.

The Diboron trioxide is the product of the decomposition of the boric acic over 300 °C and , and there are no known applications in the tanning industry.

The support document for the Tetraboron disodium heptaoxide hydrate covers the substance Disodium tetraborate anhydrous ($B_4Na_2O_7$), with EC number 215-540-4 and CAS number

1330-43-4, as well as substances / hydrates with the following CAS numbers which are covered by the EINECS entry of anhydrous form:

- CAS number 12179-04-3: Disodium tetraborate pentahydrate, [CAS name: boron sodium oxide ($B_4Na_2O_7 \times 5H_2O$)]
- CAS number 1303-96-4: Disodium tetraborate decahydrate, [CAS name: Borax ($B_4Na_2O_7 \times 10H_2O$)]
-

Among these compounds the most important is the borax, which has a wide variety of uses. It is a component of many detergents, cosmetics, and enamel glazes. It is also used to make buffer solutions in biochemistry, as a fire retardant, as an anti-fungal compound for fiberglass, as a flux in metallurgy, neutron-capture shields for radioactive sources, a texturing agent in cooking, and as a precursor for other boron compounds.

Boric acid is a weak acid of boron often used as an antiseptic, insecticide, flame retardant, neutron absorber, or precursor to other chemical compounds. It's a Lewis acid (hydroxide ion acceptor) rather than a Brønsted acid (proton donator). For this purpose the formula for boric acid is best written as $B(OH)_3$, with pKa = 9.0 at 25°C in dilute solutions only ($B \leq 0.025$ M). At higher boron concentrations, polynuclear complexes are formed and several dissociation/formation constants apply.

2. Material and Methods

In order to verify the impact on the tanning of the new classification of the boron-based compounds examination of the safety data sheets for chemicals taken from different Italian tanneries was carried out in the first.

The content analysis of total boron in the leathers samples were carried out following the procedure of the ISO 17072-2 standard Leather -- Chemical determination of metal content -- Part 2: Total metal content; in particular microwave assisted digestion (MAD) was carried out followed by ICP-MS determination. The ICP-MS was equipped with inert and high-sensitivity sample introduction system.
In order to avoid contamination, only plastic laboratory equipment was used.

3. Results and Discussion

Both Borax Decahydrate and boric acid came into use in the leather industry in the latter half of the 19th Century. It is the mild alkalinity of borax and weak acidity of boric acid that make them suitable for this application. Borax is used for soaking hides and skins, for stripping vegetable tans and for neutralizing chrome tans. Boric acid is used mainly for neutralizing limed pelts.

In a general way, it can be said that the boron derivatives can be used in the tanning process for the following applications:

1. preservative for skins (biocide); curing agent for snake skins
2. deliming,
3. neutralizer for tanning,
4. whitening,
5. dyeing auxiliary,

While it is known the potential use of boric acid and sodium tetraborate as preservative, deliming and neutralizing agents, less well known is their presence, especially in the case of borax, as ingredients in some finishing products among which the proteic ligands and pigments.

Indeed, as a result of the monitoring of safety data sheets relating to the chemicals present in some tanneries, the presence of borax in many finishing products has been detected.
On the other hand, the presence of boron compounds in deliming agents or neutralizing agents, in which they could be expected, was detected only rarely.

In this regard, in Table 1, as an example, shows the composition% of borax and other ingredients of a finishing product, such as a proteic ligand, as reported in a safety data sheet.

Component	**CAS**	**Quantity**	**Risk Phrase**	**Note**
Oleic Acid	112-80-1	1-5 %	36/37/38	
Caprolactam	105-60-2	1-5 %	20/22 36/37/38	
Casein	9000-71-9	9-30 %	36	
Borax	1303-96-4	1-5 %	60/61, 22,38,41, 48/22	Candidate list
Diethanolamine	111-42-2	< 1%		

This evidence could be explained as, in proteic finishing products, casein can be made water-soluble by an alkaline treatment with ammonia or borax. The casein exerts the action of colloid protector against pigments and makes them water-soluble.

Furthermore several statements of chemicals suppliers claim that the sodium tetraborate (borax), is present in various preparations of pigments in a concentration which can vary from a minimum of 0.26% to a maximum of 0.59% as reported in Table 2.

Finishing product	**Borax (CAS 1303-96-4) %**
White pigment	0,26 - 0,58
Brown pigment	0,36
Blue pigment	0,58
Yellow pigment	0,58
Red pigment	0,58
Green pigment	0,58
Silver pigment	0,27
Bronze pigment	0,54
Black pigment	0,44 - 0,59

The safety data sheets were, in this case together with a statement showing that "with normal levels of application of these products, finished leathers comply with the restrictions on the SVHC (0.1% in the articles)”. This type of statement, when inserted in the safety data sheet, makes the chemical provided according to REACH Regulation

From the late '90s the need to produce according to the requirements that would guarantee not only the quality of the product but also the environment has spread more and more.

In this regard, compliance with the eco-toxicological criteria should be ensured not only through the respect of the laws in charge, such as REACH, but also taking in account the limits imposed by other regulations, voluntary and sometimes private nature (eg technical standards, eco-labels, technical specifications and / or customer specifications).

From the examination of the eco-toxicological specifications and standards that govern, it is clear that the evaluation of boron and sodium tetraborate is never expected.

Conversely, under the REACH regulation is necessary to know the weight / weight percentage of boric acid and borax present in the article leather, bearing in mind that these are SVHC substances that can be used in some phases of the production process tanning.

For this reason, monitoring was performed on 75 leather samples with different origin and at different stages of processing (pickled, wet blue, crust and finished). From screening performed has emerged, on the whole, a non-negligible presence of boron in 25 leather sample (33% of the whole).

In particular, in Table 3, is an example of the values found in some semi-processed (pickled, wet blue, crust and finished) and finished leathers.

Table 3. Results of the analysis of boron in semi-finished and finished leather (values on dry matter)

	Processing stage				
	Pickled	**Wet-Blue**	**Crust**	**Semi-aniline**	**Aniline**
Total Boron	838	253	119	131	322
Boron espressed as Boric Acid H_3BO_3	4.795	1.443	678	750	1.839
Boron espressed as Borax $Na_2B_4O_7$ x $10H_2O$	7.398	2.226	1.048	1.158	2.838

As you can note, expressing the value of the boron as boric acid (H_3BO_3) and sodium tetraborate decahydrate ($Na_2B_4O_7$ - $10H_2O$), the obtained values are higher than the limit value of 0.1% (1.000 mg / Kg) provided for the substances in the SVHC articles produced and / or imported into the European Community. In the calculation of the presence of the various salts were taken into account that the amount of boron present in the boric acid is equal to 17.5%, while in Borax this value is equal to 11.3%.

Therefore, the monitoring carried out confirms the need for the analysis of boron for the respect of eco toxicological parameters provided for under the REACH legislation.

Of course there is to be noted that a substance included in the Candidate List is not a substance whose use is forbidden: therefore, there is no ban on producing or importing articles containing such substances; provided that they meet the obligations of communication to customers and possible notification to ECHA

In order to verify the application of the Reach Regulation, it is to make clear what compound of boron is present in the leather when such information is not available from safety data sheets for chemicals, as in the case of leather imported from extra-EU countries.

At this regard, with reference to the ECHA dossier for the boron compounds regulated as SVHCs, we know that the dissociation constant for disodium tetraborate anhydrous as such cannot be determined because disodium tetraborate anhydrous is converted into boric acid/borate upon dissolution in water:

$$Na_2B_4O_7 + 7H_2O \rightarrow 2\ NaB(OH)_4 + 2\ B(OH)_3$$

The dissociation constant found will be the dissociation constant for boric acid in the presence of sodium ions. At low concentrations, boric acid exists as undissociated boric acid $B(OH)_3$ at pH < 5, whereas at pH > 12.5, the metaborate ion -$[B(OH)_4]^-$ becomes the main species in solution. Both species are present at pH 5-12.5 at concentrate ions B≤0.025 M.

At higher boron concentrations (B>0.025 M), an equilibrium is formed between B(OH)3, polynuclear complexes and $B(OH)_4^-$. Again at pH<5, boron is mainly present as B(OH)3 and in alkaline solution at pH>12.5, boron is mainly present as $B(OH)_4^-$.

At in between values (pH 5-12), polynuclear anions are found as well as $B(OH)_3$ and $B(OH)_4^-$. The dissociation constant depends on temperature, ionic strength and presence of group I metal ions (Na, K).

As from the analytical point of view it is not possible to proceed to the speciation of the compounds of boron, when they exist in a leather, and according to the above information, if it is not possible to know the product used, the possible detection of boron in leather hat to be referred, from the point of view of compliance with the REACH Regulation, to boric acid.

The results reported in Table 3, show that the presence of boron becomes problematic when it is present in the imported leathers.

In fact, even the values obtained on finished leather, because of what has been shown by the analysis of safety data sheets, allow the presumption that the presence of boron derived from the use in the first stage of processing, carried out in the countries of origin of the leathers.

Notwithstanding that the best approach to the problem of the presence of boron-based compounds in the leather is the replacement of boric acid and borax in the early stages of the tanning process, still remains open the problem of imports of leathers from non-EU, which may contain compounds based on boron concentrations above the limit of 0.1% and are thus to be covered by the REACH Regulation. At the same time, is to be considered the fact that this concentration can be maintained also on the finished article.

As most of the imported semi-processed articles arrive in Italy as wet-blue, on this type of leathers some trials for the removal of boron are in progress.

Due to the high solubility of boric acid, the first tests were conducted by performing an increasing number of washings, even with the aid of the temperature. These tests have not given positive results, in practice not experiencing any removal of boron from the leathers, and therefore a complex mechanism of interaction between the boron-based compounds and leathers can be supposed.

At the time, we are studying the possibility of using complexing agents that may have a positive effect on the removal of boron.

4. Conclusions

REACH regulation provides, among others, various restrictions regarding chemicals. In particular, among the so-called SVHC (Substance of Very High Concern), there are some of them directly concerning the tanning industry and consequently also the leather and the finished articles.

Some boron compounds, such as boric acid and the sodium tetraborate, are SVHCs that can be used in leather processing; in fact the use of such compounds in deliming is reported in the scientific literature concerning the tanning process, and furthermore the acid boric is also used for the preservation of raw hides, as well as the sodium tetraborate may be present in some finishing products.

The analytical tests carried out on semi-finished skins (pickled, wet-blue and crust) and on finished leathers, have revealed the presence of boron, expressed as boric acid and/or tetraborate, in a quantity exceeding the expected limit for SVHC substances in the finished articles, equal to 0,1%.

The results show that the presence of boron becomes problematic when it is present in the imported leathers. In fact, even the values obtained on finished leather, and by the analysis of safety data sheets, the presence of boron derived from the use in the first stage of processing, carried out in the countries of origin of the leathers.

As the removal of boron from leather could be very difficult, the best approach to the problem of the presence of boron-based compounds in the leather is the replacement of boric acid and borax in the early stages of the tanning process.

5. References

Calvanese G. , Prospettive e problematiche relative alla sostituzione di sostanze chimiche nell'ambito dell'applicazione del REACH , Conferenza Tecnologica, Milano 20-21 Gennaio 2012

Candar V., Possibilità di sostituzione di alcune sostanze chimiche in campo conciario, Conferenza Tecnologica, Milano 20-21 Gennaio 2012

Consiglia G. A., L'implementazione del regolamento REACH nell'Industria conciaria; caso studio: Il polo industriale di Solofra, Tesi di Master di II livello in REACH, Università di Napoli- Federico II, Facoltà di Farmacia

Hughes I.R., Temporary preservation of hides using boric acid, JSLTC, 58, 100-103, 1974

Ministero dell'Ambiente, Le sostanze estremamente preoccupanti ai sensi del regolamento REACH, bollettino di informazione, anno 4- n°1, Febbraio 2013

Piccirillo D., Monitoraggio delle sostanze SVHC negli articoli in cuoio, Tesi di laurea in Controllo di Qualità, Università di Napoli- Federico II, Facoltà di Farmacia

Sammarco U. , Tecnologia Conciaria, Ed. Editma

Vigezzi E., L'acido borico ed il borace nella lavorazione delle pelli, CPMC, 11, 371-381, 1933

Touloumet M. L., Substitution de l'acide borique , CTCentreprise, Septembre 2009