

Workshop on the implications of the use of trivalent Chromium in functional plating with decorative character

Summary Conclusions

Webinar, 10 October 2022

Introduction and purpose of the workshop

The webinar was hosted by ECHA and included a series of speakers followed by a panel discussion (see Annex 1). 350 stakeholders participated in the workshop. Presentations are available at [ECHA website](#).

The **purpose** was to gain understanding of the potential implications of the use of trivalent chromium (Cr(III)) in functional plating with decorative character considering the following important questions:

- How is Cr(III) currently used for this specific use and to what extent are borates used in the process? Are there alternative substances/technologies available?
- What are the potential health and environmental implications of using Cr(III) and borates for this use and can mitigation measures be implemented relevant to the introduction of a SVHC?
- What sources are used for Cr(III) manufacturing and is this different from Cr(VI)?

Workshop conclusions

The following conclusions were drawn from the presentations and subsequent panel discussion:

1. *In general Cr(VI) is imported into the EU as chromium trioxide and is transformed to Cr(III) and Cr(VI) formulations in the EU. Lower volumes of Cr(III) are imported from mainly Turkey.*
2. *As a technology, Cr(III) plating with decorative character is still developing; it is regarded as a much more complex and unstable process than Cr(VI) plating with decorative character and in general consumes more Cr(III) due to a somewhat lower efficiency.*
3. *Cr(III) acceptance rate by users is still low due to the difficulty to achieve a stable product.*
4. *Cr(III) plating with decorative character is presently fully dependent on borates due to the fact that this substance fulfils a combination of specific technical properties (e.g. smoothness of the surface, buffer function, ...). This is also the case in nickel, zinc and precious metal plating.*
5. *Cr(III) hazard classification may change as a consequence of the EU substance evaluation going forward; the hazard properties of borates are well known and fulfil the SVHC criteria.*
6. *The quantity of borates needed relative to the quantity of chrome plate achieved is relatively high.*
7. *Regeneration of borates is not possible and Waste Water Treatment Plants do not eliminate borates from the waste water. Hence, at present, discharge of borates to surface waters is unavoidable.*
8. *Borates regulation is expected to become stricter – SVHC candidate listing can place legal requirements in some Member States, such as Italy e.g., on discharge to surface waters.*
9. *A quantified environmental risk assessment is unfeasible at this stage due to the lack of mass balances for plants discharging borates. A calculation from emissions to surface water based on generic assumptions indicates that there may be a local risk (PEC > PNEC). Current EU-wide regional exposure data do not demonstrate a regional risk¹.*
10. *The review of the BREF document for the surface treatment of metals and plastics' sector is underway. Boron and its compounds have been identified here as a key environmental issue.*
11. *Monitoring for worker exposure only captures the total chrome. Monitoring of borates is not conducted but is possible with a cost.*

¹ The local Borates scenario was calculated by Apeiron in September 2022 with EUSES on the basis of a standard Sewage Treatment Plant scenario for an average use of 40 t boric acid per year with an elimination efficiency of 0%. The regional assessment was done by ARCHE environmental consultants in September 2022. It used all Borate monitoring concentrations available in the 2021 edition of the European Environmental Agency "Waterbase database" and compared them, as for the local assessment, with the PNECs available in the Boric acid REACH registration file.

Scoping and challenges

The workshop focussed on the potential use of Cr(III) as an alternative to Cr(VI) for functional plating with decorative character. Other plating uses exist but were excluded from the scope. Applications for plating usually focus on the direct use of Cr(III). In this case there are potential concerns due to the use of borates in the plating bath, as well as with the manufacturing of Cr(III) from Cr(VI).

Materials flow and manufacturing pathway

The overall materials flow for chrome starts with the mining of chrome containing iron ores, mainly in Kazakhstan and South Africa. Chrome is extracted as disodium chromate and transformed into Chromic acid/chrome trioxide (both Cr(VI)) which is the main component imported in the EU. This substance is either formulated for direct use as a Cr(VI) compound or transformed (as an intermediate) as a Cr(III) compound (often CrCl₃ or Cr₂(SO₄)₃) and subsequently formulated. The main producers of Cr(III) compounds for use in Europe are located in Turkey, Italy, Germany and the UK. Details on the production pathways of Cr(III) compounds were provided during the workshop. Most important is that they all start from Chromic acid or chromium trioxide (both of which are Cr(VI) compounds) for the manufacture of Cr(III) compounds. The generic materials flow for Cr(VI) and Cr(III) use in the EU is illustrated separately on [ECHA website](#).

Hazard properties and harmonised classification under CLP

Cr(VI) compounds used in plating are formally classified as CM(R) Cat. 1B. There are indications from a recent Substance Evaluation conducted by France, that Cr(III) compounds show some hazard endpoints of concern (skin sensitisation and repeated dose toxicity) while the reprotoxicity endpoint was concluded as “unresolved”. However, no initiative for a harmonised classification has been taken or announced on the ECHA Registry of Intentions, so far.

Potential Cr(VI) impurities in Cr(III) above the classifiable level of 0.1% were also identified as a concern. Boric acid is classified in Annex VI of the CLP as reprotoxic 1B with a generic concentration limit of 0,3%. This classification applies to many borate substances belonging to this group, and more will come in the future.

Monitorability and monitoring experience

The UK started routine monitoring for chrome in 2009. The first report published in 2013 indicated that good exposure control could reduce actual exposure to close to background values. The main relevant exposure routes turned out to be dermal exposure and ingestion, due to poor personal hygiene. Despite the different plating/coating processes and steps, the general exposure for chromium workers was no more than 3 µmol/mol creatinine, on average one third of the UK BMVG, which is 10 µmol/mol creatinine, and double of the levels for non-chromium workers. A problem is that only total Cr can be measured in routine measurements, and therefore no distinction can be made between Cr(VI) and Cr(III). There is therefore only very limited specific biological monitoring data available for Cr(III) or for borates in the UK. Hence, the identification of a need for the plating sector to monitor Cr(III) and borates on a routine basis.

Advantages and disadvantages of using Cr(III) and Cr(VI) for functional decorative plating

In contrast to some other metals, chromium metal is a brittle substance and cannot be used as a base metal, hence it is rather used as a coating on a solid plastic or metal support base. One of the advantages of using Cr(VI) is its abundant availability and it being an “easy to handle” compound for etching and electroplating compared to Cr(III) compounds. The latter require more volume to achieve the same results and the baths are less stable than when using Cr(VI), therefore they require buffers (e.g. borates) and other compounds (some of which are also classified) are needed to maintain a stable performance.

Technically speaking, Cr(VI) compounds are presently the easiest way to achieve a high performance metallic chromium (Cr0) layer/coating that is also colour stable. Cr(III) is an upcoming technology but there are still some technical suitability issues with the stability of the plating process and the colour of the coated layer. The challenges in using Cr(III) for decorative plating are greater than, for example, hard chrome plating given that the layer of deposited Chromium needs to be very thin -- between 0.1 and 0.5 µm – smooth, corrosion resistant, chemical resistant, abrasion resistant and colour stable. Working conditions for the plating process are very strict and different than for other technologies where they can be much more tolerant. The process parameters of the plating bath are therefore much more constrained and require buffering and other chemicals. Those additives are added to the electrolyte to design the coating layer properties (mainly thickness, corrosion, chemical and abrasion resistance, colour, smoothness, ...).

The use of borates in the electrolyte

Borates are only used in the plating with Cr(III) given this process requires more buffering, which is one of the main (but not exclusive) role of borates. As a buffer, borates can be replaced by aluminium chloride (a substance also reviewed under a substance evaluation for potential reprotoxicity concerns). Other key roles of borates include a better deposition process, gloss-forming effect (smoothing), and other layer properties. Borates also influence the layer quality/stability itself including the complexation of iron, a key factor in corrosion resistance and colour stability required to compete with Cr(VI) coating.

There is more than 10 years' experience in efforts to substitute borates in the buffer system by alternatives like carboxylic acids and others. However, so far they still face technical and aesthetic (colour) issues. Borates also help to reduce the development of Cr(VI) impurities in the Cr(III) baths.

Up until now, borates are an indispensable ingredient in Cr(III) electroplating. Borates are also used for this purpose in Zn and Ni electroplating, where the process parameters (such as current density) are somewhat different.

Several platers with extensive experience in using Cr(III) technology indicated that Cr(III) based decorative plating represents today only approximately 5-7 % of their portfolio. The customers' drive in the end is the acceptance of the product quality. The main hurdles for them seem related to quality parameters of the end product, certainly in the high-end sector, like some sanitary ware, as well as for cosmetics. For the platers, the high product throughput required to remain economically viable is still a challenge for this new technology

It was further recalled that there is still an etching step required for chrome plating on plastics which involves Cr(VI).

Exposures and exposure control

Workplace exposure measurements of Cr(III) and borates during the Cr(III) process seem to be very low and dependent on the design of the installation. LEVs include fume extraction, complemented by high-level operator personal protection equipment as a safety measure given that, in principle, this is not needed. Overall, the same type of exposure protection equipment for workers are used for Cr(III) as for Cr(VI) based processes.

Airborne borates exposure measurements in workplaces that use Cr(III) technology are in general below the detection level (which was not specified). However, such measurements in the workplace are not routine. Measurements of borates in Zn and Ni coating processes do not identify an increased risk due to borates.

On the other hand, the amounts of **waste (and waste water)** is much higher in the Cr(III) process than for the Cr(VI) technology, due to the lower stability of the process, the use of additives and higher bath renewal rates.

At this stage, it is not possible to define a quantitative risk assessment for borates **environmental emissions from the plating sector**. A qualitative comparison of Cr(VI) and Cr(III) technology depends on how well exposure is controlled at the particular workplace. Different from Cr salts, borates are not consumed in the process and hence present under the form of acid mist in the emissions during the electrolytic process or waste waters from the rinsing and the baths renewal. Contrary to most metals, borates do not bind to organic matter and hence have different fate properties, passing through standard designed waste water treatment plants, unless waste water is concentrated (by evaporation) and eliminated. At present there is no full scale specific technology known yet that can remove boric acid efficiently from the waste water.

A calculation of emissions to surface water was made for a large production site or for a group of companies emitting into the same river. The calculation is based on reasonable worst case and resulting in PEC values > PNECs. The calculated local emissions are higher than the regional background levels measured in EU waters (see footnote 1).

Further research

Research to improve the electroplating process with Cr(III) as well as developing appropriate waste water treatment are in progress. While the Cr(III) technology is promising it is not yet generally applicable due to technical performance and stability issues. In principle, the sustainable taxonomy recommendations are a driver for safer non SVHC substitutes which could impact the use of borates. However, the use of borates and other additives are at this moment still indispensable to ensure proper technical feasibility. The lack of sufficient gloss effects, colour aspects and insufficient corrosion, chemical and abrasion protection are the main arguments used by customers to hesitate accepting the new technology. The question in the end remains what the environmental and workers exposure gains are between the two technologies when all exposure aspects are considered.

Switching the process from Cr(VI) to Cr(III) technology is a challenge for the waste water treatment due to borates. Some company figures on borates use and releases were provided and demonstrated that they can be large. Boric acid in the plating baths is usually up to a concentration of 90 g/l. Mitigation measures for borates include Local Exhaust Ventilation (LEV), and a closed waste water treatment plant circuits that are required given presently borates cannot effectively be eliminated from the waste water treatment plant effluents. Evaporation and strong ion exchangers are theoretically feasible technologies but economically infeasible given the large volumes of liquids involved. These also require high energy usage.

Learning lessons from the PANEL discussion

Panel chair: Tim Bowmer (ECHA). Panel members: Dave Elliott (CETS), Matthias Enseling (Hapoc) and Hiram Moerman (Apeiron).

Are borates really essential for the Cr(III) process?

- Cr(III) is a potentially promising technology (certainly for the job platers) but not a common practice. All Cr (III) platers use borates. They are used in the baths as a buffer and for other functions. Companies dealing with decorative plating do not see alternatives to borates.
- It was quoted that Cr(III) technology can be successfully applied in “lower end” decorative applications.

Are borates emissions or exposures a problem?

- Borates are broadly used but the amount of borates is small compared to the natural flows.

- Modelling indicates that local emissions from waste water treatment plants to surface water can cause a local risk. The calculated local emissions are higher than the regional background levels measured in EU waters.
- It was suggested to check if there is an evolution in regional concentrations (realising the sources of borates are multiple).
- The number of borates being SVHC is rising and EU taxonomy may make it more difficult to use SVHC materials like borates.
- Borates cannot be recuperated and recycled, they are either released or emitted.
- Economically feasible technologies to clean borates from waste water treatment plants and releases from plating facilities are not available. Ion exchangers are in theory possible but technically and economically infeasible.

Are Cr(III) and borates workplace emissions monitored?

- Borates in the plating sector are not routinely monitored despite the fact that SVHC identification would promote monitoring.
- The limited information available demonstrates that measurements are on average below the detection limit. This can be explained by the fact that Cr(III) processes are more sophisticated than Cr(VI) processes hence more attention for risk control.
- Borates exposure at the workplace could in principle be added to the monitoring plans at a cost. The focus should be on maintenance workers given they are exposed to higher levels.
- Acid mist at plating sites is composed of both Cr(III) and borates. Borates concentrations may therefore be estimated from the Cr levels.
- The step to produce Cr(III) from Cr(VI) is an additional exposure step. While in theory this could be done directly from the ore, this failed technically due to the too high levels of impurities

Mass flow of borates:

- Borates exiting the system via aerosol (acid mist) emissions are cleaned in a scrubber. Also rinsing water from the electroplated products contains boric acid. Scrubber and rinsing water are discharged to the waste water treatment.
- Waste and waste fluids from Cr(III) baths are larger and come from a different process.
- The replacement of the electrolyte happens more frequent for Cr (III) than for Cr (VI), due to formation of impurities.
- A good mass balance for borates in the plating sector has not been made while this information could be most useful.

Others:

- The EU is working on the review of the BREF document for surface treatment of metals and plastics². Boron and its compounds have been identified here as a key environmental issue for emissions to water. As part of the review process, data will be collected and it will be decided whether BAT-AELs³ for emissions should be derived.
- Italy has an aquatic emission standard for borates of 2 mg/l and 4 mg/l in sewage. This standard causes practical problems for platers in Italy.

² See <https://eippcb.jrc.ec.europa.eu/reference/surface-treatment-metals-and-plastics>

³ Emission level associated with the Best Available Techniques

Annex 1: Workshop Programme

Presentations are available at [ECHA website](#).

Time	Title	Speaker
14:00-14:05	Welcome!	Matti Vainio (ECHA)
14:05-14:15	The challenge	Hugo Waeterschoot (Eurometaux)
14:15-14:25	Hazard status of Cr(III) and borates	Pablo Regil (ECHA)
14:25-14:35	Monitoring possibilities and monitoring experience for Cr(VI), Cr(III) and borates. What do we know, what don't we know?	Dave Elliot (CETS)
14:35-14:45	How are Cr(VI) and Cr(III) produced	Michael Stoffers (Vopelius Chemie AG)
14:45-15:00	Cr(III) technology: <ul style="list-style-type: none"> - The function of boric acid - How are exposure and emissions of boric acid considered in the process - Impurities of Cr(VI) in Cr(III) plating 	Joachim Heermann (Max Schlöter)
15:00-15:15	Coffee Break	
15:15-15:35	Plating with Cr(III): Its use including exposure to and emissions of Cr(VI) and boric acid	Jérôme Lemoine (Qualipac) & Owe König (Eupoc, on behalf of Kesseböhmer)
15:35-15:50	Environmental emissions of borates in plating: current knowledge	Hiram Moerman (Apeiron)
15:50-16:00	Is there waste-water treatment technology to remove borates and what are the costs?	Christoph Westermann (VDMA)
16:00-17:00	Panel: Chair Tim Bowmer, Chairperson of the Committee for Risk Assessment (RAC) Dave Elliott (CETS), Matthias Enseling (Hapoc) and Hiram Moerman (Apeiron)	