

Chromium plating beyond the year 2017

Chromium(III) – a genuine alternative to chromium(VI)?

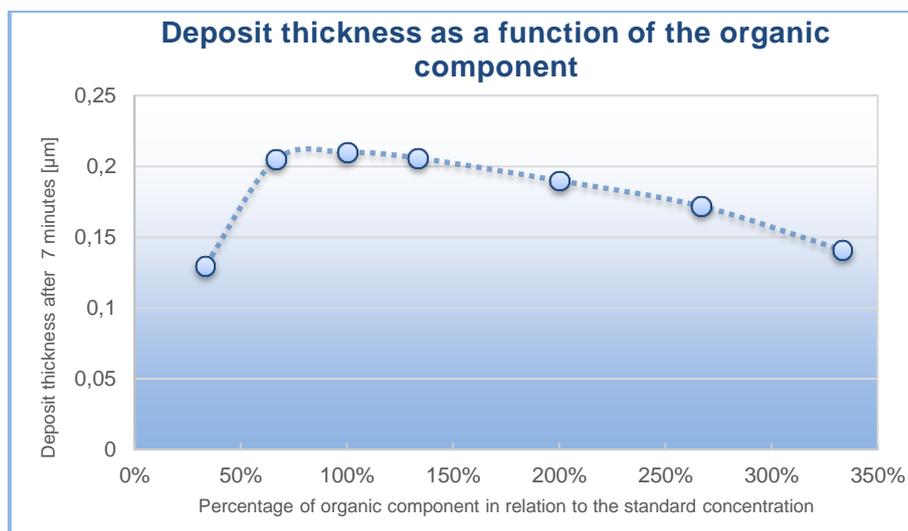
Since the inclusion of chromium (VI) in the list of substances subject to authorisation the interest in trivalent chromium plating processes has been on the increase. The following article deals with important application aspects and the performance spectrum of a sulphate-based chromium(III) process.

It is surely widely known that hexavalent chromium compounds have been under observation for years and that they were included in Annex XIV of the list of substances subject to authorisation in April 2013. Currently an investigation procedure is pending before the European Chemicals Agency (ECHA) relating to the further use or the prohibition of hexavalent chromium beyond the year 2017 with an uncertain outcome.

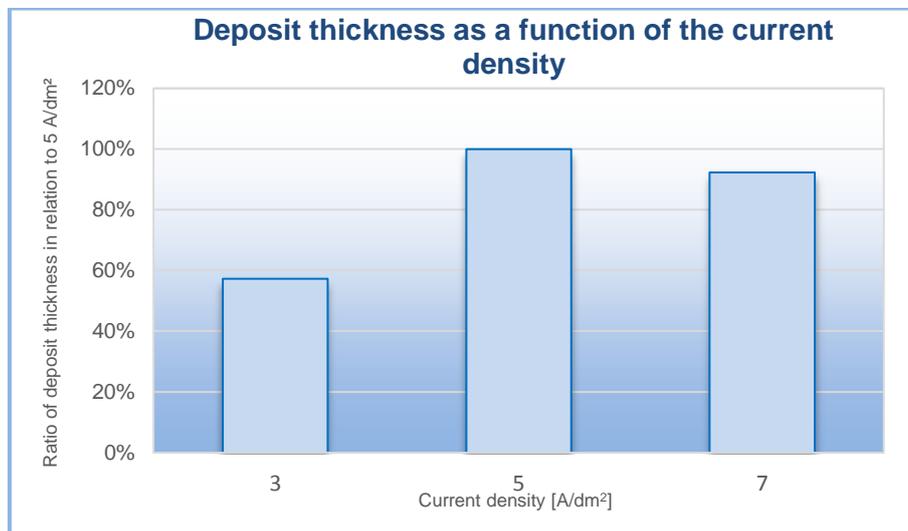
The result of this is that in the last few years the separation of chromium from trivalent chromium systems has again been dealt with intensively. For trivalent chromium plating essentially chloride and sulphate-based systems are used. These vary enormously as regards the working parameters.

Separation from trivalent chromium compounds has been known for more than 150 years. However, the details of the separation process are a subject of controversy. The two-stage mechanism in which the Cr(III) is first reduced to the bivalent and then to metallic chromium appears to be the most probable. In this case it is necessary to master several challenges in order to achieve a high-quality chromium coating on the workpiece.

First of all the very short-lived chromium(II) ion must be stabilised with suitable additives in order to ensure further reduction of the chromium. Furthermore care must be taken to ensure that the pH value rising as a result of the marked hydrogen reduction is buffered as effectively as possible in order to avoid precipitation of $\text{Cr}(\text{OH})_3$. Finally suitable anodes must be used for the Cr(III) bath in order to prevent oxidation to hexavalent chromium. Chromium (VI) not only interferes with the separation process but should not be included in the electrolyte for environmental and health protection reasons.



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For a sulphate-based electrolyte, like KIESOW's SAPHIR 2000 process, an organic component is required in order to support the two-stage reduction process. Fig. 1 shows the influence of the organic factor in the growth of the deposit. It can be easily seen that at 100%, i.e. the standard concentration of the organic factor, a maximum deposit thickness is reached.

In the SAPHIR 2000 electrolyte what are known as MMO (mixed metal oxide) anodes are used. These are essentially electrodes which are composed in such a way that they show a certain oxidation potential necessary for suppressing anodic oxidation of chromium (III) to chromium(VI). The matrix of the electrodes is mostly formed by expanded titanium metals which have varying surface coefficients, and are able to be produced in a customised manner for every plant and application.

An important criterion is the load from the current applied and the current supply of the electrode. Hence an excessively high anodic current density reduces the useful life of the electrodes. Moreover, the current supply must be adequately dimensioned in order to avoid an excessive voltage drop as the conductivity of the trivalent chromium electrolyte that contains sulphate is markedly lower than that of the hexavalent systems.

No problems in wastewater treatment

The chromium(III) content can vary from one process to the next. Excessively high chromium(III) contents cause clearly worse separation. The SAPHIR 2000 process works with relatively low chromium content and is free of complexing agents. Hence no problems are encountered in the treatment of wastewater.

The cathodic current density of the process is 5 A/dm² which is ideal for the electrolyte. On the one hand, this relatively low current density ensures that even highly structured components are completely coated and that, on the other hand, the electrolyte shows its maximum deposit growth at 5 A/dm² (Fig. 2).

When foreign metals contaminate the chromium (III) electrolyte, this can adversely affect the separation process. Therefore ion exchange resins are used for the elimination of the foreign metals. This is specifically a slightly

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acidic macroporous cation exchanger. These cationic exchange resins are present in the sodium form and have to be converted into the H⁺ form by means of treatment in dilute sulphuric acid. The resins work as a function of the pH value, the absorption of bivalent cations being clearly reduced in the case of an excessively low pH value. This must be borne in mind during use of the trivalent chromium electrolyte. The absorption of the metals by the resin is subject to certain rules, with the affinity for the absorption of copper(II) > lead(II) > nickel > zinc > iron(II) decreasing.



The sulphate-based chromium(III) electrolyte has proved efficient in practice as regards corrosion resistance and colour

The post-dip solution increases corrosion proofing

Subsequently the separated chromium deposit can be treated with a post-dip solution based on chromium(III) salts. This clearly reduces the inter-crystalline corrosion of the trivalent chromium separated. For this a chromium(III) based chemical post-dip solution is used. In this way corrosion protection values of more than 480 h NSS without any chromium corrosion are obtained. An additional use of an electrolytic system, employed after the chemical post-treatment, is currently in the practical testing phase.

Reduced deposition rate

Although decorative coating with chromium(III) electrolytes is meanwhile state of the art, there are some challenges posed by the trivalent systems. For example, the deposition rate is lower than in conventional hexavalent systems. This fact must be taken into account in the planning of plants and in the change of systems in existing plants.

For the chemical post-dip solution, if necessary for the combination of a chemical and an electrolytic solution, there must be sufficient space in existing plants. As regards the colour there are restrictions in comparison with the hexavalent systems. The L values of the LAB test demanded by the Professional Association of Galvanized Plastics (Fachverband Galvanisierte Kunststoffe (FGK)) are achieved. The trivalent chromium electrolyte requires higher maintenance expenditure and effort. As a result higher maintenance and personnel costs are incurred.

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Tried and proven in practice

In the contract finishing company Emil Weiss GmbH & Co. KG in Mitwitz-Steinach, near Kronach in Franconia, specialising in, among other things, nickel-plating and chrome-plating of project furniture and shop components, sulphate-based chromium electrolyte SAPHIR 2000 from Kiesow is used. For this the required adsorber resins and their cleaning equipment were adequately dimensioned.

After a few months of production the contract finisher is convinced of the system's efficiency and performance capability. The electrolyte is used in some case in which the chrome-plating from hexavalent systems encounters problems due to the geometry of the parts. The colour differences between the two chromium deposits are practically negligible. The SAPHIR process shows itself to be superior as regards the corrosion resistance on the specially finished interior parts.

An indispensable process

In the future, trivalent chromium-plating will increasingly finds its way into the finishing of surfaces, even if the authorisation of hexavalent chromium proceeds positively in the interest of the users. Its use in the automotive and/or sanitary sectors which consider the chromium deposits an industrial chromium coating is presently regarded with scepticism. In this case further tests, ring tests and lots more are necessary in order to more closely define the different demands on the chromium deposits and to possibly improve them. The trivalent chromium processes will continue to gain in importance, and will in future become indispensable.

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