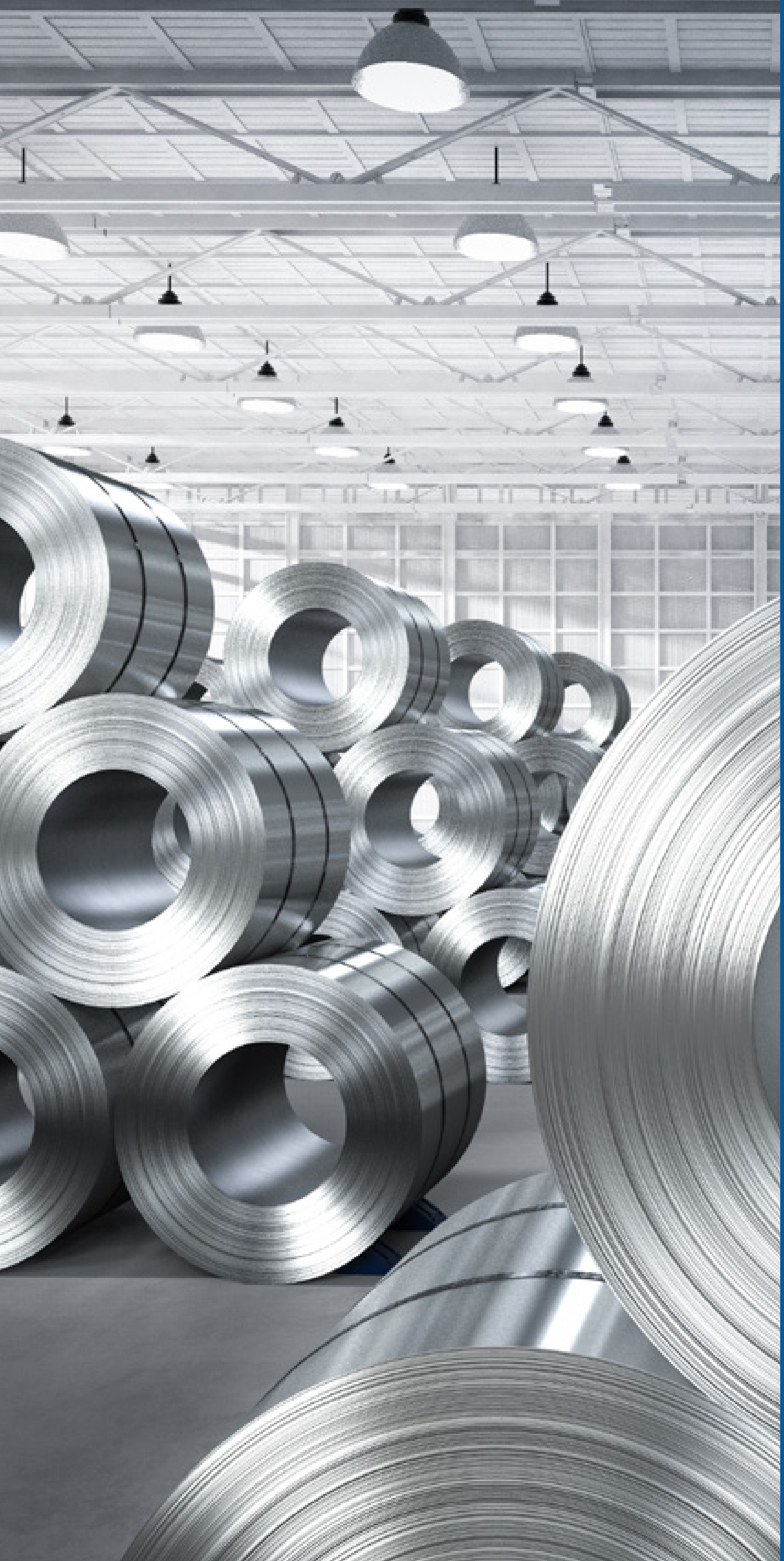


Eastman TETRASHIELD™
protective resin systems

# Removing hexavalent chromium from tin plate surface treatment

*What does that mean for your coatings?*

EASTMAN

# Regulation and context

The food metal-packaging industry is moving toward using non-hexavalent chromium surface treatment in steel and aluminum substrates. This transition is driven by growing concerns about the environmental and health impacts of hexavalent chromium compounds. Hexavalent chromium is known to be toxic and carcinogenic, raising alarms about its presence in food contact materials. Regulatory bodies and industry standards have recognized these risks, prompting the industry to explore safer alternatives.

Regulations such as Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) in Europe and Food and Drug Administration (FDA) guidelines in the United States have restricted hexavalent chromium use in food packaging. Hexavalent chromium is subject to a time-limited authorization permit in the European Union as these substances have been identified as Substances of Very High Concern (SVHCs), resulting in their inclusion in REACH Annex XIV (authorization list).[1] Current authorizations expire September 21, 2024, but authorization holders reapplied by submitting a review report to the European Chemicals Agency (ECHA). Deliberation by ECHA on whether to continue using hexavalent chromium is expected in 2023. Depending on that result, hexavalent chromium use may still be allowed beyond 2024.

Hexavalent chromium [Cr(VI)] is one of the valence states (+6) of the element chromium. It is usually produced by an industrial process. Cr(VI) is known to cause cancer and targets the respiratory system, kidneys, liver, skin and eyes.[2] Chromium metal is added to alloy steel to increase hardenability and corrosion resistance. Worker exposure to Cr(VI) occurs during "hot work" such as welding on stainless steel and other alloy steels containing chromium metal. Cr(VI) compounds may be used as pigments in dyes, paints, inks and plastics. It also may be used as an anticorrosive agent added to paints, primers and other surface coatings. The Cr(VI) compound chromic acid is used to electroplate chromium onto metal parts to provide a decorative or protective coating.

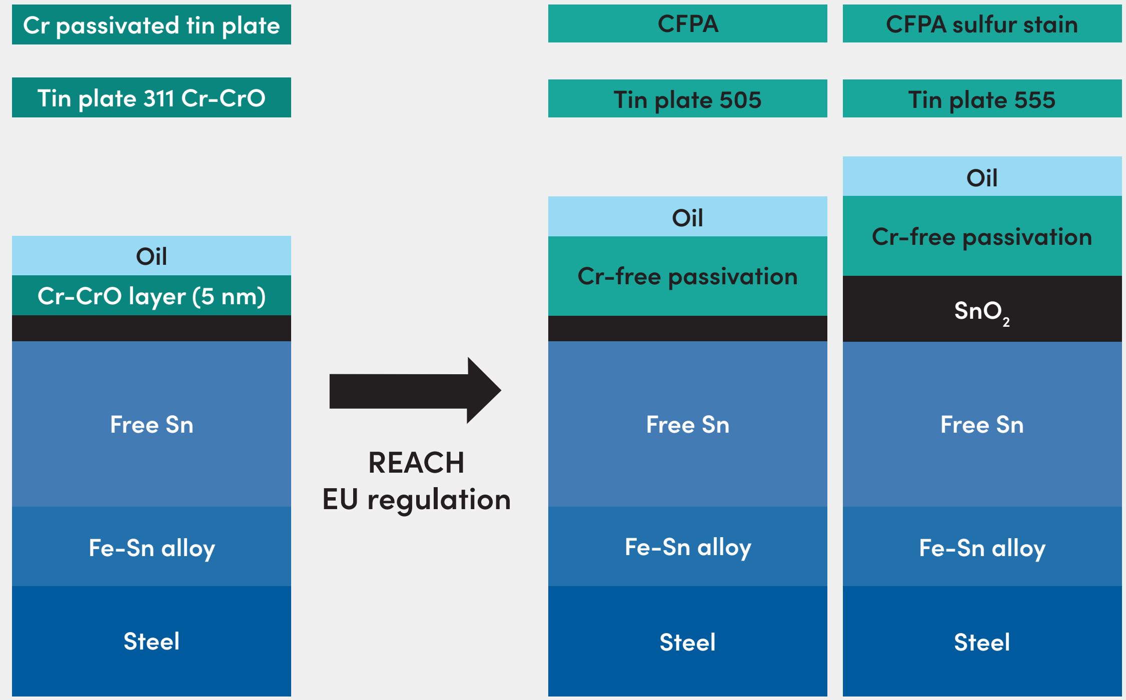
[1] *https://echa.europa.eu/applications-for-authorisation-consultation*
[2] *https://www.osha.gov/hexavalent-chromium*

## Latest news from CARB

### Hexavalent chromium banned in California

The California Air Resources Board (CARB) recently approved a landmark ban on use of the substance by the chrome plating industry. The ban requires companies to use alternative materials. The new rule makes California the first state to ban hexavalent chromium. Decorative plating businesses have until 2027 to discontinue use. These regulations have played a pivotal role in motivating manufacturers to explore non-hexavalent chromium surface treatments that offer improved safety and sustainability. Non-hexavalent chromium surface treatments not only mitigate health risks but align with consumer demands for environmentally friendly and safe packaging.

# Alternative surface treatment for tin plate without hexavalent chromium




*Classic passivation for electrolytic tin plate (ETP) and chrome-free passivation alternative (CFPA) tin plate*

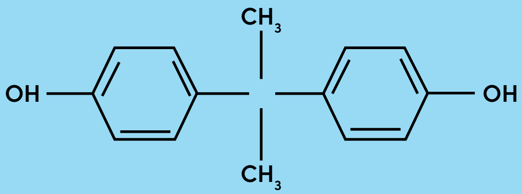
# History of metal can coatings

### More than 70 years of epoxy

In the 18th century, French confectioner Nicolas Appert developed a method to preserve food by heating and sealing glass jars to prevent spoilage. This process was used by Napoleon and his troops to transport food during their campaigns. In the 19th century, the first metal can was made of tin plate and introduced in England by merchant Peter Durand. Metal proved to be more durable than glass, and manufacturing improvements in the 19th century allowed metal food cans to be made on a larger scale in Europe and in the U.S. Further progress was made to protect the can from corrosion caused by the food while keeping organoleptic properties.

The first inner can coating consisted of a layer of tin as a barrier between the food and the can. Enamel has also been used to coat the inside of a can. Early organic coatings made of wax or shellac were used but with limited performance. Epoxy coatings were introduced in 1950, offering excellent corrosion resistance while maintaining organoleptic properties. In the late-1990s, concerns arose with bisphenol A diglycidyl ether (BADGE) and the starting monomer bisphenol A (BPA). Bans were enacted in the 2010s, and alternative coatings were developed to replace epoxy-based coatings.

### Bisphenol A (BPA)




**2,2-Bis (4-hydroxyphenyl) propane**
**$C_{15}H_{16}O_2$ = 228.29 g/mol**



# Innovation in tin plate for metal packaging industry

Non-hexavalent chromium surface treatments encompass a range of alternatives for tin plate, electrolytic chromium coated steel (ECCS) and aluminum substrates. These include a trivalent chromium passivation or a protective layer consisting of $ZrO_2/TiO_2$, phosphoric and polymeric compounds called chrome-free passivation alternative (CFPA). Trivalent chromium has gained popularity as a replacement for ECCS and has been made by Tata Steel[3] and thyssenkrupp[4] under the name Trivalent Chromium-Coating Technology (TCCT®). TCCT is produced in accordance with the revised European standard EN 10202-2022.

ArcelorMittal[5] has developed a different approach to replace ECCS. Chromium coating was primarily developed as an economic alternative to tin.

It is an electrolytic treatment in a bath of chromic acid to deposit metallic chromium and chromium oxide on the black plate. The usual name is ECCS or tin-free steel (TFS). TFS is excellent for lacquer adhesion and must always be lacquered on both faces before use. TFS is not suitable for welding or soldering. Its appearance is less attractive (lower brightness) than tinplate. The absence of tin makes TFS inappropriate for acidic food (pH < 4) because of lower corrosion resistance. To be compliant with REACH, European tinplate producers are developing alternatives to the current ECCS. ArcelorMittal proposes a low-tin in steel (LTS) with titanium/zirconium passivation and can provide any specification.

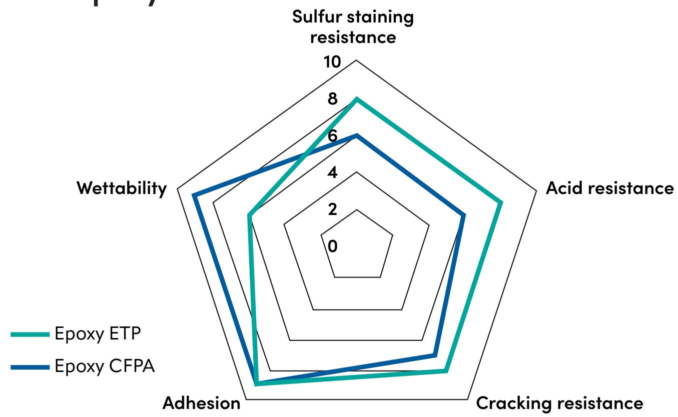
[3] *https://www.tatasteeleurope.com/sites/default/files/tata-steel-apeal-packaging-chrome-free-passivation-alternative-cfpa-EN.pdf*
[4] *https://www.thyssenkrupp-steel.com/en/innovations/materials/rasselstein-cfpa/rasselstein-cfpa.html*
[5] *https://packaging.arcelormittal.com/repository2/Unassigned/CatPack2017_170425i.pdf*

# The impact of hexavalent, chromium-free passivation on coating technologies

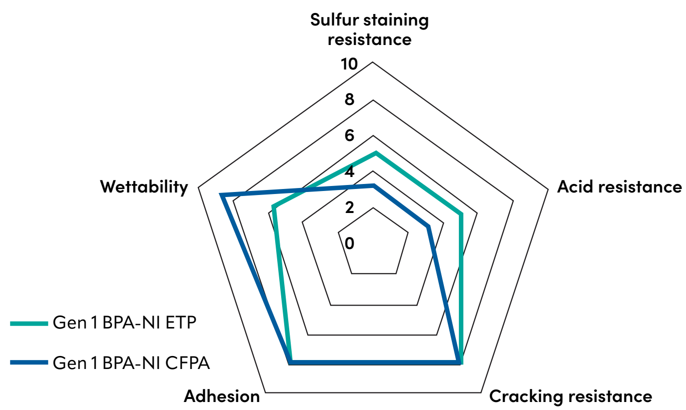
Evaluation of coatings technologies on ETP and CFPA shows the performance of Tetrashield-based coatings compared to competitive technologies.

- In some severe applications (aggressive media) and especially with gen 1 BPA-NI coating, CFPA does not perform as well as chromic passivation.
- Tetrashield-based coatings can provide enhanced performance on CFPA.

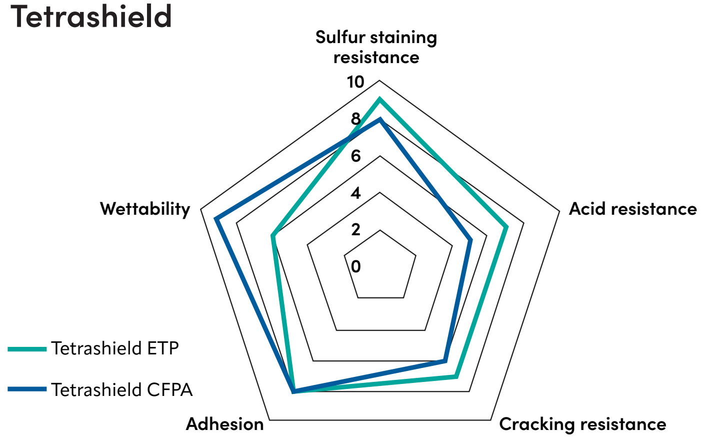
### BPA epoxy




### Gen 1 BPA-NI




### Tetrashield




# Key properties for food cans

The challenge with removing hexavalent chromium passivation is to maintain performance on critical properties after the coated sheet is transformed into a can end or body. The coating should have a good wetting on the substrate. During the transformation, a good coating adhesion to metal and suitable cracking resistance (flexibility) are necessary for the coated panel to be transformed, ensuring maximum protection of the metal while maintaining the organoleptic properties of the food inside.

Most food requires a sterilization step during the packing process. The most difficult foods to pack have a pH lower than 4. Therefore, the coating needs to withstand strong acid attacks at a high temperature. Also, certain foods contain proteins that can degrade during the sterilization process, forming hydrogen sulfide ($H_2S$). $H_2S$ can react with the tin from the substrate if the coating does not offer a perfect barrier to the food.

In the previous graphs, Eastman has evaluated a commercial coating based on epoxy BPA, a commercial coating BPA-NI called gen 1, and an experimental coating based on Eastman Tetrashield™ protective resin systems. Application of each coating was performed to electrolytic tin plate (ETP) and CFPA — supplied by thyssenkrupp by means of a drawdown bar — and baked at 195°C part metal temperature (PMT) for 10 minutes.

The coated panels were transformed into ends, coupons and a four-corner metal box with asymmetrical corners. We evaluated cracking resistance using an enamel rater measuring porosity of the film. We also tested ends and coupons after sterilization in an autoclave for one hour at 131°C using various food simulants like strong acids (2% lactic, 3% acetic) and acidified sulfur solution. The spider chart shows a direct comparison between coating performance on ETP and CFPA. For all coating technologies, CFPA is more challenging for the coatings, especially in regard to sulfur stain resistance and strong acid resistance. However, coatings based on Tetrashield perform similar to epoxy BPA.

## Summary

The regulatory landscape is continuously evolving, and companies would benefit from compliance with existing regulatory restrictions and from anticipating future bans. This paper illustrates how hexavalent chromium will be removed from various surface treatments used to prevent corrosion of metal substrates in the metal packaging industry and the alternative passivation options proposed by metal-making companies. Furthermore, it demonstrates how switching from ETP to CFPA can create a performance gap, particularly in regard to resistance to sulfur stain and strong acids.

The metal packaging industry is driving a conversion toward BPA-NI coatings and, given the drop of performance, certain commercial BPA-NI coatings might not be suitable when the industry switches from ETP to CFPA metal. Tetrashield high-performing resins deliver performance similar to that of BPA epoxy-based coatings, particularly in sulfur stains and strong acid resistance, and aim to serve as suitable alternatives. This would allow conversion to BPA-NI coatings and CFPA metal substrate without compromising food safety or shelf life.

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