

Publication 130 – E

Chemical Passivation of Metallic Coatings on Steel Sheet



Stahl-Informations-Zentrum

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1 Introduction

Passivating agents for a temporary protection of metallic coatings (hot-dip coatings, electrolytic zinc coatings) were formerly based on chrome (VI)-containing chemicals, also known as chromates. The use of these compounds has been severely restricted or even prohibited by the introduction of legislation addressing various industries. The substance bans imposed to date (March 2009) apply to materials for electronic and electrical consumer goods, passenger cars and commercial vehicles with weights not exceeding 3.5 tonnes. For Germany, the relevant regulations and exceptions are laid down in the Electrical and Electronic Equipment Act based on the “RoHS” Directive 2002/95/EC and in the End-of-Life Vehicles Act based on the “ELV” Directive 2000/53/EC.

In branches of industry exempt from such regulations, the use of coatings passivated with Cr(VI) containing agents is still an option. However, in the interests of labour safety in steelmaking and steel processing and for environmental reasons, steel-makers are endeavouring to limit the use of Cr(VI) containing chemicals even further, up to the point where they can be eliminated altogether.

The present publication is aimed at processors and users of the above-mentioned chemically passivated flat products and goods manufactured therefrom. In order to ensure that hot-dip coated and electrogalvanized products with chemical passivation can still be marketed in an altered legal situation, substitutes for Cr(VI)-containing passivating agents have been developed. Given their chemical composition and action principle, these substances tend to result in appreciably different application characteristics in downstream processing.

Table 1:
Corrosion properties
of hot-dip coatings

Corrosion behaviour	Z	ZA	AZ	AS
Undeformed surface	○	+	++	++
Bending shoulder	○	+	+	+
Cut edge	○	○	-	-

This table gives a general evaluation reflecting today's level of experience. It does not apply to all application situations. In cases of doubt the vendor should be contacted. ○ = standard

Since research and development of these substitutes is ongoing, their properties cannot be described in detail in this publication. However, they continue to provide a temporary protection of surfaces against corrosion.

2 Corrosion protection, characteristics of metallic coatings

Metallic coatings improve the application characteristics of steel sheet by enhancing its corrosion resistance. In selecting the optimal coating for a given purpose, it is necessary to consider the subsequent loading and exposure profile.

Depending on the alloy composition, metallic coatings exhibit different corrosion-inhibiting mechanisms. As a general rule, a higher aluminium content tends to diminish the cathodic protection effect while enhancing the barrier properties of the metallic coating.

Accordingly, coatings affording a high level of cathodic protection attain their maximum effectiveness

when covered with a sealing layer. Metallic coatings with a high barrier effect, especially aluminium-zinc (AZ) and aluminium-silicon (AS) coatings, exhibit very good anti-corrosion properties even when left bare. A general evaluation of the corrosion characteristics of various coatings is given in **Table 1**.

When the unprotected surface of a zinc-containing metallic coating is brought into contact with water, zinc hydroxide forms as a reaction product. If the exposure to moisture remains brief and the surface can dry fully afterwards, this compound reacts into basic zinc carbonate with CO₂ from the ambient air. The basic zinc carbonate forms a deposit on the surface which acts as a passive sealing layer. However, this natural passivation effect takes much time to develop and is quite susceptible to disturbances. The most frequent disturbance is the accumulation of moisture due to inadequate ventilation, e.g., in gaps and cavities. The water then reacts with zinc from the surface coating, with large amounts of zinc hydroxide (white rust) forming in the process, **Fig. 1**. The formation of white rust is irreversible and destroys the metallic coating. High-

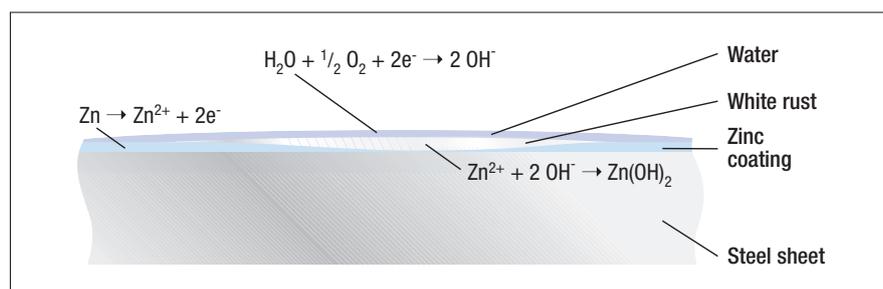


Fig. 1: Formation of white rust due to direct exposure of zinc coating to water

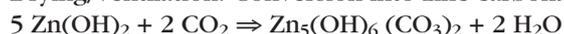
aluminium coatings are more passive due to the presence of aluminium oxide on the surface, but are likewise destroyed by lingering moisture.

Natural passivation by formation of zinc carbonate

Initial formation of zinc hydroxide:

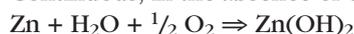


Drying/ventilation: Conversion into zinc carbonate



Formation of white rust

Continuous, in the absence of drying:



3 Temporary protection during storage and shipping

Cathodically active metallic coatings are sensitive to moisture and must therefore be protected (for further information refer to Publication 114). Effective from its ex-works delivery date, application of a temporary protection layer will keep the product corrosion-free for three months. Provided that it is properly packed, shipped, loaded and stored.

The actual protection duration depends mainly on atmospheric, shipping and storage conditions.

Common methods of protecting the surface against moisture are chemical passivation and oiling, the protective effect of which is illustrated in **Fig. 2**. In the latter treatment, a variety of user-specific oil grades are employed (see also Publication 127 – E). The quantity, type and grade of oil can be agreed upon with the steelmaker and must be stated in the purchase order.

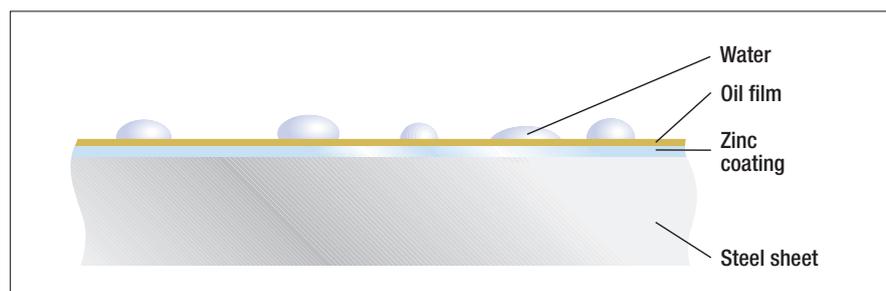


Fig. 2: Protection based on application of an oil film

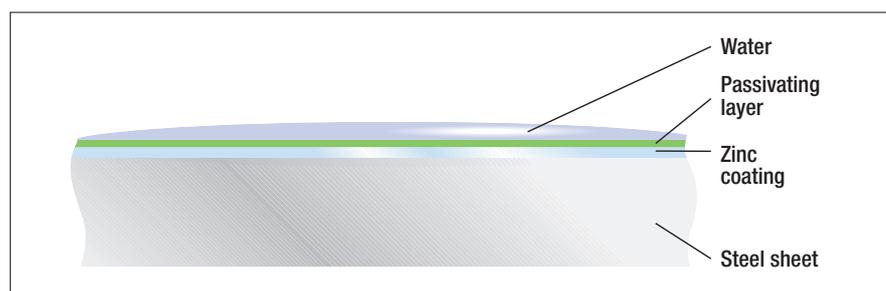


Fig. 3: Barrier effect of the passivating layer

In chemical passivation, the exterior of the metallic coating is treated with substances which initiate a conversion of the highly reactive metal surface and result in the formation of a passivating conversion layer of little reactive metal compounds. This layer acts as a barrier and protects the underlying coating metal from direct corrosion attack by moisture, **Fig. 3**. The protection is of limited duration, as with an oil film, and depends essentially on ambient conditions.

Generally, with all surface protection methods discussed here, it should be noted that a risk of corrosion damage caused by condensed water can never be ruled out. In winter, an improved corrosion resistance can be obtained by ordering suitably packed material.

In the case of unpackaged coils or panels, an abrupt temperature change from cold to warm generally causes dew to form on surfaces exposed to an airflow, and even in the air gap between coil windings. There, moisture will be retained for very long periods as a result of capillary forces.

On coils fully enclosed in film or paper, condensation will settle mostly on the packaging. However, penetration of moisture into the wrapping cannot be fully prevented. Therefore, packaged coils should **always** be unpacked as soon as the coil temperature equals that of the ambient air so that any moisture which has penetrated through the packaging can evaporate. At least two days should be allowed for thermal equalization. Every time the product is placed or shifted in storage at its destination, the potential condensation risks should be examined, **Fig. 4**.

If moisture has condensed on a coil despite all precautions (e.g., because of a large temperature difference or high humidity in the warehouse), the condensed droplets will form a continuous water film which penetrates deep into the coil windings as a result of capillary forces. To avoid irreparable white rust damage, the coil must then be processed immediately.

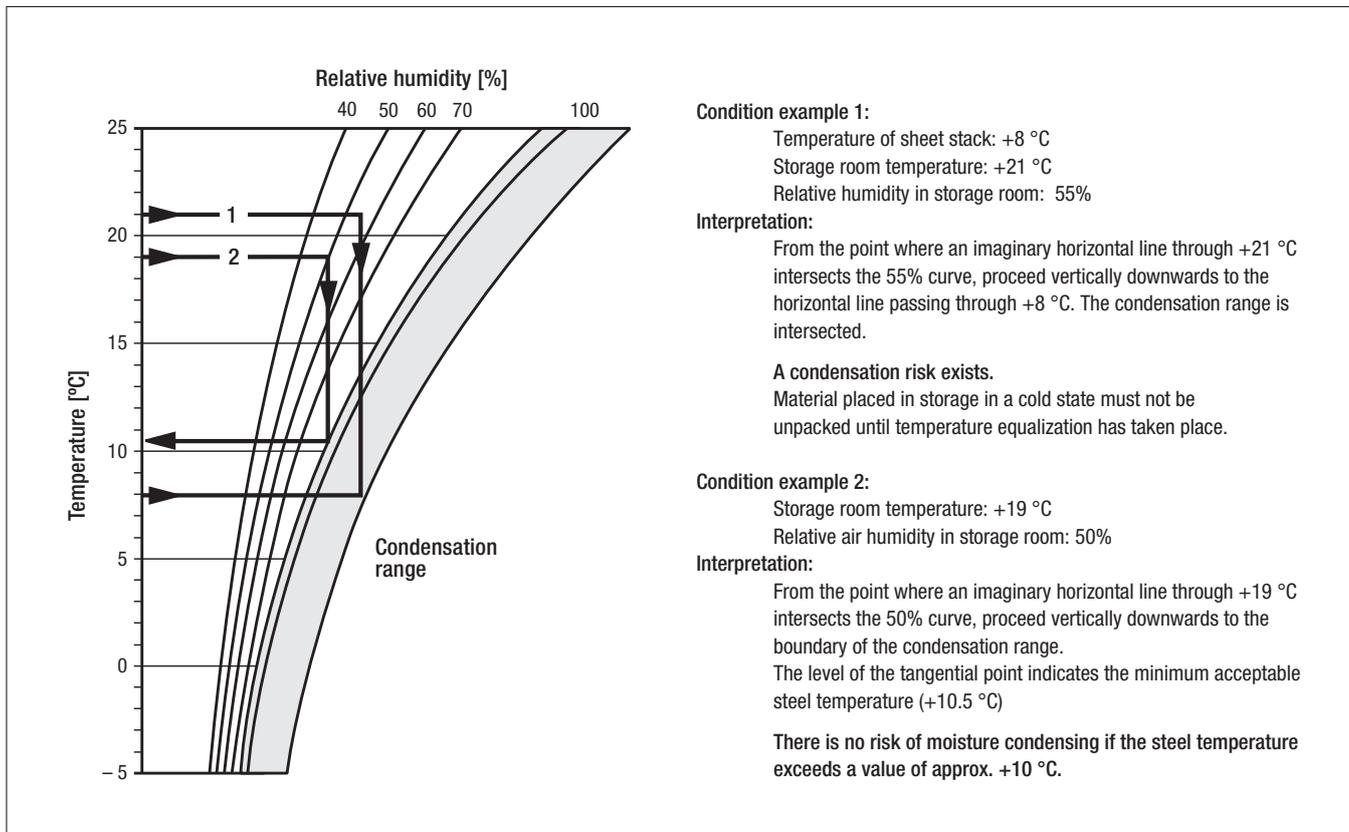


Fig. 4: Diagram for determining the condensation risk

Apart from condensed moisture, soluble salts have a highly detrimental effect on the coating. Sodium chloride – as a constituent of road salt or sea salt – accelerates the corrosion process many times over. It is therefore recommended to use export packaging where goods are loaded and shipped (whether by truck, railway or inland waterway transport) in the winter or near the sea, and the cargo-carrying vehicle should be tightly sealed.

4 Application of chemical passivating agents

On continuous coil coating lines, the passivating medium is applied to the metal coating “in line”, i.e., at full process speed (up to 250 m/min) in the processing train. This involves the physical application, quantity

control and, finally, drying of the passivating agent before the product exits the line, **Fig. 5**.

Application is by the roll method, in the spray-squeeze variant, or by Chemcoater. Drying is usually performed with hot air or, in individual cases, using NIR heater.

The type and quantity of passivating agent applied is adapted by the steelmaker so as to ensure a sufficient degree of temporary protection. Given the high process speeds involved, passivating agent splatter, streaks or stain formation cannot always be avoided. This fact is reflected in the relevant quality standards. However, such discolorations merely constitute localized visual imperfections which do not impair quality.

5 Processing of chemically passivated flat products

In processing steel sheet with a chemically passivated metal coating, interactions with the processing operation may occur. Mechanical operations (slitting, cutting to length, shaping or joining) will alter or destroy the passivation layer in the contact area. Exposure to auxiliary process fluids such as metalworking fluids or cleaning products has the same effect. Processors should therefore expect that the original corrosion protection will be lost, or at least markedly reduced, after such operations.

Conversely, passivating agent residue may be carried over, by mechanical or chemical abrasion, onto tools, equipment or process media, thus impairing their operability.

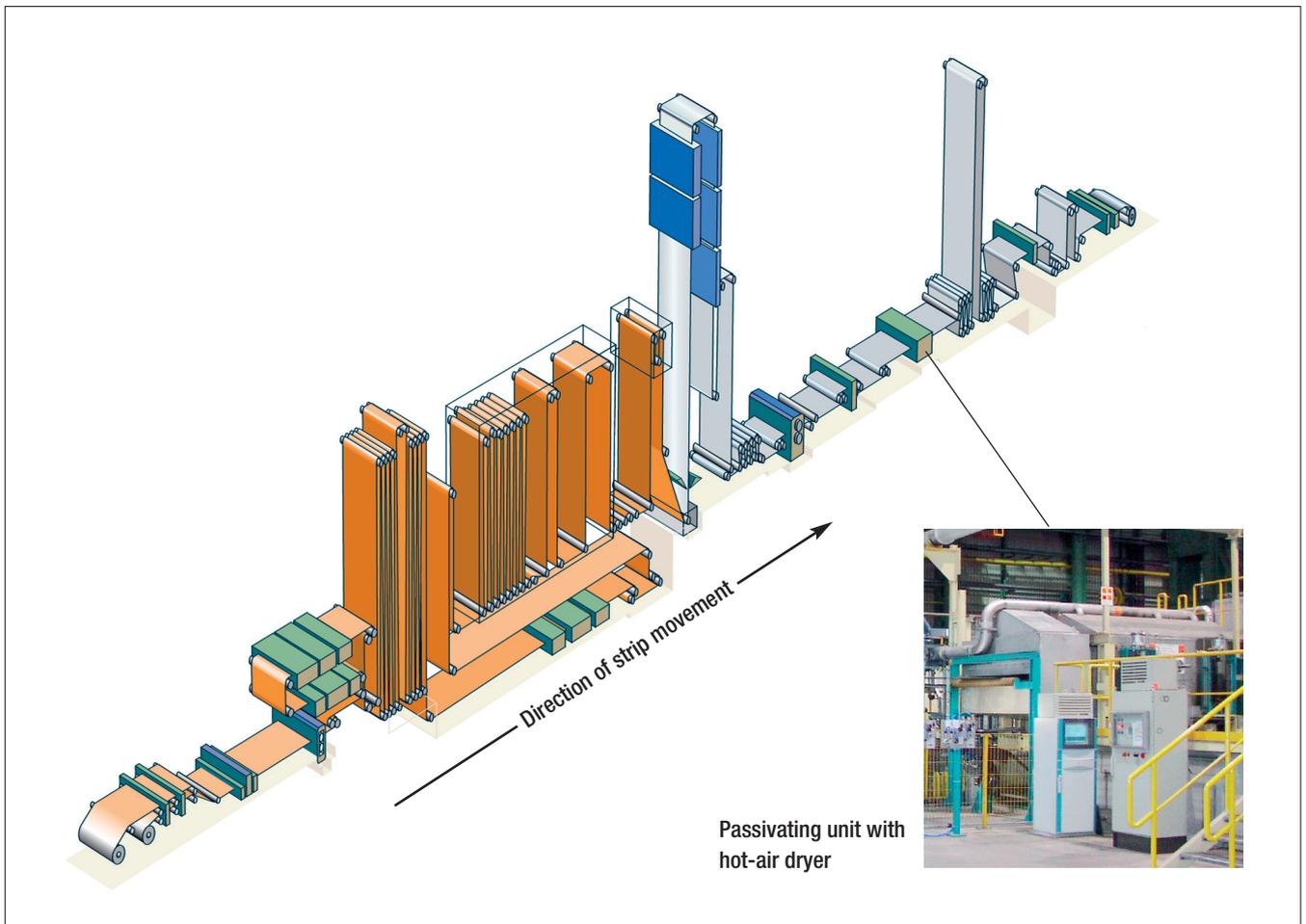


Fig. 5: Hot-dip metal coating line with passivating unit

To minimize or avoid this effect, care should be taken to ensure that the following conditions are met where aqueous auxiliary process fluids are used:

- a) The pH value of the solution or emulsion should be neutral or slightly alkaline; at pH levels > 8 the passivating film may be attacked.
- b) The medium should be prepared with deionized water to prevent precipitation of insoluble products of reaction with constituents of the passivating agent.

In general, the process capability of chemically passivated product with **surface-sensitive downstream operations** should be examined beforehand.

This is particularly true for phosphating, painting and adhesive bonding processes. For adhesive bonding, good adhesion is critical. The above-mentioned operations typically require a narrowly defined surface condition to produce the desired result. Restoring to a defined surface condition will usually be difficult after chemical passivation. As a rule, this can only be achieved by removal of the entire passivating layer and activation of the metallic surface.

The experience gained from tests with Cr(VI)-containing passivating treatments can typically not be applied to Cr(VI)-free substitutes since the latter may have an entirely different chemical composition.

Where chemical passivation is incompatible with a given downstream process, it is recommended to use oiled material instead.

6 Conclusions

For steelmakers and steel users, the transition from Cr(VI)-containing to Cr(VI)-free passivating methods constitutes a further step forward on the path towards sustainable and responsible use of surface-coated steel products. The questions arising in the context of this rapid changeover also provide an opportunity to review one's own processing routines. In the steelmaking companies, development and process departments are ready to assist customers in resolving these issues and in the subsequent optimizing.

7 Standards and regulatory instruments

EN 1623
Cold rolled strip and sheet –
Technical delivery conditions –
General structural steels

EN 10338
Hot rolled and cold rolled non-coated
flat products of multiphase steels for
cold forming – Technical delivery
conditions

EN 10152
Electrolytically zinc coated cold rolled
steel flat products for cold forming –
Technical delivery conditions

EN 10346
Continuously hot-dip coated steel flat
products – Technical delivery con-
ditions

RoHS Directive 2002/95 EC
Restriction of the use of Certain
Hazardous Substances in Electrical
and Electronic Equipment 2000/53/EC
“ELV”)

ELV Directive 2000/53/EC
end-of life vehicles

8 Further publications

For more information on this subject,
individual copies of the following
publications are available from Stahl-
Informations-Zentrum free of charge:

Charakteristische Merkmale 092
Elektrolytisch verzinktes Band und
Blech

Charakteristische Merkmale 095
Schmelztauchveredeltes Band und
Blech

Merkblatt 109
Stahlsorten für oberflächenveredeltes
Feinblech

Merkblatt 114
Verpackung, Lagerung und Transport
von unbeschichtetem und beschich-
tetem Band und Blech

Publication 122 – E
Weldable Corrosion-Protection Prim-
er – Thin Film-Coated Steel Sheets for
the Automotive Industry

Publication 127 – E
Lubrication of sheet strip and panels



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