

Surface modification by in-line thin film coating and organic/inorganic treatment of continuous galvanised steel sheet

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Protection and improvement of surface properties are the main drivers for the treatments of galvanised steel. The different galvanised steel grades require tailor made solutions to optimise the surface characteristic towards further handling and utilisation. Lubrication and corrosion protection are the major purpose for the thin inorganic and organic coatings, which are applied directly in-line as the last finishing step in galvanising lines. Each grade of galvanised surfaces chemically reacts differently due to the distinct compositions of elements and alloys and the process related texture. Each utilisation of the coated galvanised steel - for purposes in automotive manufacturing, for domestic appliance, for construction products - require special properties. Customised coating formulations, which are adjusted to the individual manufacturing process, are necessary to give specified properties to the galvanised steel surfaces. Different groups of thin film coatings are used. After-treatments have a final film thickness in the range from 50 nm up to 2 μm . For further mechanical operations like cutting and forming additional oiling is necessary. Temporary after-treatments help to conserve the surface and prepare it for the downstream processing. They are based on organic chemistry and can be removed before a final protection layer is applied. Permanent after-treatments are based on inorganic compositions which may be modified with organic components. These thin coatings support not only the subsequent manufacturing steps but will remain on the galvanised surface as part of the corrosion protection system for the final organic coating. Some organic sealing coatings are used as low cost and low performance coatings. Others represent sophisticated thin film corrosion protection systems. Their thickness counts 1 μm to 5 μm . These coatings provide good lubrication for cutting and forming and no or only little additional oiling is needed. In galvanising plus coil coating combination lines full organic coatings are applied in one or two layers with total film thicknesses of 15 μm to 40 μm . This integrated line concept is used as lean manufacturing process for mostly construction applications. The coatings raw materials must comply with existing and future legislative prerequisites. New directives like the European REACH legislation have substantial influence on the coating formulations.

Keywords:

in-line coating, passivation, thin film coating, painting, coil coating

INTRODUCTION

The market for galvanised flat steel strips is strongly growing around the globe. The additional requirements for the galvanised products are indicators for the economic strength of nations. In countries with a high GDP growth rates the demands for galvanised steel increases accordingly. In those countries with lower growth rates the request grows only moderately. Since four decades galvanised flat steel in its different varieties is increasingly integrated into fabrication and assembly of buildings and constructions, automobiles, trucks and busses, housings and domestic appliances. High quality standards from these industries on affordable cost levels would be unthinkable without the use of galvanised steel. About 640 galvanising lines are operated worldwide to serve the users. Their total nominal capacity is around 160 million tonnes. Hot

dipped galvanising lines represent 70% of the lines, which have 75% of the capacity. Electro galvanised steel strips are manufactured on the other 30% of the lines covering 25% of the capacity [1].

Without going into details, in each continuous galvanising line a number of consecutive operation steps are interlinked in the manufacturing process. The layout of the equipment and the various ways to operate the individual process steps lead potentially to a big number of varieties. Additionally, each company has its special know how about the formulation of the galvanising alloy. Despite the various possibilities to steer and control the manufacturing processes the different galvanising grades meet comparable quality ranges according to standards and norms, which define the property requirements for the different applications.

Table 1 gives an overview about the use of the different galvanised steel grades. For construction hot-dipped galvanised steel is requested. For the automotive industry hot-dipped galvanised and electro galvanised steel grades are in use. The domestic appliances industry and the manufacturer for machine and electrical equipment housings utilise hot-dipped and electro galvanised substrates.

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Type	Grade	Construction	Automotive	Appliances & Housings
Electro Galvanised	ZE Zinc		X	X
	ZN Zinc-Nickel		X	
Hot-dipped Galvanised	Z Zinc	X	X	X
	ZA Gallium	X		X
	AZ Galvalume	X		
	ZM Zinc-Magnesium	X		
	ZF Galvnealed		X	
AS Aluminium-Silicon		X		

TAB. 1
Industries using different galvanised steel grades.
Diversi gradi di acciaio galvanizzato utilizzati in alcuni settori industriali.

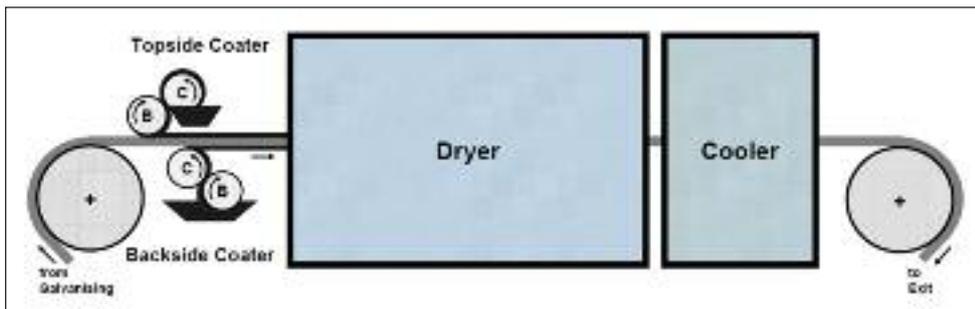


FIG. 1
Horizontal in-line coating configuration.
Configurazione orizzontale di ricoprimento in linea.

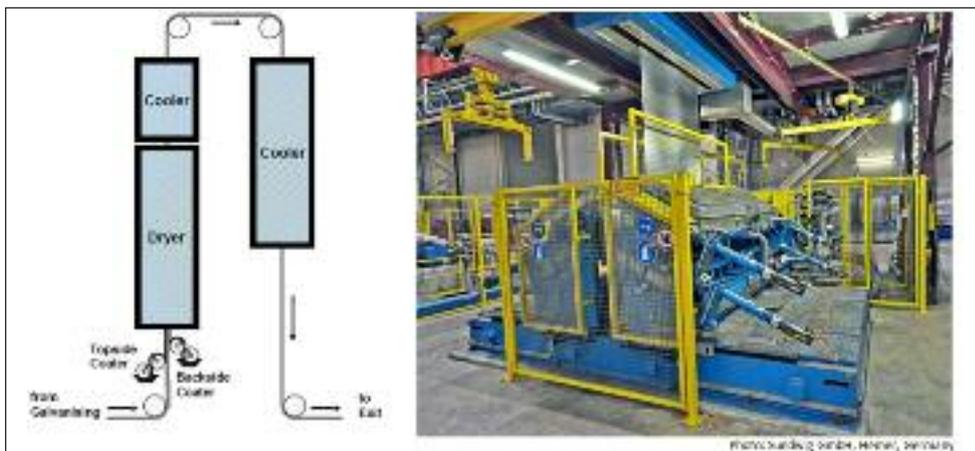


FIG. 2
Vertical in-line coating configuration.
Configurazione verticale di ricoprimento in linea.

PROTECTION AND SUPPORT FOR GALVANISED STEEL SURFACES

Due to the oxidation potential of zinc the freshly manufactured galvanised surfaces are highly reactive and will be covered with a thin oxide layer within a short time. But in many cases the oxidation would interfere with the further processing and handling. Corrosion protective layers help to suppress the oxidation and support further process steps of cutting, forming, joining, assembling and organic coating. The high variance of galvanised surfaces and the wide range of applications in the different market segments require selected layers to ensure the adequate treatment. The ideal place to treat the freshly galvanised steel strip is directly behind the skin pass step within the galvanising line. Here the surface is still not fully covered with oxides and can react with the applied treatment.

Depending on the required properties inorganic or organic treatments are applied. The simplest way is "splash and squeeze", where the liquid treatment is poured or sprayed on the horizontal strip and the excess material is squeezed off for re-use. The state of the art today is the use of chemcoaters for application. The coating of the strip is either done horizontally or vertically. In figure 1 and 2 both principals are shown in a sketch. The treatments are water based. After the coating the excess

water needs to be evaporated, what is been done through a dryer. If a higher heating temperature is required a cooling unit brings the strip temperature down prior to winding up the coil. Corrosion protection is one important motivation to treat the galvanised surface. The requirements reach from a temporary prevention of white rust to a full long term corrosion protection. Other reasons for an in-line coating include the support for forming, the prevention of staining or to prepare the surface for adhesive bonding or painting. In some galvanising lines even the final painting can be achieved. The selection of the treatment depends on the galvanising quality and the final use. Treatments to coat the galvanised steel are known since the start of the continuous strip coating with zinc and its alloys. Oil as temporary protection or for lubrication in the subsequent fabrication steps was already a well known material. But when galvanised sheets were used for more and more applications the needs for specialised surface modifications and treatments became important. Today a large variety of these chemicals are utilised. From experiences in the processing and growing knowledge about toxicological effects the treatments have been adjusted and modified over the years. In several cases materials have been phased out and substituted by new generations of sophisticated and better sustainable solutions.

TAB. 2
Overview of inorganic in-line treatments for galvanised steel.

Rassegna dei trattamenti inorganici in-linea per gli acciai galvanizzati.

Coating Type	Base Material	Thickness	Major Properties	Technical Characteristic
Passivation	Chromic Acid	50 to 100 nm	Prevent White Rust	Wide Process Window
	Chrome(III)	50 to 100 nm	Prevent White Rust	Process Window to be defined closely
	Chrome-free	50 to 100 nm	Prevent White Rust	Process Window to be defined closely
Phosphatation & Others	Phosphatation	1 to 2 µm	Support Forming	Fully compatible to Phosphatation as Pretreatment in Automotive Manufacturing
			Prepare for Painting	Not compatible to new Silanization as Pretreatment in Automotive Manufacturing
Inorganic Micro Coating	Inorganic Micro Coating	~100 nm	Support Forming (with Oil)	Compatible to new Silanization as Pretreatment in Automotive Manufacturing
			Prepare for Painting	
			Prepare adhesive Bonding	

The base for the surface coatings derives from both, inorganic and organic chemistry. It is always a mix of different ingredients which lead to the desired product quality. It may be difficult to describe exactly the substances which contribute most for the properties. But in general it can be distinguished between inorganic based treatments and those which are mainly based on organic chemicals.

INORGANIC IN-LINE TREATMENTS

Inorganic based treatments lead to permanent coatings on the galvanised surface. They react chemically with the alloys and are part of the corrosion protection system. Table 2 gives an overview on these materials and their major properties.

Passivations are the most frequently used inorganic coatings. They prevent the development of white rust on the galvanised surface. The traditional coating with chrome(VI) containing solutions is under pressure because of the strong toxic behaviour of all chrome(VI) containing materials. Only a temporary compromise is the substitution with chrome(III) based treatments. The most sustainable solution is the conversion to chrome-free formulations. For the application process of the treatment in the galvanising line chrome(VI) based materials provide a wide operational window. They are a kind of “fool-proved” systems. Both alternatives demand a much tighter controlled application process to get the optimum properties.

Passivations are being used for applications in all industries. At least in Europe the automotive industry follows the “end-of-life vehicles” directive and does not work with chrome(VI) based materials any more [2]. For the appliance and electric industry the RoHS (restriction of hazardous substances) is in force since app. 6 years for the European Union, which forbids the use of certain chemicals including chrome(VI) containing materials [3, 4].

By far the largest user for phosphated galvanised flat steel is the automotive industry. The fine crystal structure on the surface is an excellent substrate for the oil, which is been used for the forming operations in the body shops. On the other hand the phosphate layer works as pre-fabricated pretreatment and serves as adhesion promoter for adhesives and paints. Since more than 2 decades these types of pre-phosphated galvanised steel sheets are widely used for automotive applications. The zinc phosphate layer is modified with manganese and nickel to get the required fine crystallisation and with it the excellent adhesion and barrier properties [5]. But the toxic data of nickel require to rethink this technology.

During the last years very thin inorganic “micro coatings” have been developed, which are applied in-line with app. 100 nm. During the forming process in the body shop the inorganic micro

coating works as synergist with the lubricating oil. Additionally it is fully compatible with new silane based pre-treatments, which are substituting the conventional tri-cation phosphating process in the automotive painting process. This innovative technology started to substitute the conventional pre-phosphating treatment.

ORGANIC IN-LINE TREATMENTS

There are many organic treatments for galvanised steel on the market. They all have different properties and purposes. An overview is given in table 3.

Passivations based on organic chemistry have been developed as more sustainable countertype to chrome(VI) based ones [6]. They are used as temporary protection to prevent white rust. Additionally for many applications they are a reliable base for over-painting in the post-coating process.

Lubrication of the galvanised surfaces is necessary to prepare for all mechanical forming operations. Traditionally special oils are being applied. For stamping and drawing of galvanised steel a defined amount of oil is required per surface area. The accurate thickness of oil is applied in-line in the galvanising line by electrostatic devices. In many cases the oil application follows the passivation, phosphatation or inorganic coating as described above. With this two-step application the requirements from the fabricating industry can be fulfilled just in-line the galvanising manufacturing process.

Other lubricants are drylubs and hot melts. They have a more resinous, higher viscous character which brings advantages for some forming operations in the automotive body shop. Especially the 2nd generation of drylubs and hot melts are designed to support the surfaces of high strength steels at the stamping process.

Sealings are permanent thin film coatings (TFC) for galvanised steel surfaces. Anti-fingerprint coatings (AFP) are widely used to protect hot-dipped galvanised surfaces like Galvalume for building uses, if they will not be further painted. They are mostly low cost low performance organic coatings. Many of these AFPs contain chrome(VI) dispersed in a water based resin combination. This 2 to 3 µm thin coating lubricates the surface for the forming processes. Additionally it protects against corrosion to a certain degree and prevents the staining of the surface e.g. through fingerprints. In some cases AFP provides the preparation for the final painting of formed parts without an extra pre-treatment.

In the domestic appliance industry AFP coated galvanised steel is in use as well. Here chromate-free materials are mandatory for Europe, because of the RoHS legislation.

Coating Type	Base Material	Thickness	Major Properties	Technical Characteristic
Temporary Protection	Organic Resination	0.5 to 1 µm	Prevent White Rust	Base for 4th Overpainting
Lubrication	Oil	- 1 µm	Prevent White Rust	Electrostatic Application
			Support Forming	
	Powder	- 1 µm	Prevent White Rust	Oil-free Forming
			Support Forming	
Powder 2nd Generation	- 1 µm	Prevent White Rust	High Viscosity for High Strength Steel Forming	
			Support Forming	Forming Temperature > 500°C
Sealing	Anti-fingerprint	2 to 3 µm	Corrosion Protection	Mostly Chromate containing
			Support Forming	Chromate-free for Domestic Appliances (RoHS compliant in the European Union)
			Stain Resistance	
				Pretreatment for Post-Painting
Conductive Coating	1 to 2 µm	Support Forming	For Consumer Electronics	
Weldable Corrosion Protection Primer for Automotive		2 to 4 µm	Corrosion Protection	Surface conductive and weldable
			Support Forming	Future Problem Solver for Automotive instead of Corrosion Protection Concept

TAB. 3
Overview of organic in-line treatments for galvanised steel.

Rassegna dei trattamenti organici in-linea per gli acciai galvanizzati.

Coating Type	Base Material	Thickness	Major Properties	Technical Characteristic
Painting	Primer	3 to 10 µm	Full Corrosion Protection	Require Pretreatment
			Prepare for final Finish Coating	Solvents to be treated
	Singlecoats	3 to 20 µm	Limited Corrosion Protection	Require Pretreatment
			Medium Grade final Finish	Solvents to be treated
	Primer + Topcoat	20 to 35 µm	Full Corrosion Protection	2 Coater + 2 Dryer required
High Grade final Finish			Require Pretreatment	
			Solvents to be treated	
Backcoat		7 to 15 µm	Protection for the inner Side	Require Pretreatment
			Decorative for the inner Side	Solvents to be treated

TAB. 4
Overview of in-line painting in galvanizing lines.

Rassegna dei trattamenti di verniciatura "in line" nelle linee di galvanizzazione.

More high-tech materials are thin conductive coatings developed for housings and boards of consumer electronics. The galvanised steel is protected against white rust corrosion but the manufactured housing is still conductive to shield the electronic equipment and the grounding can be provided easily.

For the automotive industry special weldable corrosion protective primers have been developed in the 1990ies. These primers provide a very good corrosion protection for parts with flanges and hollow spaces. The surface is conductive enough that parts can be welded in the body shop [7, 8]. This type of primer can be applied on coil coating lines but as well in-line in galvanizing lines [9]. The outlook shows a changed rating for this technology in the future. For app 15 years it has been used as corrosion protection concept. In future it will become more a problem solver for difficult construction requirements in the automotive manufacturing.

IN-LINE PAINTING

Several steel companies operate combination lines. In the first part the steel gets its galvanised surface and in the second part the paint is applied [10]. The benefit of the combined line operation compared of manufacturing on two lines is the fast production of pre-painted galvanised steel in one run without interruptions in the process. But on the other hand the flexibility for the painting process is limited. The efficiency of the com-

bined process is dependent on the slowest operational step, which is often the painting. In table 4 the different options for in-line painting are shown.

All coating systems based on conventional coil coating paints require a pretreatment prior to the coating. This pretreatment is similar to passivations as mentioned above. They will be applied with a chemcoater. If a primer or a single coat material should be applied only one additional coater station and dryer is required. For the full two-coat system two coater stations and dryers have to be installed. Simultaneously a backcoat is applied at the backside. The sketch of figure 3 explains the different paint layers.

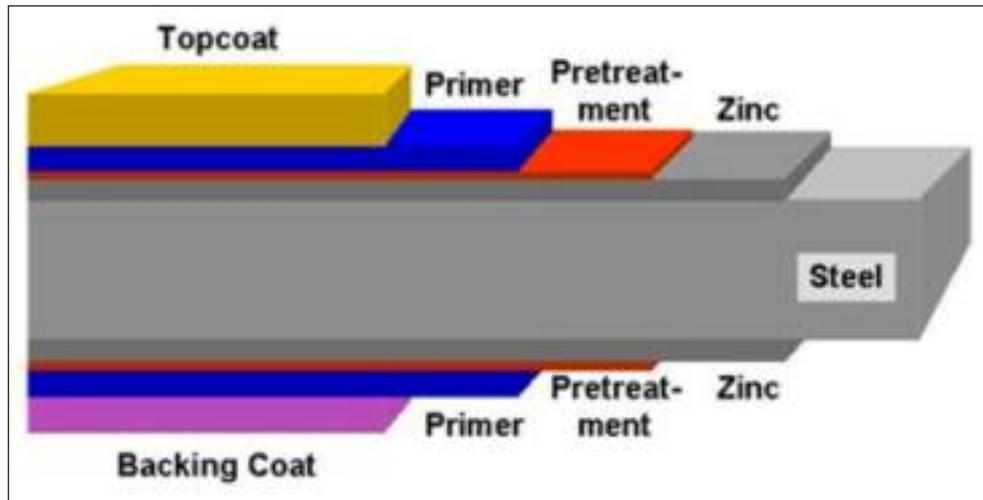
The conventional coil coating paints are solvent based. In the dryers the solvents are evaporated and the extracted exhaust requires an oxidiser for cleaning the air flow. For the dryers in a combination line one special requirement has to be obtained. Because of the coupled processes they need to be very fast responding. Therefore electrical powered induction or IR ovens are mostly utilised. They can provide start / stop operations, what cannot be done with convection ovens.

The functions of the different paint layers can be characterised in short [11]. The primer has to ensure the adhesion on the substrate and acts as adhesion promoter for the topcoats as well. The topcoats add the colour and design to the surface and act as barrier against environmental influences. On most combination

FIG. 3

Fully painted galvanised steel from in-line painting on a galvanising line.

Acciaio galvanizzato completamente ricoperto con verniciatura "in line" nell'impianto di galvanizzazione.



lines two-layer full performance coatings are applied. The target market is the building industry.

Single coats are a compromise of both layers and they are developed for the mid-quality market.

A single primer is been applied, when the galvanised steel should provide the corrosion protection already but the final finish will be coated at a later stage after fabrication.

Today on several combination lines chromate-free primers are coated. With this sustainable material most specifications for the building industry and domestic appliance manufacturers are fulfilled.

OUTLOOK AND FUTURE OPPORTUNITIES

More and more changes for the in-line treatment and painting on galvanising lines are influenced by legislations. For the member states of the European Union REACH (Registration, Evaluation and Authorisation of Chemicals) will drive the process in the next years. Some substances, which are part of the treatments or paints, are identified as CMR material (carcinogenic, mutagenic, repro-toxic). Several chrome(VI) containing substances are currently on a list of "substances of very high concern" at the European Chemicals Agency ECHA. In the evaluation process the toxicity and each single use will be investigated in the upcoming years. If an authorisation will be given it will be only for a limited time of a few years. When better sustainable alternatives are available their use will be enforced.

It will be necessary to formulate the treatments and paints with sustainable chemicals. Today some products mentioned in this paper help to convert towards better sustainability. Chromate-free passivations, AFPs, primer or inorganic micro coatings are already products for the future.

More combined hot-dipped galvanising and painting lines will get started in future. Especially for building products the benefits overweigh some disadvantages. In newer lines the two processes, galvanising and painting, will be synchronised better that no step will be a general bottleneck. By running combined lines those manufacturers who are already operating coil coating lines have a good chance to generate cost advantages for their biggest market segment, the building industry, without compromising their full portfolio offer of pre-painted galvanised steel.

Another opportunity for the future derives from the development of new primer systems, which contain an inherent pretreatment function. These primers are water based and can be dried with lower temperatures [12]. As consequence the in-line coating

equipment can be installed with a simplified layout. No pretreatment section has to be installed. The dryer for the primer needs less heat capacity and due to the low volatile organic compounds (VOC) the air exchange can be reduced drastically. The utilisation of this new technology will require a reduced investment for the painting process in the galvanising line.

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Abstract

Modifica della superficie di acciaio laminato e galvanizzato in continuo mediante rivestimento in-linea con film sottile e trattamento organico/inorganico

Parole chiave: rivestimenti, acciaio

La protezione e il miglioramento delle proprietà superficiali sono i principali scopi per il trattamento degli acciai galvanizzati. I diversi gradi di acciaio galvanizzato richiedono soluzioni su misura al fine di ottimizzare le caratteristiche superficiali in vista di ulteriori lavorazioni e dei diversi impieghi.

La lubrificazione e la protezione contro la corrosione sono l'obiettivo principale dei rivestimenti sottili inorganici ed organici, che vengono applicati direttamente in linea, come ultimo passaggio di finitura nella linea di galvanizzazione. Ogni grado di trattamento superficiale ha una reazione chimica diversa a causa della differente composizione di elementi e di leghe e della struttura ottenuta mediante i relativi processi. Ogni applicazione dell'acciaio galvanizzato rivestito - per produzione automobilistica, per elettrodomestici, per prodotti da costruzione - richiede particolari caratteristiche. Sono quindi necessarie formulazioni di rivestimenti personalizzate, che siano adeguate per ogni singolo processo di produzione, affinché le superfici di acciaio galvanizzato abbiano proprietà specifiche.

Generalmente si utilizzano diversi gruppi di rivestimenti a film sottile. I post-trattamenti permettono di ottenere rivestimenti con spessore finale che va dai 50 nm fino a 2 μm . Per eventuali successivi processi meccanici, come taglio e formatura, è necessaria un'ulteriore lubrificazione. I post-trattamenti temporanei aiutano a preservare la superficie e a prepararla per il trattamento a valle. Essi si basano su prodotti della chimica organica e possono essere eliminati prima dell'applicazione dello strato protettivo finale. I post-trattamenti permanenti sono a base di prodotti inorganici che possono essere modificati con componenti organici. Questi rivestimenti sottili non solo supportano le fasi di produzione successive ma rimangono anche sulla superficie galvanizzata come parte del sistema di protezione contro la corrosione del rivestimento finale organico.

Alcuni rivestimenti organici vengono impiegati in quanto rivestimenti a basso costo e basse prestazioni. Altri sono invece sofisticati sistemi a film sottile di protezione dalla corrosione. Il loro spessore va da 1 μm a 5 μm . Questi rivestimenti hanno una buona azione lubrificante per il taglio e la formatura e necessitano di una minima o addirittura di nessuna ulteriore lubrificazione. Nelle linee di galvanizzazione abbinate al "coil coating" i rivestimenti organici vengono applicati in uno o due strati di pellicola, con spessore totale da 15 μm a 40 μm . Questo concetto di linea integrata viene utilizzato prevalentemente per le applicazioni nel campo delle costruzioni.

Le materie prime utilizzate nei rivestimenti devono rispettare requisiti legislativi in vigore e futuri. Nuove direttive, come la legislazione europea REACH hanno una sostanziale influenza sulle formulazioni dei rivestimenti.