

1. Objectives of metal pre-treatment

Among the key objectives of every organic coating with regard to the underlying workpiece are:

- Evenly applied powder coating film
- Good adhesion to metal base materials
- High resistance to corrosive infiltration

To improve corrosion resistance and adhesion as well as to ensure an even coating, the surfaces to be coated must be pre-treated.

The treatment is usually either chemical (chapter 3) or mechanical (chapter 4), to meet the necessary substrate cleaning and adhesion requirements.

2. Test methods

The success of a chemical pre-treatment becomes evident in the long-term performance of the coated workpiece in practical applications. There are numerous test methods for the purpose of monitoring, selecting and developing pre-treatment procedures, which provide quick information. As short-term corrosion tests, the salt spray test (DIN EN ISO 9227) and testing in condensate water atmospheres (DIN EN ISO 6270-2) are considered most significant. An inadequate pre-treatment is revealed in the salt spray test by an exaggerated corrosive product infiltration of the coating starting at a scratch point. The combination of both types of stress in alternating testing create signs of corrosion that are very similar to open air weather exposure.

The corrosion assessment is standardised into DIN EN ISO 4628-8 (infiltration), DIN EN ISO 4628-3 (rust) and DIN EN ISO 4628-2 (blisters).

Powder adhesion is tested without corrosive loading using

- Mandrel bending test, cylindrical mandrel (DIN EN ISO 1519)
- Impact penetration (ISO 6272 / ASTM D 2794)
- Cupping test (EN 5020) or
- Cross-cut test (DIN EN ISO 2409)

3. Procedure for chemical pre-treatment

The chemical pre-treatment procedure is divided into the following tasks:

- Removal of harmful substances such as scale, rust, dust caused by abrasion, greases, oils, dust from the surface.
- Creation of a coat that promotes powder adhesion, for example, through phosphating, chromating or chromium-free methods, etc.
- Removal of damaging treatment substances from previous process steps by rinsing thoroughly.

3.1. Cleaning the surface

Contaminants on the metal surface prior to coating impede the adhesion between the powder coat and the metal. Therefore, contaminants such as oil and grease, as well as inorganic particles such as swarf, rust and mill scale must be removed.

Oil, grease and mechanically adhered dirt can be removed with alkaline or acid detergents.

The cleaning performance can be enhanced through higher temperatures of the active baths and through mechanical energy (particularly by spray treatment or ultrasound).

Steel can generally be cleaned using a highly alkaline cleaner, whereas mildly alkaline cleaners or mildly acidic mediums are used on galvanised steels and aluminium.

It is possible that pickling the metal surface, which actually enhances the cleaning effect, may give undesirable results when cleaning zinc or aluminium diecasts. The pickling effect can be reduced by adding special additives to the cleaner. Rust and scale can be removed by acidic pickling. The acids often contain inhibitors that prevent the bare metal from dissolving. Pickling with sulphur or hydrochloric acid are commonly used methods for descaling unalloyed steel. Rust is removed with beneficially inhibited phosphoric acid. Iron and steel materials are frequently cleaned electrolytically, supported by highly alkaline cleaner. Stainless and alloyed steels are usually pickled in a pickling solution of e.g. nitric acid and hydrofluoric acid.

Pickling with surfactants can be used for components with minimal, easily removable oil contamination, which removes rust and grease in one step. If there are no special requirements for the corrosion protection of a workpiece, subsequent phosphating can be omitted when pickling with phosphoric acid. This leaves a thin, blue shimmering phosphate film on the surface, which has good adhesion properties for subsequent coating and is suitable as temporary corrosion protection.

After pickling and/or the alkaline cleaning process, it is imperative that the components are rinsed with water.

3.2. Creating conversion coatings through phosphating

Conversion coatings are created by a chemical reaction with the treatment solution on the metal surface which forms a firmly embedded, usually inorganic coating.

3.2.1. Alkaline phosphating

When alkaline or iron (Fe) phosphating with an acidic solution of alkaline phosphates is used, a reaction takes place on the metal surface.

The aqueous solution, made up of phosphate anions, contains none of its own metal cations that play a role in the coating formation. The cations for coating formation are in the base material, which is why alkaline phosphating is often referred to as non-coating phosphating (cf. 3.2.2. Zinc phosphating). The coating created by alkaline phosphating on iron is an amorphous agglomerate made up of phosphates, oxides and hydroxides of bivalent and trivalent iron with a coating weight of 0.2 - 1.0 g/m², which corresponds to a coating thickness of approx. 0.15 - 0.8 µm.

Depending on sheet metal quality, coating thickness and the selected accelerator, the phosphatised surfaces are given a broad range of colouring, from yellow to blue shimmer, golden, or grey. However, it is also possible to beneficially treat other metals such as zinc or aluminium alloys with alkaline phosphating.

Alkaline phosphating is generally insufficient for lacquered surfaces that are permanently exposed to weathering and moisture, but is adequate as corrosion protection for powder-coated components in unexposed spaces.

3.2.2. Zinc phosphating

In contrast to alkaline phosphating as described above, phosphating with an acidic solution primarily forms zinc phosphate coatings because it creates coating thicknesses between approximately 8 and 20 µm. Zinc and/or metal ions from the phosphate solution create the coat-forming cations, while the phosphate from the phosphor solution serves as an anion. The formation of tertiary zinc and zinc-iron phosphate coatings (phosphophyllite, Zn₂Fe(PO₄)₂) on steel surfaces is accelerated by an oxidant.

The iron dissolved during coating formation is eliminated as an iron phosphate after further oxidizing. The phosphate solution is depleted of active components by the chemical reactions to the coating formation and the drag-out with workpieces. They are added continuously by adding a so-called supplement solution to the bath. To create fine crystalline coatings that have optimal characteristics, the activating agent – usually based on titanium bonds – is used as a pre-rinse prior to phosphating. These activating agents are often integrated into the alkaline cleaner, so that no additional treatment step is necessary. Phosphating based on zinc phosphate is widely used as a pre-treatment prior to a large variety of organic coating systems.

The best corrosion resistance properties for lacquer coatings on steel, cadmium-plated or galvanised steels are achieved with a zinc phosphating pre-treatment. The adhesion of the organic coating when subjected to bending or impact stress stands up to high demands. Special solutions for aluminium and other alloys are possible, but require individual baths.

3.2.3. Zinc phosphating of galvanised steel

Phosphating solutions also contain other substances, such as nickel or manganese for specific purposes – i.e. for the treatment of zinc surfaces – or fluoride for aluminium.

When phosphating galvanised surfaces, small iron ions are available for targeted integration into the phosphate coating. By adding suitable cations such as nickel, manganese or calcium, phosphating solutions that correspond to the corrosion protection effect of phosphor phyllite coatings are created. This process is sometimes referred to as the “trication” process because these phosphating solutions generally contain zinc, manganese and nickel as coat-forming cations. Nickel-free methods are therefore sometimes referred to as the “dication” process.

The addition of complex fluorides is often used to achieve even coat formation on dip-galvanised surfaces or with steel surfaces that are difficult to phosphatise. By the addition of fluorides, the aluminium ions, which are usually a component of galvanising in acidic phosphating bath solutions, are chelated.

3.2.4. Post-treatment of zinc phosphating surfaces

Post-treatment is sometimes used to increase the corrosion protection of phosphate coatings. Today, chromium-free post-passivation agents are most commonly used, which “seal” the coating by closing the open pores in the phosphate coating. When doing so, there must be discernment between organic and inorganic products:

The organic passivation agent contains polymers with chelate-forming properties; inorganic products contain complex zirconium or titanium fluorides that form insoluble phosphates on the surfaces.

3.2.5. Post-treatment of galvanised surfaces before dephosphating

Prior to the coating process, the quality of the galvanisation should be discussed with the galvanising plant. Many galvanising plants recommend post-treatment in accordance with DIN EN ISO 1461-2009 (Zinc coatings on steel applied by means of hot galvanising (piece by piece galvanising); requirements and testing), which delay and homogenise white rust formation and extend the gloss of the zinc surfaces.

Based on the experience of IGP powder technology AG, most often, these post-treatments are detrimental to good intercoat adhesion of powder coatings. Prior to coating, preliminary tests should be performed on the material to be coated.

3.2.6. Zinc phosphating prior to cathodic electrophoretic coating

The introduction of cathodic electrophoretic coating has led to an impressive increase in corrosion protection for subsequent lacquering. However, to take full advantage of the possibilities of the cathodic electrophoretic lacquer, newer zinc phosphating methods can be used. These are characterised by low zinc and high phosphate content. They create coatings of hopeite (zinc phosphate, $Zn_3(PO_4)_2$) and phosphophyllite (zinc-iron phosphate, $(Zn_2FePO_4)_2$) when sprayed on steel. For the dip method, those containing mostly phosphophyllite are used. The process time is usually somewhat longer than with conventional methods, due to the low zinc content.

3.3. Creating conversion coatings through pre-treatments with chromium content

3.3.1. Situation of pre-treatments containing chromium

At the end of 2010, chromium(VI) oxide and other chromium(VI) compounds were added to the list of candidates for the list of Substances of Very High Concern (SVHC). There are currently approval procedures pending for the further use of these substances, which will be decided by the European Commission sometime near the end of 2015.

The disadvantages of the yellow and green chromatising methods listed below are due to the diverse hazard potential of chromium(VI) oxide CrO_3 , which is a very effective oxidant and not only has oxidising characteristics, but is also highly toxic and has carcinogenic and mutagenic effects. Chromate conversion coatings are created in aqueous treatment baths containing chromic acid (dissolved CrO_3), among other substances, that are severely hazardous to water for the aforementioned reasons. This also applies to transparent chromatising as well as to both yellow and green chromatising, and chromate conversion coatings with high layer weights.

Although only chromium(VI) compounds are of toxicological and mutagenic significance, there is an increasingly scrutinising focus on green chromatising, even though the coatings created after the reaction are theoretically made up of non-toxic chromium ($CrPO_4$) and aluminium phosphates ($AlPO_4$). This is due to the facts that a) the manufacture of the treatment chemicals for yellow and green chromate coatings is always based on chromium(VI) compounds, and b) the possible remaining level of hexavalent chromium, which is approximately $0.01 \mu\text{g}/\text{cm}^2$ below the standard detection limit in a green chromatising coat.

Even if the use of chromium-based pre-treatments has not yet been excluded by national regulations, it is wise to examine the local regulations as well as the prescribed implementation provisions in the tenders prior to selecting a chromium-based pre-treatment for façade construction, particularly for public-funded construction projects.

3.3.2. Yellow and green chromatising

Yellow and green chromatising can be differentiated by the colour of the conversion coatings created with higher layer thicknesses. Both treatment solutions can be used for spray and dipping applications.

Treatment solutions for yellow chromatising have hydrofluoric acid, chromic acid, and, in addition to other substances if needed, so-called accelerators.

As a result of the primary aluminium dissolution caused by the acids, coatings are formed on the surface of the aluminium, made up of the aluminium's mixed oxides and trivalent and hexavalent chromium. The coating thicknesses of a yellow chromate coating are generally $400\text{--}1000 \text{ mg}/\text{sqm}$.

Treatment solutions for green chromatising largely contain hydrofluoric acid, chromium and phosphoric acid.

The coating reaction is also based on chromium trioxide (CrO_3) or chromium(VI) oxide, as is the case for yellow chromatising.

The fluoride concentration determines the weight of the coating. If the coating weight is not particularly high, the coating is free of hexavalent chromium. However, it is possible that high coating thicknesses will occur, especially in workpieces with indentations that divert chromate from the bath solutions, which harden after rinsing, are potentially hazardous, and which also lead to a deterioration of the adhesion.

The deposited chromate coating is made up of aluminium phosphates and trivalent chromium phosphates and does not have a crystalline structure. When being used as a pre-treatment to coating, surface weights between 400 and $1200 \text{ mg}/\text{m}^2$ are used. Both yellow and green chromatising significantly improve the adhesion and the corrosion inhibition of the subsequent applied coating.

Yellow or green chromatising are also often used to create conversion coatings on galvanised steels for a subsequent organic colour coating.

Chromatising is also used as corrosion protection without additional organic coating. In some cases, yellow and green chromate coatings can be used for decorative purposes. However, the coating weight is then higher, with 1 to $3 \text{ g}/\text{m}$.

3.3. Passivation processes with chromium (III) content

In spite of its chromium basis, chromium(III) passivation can be classified as an environmentally-friendly process as compared to yellow and green chromatising (chromium(VI) compounds). Trivalent chromium forms a reaction product on the aluminium surface that is nearly insoluble (chromium(III) oxide), which is a good corrosion inhibitor and facilitates excellent lacquer adhesion. For quite some time, trivalent chromium has been used for the passivation of zinc and zinc alloys, and is known as blue passivation. For chromium(III) process applications, a few manufacturers have recently introduced pre-treatment chemicals and/or methods that have already been certified by Qualicoat and GSB. This creates a lightly shimmering coating on aluminium, the colour of which depends on the alloy.

Prior to forming the conversion coating, the surface must be free of grease and oxides, which can be accomplished with

- cleaning by pickling or
- alkaline (pickling) degreasing and acidic etching.

Thorough rinsing must take place in between the individual pre-treatment steps, and the softest possible water should be used prior to the passivation bath. For optimal corrosion protection, the final rinse of the components after passivation should be done with purified water.

3.4. Creating conversion coatings through pre-treatments without chromium content

3.4.1. Coating components not contained in the alloy

Pre-treatments with chromium content are being replaced by chromium-free pre-treatments primarily due to the significantly reduced strain on the environment as well as to lower costs for work safety and environmental protection.

Generally, the bath monitoring and analysis is somewhat more extensive, and the rinsing processes are somewhat more laborious. The corrosion protection for possible interim storage is also usually less effective.

There are a variety of providers of chromium-free pre-treatment chemicals that can be divided based on the base chemicals as follows:

- Titanium and/or zirconium compounds
- Titanium/(fluorine) polymer compounds
- Zircon/fluorine compounds
- Organosilanes.

Most of the chromium-free pre-treatments can be applied both by means of spraying and dipping. Some are also compatible with multiple metals.

Differentiation can be made between rinse and no-rinse methods, depending on the requirement for rinsing processes after the conversion coating, or the lack thereof.

It is recommended that a pre-treatment process be selected that has been certified by GSB and/or Qualicoat and thus meets the diverse requirements in terms of process stability and applicability, in addition to many years of experience with outsourcing (example: Hoek van Holland). As with pre-treatments containing chromium, the substrates must be cleaned and rinsed in advance. Whereas acidic cleaning is sufficient for some chromium-free pre-treatments for steels and galvanised steels, aluminium substrates are subjected to an acidic degreasing pickling process. After degreasing with pickling, usually several rinse processes are required using purified water. For a no-rinse treatment, the rinse after the conversion treatment is omitted. Chromium-free methods need higher drying temperatures, both for rinse and no-rinse operation. With porous substrates, the higher temperatures have the benefit of promoting outgassing prior to coating.

3.4.2. Alloy-specific coating components - anodised oxidation

The creation of thin aluminium oxide coatings, or pre-anodisation, is an environmentally-friendly alternative to the passivation of the aluminium surface. It should be used when the coated final product is to be placed at locations with natural or artificially high corrosion potential. Examples: in an aggressive industrial atmosphere, building locations in coastal regions or atmospheres with particularly high chloride levels, such as swimming pools. The amount of chlorides plays a key role, which when combined with moisture and advantageous (reaction) temperatures, can cause the formation of electrolytes, which can create filiform corrosion as a thread-like corrosion trail under the lacquer coating. Anodic oxide coatings can be created using the dipping method on the metal serving as an anode which is dipped in an electrolyte.

Due to the effect of the electric current, atomic oxygen is created at the anode during electrolysis, with which the aluminium reacts, which causes the formation of aluminium oxide. This is firmly attached to the metal surface. The coatings consist of an impermeable protection coating and a porous top coat, the thickness and pore diameter of which depends on the current density, duration, temperature and acid concentration. Coating thicknesses between 5 to 8µm are considered suitable.

Source: GSB International <Chromium-free surface treatment for aluminium>, 2011; et al.

Pre-anodisation coating, which is produced under de-fined conditions, is internationally approved as a pre-treatment method by the two approval agencies GSB International and Qualicoat.

The following information applies to the quality of the pre-anodisation and its characteristics in terms of protective effect and intermediate adhesion to organic coatings:

- The contact points for the electrodes must be stipulated prior to the electro-chemical treatment, as they remain free.
- For profile rods, please specify which side is to be coated.
- Hydration treatment for the compression and impregnation of the surfaces after anodising must be avoided at all costs.

4. Mechanical pre-treatment

In addition to the aforementioned wet-chemical processes, mechanical cleaning and/or pre-treatments can also be used, primarily in unalloyed, low-alloy and galvanised steel. In this regard, mechanical treatment can fulfil different tasks:

- Removal of grease, dirt or corrosion products such as rust and scale
- Removal of welding residues
- Breaking of sharp (laser-)cut edges
- Enlarging the surface, particularly on ridges, edges and cut surfaces, for good paint adhesion.

Further information is also provided in DIN 55633: <Paints and varnishes - corrosion protection of steel structures by powder coating systems - assessment of powder coating systems and execution of coating>, section 6, Surface preparation and pre-treatment.

4.1. Steel blasting

In the processing of steel, the complete removal of rust down to the bare metal by mechanical brushing, grinding or blasting is one of the prerequisites for achieving a corrosion-resistant coating. Crude steel surfaces absolutely must have a surface preparation grade of Sa 2½ according to DIN 55928, section 4.

Using mechanical roughening, the adhesion of the coating to the substrate is greatly improved. Suitable abrasives include mineral and silicate abrasives such as aluminium oxide or glass. As a rule of thumb, the more edged and larger the abrasive, the rougher the surface. This is associated with better adhesion of the primer coat on the substrate, which in turn leads to better corrosion protection. Round grains are less abrasive and undergo compression, which is detrimental. To ensure good paint adhesion, the average surface roughness Rz attained should be 40µm.

4.2. Sweep of galvanised steel

Due to the surface preparation, the existing corrosion protection layer (e.g. zinc-plated strip galvanising) must not be damaged.

The process known as 'sweeping' (according to DIN EN ISO 12944-4) is very similar to compressed-air blasting. The main differences to the latter are the much lower pressure used (2.5-3 bar) and the type of blasting abrasive. This is finer (grain size = 0.25 mm - 0.5 mm) and must not contain any metallic components that can rust.

Non-metallic blasting abrasives according to DIN EN ISO 11126-3 to DIN EN ISO 11126-7 and metallic abrasives such as chromium cast granules (grit) or broken glass (grit) have proven themselves in this regard. Weld spatter and scale are to be removed with the grinder if this is permitted by the profile geometry; if necessary, they are to be reworked with a blasting pistol and a mineral abrasive (e.g. corundum).

It should be pointed out that section 6.2.3 of DIN 55633 permits not only the pre-treatment of galvanised steel using sweep blasting, but also wet-chemical pretreatment in the form of a yellow chromate coating with a layer weight of 0.5g/m² to 1.0g/m². In case of deviations and when using other pre-treatment methods with equal qualifications, this must be agreed upon separately.

4.3. After blasting / sweeping

The mechanically treated surfaces are highly oxidative due to the enlargement of the surfaces and must be processed without delay.

First, the abrasive and the contamination due to compressed air and/or chemical cleaning or chemical pretreatment are to be removed.

Compressed air usually removes only coarse dusts while – for example – a ring of galvanised steel. Due to the surface preparation, the existing corrosion protection layer (e.g. zinc-plated strip galvanising) must not be damaged.

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4.4. Corrosion protection structures

The resistance of corrosion protection systems using organic coatings as well as powder coatings is to be determined depending on the desired duration of protection and the environmental conditions defined in DIN EN ISO 12944-2. The duration of protection and the periods for the duration of protection are defined in DIN EN ISO 12944-5. The duration of protection of powder coating systems depends on several parameters:

- The design of the component and of the object
- Loading after coating (location, use)
- Condition of the steel surface or the zinc coating before preparation or pre-treatment
- Thoroughness of cleaning and effectiveness of pretreatment
- Type of coating system. A sufficient:
 - a) Number of layers (one- or two-layer structure)
 - b) Thickness of the corresponding layers
 - c) Penetration resistance of the coating system by corrosive atmospheric gases must be provided

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DIN 55633 <Paints and varnishes - corrosion protection of steel structures by powder coating systems - assessment of powder coating systems and execution of coating> defines recognised durations of protection according to the classification by DIN EN ISO 12944-5 for the two basic substrate categories – unalloyed steel and low-alloy steel – and for galvanised steel .

Tables A.1 and A.2 in Annex A list the five relevant corrosivity categories (C2, C3, C4, C5-I and C5-M) necessary to achieve the protection durations of layered structures (e.g. the number of layers and the layer thicknesses).

IGP Pulvertechnik AG fulfils these requirements with a range of various anti-corrosion primers coordinated with the substrates and topcoats. For this purpose, in the following are further IGP documents and brochures: <Safer and longer-lasting corrosion protection with IGP powder base coats> as well as IGP corrosion protection tables for coating steel and aluminium substrates.

For detailed information on corrosion protection measures and systems, please contact our trained corrosion protection inspectors and consultants.