TI100 – Pretreatment of metals

1. aims of metal pretreatment

The important objectives of any organic coating in relation to the workpiece on which the coating is based include

- Uniform powder coating film
- Good adhesion to the metallic substrate
- High resistance to corrosive infiltration

To improve corrosion resistance and adhesion, but also to ensure a uniform coating, the surfaces to be coated must be pretreated.

This is usually done chemically (chapter 3) or mechanically (chapter 4) in order to fulfil the tasks of substrate cleaning and adhesion promotion.

2. test methods

The success of chemical pretreatment is ultimately reflected in the long-term performance of the coated workpiece in practical use.
There are numerous test methods for the control, selection and development of pretreatment methods that lead to statements in a short time. Of these test methods, the salt spray tests (DIN EN ISO 9227) and the tests in a condensed water atmosphere (DIN EN ISO 6270-2) are the most important as short-term corrosion tests.

Inadequate pretreatment is shown in the salt spray test by excessive infiltration of the coating by corrosion products starting from a scratch. The combination of both types of exposure in the alternating test leads to corrosion phenomena that are largely similar to those of outdoor exposure.

The evaluation of corrosion phenomena is standardised in 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 stress by
- mandrel bending test, cylindrical mandrel (DIN EN ISO 1519)
- impact indentation (ISO 6272 / ASTM D 2794) or
- cupping test (Erichsen indentation EN 5020)
- cross-cut adhesion test (DIN EN ISO 2409)

3. process steps of the chemical pretreatment

The chemical pretreatment methods are divided into the following tasks:

Removal of harmful substances from the surface, such as scale, rust, abrasion, grease, oil, dust, etc.
Creation of a layer that promotes powder adhesion and inhibits corrosion, such as by phosphating, chromating or chromate-free processes, etc.
Removal of harmful treatment substances from previous process steps by thorough rinsing

3.1 Cleaning the surface

Contamination on the metal surface before coating impairs the adhesion between the powder layer and the metal. Therefore, contaminants such as oils and greases as well as inorganic particles such as grinding dust, rust and mill scale must be removed. Oils, greases and mechanically adhering dirt can be removed with alkaline or acidic cleaners.

The cleaning performance can be supported by higher temperatures of the active baths and by mechanical energy, in particular by spray treatment or ultrasound.

Steel can usually be cleaned with a highly alkaline medium, whereas Galvanised steel and Aluminium are treated with mildly alkaline cleaners or in a mildly acidic medium.

When cleaning zinc or die-cast aluminium, pickling of the metal surface, which actually enhances the cleaning effect, may be undesirable. The pickling effect can be reduced by adding special additives to the cleaner. Rust and scale are removed by etching in acids. These usually contain inhibitors that prevent the bare metal from dissolving. Sulphuric or hydrochloric acid pickling is commonly used for descaling unalloyed Steel, while inhibited phosphoric acid is preferably used for rust removal. Iron and steel materials are often cleaned electrolytically, supported by highly alkaline cleaning concentrates. Stainless or alloyed steels are usually etched using an etching solution consisting of nitric acid and hydrofluoric acid.

For parts with only slight, easily removable oil contamination, etching agents containing surfactants are used to remove rust and grease in a single step. If no special requirements are placed on the corrosion protection of the workpiece, subsequent phosphating can be omitted if etching is carried out with phosphoric acid. This leaves a thin, bluish iridescent phosphate film on the surface, which provides a good adhesive base for the subsequent coating and is suitable as temporary corrosion protection.

After etching and alkaline cleaning, the parts must be rinsed with demineralised water.

3.2 Building up conversion layers through phosphatisation

Conversion layers are created by chemical reaction of the metal surface with the treatment solution, forming a firmly bonded, usually inorganic layer.

3.2.1 Alkaline phosphating/iron phosphating

In alkali or iron phosphating, the metal surface reacts with an acidic solution of alkali phosphates. The aqueous solutions of phosphate anions do not contain any metal cations of their own, which are involved in the layer formation. The cations for layer formation come from the base material, which is why alkaline phosphating is often referred to as non-layer-forming phosphating. (i. Cf. 3.2.2. Zinc phosphatisation)

The layer produced by alkaline phosphating on ferrous metals is an amorphous agglomerate of phosphates, oxides and hydroxides of divalent and trivalent iron with a coating weight of 0.2-1.0 g/m2, which corresponds to a Film thickness of around 0.15 - 0.8 µm.

Depending on the sheet metal quality, Film thickness and accelerator used, the phosphated surfaces can show a wide range of colours from yellow to iridescent blue, golden or grey.

When treating zinc or aluminium alloys, there are no iron ions available to form a coating. In these cases, the alkali/iron phosphating merely acts as an etching agent.

However, it is also possible to treat other metals such as zinc or aluminium alloys advantageously using alkali phosphating processes.

Alkaline phosphating is generally not sufficient for painted surfaces exposed to weathering and permanent moisture, but is sufficient as corrosion protection for powder coated parts in unstressed areas.

3.2.2 Zinc phosphating on Steel

In contrast to the alkaline phosphating described above, phosphating with an acidic solution of primary zinc phosphate is layer-forming, as it provides Film thicknesses of around 8 - 20 µm. In this case, zinc or metal ions from the phosphate solution form the layer-forming cations, while phosphate from the phosphorus solution acts as an anion.
The layer formation of tertiary zinc and zinc iron phosphate (phosphophyllite, Zn2Fe(PO4)2) on the steel surface is accelerated by oxidising agents.

The iron dissolved during the layer formation precipitates as iron phosphate after further oxidation. The phosphating solution is depleted of active components as a result of the chemical reactions during coating formation and the discharge with the workpieces. These are continuously returned to the bath by adding a so-called replenishing solution.

To produce fine crystalline layers with optimum properties, activating agents - usually based on titanium compounds - are used for pre-rinsing before phosphating. These activating agents are also often incorporated into the alkaline cleaner so that no additional treatment step is necessary. Phosphating processes based on zinc phosphate are widely used as a pretreatment before a wide variety of organic coating systems.

Zinc phosphating as a pretreatment achieves the best corrosion resistance of paint coatings on Steel, cadmium-plated or galvanised steels. The adhesion of the organic coating under bending and impact stress also meets high standards. Special solutions for Aluminium and other alloys are possible, but require special baths.

3.3 Build-up of conversion layers through chromium-containing pretreatments

3.3.1 Situation of chromium-containing pretreatments

The disadvantages of the green chromating processes described below result from the many potential hazards. The chromate treatments are produced in aqueous treatment baths containing, among other things, chromic acid, which are highly hazardous to water. This applies to both transparent chromating and chromate treatment with a higher coating weight, i.e. green chromating.

Although the green chromating layers formed after the reaction theoretically consist of non-toxic chromium ($CrPO4$) and aluminium phosphates ($AlPO4$), it is not safe to wire them. This is partly due to the fact that chromium (VI) compounds are always assumed in the production of the treatment chemical for green chromating and partly due to the possible residual proportions of hexavalent chromium, which at around 0.01 µg/cm2 should generally be below the limit of quantification for a green chromating layer.

Even if only the use of pretreatments containing chromium VI has so far been excluded by national regulations, it is advisable to check the regional regulations and the prescribed implementation provisions in the tenders before choosing other chromium-containing pretreatments for façade components, especially for public or publicly subsidised construction projects.

3.3.2 Green chromating

Green chromating can be recognised by the colour of the conversion layers produced at higher Film thicknesses. The treatment solution can be applied by spraying or immersion.

Treatment solutions for green chromating essentially contain hydrofluoric acid, chromic acid and phosphoric acid. The layer formation reaction is therefore also based on chromium trioxide ($CrO3$) or chromium(VI) oxide, as in the case of prohibited yellow chromatising.

The fluoride concentration determines the coating weight. The coating is free of hexavalent chromium if the coating weight is not too high. However, it cannot be ruled out that high layer thicknesses occur, especially in the case of scooping workpieces, which carry chromates from the bath solutions, which are dangerous in all their potential after rinsing and also lead to a deterioration in adhesion.
The deposited chromate layer consists of phosphates of Aluminium and trivalent chromium and has no crystalline structure.

For application as a pretreatment for coating, surface weights of 400 to 1200 mg/m2 are used.

Green chromating improves adhesion and corrosion inhibition for the subsequently applied coating. Green chromating is also frequently used to form conversion layers on Galvanised steels for subsequent organic powder coating.

Chromate treatment is also used without further organic coating as bright corrosion protection. In special cases, green chromating layers can also be used for decorative purposes; the coating weights are then higher at 1 to 3 g/m2.

3.3.3 Chromium(III)-containing passivations

3.4 Build-up of conversion layers through chrome-free pre-treatments

3.4.1 Non-alloy coating components

Above all, the significantly lower environmental impact and lower costs for occupational safety and environmental protection are leading to the replacement of chrome-containing pre-treatments by chrome-free pre-treatments.
As a rule, bath management and analysis are somewhat more maintenance-intensive and the rinsing processes are somewhat more complex.
The corrosion protection for possible interim storage is also weaker in most cases.

There are various suppliers of chromium-free pre-treatment chemicals, which can be categorised on the basis of the base chemicals:
a) Titanium and/or zirconium compounds
b) Titanium/(fluorine) polymer compounds
c) Zirconium/fluorine compounds
d) Organosilanes

Most chrome-free pre-treatments can also be both sprayed and dipped. Some are also multi-metal compatible. They differ in terms of necessary or non-necessary rinsing processes after conversion coating in rinse and no-rinse processes.

It is recommended to choose pretreatment processes that have been approved by the GSB and/or Qualicoat certification bodies and thus, in addition to many years of ageing experience (e.g. Hoek van Holland), already meet a wide range of requirements in terms of process stability and suitability for processing.

As with chromium-containing pretreatments, the substrates must be pre-cleaned and rinsed. While acidic cleaning is sufficient for steels and Galvanised steels in some chrome-free pre-treatments, aluminium substrates are subjected to acidic pickling degreasing. In most cases, several rinsing cycles are indicated after pickling degreasing, whereby deionised water is used.

Rinsing after the conversion treatment is not necessary when using the no-rinse process. Chromium-free processes allow higher drying temperatures in both rinse and no-rinse operation. The higher temperatures have the advantage of promoting outgassing before coating in the case of porous substrates and generally reducing drying times.

4. mechanical pretreatments

In addition to the wet-chemical processes mentioned above, mechanical cleaning and/or pretreatment can also be used, especially for unalloyed, low-alloy and galvanised steel. Mechanical treatment can fulfil different tasks:

Removal of grease, dirt or corrosion products such as rust and scale
Removal of welding residues
Breaking sharp-edged laser and cut edges
Enlarging the surface, especially on burrs, edges and cut surfaces for good paint adhesion

Further information is also provided in DIN 55633: "Coating materials-Corrosion protection of steel constructions by powder coating systems - Evaluation of powder coating systems and execution of the coating".

4.1 Blasting Steel

When Processing 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. Raw steel surfaces must always have a surface preparation grade of Sa 2½ in accordance with DIN EN ISO12944-4. Mechanical roughening significantly improves the adhesion of the coating to the substrate. Suitable abrasives include: mineral or silicate abrasives such as corundum or glass.

As a rule of thumb, the more angular and larger the blasting material, the rougher the surface. This is accompanied by better adhesion of the primer to the substrate, which in turn leads to better corrosion protection. Round grit is less abrasive and compacts unfavourably. For good paint adhesion, the average surface roughness Rz achieved should be between 40 µm and 80 µm.

The basic prerequisite for good paint adhesion and corrosion protection is that the surface is completely free of grease and oil before blasting.

4.2 Sweep blasting of Galvanised steel

The existing corrosion protection layer (e.g. galvanic or strip galvanising) must not be damaged by the surface preparation.

Sweep blasting in accordance with DIN EN ISO 12944-4 is a process very similar to compressed air blasting. The main differences are the much lower pressure (2.5-3 bar) and the type of abrasive. This is finer (Particle size 0.25mm - 0.5 mm) and must not contain any rusting metallic components. Non-metallic blasting abrasives according to DIN EN ISO 11126-3 to DIN EN ISO 11126-7 as well as metallic blasting abrasives such as cast chrome granulate (grit) or broken glass (grit) have proven themselves as blasting abrasives.

Welding beads and scale should be removed with the grinding machine if the profile geometry allows this; if necessary, rework with a blasting gun and mineral blasting abrasive (e.g. corundum).

The basic prerequisite for good powder adhesion and corrosion protection is that the surface is completely free of grease and oil before blasting.

4.3 Post-treatment of blasted Steel

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

Firstly, the contaminants from the blasting material must be removed using compressed air and/or chemical cleaning or chemical pretreatment. Compressed air usually only removes coarse dust, while a chemical surface treatment such as iron phosphating, for example, not only removes the finest dust but also provides a certain degree of corrosion protection for steel surfaces during further processing.

A chemical surface treatment is a useful addition to the mechanical pretreatment for the subsequent powder coating and promotes adhesion to the substrate:

Phosphating processes in accordance with DIN EN 9717 "Phosphating coatings on metals" - Methods for specifying requirements, preferably zinc phosphating, should be provided for steel substrates. Chromate treatment is not possible for raw Steel.
Zinc phosphating is advantageous for galvanised steels after mechanical pretreatment by sweep blasting.

Chromium-free conversion layers based on zirconium and titanium can achieve equivalent results to classic chromate treatment.

It is advisable to obtain proof of the desired adhesion values by means of corrosion protection tests (e.g: Condensation water alternating climate according to DIN EN ISO 6270-2 and spray mist test according to DIN EN ISO 9927).

4.4 Corrosion protection structures

The resistance of corrosion protection systems using organic coatings such as powder coatings must 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 time periods for the duration of protection are defined in DIN EN ISO 12944-1. The duration of protection of powder coating systems depends on various parameters:

- Design of the component and the object
- Load after coating (location, use)
- Condition of the steel surface or zinc coating before preparation or pretreatment
- Careful cleaning and effectiveness of the pretreatment
- Type of coating system. Decisive here:
  a) Number of layers (one-coat or two-coat system)
  b) Thickness of the respective layers
  c) Penetration resistance of the coating system to corrosive atmospheres

DIN 55633-1, "Coating materials - Corrosion protection of steel constructions by powder coating systems - Evaluation of powder coating systems and execution of the coating", defines recognised durations of protection for the two basic substrate categories - unalloyed steel or low-alloy steel; hot-dip galvanised steel - in accordance with the classification in DIN EN ISO 12944-1.
For the relevant corrosion categories (C2, C3, C4, C5-I and C5-M), the layer structures required to achieve the duration of protection (e.g. number of layers and layer thicknesses) are specified there.

IGP Pulvertechnik AG fulfils these specifications with a range of various anticorrosive primers matched to the substrates and top coats.

You can obtain detailed information on corrosion protection measures and systems from our trained corrosion protection inspectors and specialist consultants.