

English version

Protection of metallic materials against corrosion - Guidance on
the assessment of corrosion likelihood in water distribution and
storage systems - Part 3: Influencing factors for hot dip
galvanised ferrous materials

Protection des matériaux métalliques contre la corrosion -
Recommandations pour l'évaluation du risque de corrosion
dans les installations de distribution et stockage d'eau -
Partie 3 : Facteurs à considérer pour les métaux ferreux
galvanisés à chaud

Korrosionsschutz metallischer Werkstoffe - Hinweise zur
Abschätzung der Korrosionswahrscheinlichkeit in
Wasserverteilungs- und speichersystemen - Teil 3:
Einflussfaktoren für schmelztauchverzinkte Eisenwerkstoffe

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Foreword

This document (EN 12502-3:2004) has been prepared by Technical Committee CEN/TC 262 "Metallic and other inorganic coatings", the secretariat of which is held by BSI.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2005, and conflicting national standards shall be withdrawn at the latest by June 2005.

This standard is in five parts:

Part 1: General;

Part 2: Influencing factors for copper and copper alloys;

Part 3: Influencing factors for hot dip galvanized ferrous material;

Part 4: Influencing factors for stainless steels;

Part 5: Influencing factors for cast iron, unalloyed and low alloyed steels.

Together these five parts constitute a package of interrelated European Standards with a common date of withdrawal (dow) of 2005-06.

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Introduction

This document results mainly from investigations into and experience gained of the corrosion of hot dip galvanized ferrous materials, used as steel tubes and cast iron fittings (galvanized products), in drinking water distribution systems in buildings. However, it can be applied analogously to other water systems.

The corrosion likelihood of galvanized products depends on the formation of a corrosion product layer, which begins to form as soon as the galvanized surface comes in contact with water. The more this layer prevents ionic and electronic exchanges between the metal and water, the more protective it will be and the higher the durability of the galvanized products.

Drinking water systems with galvanized products, although showing visible corrosion effects, are, in general, resistant to corrosion damage in normal use. However, there are conditions under which they will sustain corrosion damage.

As a result of the complex interactions between the various influencing factors, the extent of corrosion can only be expressed in terms of likelihood. This document is a guidance document and does not set explicit rules for the use of hot dip galvanized ferrous materials in water systems. It can be used to minimize the likelihood of corrosion damages occurring by:

- assisting in designing, installing and operating systems from an anti-corrosion point of view;
- evaluating the need for additional corrosion protection methods for a new or existing system;
- assisting in failure analysis, when failures occur in order to prevent repeat failures occurring.

However, a corrosion expert, or at least a person with technical training and experience in the corrosion field is required to give an accurate assessment of corrosion likelihood or failure analysis.

1 Scope

This document gives a review of influencing factors of the corrosion likelihood of hot dip galvanized steel and cast iron, used as tubes, tanks and equipment, unalloyed and low alloy ferrous materials in water distribution and storage systems as defined in EN 12502-1.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 8044:1999, *Corrosion of metals and alloys — Basic terms and definitions (ISO 8044:1999)*.

EN 12502-1:2004, *Protection of metallic materials against corrosion — Guidance on the assessment of corrosion likelihood in water distribution and storage systems — Part 1: General*.

3 Terms, definitions, and symbols

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in EN ISO 8044:1999 and EN 12502-1:2004 apply.

3.2 Symbols

$c(\text{HCO}_3^-)$	Concentration of hydrogen carbonate ions in mmol/l
$c(\text{Cl}^-)$	Concentration of chloride ions in mmol/l
$c(\text{SO}_4^{2-})$	Concentration of sulphate ions in mmol/l
$c(\text{NO}_3^-)$	Concentration of nitrate ions in mmol/l
$c(\text{Ca}^{2+})$	Concentration of calcium ions in mmol/l

4 Types of corrosion

4.1 General

Internal corrosion of galvanized products in water distribution and storage systems generally leads to the build-up of layers formed by corrosion products, which might or might not be protective. Because a metal coating produced by hot dip galvanizing is not a homogeneous layer consisting of zinc alone, but a structured system of zinc and various zinc-iron alloy phases, after some time the corrosion products will also contain iron compounds. Because of the greater solubility of the zinc compounds, the layers end up consisting of iron corrosion products (rust). In the case of non-protective layers, corrosion can lead to the impairment of the function of the system (lack of serviceability because of corrosion damage).

The most common types of corrosion are described in EN 12502-1:2004, Clause 4.

The types of corrosion considered for galvanized products are the following:

- uniform corrosion;
- pitting corrosion;
- selective corrosion;
- bimetallic corrosion.

The various possibilities are shown schematically in Tables 1 and 2.

Table 1 — Uniform corrosion and its consequences

	Low rate uniform corrosion	High rate uniform corrosion	
Corrosion effects on zinc coating	Formation of a protective layer on residual zinc coating, which remains during full service life.	Complete loss of zinc coating.	
Corrosion effects on the base metal	None	Uniform attack, low mass loss; protective rust layer	Non-uniform attack, pits, tubercles
Possible corrosion damage (during projected service life)	None	Initially high concentration of metal ions in water	Reduction in free pipe bore size

Table 2 — Localized corrosion and its consequences

	Pitting corrosion	Selective corrosion
Corrosion effects on the coating	Localized loss of coating	Intergranular attack leading to complete loss of the zinc phase
Corrosion effects on the base metal	Pits and tubercles	Non-uniform general corrosion
Possible corrosion damage (during projected service life)	Reduction of free pipe bore size, contamination of water by iron corrosion products, blockage of system components, wall perforation	Initial release of solid zinc corrosion products into water, contamination of water by iron corrosion products

For each type of corrosion, the following influencing factors (described in EN 12502-1:2004, Table 1 and Clause 5) are considered:

- characteristics of the metallic material;
- characteristics of the water;
- design and construction;
- commissioning and pressure testing;
- operating conditions.

To assess the influence of the characteristics of the water, data as described in EN 12502-1 are necessary. Therefore, the composition of the water fed into the respective installations is relevant. However, temporary variations of the water composition need to be considered. Therefore, in addition to a detailed analysis of the water, information about its variations is necessary.

4.2 Uniform corrosion

4.2.1 General

Experience shows that corrosion damage to galvanized products because of uniform corrosion can only occur if the corrosion velocity is extremely high and there is no possibility of stable protecting rust layers being formed. Uniform corrosion can manifest itself in different ways (see Table 1).

Uniform corrosion leads to the formation of layers consisting of zinc hydroxycarbonates, which, depending on the carbonic acid species concentration, can offer the product greater or lesser degrees of protection.

If the corrosion rate is sufficiently low, no complete loss of the zinc layer will occur during the projected service life. Protective layers will form on the remaining zinc phase of the metal coating.

At a higher corrosion rate, the metal coating will be completely removed during the projected service life. The concentration of iron corrosion products in the surface layer increases during the corrosion of the zinc-iron alloy phases. Further corrosion processes eventually result in the formation of a surface layer consisting predominantly of aged iron corrosion products, which provide lasting corrosion protection.

If the corrosion rate of the coating is too high, or the concentration of the components forming the carbonic acid system too low to allow the formation of a protective layer, the base metal will be non-uniformly attacked after the consumption of the metal coating. The consequence can be contamination of the water by iron corrosion products, encrustation and clogging of the pipes or wall penetration by pitting corrosion.

Although zinc corrosion products are only sparingly soluble, zinc ions are released into water.

The concentration of zinc ions because of dissolution of corrosion products will depend on:

- the concentration of the carbonic acid species in the water;
- the duration of stagnation of water in pipes;
- the age of the installation;
- the dilution caused by mixing with fresh water;
- the method of sampling.

The quantity of loosely adherent zinc corrosion products that can be removed from the tube walls will depend on:

- the duration of low water velocity;
- the extent of sudden turbulent flow.

4.2.2 Influence of the characteristics of the metallic material

Physical and chemical characteristics and surface conditions of the metallic material on the degree of uniform corrosion are not known to influence uniform corrosion.

4.2.3 Influence of the characteristics of the water

Under flowing conditions, the rate of uniform corrosion of zinc strongly depends on the pH value of the water. It increases with decreasing pH value of the incoming water.

Under stagnant conditions, the quantity of zinc ions going into solution is predominantly determined by the carbonic acid species concentration, in particular the carbon dioxide concentration.

The rate of uniform corrosion can be decreased by the addition of inhibitors, e.g. orthophosphates, or by alkalization of the water by addition of NaOH and/or Na₂CO₃, by addition of Ca(OH)₂ or by use of filters, e.g. marble, limestone, dolomite.

The rate of uniform corrosion in a water distribution system decreases in the flow direction. This is because water flowing through hot dip galvanized pipes will be depleted of oxygen and carbon dioxide by the corrosion process and becomes less corrosive than fresh water.

4.2.4 Influence of design and construction

The formation of protective layers will be favoured by regular renewal of the water, which can be facilitated by avoiding areas of stagnation.

4.2.5 Influence of pressure testing and commissioning

If pressure testing is not done according to the recommendations given in EN 12504-1, 5.5, and residual water is left in the system after draining, the likelihood for the formation of loosely adherent corrosion products is increased.

4.2.6 Influence of operating conditions

4.2.6.1 Influence of temperature

The effect of temperature on uniform corrosion of zinc is complex because of changes in the composition of the corrosion products in the surface layer. Up to temperatures of approximately 35 °C, the rate of uniform corrosion increases with temperature. Above this temperature, the corrosion rate tends to decrease because the predominant corrosion product in flowing cold water, zinc hydroxide, is converted to less soluble zinc oxide.

4.2.6.2 Influence of flow conditions

The rate of uniform corrosion under stagnant conditions in a particular water is always lower than under flowing conditions. It increases with water flow velocity.

4.3 Pitting corrosion

4.3.1 General

4.3.1.1 Manifestations of pitting corrosion

Depending on the water temperature, there are two different types of pitting corrosion that can occur on galvanized products.

4.3.1.2 Pitting corrosion in cold water

In cold water systems, pitting corrosion manifests itself mainly in the formation of pits. It results in the development of pustules, which reduce the free pipe bore size over the course of time. The water can also be contaminated by corrosion products of iron. Wall perforation rarely occurs in the case of this type of pitting corrosion, which is caused by corrosion cells, which are often induced by differential aeration (under deposits), or by contact with a more noble metal (bimetallic corrosion).

Besides the soluble ions of zinc released by uniform corrosion, iron corrosion products from pitting corrosion or from dislodged encrustations have to be taken into consideration. Encrusted corrosion products are easily dislodged into the water stream. In these cases, the analytically observed iron concentration in the water can become extremely high, especially after longer periods of stagnation and operating conditions such as high flow rates and water hammer.

4.3.1.3 Pitting corrosion in heated water

Pitting corrosion in heated water ($>35\text{ }^{\circ}\text{C}$) is characterized by sharply bounded pits within a non-corroded area. It develops from existing or corrosion-produced defects in the metal coating, under deposits or in crevices, because of the formation of zinc oxide, which forms easily in heated water. Its semi-conductive properties enhance the cathodic reaction of oxygen reduction. This is accompanied by a shift of the free corrosion potential to more noble values, which are often more positive than the free corrosion potential of iron. This effect was commonly referred to as "potential reversal" in the early literature.

Initiation of pitting corrosion in heated water is often caused by blistering; a special type of corrosion occurring within galvanized coatings. Blistering is attributed to corrosion of zinc with hydrogen evolution. The atomic hydrogen generated is absorbed and recombines to give hydrogen molecules in the region of the zinc-iron alloy phases, causing material separations and blisters. Anodes for differential aeration cells develop in the areas of blister bursts.

The effect of pitting corrosion on water quality is similar to the effect of pitting corrosion in cold water (see 4.3.1.2).

4.3.2 Influence of the characteristics of the metallic material

Chemical composition of the metal coating is not known to influence pitting corrosion in either cold or heated water.

The influence of the surface conditions is well known. This has led to the requirement of using only Type A quality pipes in accordance with EN 10240 [2]. For example, a rough surface, because of its heterogeneities, is more susceptible to the formation of local anodes than a smooth surface.

Another critical factor is the condition of the inner weld seam. An irregular shape of the seam weld can lead to anodic spots. Therefore the shape of the inner seam weld should be regular, which for most cases of manufacturing welded tubes requires machining of the inner seam weld.

A particular susceptibility is observed with electrically resistant welded pipes, which are not diameter-reduced by drawing. After removal of the zinc coating, this so-called "grooving corrosion" occurs within a restricted area of the seam and relates to a preferential corrosion of certain sulfur-containing phases in the weld metal, redistributed along the weld during the electric resistance welding process. After stabilization of a local anode, very rapid corrosion can occur because of the formation of acids at the anode by hydrolysis of soluble corrosion products. To avoid this effect, steel qualities with limited sulfur content are to be used. Besides this, a stabilizing thermal treatment is useful.

Galvanized products with the zinc-iron alloy layers located at the surface are more susceptible to blistering because hydrogen evolution is easier in the alloy layers.

4.3.3 Influence of the characteristics of the water

The influence of the water composition on the corrosion likelihood should be considered separately for the anodic and cathodic reactions.

The nature and the concentration of the anions have an important influence on the anodic partial reaction. Chloride, nitrate and sulphate ions which migrate to the anode in the electrical field of the corrosion cell do not slow down the anodic dissolution because, unlike hydrogen carbonate ions, they are not able to buffer the acidity caused by hydrolysis of the zinc or/and iron ions formed within the pit. Hydrogen carbonate ions inhibit this mechanism by buffering the acidity. The influence of the anions, therefore, is determined more by the concentration ratio, S_1 , than by the total concentration of the individual anions, where S_1 is calculated from the equation:

$$S_1 = \frac{c(\text{Cl}^-) + c(\text{NO}_3^-) + 2 c(\text{SO}_4^{2-})}{c(\text{HCO}_3^-)}$$

The likelihood of pitting corrosion increases with increasing values of S_1 . It can be reduced by altering the concentration ratio S_1 by a method such as selective membrane filtration.

NOTE According to current thinking, pitting corrosion is extremely unlikely with S_1 values below 0,5 and very likely with S_1 values above 3.

The likelihood of pitting corrosion in heated water is indirectly influenced by the amount of acidity, as the likelihood for blistering, one of the most important prerequisites for pitting corrosion, increases with increasing acidity.

High levels of suspended solids in the water resulting from corrosion of the water mains or from incomplete removal of manganese, iron or silt from the raw water, increase the likelihood of pitting corrosion under deposits on the bottom. For waters having usual oxygen concentrations ($> 0,1 \text{ mmol/l}$), the oxygen reduction, being the cathodic partial reaction of pitting corrosion, is not actually limited by the oxygen content. Pitting corrosion does not occur with $c(\text{O}_2) \leq 0,003 \text{ mmol/l}$.

Hydrogen carbonate and phosphate anions in combination with calcium cations can act as cathodic inhibitors because of the formation of non-conductive layers of calcium carbonate or calcium phosphate. The necessary concentrations are:

$$c(\text{HCO}_3^-) \geq 2,0 \text{ mmol/l}$$

$$c(\text{Ca}^{2+}) \geq 0,5 \text{ mmol/l}$$

The pH value and the concentration of total inorganic carbon indirectly influence the cathodic activity. Rapid dissolution of the zinc phase of the coating leads to the formation of layers with iron corrosion products that show a much better conductivity. Thereby, the corrosion potential increases and pitting corrosion is favoured. Therefore, in some cases pitting corrosion develops only after the appearance of the zinc-iron alloy phase on the surface. In this special case, the likelihood of pitting corrosion can be reduced by alkalization (see 4.2.3).

Furthermore, pitting corrosion can be reduced by electrolytic processes with dissolution of aluminium electrodes. This will lead to the formation of artificial protective layers with reduced cathodic activity.

4.3.4 Influence of design and construction

Deposits inducing the formation of anodic spots are often introduced during the plumbing operation when screw joints are made and too much jointing compound (e.g. hemp) is used. The typical manifestation in this case is a corrosion attack immediately beside the cut edge of the pipe in the thread of the galvanized cast iron fitting. On the other hand, insufficient application of jointing compound will leave critical crevices in the thread.

Other solid substances introduced by plumbing operations, e.g. sand and iron splinters, can be removed by efficient flushing (e.g. with pressurized water/air mixture). The contamination of the system by splinters or turnings produced by thread cutting can be prevented by their removal from the pipe ends immediately after the cutting operation.

Particles of solid substances originating from the water main systems can promote corrosion. This effect can be avoided by filtration.

Threading fluids based on mineral oil cause non-uniform wetting and formation of heterogeneous surface layers. The mineral oil coated area can act as a more active cathode than the areas with layers of non-conductive corrosion products. Water soluble products used as threading fluids are preferable.

The influence of mixed installation on pitting corrosion is dealt with in 4.5.

4.3.5 Influence of pressure testing and commissioning

The long-term corrosion behaviour is substantially determined by the formation of a protective layer formed in the initial period after the system is put into operation.

The corrosion likelihood increases if the formation of the protective layer is disturbed or prevented in any way. The removal of foreign substances, e.g. any debris or sand, can be achieved by appropriate flushing (preferably with an air/water flushing device) of the system immediately after the first filling.

If pressure testing is not done according to the recommendations given in EN 12502-1:2004, 5.5, leading to residual water being left in the system after draining, the likelihood of pitting corrosion is increased.

4.3.6 Influence of operating conditions

4.3.6.1 Influence of temperature

The likelihood of pitting corrosion is influenced predominantly by the water temperature. As very often the anodes are formed by cracked blisters in the zinc phase of the coating and the likelihood of blistering increases with the temperature, the likelihood of the formation of such anodes also increases with temperature. In addition, the influence of temperature on the cathodic reaction is because of the fact that the portion of zinc oxide in the surface layer increases with increasing temperature. Zinc oxide has semi-conductive properties leading to enhanced activity of the oxygen reduction. Experience indicates that the likelihood of pitting corrosion increases markedly with increasing temperature in heated waters.

Sudden temperature changes can cause spalling of corrosion products because of the differential expansion between the corrosion product layer and the base metal. If the water in the tube of a cold water line after stagnation over night at room temperature is replaced by fresh flowing water with a temperature possibly 10 °C lower, or if the water in the line between a circulating heated water system and the tap is replaced by fresh flowing water with a temperature possibly 30 °C higher, dislodging of corrosion products is promoted.

4.3.6.2 Influence of flow conditions

Pitting corrosion is favoured in stagnant water, because local anodes become stabilized under these conditions. When stabilization of anodes is completed, the progress of pitting corrosion is promoted by water flow, because the transport of oxygen is facilitated.

4.4 Selective corrosion

4.4.1 General

4.4.1.1 Manifestations of selective corrosion

Selective corrosion of galvanized products predominantly occurs in cold water. It is characterized by a preferential corrosion along grain boundaries in the zinc layer of the metal coating. As a result, a thick layer of only loosely adherent corrosion products is formed from which granular particles can be transferred into the water. These particles consist of solid zinc corrosion products that can still contain metallic zinc or zinc-iron alloy. After destruction of the metal coating, corrosion proceeds normally as non-uniform general corrosion.

4.4.1.2 Effect of selective corrosion on water quality

The quantity of dispersed solid zinc corrosion products that can be removed from the tube walls will depend on the duration of time with low water velocity and the extent of sudden turbulent flow. With proceeding corrosion, the colour of the corrosion products will change from grey to brown.

4.4.2 Influence of the characteristics of the metallic material

The chemical composition of the coating is not known to have influence, although the preferential corrosion is supposed to be because of enrichment of some minor constituents along the grain boundaries.

The size of the granular particles transferred into the water is influenced by the structure and the thickness of the coating. Bigger particles are observed with galvanized tubes with rough coatings, as they come out of production lines that use air blasting instead of steam blasting.

4.4.3 Influence of the characteristics of the water

The likelihood of selective corrosion is influenced in different ways by the concentrations of inhibiting nitrate ions and stimulating chloride and sulphate ions. Selective corrosion is possible only within a certain range when the concentration of nitrate ions is high enough to passivate the grain surface of the zinc against the activating power of chloride and/or sulphate ions, but not high enough to passivate also the grain boundaries. The conditions for selective corrosion can be characterized by the concentration ratio S_2 , which is calculated from the equation:

$$S_2 = \frac{c(\text{Cl}^-) + 2 c(\text{SO}_4^{2-})}{c(\text{NO}_3^-)}$$

NOTE The likelihood of selective corrosion of this type is considered to be low when S_2 is below 1 or above 3 or when $c(\text{NO}_3^-)$ is below 0,3 mmol/l.

The extent of selective corrosion can be reduced by altering the ratio S_2 by, e.g. anion exchange.

4.4.4 Influence of design and construction

Design and construction does not directly influence the likelihood of selective corrosion, except that a design favouring long stagnation periods will be disadvantageous.

4.4.5 Influence of pressure testing and commissioning

Pressure testing and commissioning is not known to influence the likelihood of selective corrosion.

4.4.6 Influence of operating conditions

The operating conditions do not apparently influence the process of selective corrosion, but markedly influence the effect of selective corrosion on water quality (see 4.4.1.2).

4.5 Bimetallic corrosion

4.5.1 General

In the case of galvanized products, bimetallic corrosion can be a result of mixed installation involving galvanized products and materials that have a more positive corrosion potential (e.g. stainless steel, copper and copper alloys). In such cases, the galvanized product becomes anodically polarized. As a result, the likelihood of pitting corrosion in cold and in heated water is increased.

Bimetallic corrosion can occur because of either direct coupling or indirectly where noble metals are electrodeposited on the zinc surface.

4.5.2 Influence of the characteristics of the metallic material

The characteristics of the metallic material do not have any known effect on bimetallic corrosion.

4.5.3 Influence of the characteristics of the water

The influence of the water composition on the bimetallic corrosion is similar to the influence on the cathodic reaction of pitting corrosion. An increase in electrical conductivity normally increases the likelihood of bimetallic corrosion. However, the presence of calcium hydrogencarbonate, which also increases the conductivity, decreases the bimetallic corrosion likelihood by enabling the precipitation of inhibiting calcium carbonate layers on the more noble material.

4.5.4 Influence of design and construction

Influencing factors of the design on bimetallic corrosion are the anode-to-cathode area ratio and the geometry.

Mixed installation with copper-zinc alloys (brass) is less critical than mixed installation with copper-tin alloys (gun-metal), because the zinc content of the brass leads to the formation of less conductive zinc hydroxycarbonate layers that increase the polarization resistance. Mixed installation with stainless steels can lead to bimetallic corrosion, especially if the cathode/anode area is high. However, this does not lead to such a severe acceleration as could be expected by the difference of the corrosion potentials, as the cathodic polarization resistance of stainless steel is normally rather high.

A special influence is observed in mixed installations with copper compounds. Components made of copper or copper alloys or components brazed with large amounts of copper filler metal can transfer copper ions into the water. These ions increase the likelihood of pitting corrosion of galvanized products by precipitation of copper on metallic zinc to form spots of metallic copper with very high cathodic activity.

Components of copper and copper alloys installed upstream of components made of galvanized products increase the likelihood of this type of bimetallic corrosion. This is also valid when these components are installed downstream of the galvanized products in systems without no-return device, because of recirculation and convection of water.

The normal use of valves made of copper alloys in a water distribution system is not critical in this context because of their relatively low surface area.

NOTE In investigations into the cause of any corrosion damage because of pitting corrosion, the quantity of copper per unit area provides information on whether the damage is influenced by the use of mixed copper-zinc plumbing. An important influence should be assumed if the copper content in areas adjacent to the pit is higher than 1,0 g/m.

4.5.5 Influence of pressure testing and commissioning

Pressure testing and commissioning are not known to influence the likelihood of bimetallic corrosion.

4.5.6 Influence of operating conditions

The operating conditions influence bimetallic corrosion in the same way as the pitting corrosion (see 4.3.6).

5 Assessment of corrosion likelihood

In order to assess the corrosion likelihood of hot dip galvanized steel in a water distribution and storage system, all the influencing factors, listed in EN 12502-1:2004, Table 1, and their possible interactions should be taken into consideration. This assessment should be carried out separately for all types of corrosion relevant to the specific corrosion system. Because of the complexity of the influencing factors and of their interaction, in most cases only a qualitative assessment is possible.

Bibliography

- [1] EN 12504-1:2000, *Testing concrete in structures. Part: 1 Cored specimens. Testing, examining and testing in compression.*
- [2] EN 10240, *Internal and/or external protective coatings for steel tubes — Specification for hot dip galvanized coatings applied in automatic plants.*