

Phosphating metals
Principles and testing

DIN
50942

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Descriptors: Corrosion protection, phosphating, metals, coatings, testing.

Phosphatieren von Metallen – Verfahrensgrundsätze, Prüfverfahren

This standard, together with DIN EN ISO 3892, June 1996 edition, supersedes May 1987 edition.

In keeping with current practice in standards published by the International Organization for Standardization (ISO), a comma has been used throughout as the decimal marker.

In this standard, the symbol % means percentage by mass.

The density values given refer to a temperature of 20 °C.

Foreword

This standard has been prepared by the *Normenausschuß Materialprüfung* (Materials Testing Standards Committee).

As DIN EN ISO 3892 only covers gravimetric testing and does not deal with the other types of test method previously dealt with in DIN 50942, the responsible technical committee has decided to issue a revised version of this standard.

Amendments

In comparison with the May 1987 edition of DIN 50942, the text has been rearranged and the passages covering determination of mass per unit area by differential weighing have been omitted.

Previous editions

DIN 50942: 1955-11, 1973-11, 1987-05.

1 Scope and field of application

This standard describes the principles of phosphating products made from or coated with ferrous materials, zinc, aluminium, cadmium, and their alloys. The phosphate conversion coatings produced may serve as corrosion protection, to promote the adhesion of paints and similar materials (including plastic film), to provide lubrication during cold-forming operations such as drawing, shaping, forming, extrusion, etc., to reduce friction, or as electrical insulation.

This standard does not cover pickling methods using phosphoric acid, rust conversion, or phosphating methods involving stoving.

Continued on pages 2 to 13.

Translation by DIN-Sprachendienst.

In case of doubt, the German-language original should be consulted as the authoritative text.

2 Normative references

This standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate place in the text and the titles of the publications are listed below. For dated references, subsequent amendments to or revisions of any of these publications apply to this standard only when incorporated into it by amendment or revision. For undated references, the latest edition of the publication referred to applies.

DIN 12331	Beakers for laboratory use
DIN 12680-1	Graduated cylinders for laboratory use
DIN 12700-1	Burettes for laboratory use – General requirements
DIN 50014	Artificial climates in technical applications – Standard atmospheres
DIN 50017	Artificial climates in technical applications – Condensation water test atmospheres
DIN 50021	Corrosion testing – Spray tests with different sodium chloride solutions
DIN 50960-1	Electroplated and chemically applied coatings – Designation and information in technical documentation
DIN 53135	Filter paper for chemical analysis – Classification, designation, properties, testing
DIN 53167	Salt spray testing of organic coatings
DIN 53209	Designation of the degree of blistering of paints, varnishes and similar coatings
DIN 53210	Designation of the degree of rusting of paints, varnishes and similar coatings
DIN EN 605	Paints and varnishes – Standard panels for testing (ISO 1514 : 1984, modified)
DIN EN ISO 2178	Non-magnetic coatings on magnetic substrates – Measurement of coating thickness by the magnetic method (ISO 2178 : 1982)
DIN EN ISO 3892	Conversion coatings on metallic materials – Determination of coating mass per unit area with gravimetric methods (ISO 3892 : 1980)

DVV Code of practice *Charakteristische Merkmale für elektrolytisch verzinktes Feinblech in Tafeln und in Rollen* (Characteristics of galvanized sheet metal in the form of panels or coils*)

3 Concept

Phosphating is the formation of a phosphate conversion coating on a metal substrate by immersion in an aqueous phosphoric acid solution. The phosphate anions found in such coatings are provided by the solution, while the cations are provided by the solution and/or the substrate material.

4 Principle

4.1 Substrates to be phosphated are to be completely free of corrosion products. Unless the phosphating bath also serves to clean and degrease the substrate, the latter shall also be free of oil, grease, fingerprints and other impurities or foreign matter.

4.2 Phosphate coatings can be applied by immersion in a still or agitated solution, by curtain coating or by spraying. Roll coating may be used for phosphating steel strip, whether it is galvanized or not. Details of the application procedure are to be taken from the relevant instructions. After phosphating, the coated products are usually rinsed with water and dried; supplemental coatings of oil, grease, wax or paints and similar materials (including plastic film) are applied if necessary.

4.3 When using conventional phosphating methods, the hydrogen embrittlement of steel components having a tensile strength of 1 200 N/mm² or greater cannot be completely prevented (cf. Explanatory notes). However, the risk of embrittlement can be reduced by choosing materials of adequate ductility and by subjecting products, either before and/or after phosphating, to an appropriate form of heat treatment, such as

- a) stress-relief annealing after cold forming, in order to eliminate residual tensile stresses;
- b) heating to a temperature of 130 to 150 °C for at least two hours after phosphating, in order to expel the hydrogen which has been absorbed during phosphating.

5 Designation

The designation of phosphate coatings shall be as specified in DIN 50960-1.

Unless otherwise specified, the mass per unit area shall be as given in tables 2 to 4.

*) Issued by and obtainable from *Deutscher Verzinkerverband e.V.*, Düsseldorf, 1979.

6 Coating types

The type of phosphate coating produced (i.e. its mass per unit area and apparent density) will depend on the material and quality of the substrate being coated, the mechanical and chemical treatment of the products prior to phosphating, the composition of the phosphate bath, and the working conditions during phosphating. All phosphate coatings have pinholes, most of which are closed when an additional coating is provided.

Table 1 shows several types of phosphate coating.

Solutions based on $Zn(H_2PO_4)_2$ and $Mn(H_2PO_4)_2$ produce zinc phosphate and manganese phosphate coatings, respectively. Zinc calcium phosphate coatings are obtained with solutions based on $Zn(H_2PO_4)_2$ and $Ca(H_2PO_4)_2$. Alkali metal phosphate solutions give coatings which mainly consist of the phosphate of the treated metal mixed with that metal's oxides. When ferrous materials are treated with a solution containing NaH_2PO_4 , for example, an iron phosphate coating is produced.

In this standard, the following symbols are used to denote the various coating types:

Zinc phosphate: Znph
Zinc calcium phosphate: ZnCaph
Manganese phosphate: Mnph
Iron phosphate: Feph

Table 1: Types of phosphate coating

Main constituent of bath	Coating type produced	Colour of coating	Mass per unit area, in g/m ² , produced on			
			ferrous materials	aluminium	zinc	cadmium
$Zn(H_2PO_4)_2$	Zinc phosphate	Light to dark grey, crystalline	1 to 60	1 to 15	1 to 60	1 to 60
$Zn(H_2PO_4)_2 + Ca(H_2PO_4)_2$	Zinc calcium phosphate	Light to dark grey, fine crystalline	1 to 15	-	1 to 10	-
$Mn(H_2PO_4)_2$	Manganese phosphate	Dark grey, crystalline	1 to 60	-	-	-
$Me(I)(H_2PO_4)^1)$	Phosphate of metal treated (plus iron oxides, in the case of ferrous materials)	Coatings of 0,1 to about 1 g/m ² : Iridescent (e.g. yellowish to bluish grey). Coatings of more than 1 g/m ² : grey.	0,1 to < 1	< 0,3	0,1 to 2	-

¹⁾ Me(I) means cation of an alkali metal or NH₄⁺.

6.1 Coatings for corrosion protection

All of the above-mentioned coating types can be used for corrosion protection. The coating type and mass per unit area should be selected according to the nature of the metal to be phosphated and the degree of corrosion protection required in service.

Phosphate coatings used for corrosion protection may be given a final rinse with aqueous solutions containing chromium compounds. However, without a supplemental coating, the corrosion protection afforded by phosphate coatings is of only limited duration. To obtain effective long-term protection, additional coating geared to the intended use of the phosphated metal surfaces is necessary. Such coatings may consist of anti-corrosion oil, grease or wax, or paints or similar coating materials (including plastic film). It is recommended that subsequent coating be carried out immediately after phosphating.

Phosphated surfaces that are to be coated with paints or similar materials shall be free of water-soluble substances as these cause blistering of the top layer. For this purpose, phosphate coatings shall be given a final rinse with double-distilled water. Before coating, it is essential to avoid any contamination of the phosphate coating (e.g. by dust or fingerprints).

Table 2: Phosphate coatings for corrosion protection

Metal to be protected	Phosphate coating		Supplemental coating required	Extent of protection	Examples of applications
	Recommended coating type	Recommended mass per unit area, in g/m ²			
Ferrous materials	Feph Znph	0,1 to less than 1 1 to 5	None None	Temporary corrosion protection in dry environments free of condensation	Short-term indoor storage of machine components
	Znph and Mnph	Greater than 5, preferably greater than 10	None	Long-term corrosion protection in dry environments free of condensation	Long-term indoor storage of machine components
	Znph and Mnph	Greater than 5, preferably greater than 10	Anti-corrosion oil or wax, etc. (where appropriate, applied after staining of coating)	Permanent protection in dry environments free of condensation, temporary protection outdoors under cover	Corrosion protection during transportation or long-term storage, and at points of contact of nuts, bolts, fittings, etc.
	ZnCaph	Greater than 5			
Ferrous materials, zinc, aluminium or cadmium (where appropriate)	Znph and ZnCaph	1 to 10, preferably 1 to 5	Paint or similar materials	Permanent protection outdoors and in highly corrosive environments	Automobile and truck bodies, refrigerator and washing machine housings
Ferrous materials	Feph	0,1 to less than 1	Paint or similar materials	Permanent protection outdoors and in highly corrosive environments, in particular when the applied organic coating will be subjected to flexural stress	Automobile and truck bodies, sheet and strip which are to be shaped after coating
Zinc	Znph	0,1 to 2			

Table 3: Mass per unit area of zinc phosphate coatings used to facilitate cold forming

Application	Preferred mass per unit area, in g/m ²
Drawing of steel wire	1 to 10
Drawing of welded steel tubes	1 to 10
Drawing of precision steel tubes	4 to 10
Cold extrusion	Over 10
Deep drawing without wall thickness reduction	1 to 5
Deep drawing with wall thickness reduction	4 to 10

6.2 Coatings applied to facilitate cold forming

Zinc phosphate coatings are often used to facilitate cold forming. Table 3 gives values for the preferred mass per unit area for various applications. It is recommended that the coatings be neutralized using a slightly alkaline solution after rinsing.

Suitable lubricants shall be used during the forming process.

6.3 Coatings applied to reduce friction

Used in conjunction with suitable lubricants, phosphate coatings can help reduce friction and narrow the coefficient of friction range.

In this case, coatings are to be selected according to their type (manganese phosphate and zinc phosphate coatings are preferred for this purpose), thickness (i.e. mass per unit area), structure and the lubricant used. The mass per unit area is to be selected as a function of the dimensional tolerances specified for the coated components (see table 4).

Table 4: Mass per unit area of phosphate coatings used to reduce friction

Application	Preferred mass per unit area, in g/m ²
Components with small clearance fits (pistons of refrigerator compressors, or threaded components)	1 to 3
Components with large clearance fits (gearwheels, ring gears, pinions of gearboxes and differentials)	5 to 20

6.4 Coatings for electrical insulation

Zinc phosphate coatings are preferably used for electrical insulation purposes. The mass per unit area shall be a function of the required surface resistivity; at an electrode contact pressure of 100 N/cm² this can be between 10² and 10⁴ Ωcm².

7 Testing

7.1 Appearance

The coating structure, colour and homogeneity of the coating shall be visually examined.

When coatings are examined with the naked eye or with a magnifying glass with X6 magnification, a crystalline structure is visible in most zinc phosphate and manganese phosphate coatings. However, the very fine crystalline structure of zinc phosphate, manganese phosphate and zinc calcium phosphate coatings is not detectable by this procedure. As iron phosphate coatings do not exhibit a crystalline structure, they can only be identified by their iridescent colour (e.g. yellowish to bluish-grey). Zinc phosphate and zinc calcium phosphate coatings shall be light grey to dark grey, and manganese phosphate coatings shall be dark grey.

Zinc phosphate, zinc calcium phosphate and manganese phosphate coatings shall appear to cover the substrate uniformly, and shall not exhibit any white patches, corrosion products or fingerprints. Slight fluctuations in the appearance of phosphate coatings, which may be caused by variations in the substrate structure, by contact with supports or with other components while in the phosphating drum are permitted.

7.2 Chemical composition of coating

In addition to the methods specified in this standard, other analytical methods with at least the same precision may be used.

The detection of phosphate in a coating shall be taken as proof that it is a phosphate coating.

To establish that a coating is a manganese phosphate coating, it is sufficient to establish the presence of manganese (for ferrous substrates only).

To establish that a coating is a zinc phosphate or a zinc calcium phosphate coating, it is sufficient to establish the presence of zinc or zinc and calcium, respectively (for zinc-free substrates).

If neither manganese nor zinc has been detected in a phosphate coating on a substrate of ferrous material, then the coating is certain to be an iron phosphate coating.

7.2.1 Reagents

Unless otherwise specified, only distilled or double-distilled water shall be used to prepare the solutions.

The following reagents, of analytical grade, shall be used.

- a) **5 % sodium hydroxide solution**, NaOH.
- b) **40 % nitric acid solution**, HNO₃, prepared by mixing one part by volume of nitric acid with a density of 1,4 g/cm³ and one part by volume of water, for example.
- c) **Ammonium molybdate solution**, prepared by dissolving 88,3 g of ammonium heptamolybdate tetrahydrate, (NH₄)₆Mo₇O₂₄ · 4 H₂O, 30 ml of 25 % ammonia solution, NH₃, and 240 g of ammonium nitrate, NH₄NO₃, in water and making up to 1 litre.
- d) **25 % hydrochloric acid solution**, HCl.

- e) **5 % potassium hexacyanoferrate (II) solution**, $K_4[Fe(CN)_6]$.
- f) **17 % nitric acid solution**, HNO_3 , prepared by mixing one part by volume of nitric acid with a density of $1,4 \text{ g/cm}^3$ and four parts by volume of water, for example.
- g) **3 % hydrogen peroxide solution**, H_2O_2 .
- h) **Bismuth sodium trioxide**, $NaBiO_3$.
- i) **Ammonium nitrate**, NH_4NO_3 .
- j) **12 % aqueous ammonia solution**, NH_3 , prepared by mixing one part by volume of concentrated ammonia solution containing 25 % of NH_3 with two parts by volume of water, for example.
- k) **Ammonium oxalate**, $(NH_4)_2C_2O_4 \cdot H_2O$.
- l) **Ammonium chloride**, NH_4Cl .
- m) **10 % hydrochloric acid solution**, HCl , prepared by mixing one part by volume of hydrochloric acid with a density of $1,19 \text{ g/cm}^3$ and three parts by volume of water, for example.
- n) **45 % sulfuric acid solution**, H_2SO_4 , prepared by mixing one part by volume of sulfuric acid with a density of $1,84 \text{ g/cm}^3$ and two parts by volume of water, for example.
- o) **5 % potassium permanganate solution**, $KMnO_4$.

7.2.2 Testing for the presence of phosphate

To test for the presence of phosphate in the coating, treat a coated test piece having a surface area of about 100 cm^2 with 100 ml of a 5 % sodium hydroxide solution at 80 to 90 °C until either the coating has been stripped or it has at least been noticeably attacked. If necessary, scrub the coating off with a rubber wiper. Filter the resulting solution and acidify 25 ml of the filtrate with 40 % nitric acid. Add 10 ml of the ammonium molybdate solution and 5 g of ammonium nitrate to the acidified filtrate, and leave the mixture to stand for at least 15 minutes. A yellow precipitate indicates the presence of phosphate.

7.2.3 Testing for the presence of manganese

To test for the presence of manganese, dissolve the filter residue obtained as described in subclause 7.2.2 with warm 17 % nitric acid, to which a few drops of 3 % hydrogen peroxide have been added. To decompose the excess hydrogen peroxide, boil the resulting solution for a few minutes and then cool it to ambient temperature. Using half of the solution, test for manganese by adding 0,5 g of bismuth sodium trioxide, thus oxidizing any manganese present to permanganate; a reddish violet colour indicates the presence of manganese.

Use the other half of the solution to test for the presence of calcium as described in subclause 7.2.5, if necessary.

7.2.4 Testing for the presence of zinc

To test for the presence of zinc (only for coatings on zinc-free substrates), use 25 % hydrochloric acid to slightly acidify 25 ml of the filtrate obtained as described in subclause 7.2.2, and then add 5 ml of 5 % potassium hexacyanoferrate (II) solution. A white precipitate, which may have a slight green tinge due to the presence of a small amount of iron, indicates the presence of zinc.

7.2.5 Testing for the presence of calcium

To test for the presence of calcium, take 5 ml of the alkaline filtrate obtained as described in subclause 7.2.2 and combine it with the remaining half of the solution obtained as described in subclause 7.2.3. Prepare a clear solution by adding a few drops of 17 % nitric acid and then buffering it to a pH value between 2 and 3 by adding a few drops of 10 % ammonia solution (check the pH with special indicator paper, e.g. ion-specific indicator paper). After heating the solution to about 80 °C, dissolve into it 1 g of solid ammonium oxalate, thus changing the pH of the solution to between 5 and 6 (check again with indicator paper). If necessary, adjust the pH to the desired level by adding solid ammonium chloride.

If calcium is present, a fine white crystalline precipitate of calcium oxalate forms when the solution is heated to 80 °C. Filter off this precipitate after about 10 minutes of heating, rinse it with hot distilled water to which some ammonium oxalate (2 g/l) has been added, and then purify it by reprecipitation as follows: Redissolve the precipitate on the filter in hot 10 % hydrochloric acid, heat the resulting solution to 80 °C, adjusting it to a pH value of between 5 and 6 by adding 10 % ammonia solution; the calcium then reprecipitates as fine crystalline calcium oxalate. Filter this off after 10 minutes of heating and rinse thoroughly with hot distilled water.

To identify the purified white precipitate as calcium oxalate, remove it from the filter by spraying with hot distilled water, and then add about 50 ml of distilled water. Add 5 ml of 45 % sulfuric acid to dissolve the precipitate and treat it at about 80 °C by adding some drops of 5 % potassium permanganate solution. Decoloration of the permanganate solution identifies the precipitate as calcium oxalate, thus indicating the presence of calcium in the coating.

7.3 Determining mass per unit area

The mass per unit area of phosphate coatings is to be determined by dissolving the coating off a surface with a known area and then using one of the two methods specified below to measure the quantity of dissolved coating.

7.3.1 Differential weighing (gravimetric method)

For procedure, see DIN EN ISO 3892. Suitable solvents and dissolving conditions are given in table 5.

Table 5: Conditions for dissolving phosphate coatings (gravimetric method)

Substrate material	Type of phosphate coating	Solvent constituents, as percentages by mass	Dissolving temperature, in °C	Dissolving time, in minutes	Amount of substrate or coating removed, in g/m ² every 10 minutes
Iron	Znph, ZnCaph, and Fe-ph	4% triethanolamine, 12% Na ₄ EDTA ²⁾ , 9% NaOH, 75% H ₂ O	70	5	About 0,1
	Znph and Mnph	5%, 95% H ₂ O	70	15	Less than 0,05
Aluminium	Znph	65% HNO ₃ , 35% H ₂ O	25	15	For Al 99: about 0,02 For AlCuMg: about 0,08
			75	5	For Al 99: about 0,02 For AlCuMg: about 0,08
Zinc	Znph	2,2% (NH ₄) ₂ Cr ₂ O ₇ , 27,4% NH ₃ , 70,4% H ₂ O	25	5	For Zn 98,5: less than 0,01
	Znph and ZnCaph	5% CrO ₃ , 95% H ₂ O	25	5	For Zn 98,5: about 0,05
Cadmium	Znph	4% triethanolamine, 12% Na ₄ EDTA ²⁾ , 9% NaOH, 75% H ₂ O	70	5	About 0,1

²⁾ Ethylenediaminetetraacetic acid.

7.3.2 Back-titration method

7.3.2.1 Principle

The phosphate coating is dissolved off the substrate using a hot sodium hydroxide solution. The PO₄³⁻ ions present are then precipitated in the form of yellow ammonium molybdophosphate. The yellow precipitate is filtered off, rinsed and dissolved in a given excess amount of NaOH solution. The excess is titrated back with sulfuric acid, and the quantity of phosphate coating which has dissolved is calculated from the amount of NaOH solution consumed during precipitation. This is reported as the mass per unit area, expressed in g per m² of the coated surface area.

7.3.2.2 Reagents

Unless otherwise specified, only distilled or double-distilled water shall be used to prepare the solutions.

The following reagents, of analytical grade, shall be used.

- 25 % sodium hydroxide solution**, NaOH.
- 40 % nitric acid solution**, prepared by mixing one part by volume of nitric acid of 1,4 g/cm³ density with one part by volume of water, for example.
- 4,5 % nitric acid**, prepared by mixing one part by volume of nitric acid of 1,4 g/cm³ density with 19 parts by volume of water, for example.
- 10 % ammonia solution**, prepared by dissolving NH₃ of 0,957 g/cm³ density in water.
- Ammonium molybdate solution**, prepared by dissolving 80 g of ammonium heptamolybdate tetrahydrate, (NH₄)₆Mo₇O₂₄ · 4 H₂O, in 400 ml of water. In a second container, dilute 415 ml of concentrated nitric acid (of 1,4 g/cm³ density) with 400 ml of water, and mix with 140 ml of concentrated ammonia solution (of 0,91 g/cm³ density). After the two solutions have been cooled to ambient temperature, add the ammonium heptamolybdate solution to the acid solution and make up the mixture to two litres with water.

- f) **Ammonium nitrate**, NH_4NO_3 .
- g) **1 % potassium nitrate solution**, KNO_3 .
- h) **1 mol/l sodium hydroxide solution**.
- i) **1 mol/l sulfuric acid**.
- j) **0,1 % phenolphthalein solution**, prepared by dissolving phenolphthalein in ethanol.

7.3.2.3 Apparatus

The following shall be used for testing.

- a) 50 ml-burettes (e.g. as in DIN 12700-1).
- b) DIN 12680 – ME 100 graduated cylinders.
- c) Wash-bottles.
- d) Dropping bottle.
- e) DIN 12332 – NF 600 beaker.
- f) Funnel.
- g) DIN 53135 – 2b filter paper.

7.3.2.4 Procedure

To dissolve the phosphate coating, immerse coated test pieces having a total surface area of 200 cm² (to be determined as accurately as possible) in a 600 ml beaker containing enough 25 % sodium hydroxide solution to completely cover the test piece (about 100 to 150 ml) for half an hour at 50 to 60 °C. Shake or stir the liquid to ensure that the solution acts uniformly on all parts of the coating. Then, dilute the solution by making up to about 200 ml with distilled water.

To ensure that the coating is thoroughly removed, take the test piece out of the beaker using plastic or chromium-nickel steel pincers, and rinse it over the beaker, first with distilled water, then with 4,5 % nitric acid, and finally once more with distilled water, using wash bottles each time so that the rinse water is added to the main solution. When removing manganese phosphate coatings, it may be necessary to wipe off any residual coating material with a strip of filter paper before the nitric acid rinse, adding the filter paper to the beaker of solution.

Neutralize the solution with 40 % nitric acid, then immediately acidify it by adding a further 20 ml of nitric acid of the same concentration and boiling for fifteen minutes. Make up to a volume of 400 ml by adding distilled water, add 5 to 10 g of solid ammonium nitrate and cool to a temperature of 50 to 60 °C. Remove any turbidity in the solution (e.g. due to undissolved manganese dioxide in the case of manganese phosphate coatings) by filtering the solution. Precipitate the PO_4^{3-} -content as a yellow precipitate of aqueous ammonium molybdatophosphate ($(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$) by slowly adding 100 ml of the ammonium molybdate solution, stirring vigorously. As soon as the yellow precipitate has settled, add the ammonium molybdate solution dropwise to the supernatant clear solution; if the solution does not become turbid, precipitation is complete.

After leaving the solution to stand for at least ten hours (e.g. overnight), filter it through DIN 53135 – 2b filter paper. Rinse both the precipitation vessel and the yellow precipitate remaining on the filter with 1 % potassium nitrate solution and wash them until they are free of acid (check by testing the rinse water and filter edge with indicator paper). Transfer the yellow precipitate and the filter to a beaker, add 150 ml of distilled water and titrate with 1 mol/l sodium hydroxide solution until the yellow precipitate has dissolved completely and an excess of sodium hydroxide is present (consumption, *a*, in ml). After adding a few drops of phenolphthalein solution as an indicator, back titrate the solution in the beaker with 1 mol/l sulfuric acid (consumption, *b*, in ml) until it becomes colourless. The amount of 1 mol/l sodium hydroxide solution consumed by the yellow precipitate of ammonium molybdatophosphate is given by the difference between *a* and *b*, in ml.

Alternative procedure

If test results are required on the same working day (i.e. solution cannot be left to stand overnight for ten hours), the time needed for the procedure can be shortened by reprecipitating the ammonium molybdatophosphate as follows.

As soon as the yellow precipitate has settled, check to see if precipitation is complete using the method described above. Then filter the solution through DIN 53135 – 2b filter paper and rinse the precipitate remaining on the filter with 4,5 % nitric acid. Place a beaker underneath the funnel and filter, and dissolve the precipitate by adding drops of 10 % ammonia solution, using a dropping bottle; collect the resulting solution in a beaker.

When the yellow precipitate has completely dissolved, wash the filter out with distilled water, combining the wash water with the solution in the beaker. Add 12 ml of ammonium molybdate solution, followed by an excess quantity of 40 % nitric acid. Add five more drops of 40 % nitric acid and leave the solution to stand in a warm environment for about fifteen minutes until the precipitate has settled.

Filter the solution again through DIN 53135 – 2b filter paper. Rinse the precipitate and filter with 1 % potassium nitrate solution and wash them until they are free of acid (check by testing the rinse water and filter edge with indicator paper). Transfer the yellow precipitate and the filter to a beaker, add 150 ml of distilled water and titrate and back titrate as described above.

7.3.2.5 Evaluation

Calculate the quantity, m , of the dissolved phosphate coating, in mg, by determining the amount of sodium hydroxide solution needed to dissolve the yellow precipitate (i.e. $a - b$) using the following equation:

$$m = (a - b) \cdot f$$

where f is a conversion factor taken from table 6.

Calculate the mass per unit area of the coating, m_A , expressed in g/m^2 , using the following equation:

$$m_A = \frac{m}{A} \cdot 10$$

where

m is the quantity of dissolved coating, in mg;

A is the surface area tested, in cm^2 .

7.4 Determining coating thickness

Information on the coating thickness is frequently required in practice for characterizing phosphate coatings. Since most thickness measurement methods involve a considerable uncertainty of measurement, the type of information required and measurement method to be used shall be subject to agreement (cf. Explanatory notes).

Depending on the nature of the substrate material, magnetic or electrical methods may be used. Mechanical measurement is suitable for all types of substrate material.

It should be noted that even with so-called non-destructive methods in which a probe touches the coating, the fine crystalline structure of the coating may be damaged as a result of contact pressure, resulting in erroneously low results. For instance, values obtained from magnetic measurement may be more than 50 % lower than the expected value, depending on the pressure exerted by the probe, its design, and the specific structure of the coating in question. This systematic error cannot be eliminated statistically.

As a whole, current probe-based methods of measuring the thickness of phosphate coatings are unsuitable for obtaining precise results.

7.5 Performance testing

7.5.1 Testing the corrosion protection afforded by coatings

Normally, the corrosion protection provided by phosphate coatings is tested by subjecting phosphated and non-phosphated test pieces to a comparative test. In this case, sampling details are to be agreed (i.e. as to whether test pieces are to be the products as delivered, sections cut from the products, or panels of the same material as the products).

If different phosphating methods are compared, reproducibility of the test results is to be ensured by using materials of the same chemical composition and having the same surface finish, and by using the same surface treatment method prior to phosphating.

For comparative testing, test pieces are to be 100 mm x 200 mm DIN EN 605 standard test panels made of steel, hot-dip galvanized steel or aluminium. Panels of electroplated sheet metal shall be about 0,75 mm thick, of special deep-drawing grade 7,5 B, and oiled, as specified in the DVV Code of practice *Charakteristische Merkmale für elektrolytisch verzinktes Feinblech in Tafeln und in Rollen*.

NOTE: This requirement applies until a DIN Standard on electroplated sheet metal is published.

7.5.1.1 Coatings without supplemental coating

Testing shall be by the salt spray test (SS test) as in DIN 50021. Test pieces shall be placed in the spray cabinet while it is in operation, and removed again after the agreed exposure times have elapsed. Table 7 gives the minimum times during which phosphate coatings on ferrous materials without additional coatings may be exposed before the first signs of corrosion appear.

7.5.1.2 Coatings in conjunction with oil, grease or wax coatings

7.5.1.2.1 Application

In most cases, the phosphated test pieces are immersed in an anti-corrosion oil, grease or wax that either complies with relevant standards or that has been agreed upon as being suitable in practice. The supplier's instructions are to be observed. The liquid, semi-solid or waxy film formed on the substrate shall be free of blisters. Before testing, the treated test pieces shall be suspended in a dry, dust-free and draught-free room at an ambient temperature of 18 to 28 °C as in DIN 50014 for at least 24 hours so that excess oil can drip off and any solvents can evaporate.

If test pieces are to be coated with oil, a standard reference oil³⁾ shall be used. To apply the oil, first dry the test pieces at 100 to 120 °C and cool to ambient temperature. Then, suspend them on plastic or insulated steel hooks and immerse them in the oil at (25 ± 2) °C for one minute. Agitate them gently for 30 seconds and then remove. A closed oil film which is free of air bubbles should have been formed on the phosphate coating. Suspend test pieces to dry in a dry, dust-free and draught-free room at an ambient temperature of 18 to 28 °C (not exceeding 25 °C, where possible) for at least 24 hours before testing.

Table 6: Conversion factors (for determining mass per unit area)

Substance tested for	P ₂ O ₅	Zinc phosphate Zn ₃ (PO ₄) ₂ · 4 H ₂ O	Zinc calcium phosphate Zn ₂ Ca(PO ₄) ₂ · H ₂ O	Manganese sulfate (MnFe) ₅ H ₂ (PO ₄) ₄ · 4 H ₂ O
Conversion factor, <i>f</i> , in mg/ml	3,086	9,96	8,62	10,96
A conversion factor cannot be given for iron phosphate coatings as their composition may vary too greatly.				

Table 7: Minimum exposure times for phosphate coatings on ferrous materials without supplemental coating

Type of phosphate coating	Zinc phosphate	Manganese phosphate
Symbol	Znph	Mnph
Mass per unit area, in g/m ²	Over 10	Over 16
Minimum exposure time, in hours	2	1,5

Table 8: Minimum exposure times for phosphate coatings on test panels coated with standard reference oil

Type of phosphate coating	Zinc phosphate	Zinc phosphate	Zinc calcium phosphate	Manganese phosphate
Symbol	Znph	Znph	ZnCaph	Mnph
Mass per unit area, in g/m ²	5 to 10	Over 10	5 to 15	Over 16
Minimum exposure time, in hours	24	48	24	36

7.5.1.2.2 Testing and evaluation

Testing shall be by the salt spray test (SS test) as in DIN 50021.

Test pieces shall be removed from the spray cabinet at regular intervals and visually assessed for any apparent corrosion (interim checks). It may be agreed that the agent (oil, grease or wax) be removed before visual examination.

The exposure times up to the appearance of the first signs of corrosion vary widely for the same type of coating (cf. Explanatory notes), depending on the composition of the agent and its mass per unit area. Therefore, the minimum exposure time given for phosphate coatings provided with supplementary coatings shall always refer to the particular agent used and its known mass per unit area (in g/m²).

Table 8 gives the minimum times during which phosphate coatings that have been coated with standard reference oil may be exposed before the first signs of corrosion appear.

7.5.1.3 Coatings in conjunction with paints or similar materials

7.5.1.3.1 Application

Additional coatings of paints or similar materials (including plastic film) shall be applied to test pieces in accordance with the relevant standards or any special agreements made regarding the type of coating material and technique used, and the number and thickness of individual layers.

Testing shall not begin until at least 48 hours after the end of the drying time specified by the manufacturer of the material used for the final coat.

7.5.1.3.2 Testing and evaluation

The corrosion protection of phosphate coatings in conjunction with paints or similar materials shall be established either by salt spray testing as in DIN 50021 or by testing in an artificial atmosphere as in DIN 50017 (cf. Explanatory notes).

³⁾ Information on sources of supply is obtainable from: *DIN-Bezugsquellenverzeichnis für normgerechte Erzeugnisse im DIN*, Burggrafenstraße 6, D-10787 Berlin.

Salt spray testing

DIN 50021 specifies the test temperature, the concentration, pH value and amount of the sodium chloride solution to be sprayed, and the arrangement of the test pieces in the spray cabinet.

Unless otherwise agreed, DIN 53167 applies with regard to test piece preparation, the test procedure and evaluation.

The exposure times and the intervals between interim checks shall be subject to agreement unless otherwise specified in a relevant standard.

The following shall be assessed as a function of the exposure time:

- a) the extent of changes to the coating occurring near the scratches, including any disbonding or blistering;
- b) changes occurring elsewhere on the surface, such as blistering (to be assessed as specified in DIN 53209) or corrosion (to be assessed in accordance with DIN 53210).

Testing in an artificial atmosphere

The coated test pieces are to be exposed to a constant moisture condensation water atmosphere as in DIN 50017 (KK test).

The exposure times and the intervals between interim assessments shall be subject to agreement unless otherwise specified in a relevant standard.

The following shall be assessed as a function of the exposure time:

- a) the degree of blistering, assessed as described in DIN 53209, including any ring- or chain-like blister patterns or any indication of the presence of fingerprints;
- b) the degree of corrosion, assessed as specified in DIN 53210.

It may be stipulated by separate agreement that a scratch test as specified in DIN 53167 (or elsewhere) be performed, in which case the extent of the disbonding occurring near the scratches shall be assessed in accordance with DIN 53167.

7.5.2 Testing the suitability of coatings to facilitate cold forming

Testing the suitability of phosphate coatings to facilitate cold forming requires an extremely accurate simulation of in-service conditions, which can vary widely. For this reason, no test method is specified here.

7.5.3 Testing the suitability of coatings to reduce friction

Testing the suitability of phosphate coatings to reduce friction requires an extremely accurate simulation of in-service conditions, which can vary widely. For this reason, no test method is specified here.

7.5.4 Testing the suitability of coatings for electrical insulation

To test the suitability of phosphate coatings for electrical insulation purposes, the surface resistivity is to be determined.

8 Test report

The test report shall include a reference to this standard and any other relevant standards and shall provide the following information:

- a) type and designation of phosphated materials;
- b) type and designation of the phosphate coating produced, phosphating method used (designation as in DIN 50960-1), and mass per unit area determined as specified in subclause 7.3;
- c) coating thickness, in μm , and method of measurement used (cf. subclause 7.4), if so agreed;
- d) intended function of the phosphate coating;
- e) type of supplemental coating (designation as in DIN 50960-1), where applicable;
- f) in the case of coatings of oil, grease or wax: type and mass per unit area of agent used, in g/m^2 ;
- g) in the case of supplemental coatings of paint or similar materials:
 - 1) type and description of coating material(s);
 - 2) number and thickness of coating layer(s);
 - 3) application method, including drying method, time and temperature;
- h) In the case of salt spraying or artificial atmosphere testing:
 - 1) exposure time;
 - 2) intervals between interim checks;
 - 3) length of disbonded zone at scratches, w_d , in mm, or w_t , in mm^2 , assessed as in DIN 53167;
 - 4) degree of corrosion, rated as in DIN 53210;
 - 5) degree of blistering, rated as in DIN 53209, including any ring- or chain-like blister patterns or any indication of the presence of fingerprints.

Where specified values of mass per unit area or a specific degree of corrosion protection is the subject of standard or special agreements, these values shall be given as reference values against which the actual values determined in the test are compared.

Explanatory notes

Re subclause 4.3

Hydrogen embrittlement (also called 'hydrogen-induced cracking' or 'hydrogen stress cracking') is the brittle fracture of metals or alloys due to the combination of absorbed atomic hydrogen and tensile stress. Hydrogen can be absorbed during the pickling and phosphating of steel or during corrosion reactions. Susceptibility to hydrogen embrittlement rises with increasing steel strength [1].

Re clause 6

In keeping with international standards practice with regard to coatings produced by chemical methods on metal, this standard uses the mass per unit area, expressed in g/m^2 , rather than thickness as a means of characterizing phosphate coatings.

Re subclause 7.3

The mass per unit area of phosphate coatings is a measure of the amount of coating present on the metal substrate. Determining the mass per unit area by means of dissolving methods gives values which are not affected by the actual structure of the coatings or the roughness of the substrate.

Re subclause 7.3.1

The gravimetric method specified in DIN EN ISO 3892 may be used for determining the mass per unit area of coatings on test pieces that can be weighed to the nearest 0,1 mg, provided that the mass of the dissolved coating is not too small compared with that of the test piece. This method is therefore particularly suitable for sheet metal and sheet metal sections, and hollow cylindrical objects. It is less suitable for thick-walled or very heavy objects.

Subclause 7.3.2

The back-titration method of determining mass per unit area specified here is universally applicable, and is particularly suitable for phosphate coatings on wires, nuts, bolts and other small parts. Only this method can be used for plate and similar components which, owing to their excessive mass, cannot be weighed with sufficient accuracy.

Subclause 7.4

The magnetic method of measuring the thickness of non-ferromagnetic coatings on ferromagnetic substrates as specified in DIN EN ISO 2178 is one of the most common methods of coating thickness measurement.

As stated in DIN EN ISO 2178, the uncertainty of measurement using this method is reported to be about $\pm 10\%$ at a confidence level of 95 % for coatings with a thickness greater than $5\ \mu\text{m}$, and an uncertainty of $\pm 1\ \mu\text{m}$ for coatings less than $5\ \mu\text{m}$ thick; the latter uncertainty is considered too great to allow a satisfactory characterization of extremely thin coatings.

In the case of phosphate coatings, an uncertainty of $\pm 10\%$ when measuring coatings more than $5\ \mu\text{m}$ thick is unfortunately unrealistic due to the special structure of phosphate coatings, which consist of aggregates of very small crystallites. In fact, there is no truly non-destructive means of measuring phosphate coatings using probes, since the corners and edges of the crystallites are broken off or forced inwards by the pressure exerted upon contact; for more information on this topic, see [2].

Reducing the risk of surface damage improves the reproducibility of contact methods of measuring coating thickness. For instance, it is important to use only probes with tips of sufficiently large radius. In all cases, probes should be slowly and steadily lowered at a right angle to the surface with as little contact pressure as possible, taking care to avoid any scratching or thrusting movements.

The coating thickness serves to determine the mass per unit area as a function of apparent density, as discussed below.

All phosphate coatings are porous, with the degree of porosity depending on a large number of factors. This varying porosity results in varying values of apparent density. Whereas the density of the mineral phases which form the coatings lies within a range between $3,0$ and $3,2\ \text{g/cm}^3$, the coating's apparent density can never reach this value because of its porosity.

In addition, all phosphate coatings are rough to a certain degree, due to a number of factors. This varying roughness means that the surfaces of the coatings are damaged when probes are placed on them.

Allowing for the fluctuations in porosity and roughness, apparent density values of $2\ \text{g/cm}^3 \pm 50\%$ are obtained when converting the measured coating thickness into mass per unit area, based on the following relationship: coating thickness (in μm) \times apparent density (in g/cm^3) = mass per unit area (in g/m^2).

Using this formula, the following values of mass per unit area have been calculated for phosphate coatings as a function of the measured coating thickness (see table 9).

Table 9: Mass per unit area of phosphate coatings as a function of coating thickness

Measured coating thickness, in μm	Mass per unit area, in g/cm^2
5	5 to 15
10	10 to 30
15	15 to 45

Factors determining the roughness and porosity of phosphate coatings include:

- composition, crystalline structure, roughness and chemical reactivity of the substrate;
- type of pretreatment prior to phosphating, such as blasting, grinding, cleaning, pickling or rinsing;
- phosphating method used (e.g. bath composition and temperature, duration of treatment, type of treatment such as dipping, spraying, etc.).

A greater number of constant factors ensures fewer fluctuations in apparent density. For this reason, it is frequently possible to measure the thickness of phosphate coatings with sufficient accuracy rather than determining the mass per unit area (e.g. for in-process testing). The values for apparent density used in the conversion of thickness into mass per unit area should always be determined separately and be subject to agreement.

Re subclause 7.5.1.2

Anti-corrosion oil, grease or wax are often used to increase the corrosion protection of phosphate coatings. Some of these agents are used undiluted, some as an aqueous emulsion, whilst others are diluted with organic solvents. Some produce oily films of varying viscosity, and others leave greasy films or non-slip films.

Because the type of anti-corrosion agent used varies so widely, salt spray test exposure times may range from 24 hours to over 1 000 hours, depending on the type of coating and its mass per unit area, and the nature, composition and mass per unit area of the anti-corrosion agent.

Re subclause 7.5.1.3

Applying additional coatings of paints or similar materials to phosphate coatings provides effective long-term protection, even against fairly severe corrosion.

Owing to the diversity of the intended applications of phosphated components provided with additional coatings, definite exposure times cannot be specified for the salt spray or artificial atmosphere tests. Unless otherwise specified, these times shall be subject to agreement on a case-by-case basis.

Re subclause 7.5.1.3.2

The salt spray test serves to determine the ability of phosphate coatings to prevent any corrosion resulting from scratches in the coating (e.g. disbonding or blistering), as well as the overall corrosion protection afforded by the entire phosphate-paint coating system in severe conditions (i.e. saltwater).

With the artificial atmosphere test, it can be established whether phosphating, including all rinse cycles, has been carried out with care so that the phosphated surfaces are free of harmful water-soluble substances. During the moisture condensation test, residues of such substances cause blisters to form in the coating within a relatively short time. The same applies to fingermarks left on the phosphate coatings; these can manifest themselves clearly after as few as 24 hours' testing, usually in the form of blister chains.

By contrast, the protection afforded by properly applied coating systems usually deteriorates much later. This deterioration is detectable by the formation of large or small blisters, which are not locally confined in the forms of rings or chains, and/or by the deposition of corrosion products on the substrate, some of which penetrate the paint.

Bibliography

[1] *Vermeidung einer Wasserstoffversprödung galvanisierter Bauteile* (Preventing hydrogen embrittlement in electroplated products), issued by the *Deutsche Gesellschaft für Galvanotechnik*, Kreuzstraße 34, D-40210 Düsseldorf.

[2] Kaysser, F. *Über die Kennzeichnung der Auflagestärken von Phosphatschichten durch Angabe der Flächengewichte und der Schichtdicken* (Determining the thickness of phosphate coatings on the basis of mass per unit area and coating thickness), *Galvanotechnik*, 1972: 63(1), 11-23.