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Adhesives — Guidelines for the surface preparation of metals

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 4588 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 11, *Products*.

This second edition cancels and replaces the first edition (ISO 4588:1989), which has been technically revised.

Adhesives — Guidelines for the surface preparation of metals

1 Scope

This International Standard describes the usual procedures for the laboratory preparation of metal surfaces for adhesive bonding and testing of the bond. Prebonding surface treatments are given for the following materials:

- a) aluminium and aluminium alloys;
- b) chromium;
- c) copper and nickel and their alloys;
- d) magnesium and magnesium alloys;
- e) steel (mild);
- f) steel (stainless);
- g) tin;
- h) zinc and zinc alloys.

Mechanical treatments such as grit blasting are widely applicable, but it is not possible to present one chemical method that is applicable to all metals. Several methods are listed so that the user will have a greater choice in selecting a treatment appropriate to a particular metal.

The surface treatments described comprise degreasing and cleaning methods, mechanical cleaning (abrasion), chemical cleaning (etching) and chemically based surface modification techniques. When used together, these treatments should normally be used in the following order: cleaning to remove gross contamination, then abrasion and finally etching to achieve the optimum surface for bonding. Alternative sequences may, however, be used, especially when the surface is to be chemically modified. In such

cases, the sequence used shall be clearly described in the test report.

WARNING — The procedures described do not necessarily detail all the precautions necessary for health and safety in a particular country. Because of the hazardous nature of some of the chemicals used, national and local legislative requirements for safe handling and disposal of these materials shall be observed. Refer to the material safety data sheet prior to use for details of the hazard and the personal-protection equipment to be used. (See also clause 7.)

2 Handling and storage

2.1 Handling

All parts shall be handled as little as possible during and after processing and before bonding, and the use of bare hands shall be avoided. Use clean hand coverings that will not contaminate the surface, such as lint-free cotton and nylon fabric gloves, and handle parts by edges or non-treated areas.

2.2 Storage conditions

2.2.1 In the laboratory

Prepared surfaces shall be stored at $23\text{ °C} \pm 2\text{ °C}$ and $(50 \pm 5)\%$ relative humidity, except for metals such as carbon steels which cannot sustain these conditions without prejudicial oxidation. If necessary, the air shall be filtered to remove dust.

The time between, and conditions of, surface preparation and bonding are critical. For sensitive surfaces, the storage time shall not exceed 8 h and parts shall be covered with or wrapped in unbleached kraft paper or other suitable coverings. When possible, prepared

surfaces shall be stored in a conditioned container without surface contact.

2.2.2 At industrial production facilities

Economic and practical considerations may prevent production facilities from following laboratory practice. Nonetheless, the possibility of re-contamination must be borne in mind and its consequences taken into account.

3 Initial preparation

3.1 Cleanliness

Do not carry out contaminating operations in the work area. Painting or other spraying operations, processes using powder materials, the presence of oil vapours from pumps and other machinery, the spraying of mould release agents, etc., are especially detrimental.

3.2 Preliminary cleaning

Remove ink markings or printed identifications from the metals by wiping with a cloth wetted with an appropriate solvent such as acetone, methyl ethyl ketone (butan-2-one) or a permitted hydrocarbon mixture.

3.3 Degreasing

NOTE 1 Solvent degreasing was included as a standard method in the previous edition of this International Standard. For health and safety as well as environmental reasons, however, this method is no longer recommended. An alternative method such as alkaline degreasing should prove to be equally satisfactory.

3.3.1 Detergent degreasing

Scrub the joint surfaces in a solution of liquid detergent. Wash with clean, hot water and allow to dry thoroughly — preferably in a stream of hot air from e.g. a domestic forced-air heater.

NOTE 2 Non-ionic detergents generally give good results.

3.3.2 Alkaline degreasing

Alkaline degreasing is an alternative to detergent degreasing.

The ingredients are selected from sodium or potassium hydroxide, carbonates, phosphates, borates, complexing agents (such as EDTA, gluconates,

heptonates, polyphosphates and cyanides) and organic surfactants. They may be used hot or cold, with or without an applied current which may be either anodic or cathodic. The joint surfaces shall be washed very thoroughly, possibly followed by neutralization to remove any residual traces of the alkaline cleaner.

NOTE 3 The cleaning action is based on the saponifying and emulsifying properties of aqueous alkalis, which are often reinforced by sequestering, complexing and surface-active agents. It is also effective in removing soaps and salts.

3.3.2.1 Strongly alkaline cleaners

These cleaners may contain any of the ingredients given in 3.3.2 above. Heavy-duty types may contain a high proportion of caustic alkali.

Strongly alkaline cleaners shall be used as soak cleaners or used electrolytically, preferably anodically, and are suitable for use on all metals except aluminium, lead, tin and zinc, each of which is attacked by strong alkalis. Simultaneous cleaning and etching of aluminium in caustic soda or other alkaline solutions may be employed only when agreed between the various suppliers (of the metal, the cleaning agent, the adhesive, etc.) and shall be strictly controlled.

NOTE 4 Metallic soaps can be removed by strongly alkaline cleaners.

3.3.2.2 Mild alkaline cleaners

Mild alkaline cleaners shall be used as soak or spray cleaners.

They are suitable for all metals. They are essentially free from strong alkali and may contain inhibitors such as silicates to prevent the metal being attacked.

Applied current may be used in immersion applications, but is less effective than with strongly alkaline cleaners.

3.3.3 Ultrasonic degreasing

This treatment may be employed when appropriate and is generally used for the preparation of small specimens.

4 Abrasion

Abrasion may be used as the principal surface treatment, or prior to etching, to remove oxide and to roughen the surface.

4.1 Preliminary treatment

Degrease the surface using one of the procedures described in clause 3 to remove gross oily contamination.

4.2 Dry-blasting method

4.2.1 Dry-blast with an appropriate abrasive such as clean, dry, sharp-edged alumina, silicon carbide, sand or similar abrasive of particle size 106 µm to 45 µm. Do not use steel shot or steel-contaminated abrasive to blast-clean aluminium, copper or stainless steel. The blasted surface shall be visually uniform. The air used for blasting shall be clean, degreased and dry.

4.2.2 Blow-clean parts with clean, dry, filtered air or nitrogen to remove particulate matter. Alternatively, use a degreasing method.

4.3 Wet-blasting method

Wet-blast with water or steam containing suspended grit particles of mesh size 1 000 or smaller. The angle of the water or steam jet shall be 90°

NOTE 5 This can be very effective and does not warp the parts if done carefully. Wet-blasting is recommended for small items only.

Wet-blasting equipment usually contains flow modifiers and corrosion-resistance additives. Rinse the wet-blasted parts thoroughly in water and clean solvent, or vapour-degrease, prior to drying and bonding.

4.4 Hand-abrasion method

4.4.1 Abrade the surface to be bonded with abrasive paper or cloth, using alumina, silicon carbide, emery or other suitable material of particle size 106 µm to 45 µm. This abrasion may be carried out wet or dry.

Use the following sequence of abrasive operations:

- a) straight across the part in a direction parallel to any one side;
- b) at right angles to the first direction until all signs of the first abrasion operation have been removed;
- c) circular motion of diameter approximately 80 mm to 100 mm, until a pattern has been produced consisting only of circular abrasion marks superimposed one upon the other and the surface appears visually uniform.

4.4.2 Blow-clean parts with clean, dry, filtered air or nitrogen, or brush with a clean, dry brush, to remove particulate matter.

If wet abrasion is used, wipe the surface with a cloth dampened with an appropriate solvent, or wipe with a clean, dry cloth.

4.5 Silination method

This is a derivative of abrasive blasting. There are two variants, both using proprietary materials after general cleaning and pre-blasting.

4.5.1 Silane-coated corundum

Following initial treatment, the surface is blasted with silane-coated corundum grit. The surface may subsequently be treated with a suitable primer prior to bonding.

4.5.2 Flame treatment

Following initial preparation, the surface is subjected to the action of a flame generated by the combustion of proprietary materials.

4.6 Wet-abrasion method

Surfaces are abraded as in 4.4.1 but in the presence of proprietary solutions which modify the surface by reacting with it during the course of abrasion. The reaction usually involves a silane coupling agent which has the ability to react chemically with both the metal surface and the adhesive.

Some proprietary solutions will also indicate whether or not the surface has been cleaned sufficiently to ensure that the subsequent bonding process will be satisfactory. (See 5.2.4.)

5 Etching

5.1 General

Etching may be preceded by abrasion (see clause 4) and/or by a chemical deoxidizing treatment.

5.2 Apparatus, materials and procedures

5.2.1 Apparatus

All vessels and other equipment shall be resistant to the etching solutions used.

5.2.2 Water

Water for preparing etching solutions, such as distilled water or demineralized water, shall not contain more than 50 mg/kg of solids and shall have a pH between 5,5 and 7,5 and a conductance of less than 20 μ S.

5.2.3 Monitoring of etching solutions

The useful life of the solutions depends upon the number of parts being treated and their dimensions. The solutions shall be sampled periodically and analysed for materials pertinent to the particular treatment, such as hexavalent chromium (CrO_3), iron, chlorides or aluminium. Compliance with the purity specifications shall be established for each batch and each vessel containing solution.

Records shall be kept indicating the date of preparation of each solution, any change in concentration with time, and the amounts of contaminants present.

The solutions may be made up from technical- or reagent-grade chemicals and, unless otherwise specified, with water as specified in 5.2.2. Except for water, all constituents shall be weighed to within ± 1 %.

5.2.4 Rinsing

Rinsing may be done by spraying or by dipping in a tank of water (5.2.2) which is circulated round an overflow circuit so that it is constantly renewed.

Rinsing shall be sufficiently long and vigorous to ensure the removal of all traces of chemicals, dirt or other particulate matter. Wiping with a clean cloth or brushing with a brush shall be avoided if possible. Any temperature limit specified for the rinsing water shall be respected.

After rinsing, the water-break test is commonly used to determine whether the surface of the metal is clean. The surface under test is completely immersed in water and then withdrawn; if the water film is continuous and does not break up into droplets within 30 s, then the surface may be assumed to be free of contamination.

If the water film is discontinuous, this indicates that the cleaning treatment was unsatisfactory, and it shall therefore be repeated. The number of times that cleaning may be repeated depends on the amount of

metal removed in relation to the tolerance requirements for the part and whether coated or bare metal is involved. Generally, not more than two repeat treatments are permitted.

NOTE 6 Even if the cleaned metal surface is wetted by water, this gives no information as to the likely strength of an adhesive bond made with the metal surface. At best, it is a necessary, but not a sufficient, requirement for the achievement of high bond strength.

A variant of the water-break test is the use of proprietary materials which, because of their specific surface tension, indicate whether or not the surface is sufficiently clean for the subsequent bonding process. Such materials may also contain silane coupling agents which modify the surface. (See also 4.6.)

6 Procedures to be used for specific metals

WARNING — Some of the procedures given hereafter involve the use of chromates. Great care should be taken in handling such compounds (see also clause 7).

6.1 Aluminium and aluminium alloys

6.1.1 Anodized material

Chromic-acid-anodized or phosphoric-acid-anodized material has the best surface properties for bonding directly after completion of the anodizing process. The material must be bonded within a few hours of anodizing. Aluminium alloy anodized by the normal chromic acid or sulfuric acid methods may be bonded after degreasing and light abrasion.

Hard-anodized aluminium alloy requires stripping either by abrasive blasting or by etching in the sulfuric acid/sodium dichromate (or chromium trioxide) solution specified in 6.1.2.1.

NOTE 7 The unstripped material is unsuitable for bonding.

6.1.2 Non-anodized material

Degrease in accordance with clause 3. Then either abrade in accordance with clause 4 or etch in a sulfuric acid/sodium dichromate solution, and/or use a primer, or etch in a sulfuric acid/hydrofluoric acid solution.

6.1.2.1 In the case of etching with sulfuric acid/sodium dichromate, use a solution of the following composition:

Water	30 parts by mass
Concentrated sulfuric acid ($\rho \approx 1,84$ g/ml)	10 parts by mass
Sodium dichromate	2 parts by mass

Immerse for 10 min at 65 °C to 71 °C, rinse with clean, cold running water, air-dry for 15 min, and dry with hot air for 10 min at 62 °C to 68 °C.

NOTE 8 Proprietary chromium-based oxidizing agents may also be used (see clause 7).

6.1.2.2 The use of proprietary coupling agents (see 4.6) is an alternative to chemical pretreatment for aluminium and aluminium alloys. In some cases, treatment with coupling agents is carried out in addition to etching, the coupling-agent treatment following the etching procedure.

Resin-based coating primers may also be used as a supplement to any of the methods given in clause 4. However, in all cases the user shall ensure compatibility between the proprietary materials, the metal surfaces and the adhesive.

6.1.2.3 An aqueous solution of the following composition is used for pickling degreased aluminium alloys:

Concentrated sulfuric acid ($\rho \approx 1,84$ g/ml)	100 ml/l
Hydrofluoric acid [40 % (m/m)]	15 ml/l

Immerse parts in the above solution at a temperature not exceeding 50 °C until clean. Rinse in cold water and transfer to a cleaning solution such as a cold aqueous solution containing approximately 500 ml of concentrated nitric acid ($\rho \approx 1,42$ g/ml) per litre for approximately 1 min and then wash thoroughly in clean water at a temperature not exceeding 50 °C.

WARNING — Great care should be taken in handling hydrofluoric acid. It is essential that the manufacturer's instructions be followed to the letter as burns due to contact with the acid may be apparent only after several hours.

6.2 Chromium

Degrease in accordance with clause 3. Then either abrade in accordance with clause 4 or etch in a solution of the following composition:

Water	5 litres
Concentrated hydrochloric acid ($\rho \approx 1,18$ g/ml)	4,25 litres

Immerse for 1 min to 5 min at 90 °C to 95 °C, wash with clean, cold running water, followed by clean, hot water, and dry with hot air.

WARNING — Concentrated hydrochloric acid is highly corrosive. Particular care is needed when handling this acid (see clause 7).

6.3 Copper and nickel

6.3.1 Nitric acid

Degrease in accordance with clause 3. Then either abrade in accordance with clause 4 or etch at room temperature in nitric acid as specified in table 1.

Table 1 — Conditions for etching in nitric acid

Material	Copper and copper alloys	Nickel and nickel alloys
Etching solution	Conc. nitric acid ($\rho \approx 1,42$ g/ml) and water in the ratio 1:3 by volume	Conc. nitric acid ($\rho \approx 1,42$ g/ml), undiluted
Immersion time	30 s	5 s

Wash with clean, cold running water, followed by clean, hot water, and dry with hot air.

WARNING — Concentrated nitric acid is highly corrosive and a powerful oxidizing agent. Particular care is needed when handling this acid (see clause 7).

In the case of cupronickel alloys, trials are recommended to establish the optimum solution concentration and immersion time for the particular alloy.

6.3.2 Ammonium persulfate

6.3.2.1 Surface preparation

a) Remove oil or grease contamination with solvent.

- b) Immerse the item for 1 min to 2 min at room temperature in an etching solution.
- c) Remove item from solution and rinse thoroughly in cold distilled or deionized water.
- d) Dry using clean, cold pressurized air. Hot air will discolour the surface.
- e) Bond without delay.

6.3.2.2 Etching solution

When preparing this solution, use only apparatus made of polyethylene, polytetrafluoroethylene or polypropylene.

Composition:

Aqueous iron(III) chloride solution [42 % (m/m)]	15 parts by mass
Concentrated nitric acid ($\rho \approx 1,42$ g/ml)	30 parts by mass
Distilled or deionized water	197 parts by mass

An alternative etching solution may be prepared by dissolving 1 part by mass of ammonium persulfate in 3 parts by mass of water. If this solution is used, shorten the immersion period by 30 s.

Preparation:

Add the iron(III) chloride solution to the water and then cautiously add the acid, stirring continuously.

WARNING — Always add acid to water, never water to acid.

Acid, iron(III) chloride and ammonium persulfate are toxic and corrosive. Follow approved procedures for disposal.

6.4 Magnesium and magnesium alloys

6.4.1 Surface preparation

- a) Remove oil or grease contamination with solvent. Wherever possible, use isopropyl alcohol. Other-

wise, use a ketone (MEK or MIBK) or an approved halogenated solvent.

- b) Immerse the part in sodium hydroxide solution (6.4.2.1) for 10 min at 70 °C. Wash in cold running water.
- c) Immerse the part in the etching solution for 10 min at room temperature.
- d) Wash with cold running water. Wash again with distilled or deionized water. Dry in a hot (65 °C) air stream.
- e) Bond immediately to reduce surface oxidation.

WARNING — Alcohols and ketones are flammable, particularly ketones. All are toxic at high concentrations. Ventilate properly, take account of vapour density and draw fumes away from the operator.

Do not allow solvent to come in contact with the skin. Abuse may lead to dermatitis.

Wear eye protection and protective clothing.

Fire hazard — never place magnesium components in a vapour bath and never abrade.

6.4.2 Solutions

6.4.2.1 Sodium hydroxide

Composition:

Sodium hydroxide	1,0 parts by mass
Distilled or deionized water	12,0 parts by mass

Preparation:

Add the sodium hydroxide to the water and stir until dissolution is complete.

WARNING — Sodium hydroxide is both toxic and corrosive. Follow approved procedures for disposal.

6.4.2.2 Etching solution

When preparing this solution, use only apparatus made of polyethylene, polytetrafluoroethylene or polypropylene.

Composition:

Sodium sulfate (anhydrous)	1,8 parts by mass
Calcium nitrate	2,1 parts by mass
Chromium trioxide	24,0 parts by mass
Distilled or deionized water	123,0 parts by mass

Preparation:

Add the materials to the water in the order given above and stir until dissolution is complete.

WARNING — Chromium trioxide is both toxic and corrosive. Follow approved procedures for disposal.

6.5 Steel (mild)

Degrease in accordance with clause 3. Then either abrade in accordance with clause 4 (especially by the methods specified in 4.5 and 4.6) or etch.

In the case of etching, use a solution of:

Industrial methylated spirit	2 litres
Orthophosphoric acid ($\rho \approx 1,7$ g/ml)	1 litre

Immerse for 10 min at 60 °C, remove from the solution and then, under clean, cold running water, brush off the black deposit with a clean stiff-bristle nylon brush. Absorb residual water by wiping with a clean cloth soaked with clean industrial methylated spirit or isopropyl alcohol. Heat for 1 h at 120 °C.

6.6 Steel (stainless)

Degrease in accordance with clause 3. Then either abrade in accordance with clause 4 (especially methods indicated in 4.5 and 4.6), or etch for 5 min to 10 min at 55 °C to 65 °C.

In the case of etching, trials are recommended with the particular stainless steel to establish the optimum immersion conditions and the optimum composition of the etching solution. If no trials are carried out, use a solution of the following composition:

Water	3,5 litres
Oxalic acid [(COOH) ₂ ·2H ₂ O]	0,5 kg
Concentrated sulfuric acid ($\rho \approx 1,84$ g/ml)	1,6 litres

Baths in use for the pretreatment of aluminium alloys shall not be used concurrently for the pretreatment of steel.

NOTE 9 The oxalic acid will dissolve completely at the etching temperature.

Prior conditioning (e.g. passivation) of the steel surface may delay the reaction between the steel and the etching solution. The etching treatment shall therefore be timed from the onset of the reaction.

Wash with clean, cold running water, then remove the black deposit by immersing for 5 min to 20 min at 60 °C to 65 °C in the sulfuric acid/sodium dichromate (or chromium trioxide) solution specified in 6.1.2.1.

Alternatively, remove the black deposit by brushing, under clean, cold running water, with a stiff-bristle nylon brush, and dry with hot air. Highest bond strengths, however, are obtained after removal of the black deposit by the chemical treatment given above.

6.7 Tin

Degrease in accordance with clause 3, then abrade in accordance with 4.2 or 4.4. Remove fine debris with an appropriate solvent using lint-free cloth or tissue.

6.8 Zinc and zinc alloys

Degrease in accordance with clause 3, then abrade in accordance with clause 4 (especially by the methods specified in 4.5 and 4.6), and apply the adhesive immediately.

7 Safety precautions

Concentrated acids, oxidizing agents (e.g. chromium trioxide, dichromates) and caustic soda are highly corrosive chemicals. Spillages and splashes can cause severe damage to eyes and skin, and attack ordinary clothing. Operators shall wear goggles (or a visor) and protective clothing where these chemicals are in use.

Since chromates are recognized as being carcinogenic to humans, they must be handled in accordance with local safety regulations.

The manufacturer's handling precautions shall be observed.

IMPORTANT — Never pour water into acids. Always pour the acid in a slow, steady stream into the water, stirring continuously. Bear in mind that the handling hazard is greater when the acid is hot.