

PUBLICLY AVAILABLE SPECIFICATION



**Printed board assemblies –
Part 10: Application and utilization of protective coatings for electronic
assemblies**

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PRINTED BOARD ASSEMBLIES –

Part 10: Application and utilization of protective coatings for electronic assemblies

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IEC-PAS 61191-10, submitted by GfKORR – Gesellschaft für Korrosionsschutz e.V. was processed by IEC technical committee 91: Electronics assembly technology. It is based on *Guidelines for the application and utilization of protective coatings for electronic assemblies – Selection, fields of application, requirements and application recommendations – provided by the working party "Corrosion protection in electronics and microcircuitry"*. The structure and editorial rules used in this PAS reflect the practice of the organization which submitted it.

The text of this PAS is based on the following document:

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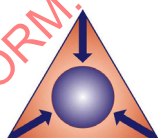
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APPLICATION AND UTILIZATION OF PROTECTIVE COATINGS FOR ELECTRONIC ASSEMBLIES

**Selection, fields of application,
requirements and application
recommendations**

Provided by the working party

“Corrosion protection in electronics and microcircuitry”



GfKORR – Gesellschaft für Korrosionsschutz e.V.

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FOREWORD

GfKORR and its working group "Corrosion protection in electronics and microsystems technology" as initiators of this guideline

GfKORR - Gesellschaft für Korrosionsschutz e.V., a non-profit technical-scientific association, which was formed in 1995 from the merger of two predecessor organizations, has set itself the goal of collecting, expanding and disseminating knowledge about corrosion, corrosion mechanisms and corrosion protection possibilities to prevent corrosion damage with the participation of all persons, institutes, companies and facilities involved in corrosion and corrosion protection. This project is to be realized on the one hand through joint conferences, seminars and workshops and on the other hand through constructive work in working groups with special orientation and topics. Further information about GfKORR and its work can be found at <http://www.gfkorrr.de>

The constantly increasing number of different electronic assemblies and miniaturized systems made of various materials and their use, especially in motor vehicles, telecommunications, aircraft, building services and even toys, is also associated with increasing expectations for the functional reliability and long-term stability of the products. In addition, the progressive miniaturization of components places ever greater demands on purity during manufacture and assembly. Furthermore, both electronics and the microcomponents are increasingly exposed to changing climatic conditions such as humidity, temperature changes and temperature shock. Based on long-term warranty requirements and worldwide marketing, an effective assurance of the reliability of electronic products is only conceivable with the help of in-depth knowledge of the mechanisms of action of corrosion of electronic and microsystem components and corresponding corrosion protection measures.

In the spring of 1998, GfKORR founded the working group "Corrosion protection in electronics and microsystems technology" with a view to discussing such ever-increasing issues and problems. It is currently headed by Dr. Helmut Schweigart, Dr. O.K. Wack Chemie GmbH, Ingolstadt; his deputy is Dr. Michael Popall, Fraunhofer Institute for Silicate Research, Würzburg. The working group meets twice a year in Würzburg in spring and autumn (for further information and contact details, see the list of authors and the Internet on the GfKORR homepage).

The working group includes representatives from industry (such as ALTANA Chemie AG, CiS Institut für Mikrosensorik gGmbH, Continental AG, Dage Electronic Europa Vertriebs GmbH, Dow Corning GmbH, GTL Knödel GmbH, Hella KGaA, ISO-ELEKTRA Elektrochemische Fabrik GmbH, KC-Kunststoff-Chemische Produkte GmbH, Lackwerke Peters GmbH & Co. KG, Nordson-Asymtek, Specialty Coating Systems, Stannol GmbH, Wevo-Chemie GmbH, Würth Elektronik GmbH & Co. KG, Zollner Elektronik AG...) as well as employees of various research institutions and service providers (such as the Fraunhofer Institute for Applied Materials Research (IFAM), for Silicate Research (ISC) and for Silicate Technology (ISiT) and the Karlsruhe Research Center GmbH).

The goals of the working group are:

- the deepening of the understanding of the mechanisms leading to functional hazards,
- the interdisciplinary exchange on the state of science and technology in the working fields of the working group in cooperation with industry and other scientific-technical societies,
- damage assessment and prevention, and
- the provision of competent contact persons for acute questions.

An important point that the working group has already dealt with in the past and must continue to deal with is the current test methods for characterizing the protective coatings applied to printed circuit boards and components. Here it is important to make further developments, which, however, can only be pursued jointly by coating manufacturers and users.

The GfKORR working group "Corrosion protection in electronics and microsystems technology" has in recent years focused its work on the compilation of the present guideline and discussed individual points controversially. This guideline, entitled "Application and processing of protective coatings for electronic assemblies - selection criteria, areas of application, requirement profiles and application notes", is based on the knowledge that a comprehensive and fundamental understanding of the coating and its function on electronic assemblies is required. For this, it is necessary to analyze the entire process. This guideline is intended to provide practical assistance in considering this process, starting with the layout up to the functional test of the assembly after the coating.

In order to achieve optimum results in the application of protective coatings, it is also desirable that both manufacturers and assemblers of electronic assemblies and users of protective coatings discuss and implement the desired properties and the necessary and possible process steps together with the manufacturers of protective coatings. Only with such "round-table" discussions can successful solutions be developed for each individual application. It is then also possible to update and improve this guideline at regular intervals through such meetings and discussions.

September 2018

The authors of the guideline

INTRODUCTION

During their production and use in the field, electronic equipment and assemblies are exposed to the influence of moisture and environmental conditions (air, weather, location of the assembly, storage and cleaning). Air, humidity and water lead to an electrical conductive connection of adjacent metal surfaces, which may have different electrical potentials and may thus cause disorder of the electrical insulation by developing additional electrical pathes. Other influences like fluctuations of temperature or strain caused by harmful substances, vibrations and mechanical strain lead to changes in the electrical conduction properties and changes and destruction of the conductor and insulation materials.

Disorder caused by water or moisture often disappears in a dry environment. Also changes of the electrical conductivity caused by temperature disappear when used at moderate ambient temperatures. However, the material, which was destroyed by thermal or mechanical strain, remains in its destroyed condition. A disorder caused by moisture may therefore disappear in favourable cases, however, in view of functional safety considerations of electronic assemblies also such damages must be avoided.

An electronic assembly is only suitable if a safe performance is guaranteed for a specified time. The majority of assemblies is installed in final equipment without any insulation and operate throughout their lifetime without failure. However, the assembly is increasingly used under more difficult conditions. In such cases, safe operation of an assembly is only guaranteed by a protective coating.

Reliability of an electronic product and customer satisfaction are of utmost importance for the success on the market. Product liability requires the manufacturers to take the necessary steps in order to ensure safe operation of electronic equipment also under such heavy conditions. This mainly applies to assemblies which are used in space technology and aviation, defence technology, medicine and automotive industry.

Generally, the coating of the assembly is the last step in the value-added chain of the assembly. Any fault during this step may become very cost intensive and in the worst case may cause disastrous results in the field. Therefore, these guidelines represent a co-operative effort by design engineers, producers, coating engineers and users of electronic equipment. It was decided to establish these guidelines because of the fact that comprehensive and elementary knowledge of the coating and its performance on electronic assemblies is vital. For this purpose, it is necessary to analyse the entire process critically.

These guidelines shall help control in practice the application of protective coatings from the layout to the functional test of the assembly after coating.

Nowadays, coating materials for electronic assemblies are nearly exclusively available in liquid form. The application of powder to certain components as well as full body or partial application of molten foils is limited to exceptional cases. Besides the complete sealing of electronic assemblies, the protective coating offers a cost-effective and user-friendly alternative.

Therefore, the present guidelines especially deal with the requirements for the protective coating, its properties, as well as the application of liquid coating materials. ¹.

The German terms „Lacke“ and „Anstrichstoff“ are generally and synonymously used for pigmented and non-pigmented coating materials. The coatings for the protection of electric assemblies described herein are non-pigmented paints. However, a non-pigmented paint should be called clear paint.

In order to stay as neutral as possible, the generic terms coating material and coating process were used herein if further definitions were not expressly required. If more emphasis is placed on the properties of the protective coatings especially described herein, then the term protective paint is used.

In order to set out the scope of these guidelines, the following limitations were made:

- The protective coatings described in these guidelines are protective paints (Conformal Coatings, CC^{2,3} or Protective Coatings, PC).
- Protective coatings are polymer layers which protect assemblies against negative influences in service in order to extend their lifetime and operating time, resp.
- If the contours of the assembly are still visible, the polymer coating is defined as protective paint and protective coating resp.- conformal coating -.
- If the contours are entirely covered, then coating resins, casting resins and/or sealing compounds are concerned.
- The entire sealing of an assembly and the processes to be used are not part of these guidelines (see also [Kli05a, Ott05, Ott07 Pie07 HdT07]).

The coating of electronic assemblies is a part of the assembly production developing continuously and quickly. It is therefore planned to update the guidelines on a regular basis and to add more chapters by the GfKORR study group. ⁴.

¹ According to DIN EN 971-1 (1996-09; „Lacke und Anstrichstoffe – Fachausdrücke und Definitionen für Beschichtungsstoffe – Teil 1: Allgemeine Begriffe“; in the meantime replaced by DIN EN ISO 4618 (2003-12) „Beschichtungsstoffe – Begriffe“) coating material is defined as follows: „Coating material is either a liquid product, or a paste or powder which, when applied to a surface, provides a coating with protective, ornamental and/or other specific properties.“.

Note: The German term „Beschichtungsstoff“ acc. to this specification is the generic term for paints, coatings and similar products. According to the supplement of the DIN EN 971-1 coating materials are also materials for the production of synthetic resins, filler compounds, floor coating compounds, as well as similar materials. The terms coating material, coatings and paint are used alternatively. This also applies to the term „Anstrichmittel“ [Zor98] which is not standardized and should hence be avoided. .

² The term “conformal coating” is used in the English and American language and acc. to IPC-CC-830 is defined as follows: “For the purpose of this specification (IPC-CC-830) the term conformal coating is used herein when referring to a type of protective coating for use on printed board assemblies. The conformal coating is intended to provide protection from moisture, contamination and provide electrical insulation; not as a sole source of mechanical support.” The same applies to conformal coatings acc. to UL 746 C („Standard for safety for polymeric materials – use in electrical equipment evaluations“).

³ The term „conformal coating“ was introduced and used for full body coatings, therefore the term shall be used herein, although nowadays “conformal coating” is very often used by mistake in case of one-sided selective coating of electronic assemblies.

⁴ The first edition of the guidelines is dated November 2005. This is the second edition dated June 2007, updated and extended for the first time by 30 pages.

REQUIREMENTS FOR THE COATING OF ASSEMBLIES

- 1 General requirements**
- 2 Climate impact requirements**
- 3 Regulations for protective coating**
 - 3.1 Reference to the general requirements
 - 3.2 Reference to climate impact

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1 General requirements

Due to the continuous miniaturization of printed circuit boards in recent years, live components and conductors are moving ever closer together, increasing the risk of leakage current formation under moisture. Due to the good dielectric properties of protective coatings, minimum distances between live conductors can be reduced.

In addition, depending on the coating system used, protection against

- mechanical abrasion, vibration and impact,
- atmospheric humidity and hand perspiration,
- chemicals and environmental gases,
- mold infestation in tropical conditions,
- metal splinters/particles.

can be achieved. The surfaces to be coated on assemblies can be of very different types, e.g.

- metal surfaces (tin, tin lead, gold, nickel, copper etc.),
- plastic surfaces (solder resist, PCB base material, component housing, etc.) or
- residues from various soldering processes (HAL = Hot Air Levelling, reflow soldering, solder paste residues, etc.), welding, gluing and other processes.

Very different surface topographies must be taken into account:

- plane surfaces (horizontal, inclined and partly vertical),
- inner edges, outer edges and corners,
- tips and pods,
- wires, curved terminal frames (component connections),
- shadow areas that are not accessible in a straight line, and
- narrow gap (expansion gap).

In general, very high demands are placed on optimum protective coatings, e.g.

- protection against moisture by forming an electrically insulating material barrier,
- avoidance of corrosion phenomena through a coating,
- good adhesion of the coating to the various metal and plastic surfaces,
- simple, cost-effective, fast coating process,
- cost-effective coating material, as little material input as possible,
- complete curing and/or drying under moderate conditions in a short time, even under the components,
- all areas to be protected must be coated;
- as uniform and homogeneous layer coating thickness as possible at all points,
- reparability should be possible,

- simple visual control of the presence of the coating,
- easy determination of the thickness of the coating at any point.

These requirements can be largely covered with thin-layer protective coatings. In case of additional loads, especially in aggressive industrial atmospheres, high potential differences and other possible loads, thick-film coatings or casting compounds are used to protect the electronics.

Most protective coatings are applied in liquid form and only achieve their specified properties after drying and, depending on the coating material, after chemical curing. This means that a fixed time requirement and corresponding ambient conditions for curing or drying are necessary. The aim is to minimize the time required to coat the assembly and to cure it safely and quickly. Considering the protective coating in terms of cost, application time and environmental impact, the requirements are slightly different, e.g.:

- as solvent-free as possible (solvents have a hazard potential and must be safely removed);
- free of prohibited hazardous substances (e.g. ELV, RoHS Directive¹),
- drying and curing under normal room conditions if possible (a need for heat etc. increases the coating effort),
- complete drying and/or curing within a short time (long curing times or slower curing with thick layers also increase the effort),
- maximum adhesion and maximum electrical insulation after a short time,
- good robustness of the protective coating during further production and protection of the assembly against the expected loads.

2 Climate impact requirements

The protection of the electrical assemblies against ambient humidity and/or condensation is the most important requirement for the protective coating. This becomes understandable when one considers the use of one and the same assembly under all geographically and climatically possible conditions.

Different climatic stresses - in terms of environmental parameters - under which an electrical assembly must function are:

- low/high humidity,
- low/high temperature,
- different air pressures,
- rapid climate changes,
- condensation,
- microbiological contamination and
- low/high pollution.

The following model illustrates the occurrence of an electrical fault in the presence of wa-

¹ RoHS = Restrictions on Hazardous Substances; Directive published in the Official Journal of the European Union L 214/65 of 18.08.2005

ter or moisture (see Fig. B1). Two closely adjacent metal surfaces have different electrical potentials. In the presence of a connecting water bridge, a current flows due to the potential difference, which can be transported due to the natural conductivity of the water and additionally substances dissolved in the water such as ions and acid components. The disturbance of the function due to electrical lines connected to water depends on the level of the electrical potential difference, the tolerance sensitivity of the electrical quantities, the duration of the presence of water, the conductivity and the cross-section of the aqueous bridge. The current flow over an aqueous bridge can be estimated mathematically if the potential difference is known, the specific conductivity of the water involved, the cross-section of the water connection and the distance between the adjacent metal surfaces.

When the surfaces dry off again, the flow of current through the aqueous compound stops and the interference can disappear again.

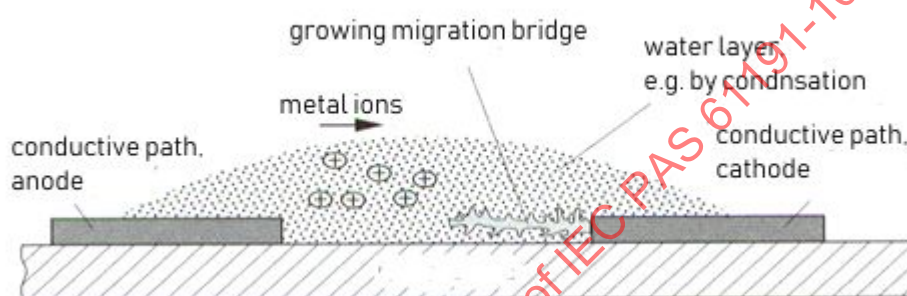


Fig. B1: Model of the development of a water-related electrical disturbance:
 (a) There is charge transport in the liquid medium water
 (b) Metal ion transport to the cathode can cause dendrite growth, i.e. metallic and oxidic material deposits are formed

Possible causes for such influences of water can be:

- Water absorption of materials,
- warm humid air,
- cooling air until condensation (see Fig. B2), rain,
- splash water,
- high pressure cleaning and
- leaking liquids.

In the case of fully assembled structures, the assembly connections, their soldering and their transition into the component are added as additional relevant surfaces, which can have an influence on the behavior under moisture.

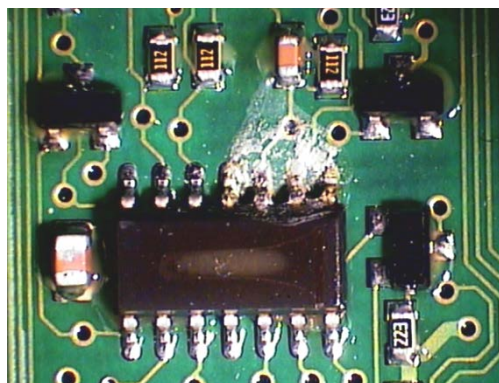


Fig. B2: Possible fault pattern on an assembly after electrical operation with clear condensation (white-colored area shows a large accumulation of corrosion products)

Examples of possible malfunctions of electronic control units due to the presence of moisture could be:

- Sensitive signals exceed the tolerance limits; the control unit switches off.
- High-resistance components are bridged by a low-impedance water bridge; the electrical control changes.
- Closely adjacent conductor tracks or connections and high potential differences cause leakage currents in the presence of moisture. This can increase overall power consumption. As long as the power supply is not interrupted or limited by a fuse or electronic control, this can lead to unforeseen heating of the conductors and their insulation.

3 Regulations for protective coating

3.1 Reference to the general requirements

The general requirements for protective coatings are included in many national and international regulations. The following list provides a brief overview of these rules and regulations:

- **IEC 61086-1** "Coatings for loaded printed wire boards (conformal coatings) – Part 1: Definitions, classification and general requirements"
- **IEC 61086-2** "Coatings for loaded printed wire boards (conformal coatings) – Part 2: Methods of test"
- **IEC 326-3** / IEC 326-3A (1982) / DIN IEC 326 Part 3 (03:1985) "Printed Circuits, Circuit Boards, Design and Application of Printed Circuit Boards".
- **IEC 60464-3-1 Ed. 2.0 b** „Varnishes used for electrical insulation - Part 3: Specifications for individual materials - Sheet 1: Ambient curing finishing varnishes"
- **DIN 46449 (1970-04)** RETRACTED "Insulating varnishes and insulating resin compounds in electrical engineering, coating varnishes, test methods".
- **DIN EN 60664-1 (2008-1)** DIN EN 60664-1 (2008-1 2003-11) "Insulation coordination for electrical equipment in low-voltage systems - Part 1: Principles, requirements and tests"
- **DIN EN 60664-3 (2017-11)** DIN EN 60664-1 (2008-1 2003-11) "Insulation coordination for electrical equipment in low-voltage systems - Part 3: Use of coatings, pouring or encapsulation to protect against contamination"

- **IPC-CC-830** "Qualification and Performance, Insulating Compounds for Printing Circuits Assemblies"
- **IPC-SM-840** "Qualification and Performance of Permanent Solder Mask – with Amendment 1"
- **IPC HDBK-830** "Guidelines for Design, Selection and Application of Conformal Coatings" ²
- **IPC-TM-650** "Test Methods Manual" (Update service for two years)
- **UL 94** "Tests for Flammability of Plastic Materials for Parts in Devices and Appliances"
- **UL 746 C** "Polymeric Materials – Use in electrical Equipment Evaluations"
- **UL 746 E** "Polymeric Materials – Industrial Laminates, Filament, Wound Tubing, Vulcanized Fibre and Materials used in Printed Wiring Boards"
- **MIL-I-46058** "Insulating Compound, Electrical" (for Coated Printed Circuit Assemblies); has been discontinued and replaced by IPC-CC-830B

The above standards mainly refer to an evaluation of the coating system. Requirements for the complete assembly and its production process can be found in the specifications of the users, especially from the automotive, aerospace and aerospace industries. The OEM specifications (Original Equipment Manufacturing) mainly describe the requirements for lifetime reliability in the respective end applications.

3.2 Reference to climate impact

The reliable functioning of an assembly under climatic conditions is decisive for the need for a protective coating. For this reason, the following information is limited to the contents of the regulations that describe climatic loads and their requirements.

The climatic resistance can be tested by measuring mechanical, chemical and/or electrical properties. In the regulations, climate resistance is defined mainly by the change in electrical resistances in a test cycle. Among other things, there is a requirement to maintain electrical insulation through the protective coating. Here, for example, the following load parameters and limit values can be found:

IPC-CC-830:

Insulation resistance: **During and after Moisture**

Class A: 100 MOhm

Class B: 500 MOhm

"climatic or test conditions": Alternating test 65°C / 25°C at 90 - 98 % r. H.³ (defined times and ramps), measured on a defined IPC test plate.

The Class B requirement applies to hydrolytically stable protective coatings and Class A to non-hydrolytically stable protective coatings.

IEC 1086-1 to -3:

Insulation resistance after damp heat: $> 1 \times 10^{10}$ Ohm

"climatic or test conditions": 10 days constant climate 40°C at 93 % r. H., measured on a defined IPC test plate after reconditioning at room temperature.

² For the content of the IPC-HDBK-830 and the link to the GfKORR Guide, see Part N of the Guide.

³ r. H. = Relative humidity

IEC 1086-1 distinguishes between general requirements (Class I) and high reliability (Class II), but makes no difference in this test.

IEC 60464-3-1:

Contact resistance after immersion:

Before: $> 10^{12}$ Ohm x cm

After: $> 10^8$ Ohm x cm

Effect of immersion on dielectric strength:

After: > 40 kV/cm

"climatic or test conditions": Constant 23°C water temperature for 7 days (dist. water).

DIN 46449 (withdrawn see DIN EN 60544):

Specific volume resistance as a function of storage in water after 24, 48, 96 and possibly 240 h.

No limit values are specified.

DIN VDE 0110-3 ⁴:

Insulation resistance: ≥ 100 MOhm

"climatic or test conditions": 4 days constant climate 40°C at 93 % r. H., measured on a defined IPC test comb.

UL 746 C:

The measured variables are the dielectric strength, at least 50% of the value for the unconditioned sample and at least 1 kV for 60 s.

UL 746 C distinguishes between two conditionings:

o *Environmental Cycling Conditioning*

This conditioning distinguishes between indoor and outdoor applications:

- "indoor end-use application": 24 h service temperature, 96 h at 35°C / 90 % r. H., 8 h at 0°C
- "outdoor end-use application": 24 h water storage at 25°C, 24 h service temperature, 96 h at 35°C / 90 % r. H., 8 h at -35°C

o *Humidity Conditioning*

"climatic or test conditions": 7 days constant climate 35°C at 90 - 95 % r. H., measured within 2 minutes after removal from the air conditioner on a special UL test plate.

⁴ DIN VDE 0110-3 (valid up to 2006-04) = DIN EN 60664-3 (2017-11) "Insulation coordination for electrical equipment in low-voltage systems - Part 3: Use of coatings, pouring or encapsulation to protect against contamination".

Not to forget the IEC series "*Basic Environmental Testing Procedures*", of which there is a series of around 70 test procedures covering a wide variety of climatic and mechanical stresses.

The presentation of further tests for climate resistance by means of measurements of mechanical, chemical and/or other electrical properties would go beyond the scope at this point. An additional list is therefore not included.

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CLASSIFICATION OF PROTECTIVE COATINGS

1 Subdivision according to binding agent

- 1.1 Acrylates
- 1.2 Alkyds
- 1.3 Epoxides
- 1.4 Polyesters
- 1.5 Polyurethanes
- 1.6 Silicones
 - 1.6.1 Chemical structure
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- 1.7 UV acrylic hybrids
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2 Subdivision according to solvent

3 Subdivision by drying and curing mechanism

- 3.1 Physically drying coating materials
 - 3.1.1 Solvent-dilutable coating materials
 - 3.1.2 Water-dilutable coating materials
- 3.2 Oxidatively curing coating materials
- 3.3 Chemically curing coating materials
- 3.4 (UV-)radiation-curing coating materials

4 Subdivision according to coating thickness

If the coating materials usually used in electronics - protective coatings or conformal coatings - are distinguished, they can - depending on which aspect is in the foreground - be subdivided according to different aspects. In general, the following schedule lines can be made:

- differentiation according to the type and chemistry of the binding agent,
- differentiation according to the solvent,
- differentiation according to the drying or curing principle and
- differentiation according to coating thickness.

1 Subdivision according to binding agent

The properties of the dried and/or cured coating are essentially determined by the type of polymer, which is the binding agent base of the coating material. If the basic polymer structure of the coating materials is subdivided, five base polymers are obtained: (poly)acrylate, polyurethane, epoxy, polyparaxylene and the silicones (polysiloxanes). The first four are combined into so-called organic polymers, which distinguishes them from silicones, which have an inorganic backbone.

Hybrid systems are polymer combinations - usually made of (poly)acrylate, polyurethane, epoxy and silicones (polysiloxanes). An overview of the essential basic properties is given in the following chapters.

1.1 Acrylates

Acrylic resins or acrylate resins, herein after referred to as acrylate resin, are produced by homo- or copolymerization of methacrylic or acrylic acid esters. So-called pure acrylic resins are homopolymerized exclusively on the basis of (meth)acrylic monomers. Acrylate coating was one of the first coating materials used to protect electronics¹.

By far the largest part of the acrylate resin coatings used today are solvent-based one-component coatings. Film formation usually follows the principle of physical drying and takes less than an hour. In mass production, the drying process can be accelerated by the influence of heat. A typical feature of physically dried coatings is their permanent susceptibility to their own solvents. Depending on the application, this can be both a negative and a positive aspect. In the case of very expensive printed circuit boards, it is desirable for repair purposes to be able to remove the coating with solvents.

Acrylate resin coatings only adhere to contaminated surfaces to a limited extent and their resistance to mechanical wear varies from medium to good depending on the coating modification. The higher the mechanical wear resistance is set, the harder and therefore also brittle the coatings are. If thermal cycling occurs, there is a risk of tearing. As a result, the coating loses its protective effect. Moisture can penetrate the cracks and lead to corrosion.

The advantage of acrylate resin coatings is their easy handling and application. Acrylic resin coatings offer very good electrical insulation properties and are UV-resistant and hydrolysis-resistant. In the sum of their properties, acrylate resin coatings can thus be used cost-efficiently.

¹ The term "acrylate" should be used if it is not UV-curing polymers or coating materials.

1.2 Alkyds

Alkyd resins (also abbreviated AK) is a collective term for synthetic resins which can be produced from polycondensation of polyols (e.g. glycerol, pentaerythritol) and polyvalent carboxylic acids (e.g. phthalic acid, adipic acid), at least one OH group being esterified with an unsaturated fatty acid. The unsaturated fatty acids are responsible for the characteristic curing process - oxidative curing.

Partial replacement of these three components produces modified alkyd resins whose properties are determined by the modifying component. If some of the polyols are replaced by low-molecular epoxy resins, so-called epoxy esters are obtained. By replacing some of the dicarboxylic acids with diisocyanates, however, the urethane-modified alkyd resins are obtained. The acrylic-modified alkyd resins are produced by copolymerization with acrylic acid. Due to this modification, the range of properties of alkyd resins and coating materials based on alkyd resins is variable and adjustable over a very wide range.

1.3 Epoxides

Epoxy resins are polycondensation resins consisting of bisphenols and epichlorohydrin with different molecular weights. They alone do not have sufficient film-forming properties, so that they are crosslinked with polyamines and their adducts or with polyisocyanates in two-component systems. The proportion of two-component epoxy systems in the protective coatings for electronic assemblies is not very high, they dominate the heavy corrosion protection in steel plant and hydraulic steel construction. They can also be found as coating materials for various components (resistors, IC's, Glob Tops, etc.).

Instead of the classic thin-film coatings, which are dependent on a solvent or water to reduce viscosity, epoxy-based coating systems were developed which contain no solvents and are largely VOC-free². The working viscosity of these is low enough to allow this type of coating material to be processed in the main systems currently in use with few exceptions.

The various products are transparent one-component coatings based on a modified epoxy resin system with the following chemical structure. A Lewis acid holds the epoxy used to form a carbonium ion, the ion in turn reacts with the next epoxy group. These reactions take place very quickly. Since the intermediates are highly reactive, they lead to a series of secondary reactions, which in turn lead to further side reactions. The network formed in this way is irregular, so that the mechanical properties, especially the flexibility, are moderate. On the other hand, the polyether structure ensures good adhesion of the film to most materials.

Since the Lewis acid used for heat curing is a boron trifluoride complex, sufficient storage stability of 6 months at room temperature is ensured. During UV curing, the Lewis acid is formed by a photoreaction. The epoxy resin has a cycloaliphatic structure that can be modified for optimum processing.

The essential properties of the cured film are:

² VOC = Volatile Organic Compound; The VOC Directive was adopted in the 31. BImSchV Point 2.1. into German law within two years. (Directive 2004/42/EC of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain coatings and varnishes and vehicle refinishing products and amending Directive 1999/13/EC)

- a film thickness of 60 to 200 µm,
- reliable adhesion and compatibility with solder resists, solder paste printing and fluxes,
- high performance in terms of thermal and electrical properties even under adverse environmental conditions, and
- good stability against polluted atmospheres when used in automotive and marine engines.

Hardening of the resin is emission-free without degradation products and without VOCs. When handling epoxy resins, the usual measures against skin contact are required³.

1.4 Polyesters

Polyesters are divided into saturated and unsaturated types. According to DIN 55958⁴, saturated polyesters are defined as resins in which the components - polybasic carboxylic acids and polyhydric alcohols - contain no polymerizable double bonds. Unsaturated polyesters (UP resins) and alkyd resins contain such double bonds. In alkyd resins, the double bonds usually originate from natural fatty acids, which can be cured (= cross-linked) using siccatives, e.g. cobaltoctoate. In UP resins, the double bonds come from maleic or fumaric acid, which are often copolymerized with styrene as reactive diluent during cross-linking..

Saturated polyesters are also known as "oil-free alkyd resins". As a basic reaction, linear diols are reacted with difunctional carboxylic acids or carboxylic anhydrides.

Monofunctional and more than difunctional basic raw materials are often used in proportion. Monofunctional educts limit the molecular weight because they act as chain breakers. If trifunctional starting materials are used too much, the manufacturer runs the risk of the entire batch gelling. The first saturated polyesters were the so-called glyptal resins from glycerine and phthalic anhydride. The disadvantages for the user were low solubility and high hardness combined with high brittleness.

By modifying the alcohol component or the acid or anhydrides, saturated polyesters with almost infinite properties can be produced. In coating applications, saturated polyesters are usually cured with a crosslinker resin (e.g. amino resin, polyisocyanate, epoxy resin), but physical drying from solutions is also possible.

Unsaturated polyesters can be adjusted to a suitable processing viscosity with monomers such as styrene, alpha-methyl styrene or diallylphthalate. These monomers cause cross-linking during the radical polymerization of the C=C double bonds in the polyester prepolymers. Although styrene is still widely used as a reactive diluent, it is often undesirable due to its toxicity combined with high vapor pressure and low odor threshold. Styrene forms styrene epoxide in the organism, a proven mutagenic metabolite. Unsaturated polyesters, however, do not play a role in the protective coatings for electronics covered in this guideline.

³ When handling coating materials, the information in the relevant safety data sheet must be observed for all protective coatings mentioned in the guideline. Further safety instructions are discussed in Part H.

⁴ DIN 55958 (1988-12) "Resins; Terms" now retracted, replaced by DIN V 55650 (1998-05) "Binding agents for paints and other coating materials –Terms" and DIN EN 923:2016-03 "Adhesives – Terms and definitions" and by DIN EN ISO 4618:2015-01 "Coating materials – Terms".

Urethane- and silicone-modified polyester resins achieve particularly good weathering and UV resistance.

1.5 Polyurethanes

The properties of crosslinked polyurethanes (PUR) can be varied over a wide range. In addition to the classic two-component reactive coatings, the range today also includes reactive and non-reactive one-component PUR systems. Depending on the type of binder, the film on the substrate can therefore be formed by a two-component reaction, by photopolymerization, by baking or purely physically by solvent evaporation. Systems are also offered in which curing mechanisms complement each other, for example physical drying by evaporation of a solvent with simultaneous reaction of the prepolymer binder with air humidity⁵. Depending on the type of starting polymer, hard, tough or soft-elastic films can be produced. In general, polyurethane resins are characterized by their outstanding permanent elasticity. In general, the degree of crosslinking and hardness increase with the content of reactive groups, but without reaching the hardness of a two-component epoxy system.

Polyurethanes are formed by polyaddition reactions of isocyanates with polyalcohols. Isocyanates have the end groups $-N=C=O$, in which the nitrogen atom has the ability to attach the hydrogen atoms from adjacent molecules to itself and to cause a connection to polymers through the valencies that are released. If the starting materials are bifunctional, linear polyurethanes result. An example of this is the addition reaction of a diol with a diisocyanate. Other reactive groups in polyalcohol and isocyanate are advantageous for three-dimensional crosslinking and for the formation of hard protective layers, so that, in addition to extending the chains, crosslinks are also formed.

Polyurethane resins also include one-component polyisocyanate resins. These are so-called prepolymers with urethane structures which still contain free isocyanate groups. These isocyanate groups react with humidity to form a polymeric network. Although strictly speaking a urea group is formed in this reaction, the term polyurethane resin has generally become commonplace. Coating materials based on these polyisocyanates are characterized by the fact that they show performance and protective effects like 2-component systems, but are to be handled like 1-component systems. The second component is the moisture always present in the surrounding air. Under Central European climates no humidity needs to be supplied.

The following table compares the advantages and disadvantages of one-component polyurethane coating materials.

Tab. C1: Advantages and disadvantages of one-component polyurethane coating materials

Advantages	Disadvantages
• Good dielectric properties • Good moisture resistance • Solvent resistance • Abrasion resistance (film toughness)	• Solvent-containing (or aqueous dispersions are also available) • Long drying time • Risk of hydrolytic decomposition

⁵ Strictly speaking, the reaction of isocyanates with humidity does not lead to polyurethanes, but to polyurea fumes according to the reactions: $R-NCO + H_2O \rightarrow R-NH-COOH$ (unstable carbamic acid) $\rightarrow CO_2$ (gas) + $R-NH_2$ (amine intermediate) followed by: $R-NH_2 + OCN-R' \rightarrow R-NH-CO-NH-R'$ (urea derivative).

The basic structure of UV-curing polyurethane-based coating materials is comparable to that of urethane-modified solvent-based coating materials. In this case, crosslinking is effected by UV-reactive acrylate groups (or methacrylate groups) whose crosslinking density is higher in comparison. Advantages and disadvantages are shown in tabular form.

Tab. C2: Advantages and disadvantages of UV-curing polyurethane coating materials

Benefits	Disadvantages
• Solvent-free • Good dielectric properties • Good moisture resistance • Solvent resistance • Abrasion resistance (film toughness) • Fast curing and processing	• Application of excessive coating thicknesses • Risk of hydrolytic decomposition • Necessity of a powerful UV irradiation unit

1.6 Silicones

1.6.1 Chemical structure

Silicones - more precisely referred to chemically as polyorganosiloxanes - are synthetic polymeric compounds in which the silicon atoms are linked via oxygen atoms, so that an alternating Si-O-Si bond is present as the chemical backbone. The Si-O-Si chain takes over the backbone function of the C-C chain found in classic coatings (see Fig. C1). This Si-O-Si framework in particular stands for the outstanding electrical and thermal properties of this substance group. The remaining valences of silicon are more or less saturated by different organic groups or by hydrogen.

In these compounds, the four-bond silicon atom has certain parallels to the structure of the quartzes, which form an "inorganic" structural unit. The "organic" structural unit can be found in the side valences. The inorganic structural units stand for the excellent temperature resistance and the high rotational mobility of the side chains for the elasticity and the low dielectric constant as well as for the low dielectric loss angle.

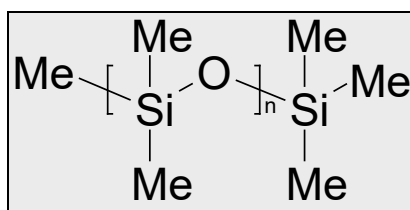


*Fig. C1: Bond ratios / polymer structure of silicones (dimethylpolysiloxane).
(The number $n+1$ of Me_2SiO groups describes the degree of polymerization)*

The combination of these inorganic and organic structural units supplies linear products (silicone oils), wide-meshed networks (silicone gels and silicone rubbers) or highly crosslinked products (silicone protective coatings), which are used in a wide variety of formulations.

Silicones are characterized on the one hand by their outstanding temperature stability and the wide temperature range in which they can be used, and on the other hand by their

mechanical properties. Silicones have a significantly lower Young's modulus than other polymers and also a significantly lower glass transition temperature.

1.6.2 Crosslinking systems and product groups

There are the following differences in chemical crosslinking between the casting compounds and silicone based protective coating or adhesives available on the market:

RTV-1 - **Room-Temperature-Crosslinking**, 1-component

RTV-2 - **Room-Temperature-Crosslinking**, 2-component

HTV - **High Temperature Crosslinking** (1-component)

If one considers the chemical mechanism of cross-linking, a differentiation into

- addition crosslinking,
- condensation crosslinking and
- UV-crosslinking

is possible. For example, we also find solvent-free coating systems for silicones of type RTV-1, whose curing takes place through a reaction with air humidity. This reaction produces specific cleavage products - hence the term "condensation-curing" silicones. Depending on the condensation product, these can in turn be divided into acidic, basic and neutral systems. While in the sanitary sector, for example, the cheaper acidic - acetic acid splitting - systems have become established, such products are of course not suitable for use on electronic assemblies. For electronics, the neutral systems, i.e. the oxime or alcohol-releasing systems, are mainly used, with the alcohol-releasing systems dominating. They show a quite wide range of applications, which can cover a temperature range from below -40°C to over 150°C (for hybrid printed circuit boards), especially for vehicle electronics under the bonnet. Special precautions must be taken for applications in hermetically sealed housings containing open relays or sliding contacts (spark discharges) [Gub05]. In addition-crosslinking silicones, we find either 2-component systems or so-called HTV silicones as 1-component systems. These silicones are usually solvent-free. The elastic products of this family can also be found as products in electronic applications. Since these products require a special platinum catalyst for crosslinking, they are sensitive to catalyst-inhibiting organic compounds, so-called catalyst poisons.

1.7 UV acrylic hybrids

The basic properties of the term "acrylic" used for UV-curing coating materials are not comparable with those of solvent-based acrylate coating materials. The "acrylic" in the name of this binder group usually refers to the UV-reactive grouping and gives an indication of the cross-linking mechanism of the UV binders. In connection with UV-curing binders, the term "acrylic" should preferably be used and the term "acrylate" should be reserved for physically drying binders.

The polymer backbone is often mentioned separately, as with acrylic/urethane or acrylic/silicone; however, UV coating materials based on pure acrylic/acrylate are also possible. Here the basic structure is an acrylate resin combined with the UV-reactive acrylic group.

Acrylic-modified coatings contain radically curing polymers that are started via a photoinitiator and cure in seconds. This acrylic function cures only with UV light. In shad-

low areas, no reaction takes place and it cannot be initiated thermally. It therefore differs from the ionic UV curing of epoxy chemistry. The same applies to methacrylic systems, which are somewhat more reactive. However, they have hygienic advantages as they are less irritating to the skin and eyes.

UV-curing coating materials contain so-called photoinitiators, which are stimulated to react by UV radiation. These photoinitiators require different specific wavelengths for excitation. The manufacturer's instructions must be observed. A coating material formulated for short-wave UV radiation produces insufficient curing results with long-wave UV radiation and, conversely, a coating material formulated for long-wave UV radiation produces insufficient crosslinking with short-wave UV radiation. All UV coating materials require a so-called secondary curing mechanism, which ensures complete curing in the unavoidable shadow areas on an assembly. Ensuring complete curing is indispensable for the subsequent functional reliability of the assembly under the expected environmental conditions. For this secondary hardening - shadow hardening - different hardening mechanisms are available. On the one hand, these are thermosetting crosslinking mechanisms and, on the other hand, chemical crosslinking via the moisture reaction of isocyanate groups in the molecule.

The secondary moisture reaction is used in the so-called TwinCure[®] cross-linking process for curing under building elements. The air humidity required for this diffuses through the polymer and leads to secondary crosslinking via the isocyanate groups. This also ensures sufficient networking in shadow areas.

The "Double Cure Process", established 20 years ago, combines radical polymerization triggered by photosensitizers and co-initiators (e.g. benzophenone) with UV light, with classic radical polymerization triggered by the thermal decomposition of peroxides or azo compounds.

1.8 Thixotropic protective coatings

Structural viscosity is the term used to describe the flow behavior of substances whose viscosity is lower at higher shear stresses or higher speed gradients than at lower values. The viscosity decreases under the influence of external forces and increases again when the force is reduced.

Thixotropy is the term for a flow behavior in which a viscosity decreases over time under constant shear intensity. Thixotropy is often confused with structural viscosity, where viscosity also depends on the speed gradient but not on the shear duration. True thixotropy is a consequence of the reversible structure of a spatial structure within the substance⁶.

The best-known example of this decrease in viscosity after the application of force (thixotropy) is ketchup in the bottle, which first needs to be shaken vigorously in order to have a flowable product.

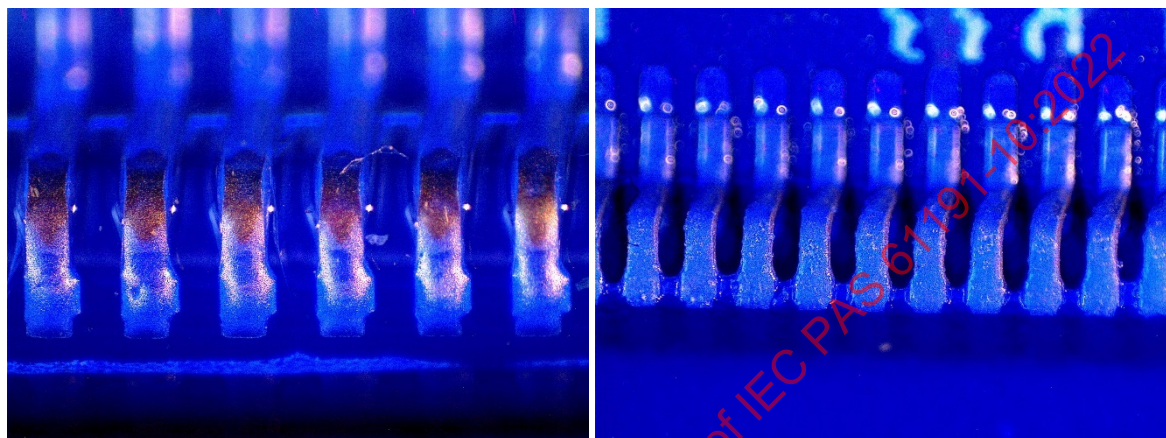
In the coating processing industry, the pseudoplastic and thixotropic flow properties are often used to apply high coating film thicknesses with low tendency to run off on vertical surfaces.

The shear forces occurring during application reduce the viscosity, so that a closed homogeneous coating film can form on the substrate. Subsequently, the viscosity increases again when the coating film is at rest, thus reducing the tendency to run off.

⁶ Römpp-Lexikon Lacke und Druckfarben, Editor Ulrich Zorll, 10th Issue, 1998, Georg Thieme Verlag, Stuttgart

When used in electronics, dam and fill applications usually encounter very highly thixotropic systems. With a highly thixotropic material, a Dam is placed around the area to be filled with a dispenser. The thus limited area is then filled with a low-viscosity, well-wetting and penetrating material.

But thixotropic systems also offer major advantages in the protective coating of electronic assemblies. The known edge alignment or the run-off of the material on sharp-edged component legs can be significantly minimized or eliminated, thus improving the protective effect.



Dip coating of classic acrylic coating⁷

Spray coating thixotropic acrylic coating⁷

While, for example, during dip coating or coating with the film coater with a conventional coating, the coating thickness at the edges is reduced to a few μm , an almost uniform coating can be achieved by targeted thixotropy.

At the same time, however, protective coatings should also wet and protect the "poorly accessible areas", such as the rear sides of the component legs or areas below the components. This is usually achieved by the so-called capillarity. The thixotropy of the protective coating system must be adjusted in such a way that the capillary forces still ensure comprehensive coating of the component legs.

With a further increase in thixotropy (very highly thixotropic coatings), gels are obtained which can be applied with pinpoint accuracy or as dams. These coatings can be used to protect areas such as plugs into which conventional protective coating systems would run due to capillary forces from a protective coating that would impair their function by pulling a dam.

With regard to the application of thixotropic protective coatings, there are some restrictions to be observed.

Optimum utilization of the thixotropic setting is achieved in particular in all common atomizing processes.

Film coaters are limited in the use of thixotropic coatings, as the formation of the film curtain is impaired.

Thixotropic coatings are not suitable for dipping processes.

⁷ Factory image Lackwerke Peters, Kempen

1.9 ORMOCER[®]e

1.9.1 Material class

More than 20 years ago, silicate-based inorganic-organic hybrid polymers (ORMOCER[®]s; registered trademark of the Fraunhofer Gesellschaft für Angewandte Forschung e.V.) were developed at the Fraunhofer Institute for Silicate Research (FhG-ISC) in Würzburg as a novel class of substances from which a wide variety of coating and volume materials can be produced. ORMOCER[®]s can be considered as inorganic-organic composites on a molecular scale. The appeal of these materials lies firstly in the variable chemistry on which the synthesis of ORMOCER[®]s is based and which can influence the material properties in many areas. On the other hand, this type of chemistry allows them to be adapted to a wide variety of processing and structuring techniques. Through the targeted incorporation of organic groups and by controlling the structure of the inorganic network at the molecular level, multi-functionality with regard to intrinsic material properties and processability is achieved. Due to the possibility of incorporating photochemically polymerizable groups, optical structuring processes can also be used in addition to a wide variety of printing processes. Not only planar structures can be created by mask exposure processes, but also any three-dimensional structures [Hou04].

The physical and chemical properties of ORMOCER[®]s result synergistically from their hybrid nature: they combine properties of organic polymers (e.g. toughness, functionalization possibilities and processing at low temperatures) with those of glassy materials (e.g. hardness, chemical and thermal stability and transparency) at the molecular level [Haa00]. This makes it possible to achieve material properties that are difficult or impossible to achieve with pure polymer or composite materials.

ORMOCER[®]s are the result of a wide variety of combinations and proportions of chemical assemblies (Fig. C2). The inorganic Si-O-Si network is built up in the sol-gel process by controlled hydrolysis and (poly)condensation of substituted silicic acid or other metal esters and metal oxides in solution. Synthesis is controlled by suitable catalysts, temperature, solvents or the ratio of the various precursors in such a way that no further hydrolysis/(poly)condensation processes occur that correspond to a gel in a classical sol-gel process. The Si-O-Si units produced in this way are organically modified nanoscale units whose size ranges from less than 1 to over 10 nm. At this stage, the materials are available as storage-stable resins with different viscosities. (Meth)acrylic, styryl or epoxy groups are often used as organic groups, with the help of which the material can be organically photochemically and/or thermally crosslinked (organically polymerized). The choice of precursors with their organic groups (e.g. aromatic, aliphatic,...) as well as the catalytically controlled synthesis lead to an adjustment of material properties within certain limits for applications in the field of microelectronics [Rob98, Frö02], passivation [Hou01, Hou03], optics or also energy generation/storage [Pop98, Dep00]. There are ORMOCER[®]s for various applications on the market, ranging from scratch-resistant coatings [Amb91, Ros95] to a range of dental ORMOCER[®]-based fillers [Wol94] and materials for optical applications [Uhl95, Str02]. The inorganic oxide network has a decisive influence on mechanical strength, thermal stability and the coefficient of thermal expansion (CTE). Additional organic groups can be incorporated by appropriate derivatized silicic acid esters. By varying the organic components and inorganic network formers such as silicon, aluminum, titanium, zirconium, etc., the material properties can be varied over a wide range.

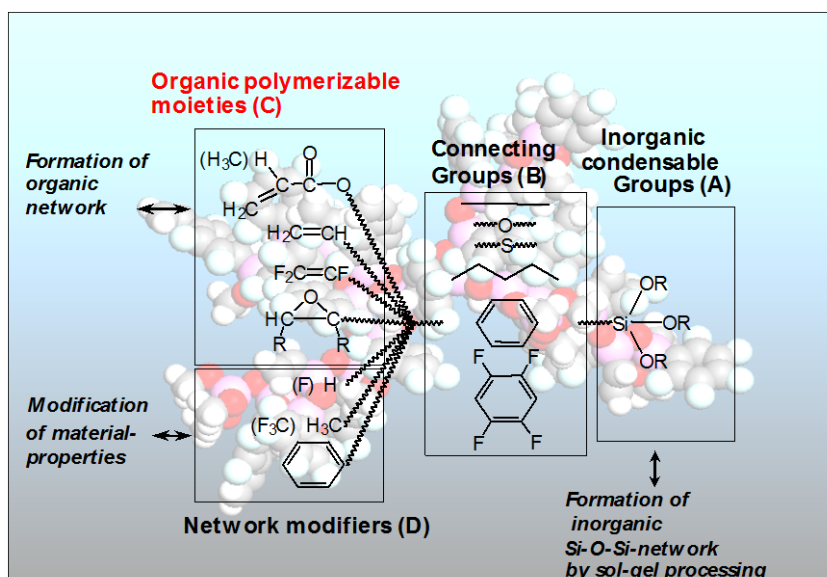


Fig. C2: Schematic drawing of typical starting products (alkoxysilanes) for the production of ORMOCER[®]s, e.g. for (micro-)electronics⁸

1.9.2 Properties

Already during the development and modification of ORMOCER[®]s (synthesis), the requirements for the properties of the material with regard to the intended application and subsequent process control are taken into account. In addition to the dielectric or barrier-typical parameters that must be achieved for special applications, questions of adhesion to the substrates specified by the user, thermal stability, chemical resistance and process control typically play a role. Since ORMOCER[®]s are composed of organic and inorganic components, they have very good adhesion properties on both polymers and inorganic materials such as metal and glass. They are exceptionally well suited for assembly and connection technology. ORMOCER[®]s can be applied with the usual coating processes, such as spinning, doctoring, dipping, flooding or spraying. They are cured thermally from 80 to 100°C and/or photochemically by UV radiation. Although their temperature stability can reach up to 400°C in some cases, they can be crosslinked during the thermal cross-linking process at temperatures rarely higher than 150°C. This means that they can also be used on temperature-sensitive substrates such as printed circuit boards or films. ORMOCER[®]s as coating materials for microelectronics have high surface and continuity resistances. They are also resistant to organic solvents and environmental influences. They absorb hardly any water and show good barrier properties against water vapor. The resulting layers are colorless and transparent.

1.9.3 Application in microelectronics

As already mentioned, variable material and processing properties are a consequence of multi-functionality. This is particularly important for applications in the field of assembly and connection technology.

⁸ The condensation of the inorganic part of the alkoxysilanes leads to organically functionalized inorganic units including polymerizable groups such as methacrylates or epoxy functionalities.

The main features for applications in the field of microelectronics / passivation are:

- Combination of ORMOCER[®]s as dielectric and passivation layers for electrical systems and components with high integration capability.
- Thermal final curing at temperatures between 80 and 150°C allows not only the use of semiconductor or glass substrates, but also of low-cost substrates such as printed circuit boards and films.
- Possibility of adaptation in the thin and thick film range as well as to the most diverse processing conditions.

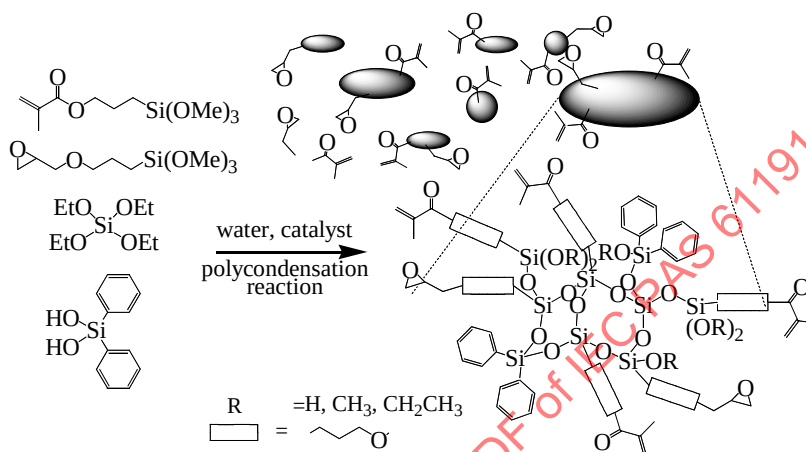


Fig. C3: General scheme of ORMOCER[®] A-synthesis for (dielectric) passivation⁹

The following material example focuses on thin layers (< 20 µm) for passivation against environmental influences, e.g. moisture. At the same time, the material shows very good dielectric properties, which will be demonstrated by means of examples. Fig. C3 shows a generalized synthesis scheme [Hou01]. The material (ORMOCER[®] A) consists of four different co-condensed alkoxy-silanes: 3-glycidyloxypropyl trimethoxysilane (G), 3-(methacrylic-oxypentyl)trimethoxysilane (M), diphenylsilanediol (P2) and tetraethoxysilane (T). In addition to its excellent passivation and dielectric properties, the material, like all ORMOCER[®]s for microsystems technology, can be crosslinked not only thermally but also by UV lithography. This is used, for example, in the area of dielectric on-chip passivation (see Fig. C4) in order to offer a cost-effective alternative to the PVD layers of SiO₂ or Si₃N₄ that are normally used.

In general, materials for the AVT must meet the highest purity requirements, so that, for example, ionic impurities are avoided by upstream purification of the ORMOCER[®] precursors during synthesis. This passivation material offers the possibility of significantly reducing the coating thicknesses of >> 100 µm or more (for classic casting compounds) typically used for good passivation of components. The material can be used reliably as a barrier layer against moisture in the coating thickness range between 1 and 20 µm. This coating thickness range has proven to be ideal, as the very good adhesion to the substrate within the interface layer/substrate is maintained even when the temperature is cyclized.

⁹ The organically functionalized oligomers (ellipses and circles) represent the resin, which can be further processed by organic cross-linking.

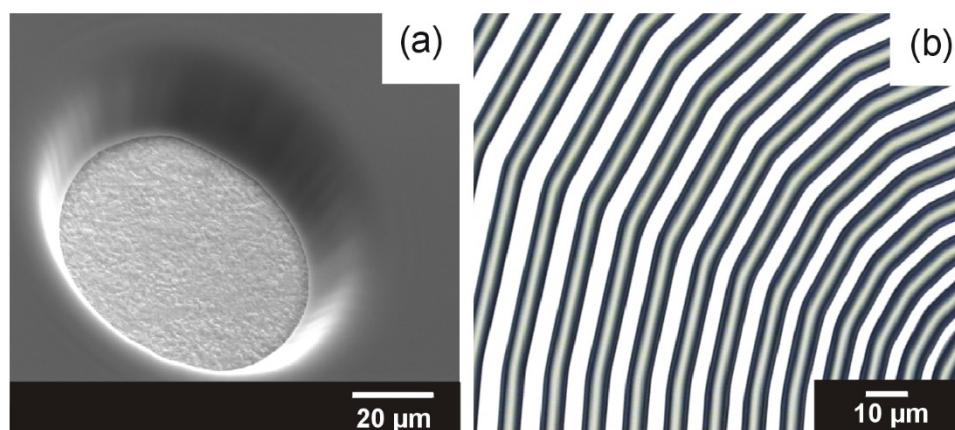


Fig. C4: (a) SEM image of a through-hole in ORMOCER®A on a Ti/Cu/Ti metallization layer; (b) Light microscope image of dielectric-passivated Guard rings (dark) in Si detectors on an Si/SiO₂ substrate (light). The layers were applied by centrifugation

Passivation of assemblies and assembled boards is carried out to reduce or avoid corrosion due to environmental influences which would inevitably lead to component failure. One of the most important prerequisites for avoiding corrosion is very good adhesion of the passivation materials used to the components or circuit boards. The better the adhesion, the more the condensation of water vapor or the diffusion of salts to or along the coating material/substrate interface is reduced. The best adhesion is generally achieved for clean surfaces, i.e. surfaces that are free of contamination, e.g. by flux from assembly processes. Any contamination prevents direct bonding of the passivation material to the components or circuit boards. ORMOCER® has particularly good adhesion to metals due to the reaction of Si-OH/Si-OR groups with the oxo-hydroxo groups of the metal. In addition, hydrogen bonds may occur which have a higher bond strength than van der Waals bonds.

To provide very good corrosion protection, the water vapor permeation, which is the product of water vapor diffusion and water solubility in the material, must be very low in addition to good adhesion of the passivation material to the coated components or circuit boards. The water vapor permeation rate for ORMOCER®A is below 3 g/(m²d), based on a coating thickness of 100 μm [Pol85]. The water absorption of the material is significantly less than 0.5% by weight. It should also be mentioned that water vapor permeation cannot be completely avoided in polymeric materials. This is due to the fact that polymers generally have mobile groups and therefore free volume. Therefore, in the synthesis of passivation materials, care is taken to achieve very low water solubility and thus low water absorption in the passivation layers, combined with good adhesion to prevent condensation at the interface between passivation material and substrate.

For the application of ORMOCER®A as passivation layer in assemblies or complete boards, processes such as dip or curtain coating as well as spraying are predominantly used. These coating techniques guarantee a uniform coating, although smaller coating thickness variations can occur on sharp edges of e.g. SMT components. In addition, these processes can also be used to coat the undersides of components on assembled circuit boards without air bubbles due to the low viscosity of the materials. Since UV exposure cannot be used for this, the ORMOCER® is thermally crosslinked at low temperatures (< 120°C) using suitable thermal initiators such as azobisisobutyronitrile or aliphatic amines. This also removes solvents that are added to the resin to adjust the viscosity from the coating.

SMT thin film capacitors [Pop92] (Fig. C5a) were chosen as an example for demonstrating

the passivation properties of ORMOCER®A. They consist of stacked metallized PET foils with outer contact electrodes made of a nickel alloy. The ORMOCER® was used here to prevent aluminium corrosion. Hexahydrophthalic acid anhydride was added to the ORMOCER® as thermal initiator for thermal crosslinking. The passivated components passed all stability tests, such as thermal cycling (-40°C / $+125^{\circ}\text{C}$, 100 cycles) and reflow soldering (270°C for 30 s). The passivation properties were tested by a modified Bellcore test: instead of 85 % relative humidity / 85°C 100 % relative humidity / 95°C were used to shorten the test duration until the capacitors failed. For each test, 100 capacitors were dewed and measured.

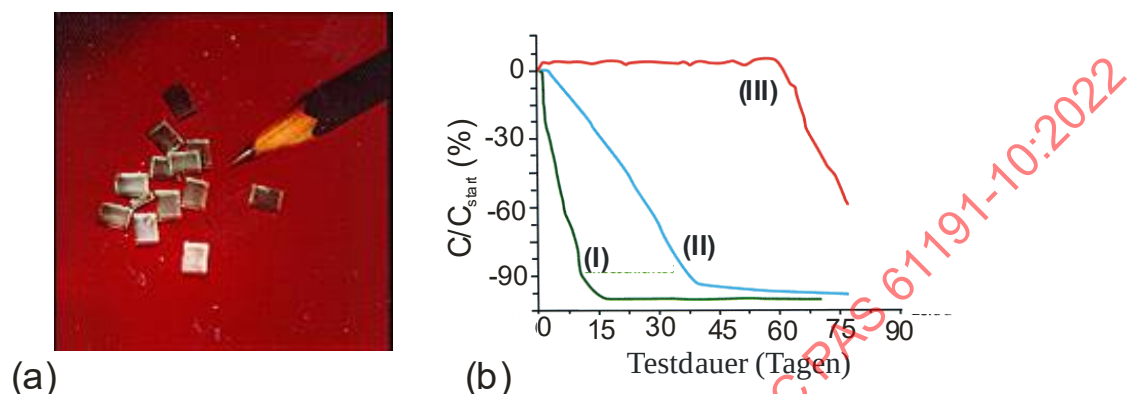


Fig. C5: (a) passivated thin film capacitors; (b) change in capacitance of uncoated (I), conventionally encapsulated (II) and ORMOCER®A coated (III) thin film capacitors depending on the test duration. The test conditions were 95°C / 100 % relative humidity

Fig. C5 shows the thin-film capacitors coated with ORMOCER®A and a comparison of the percentage reduction of capacitance for uncoated capacitors cast with epoxy (coating thickness more than 1 mm) and ORMOCER®A-coated (coating thickness approx. $2\text{ }\mu\text{m}$) depending on the test duration. While uncoated capacitors failed after approx. 15 days, the encapsulated capacitors failed after approx. 37 days. The capacitors coated with ORMOCER®A showed an initial reduction in capacitance after approx. 60 days, whereby the complete failure only occurred after 105 to 120 days. The data impressively demonstrate the significant increase in service life due to the $2\text{ }\mu\text{m}$ thick ORMOCER® passivation layer. Table C3 summarizes the most important properties of ORMOCER®A.

Tab. C3: Select properties of ORMOCER®A

Adhesion to Al₂O₃, Si, Cu, Al (in acc. with DIN 53151 ¹⁰)	0-1, 1-2, 0-1, 0-1
Permittivity ϵ_r (10 kHz)	3,4
Dielectric loss $\tan \delta$ (10 kHz)	< 0.006
Specific resistance	> 10 ¹⁶ Ωcm
Dielectric strength (auf Cu)	400 V/ μm
Young's module	2.5 GPa (adjustable)
Solder stability (reflow)	270°C / 1 h
Degradation (TG, heating rate 5 K/min)	> 270°C
Water absorption	< 0,5 masses-%
Water vapor permeation rate (based on 100 μm)	< 3 g/(m ² ·d)

1.10 Parylene

1.10.1 Introduction

The role of polymers in electronics and medical fields, particularly in miniaturized device and components, continues to grow rapidly due to increasing demand for more reliable products and advances in other technical fields. With the number of medical (implantable and non-implantable) and electronics devices increasing, the challenges related to making these devices safe and effective are also increasing. Advancements in materials technology have led to the development of several materials that are inherently stable but that tend to degrade when subjected to harsh environments. As miniaturization of medical devices and electronics continues, the required performance of these devices in different type of harsh environments has led many packaging companies and manufacturers to the world of advanced materials and polymeric conformal coatings.

Conformal coatings, which conform to the shape of the substrate they are applied to, can broadly be divided into two main categories: inorganic and organic conformal coatings. All polymeric coatings (liquid and vapor phase coatings) that are applied on PCBs, medical devices and their respective components to protect them from corrosion and their harsh operating environments are referred as conformal coatings. Although research work continues for the development of new materials, the most commercially available conformal coating types include urethanes, silicones, acrylics, epoxies and Parylenes. The choice of which material to use depends on the application, quality, cost and operating conditions.

Among the available conformal coatings, Parylenes (vapor phase deposited organic coatings) have played a significant role in packaging and protection of electronic devices and enhancement of their overall reliability in harsh environments. Parylenes have also been very effective on non-implantable and implantable medical electronic devices, providing protection from adverse environmental effects. Examples of Parylenes in medical electronic devices include ocular implants, implantable cardiac defibrillators, neurostimulator

¹⁰ DIN 53151 → EN ISO 2409 2013-6 EN ISO 2409:2005 Coating materials - Cross-cut test (ISO/DIS 2409:2005): The cross-cut test is used to assess the strength of single and multi-layer coatings (coating systems) on their substrate and the adhesion of the layers to each other. The coating is provided with a cross-shaped, continuous cutting strip of six cuts each, so that a grid with 25 squares is formed. The grid section characteristic "GT" is determined by visual comparison with the evaluation table.

pulse generators, RFID implants, transdermal drug delivery devices, digital dental imaging equipment, cochlear implants, ingestible sensors/transmitters, and implantable radiation dosimeters [Kup15, Liu13, Lah02, Cha05, Cha05a].

Parylene polymers have also been considered an integral part of medical devices by many biomedical engineering researchers as electronic devices are made of Parylene through MEMS technology [Men03, He03, Men05, Men01]. Parylenes have drawn considerable attention as a structural material for microfluidic devices because of their exceptional properties, including stress-free, truly conformal deposition, chemical inertness, bioacceptability and optical transparency. Examples of such developments include mass flow controller (consisting of an electrostatically actuated microvalve) [Xie03, Men03a], Parylene micro-nozzle for electrospray [Wan99], Parylene flapping wing [Por01], Parylene electrophoretic channel and electrostatic actuators [Web00]. Such advancements in Parylenes, coupled with existing coating capabilities, will enhance the role of micro and nano electronics in many medical applications.

As we move towards a more energy-efficient economy, the use of electronics and sensors in automotive, aerospace, military, medical and marine industries has been increasing. These sensitive electronic components are packaged into smaller devices, and the ability to repair these devices has become more difficult. Extended warranty requirements impose higher reliability and longevity standards. On top of that, environmental legislation is setting limitations on the use and/or applicability of certain VOC (volatile organic component) materials. The demands on these industries, where organic materials have been used for decades, continue to evolve.

Advancements in Light Emitting Diode (LED), Organic Light Emitting Diode (OLED) and Flexible Organic Light Emitting Diode (FOLED) technologies have led to the development of various display and electronics applications in military, aerospace, automotive, electronics, signage and medical fields. Such advancements have had a positive impact on human life, and are commercially successful due to their energy-efficiency and cost-effective operation. However, there are still many stability, reliability and environmental challenges, particularly when LED devices are subjected to outdoor and other harsh environments where they must survive extreme temperatures, moisture and UV light exposure.

Wafer-level packaging (WLP) is a key technology in the introduction of a new class of devices (e.g., 3D products, MEMS, etc.) that faces numerous challenges, including integration of multichip, chip passives, embedded passives, hermetic sealing on wafer-level, gap filling, and overall long-term reliability. As this technology moves forward, a variety of wafer-level packages have been developed, including thin film redistribution and bumping, encapsulated packaging, compliant interconnecting, wafer-level underfilling, use of through-wafer-vias, wafer thinning, and the ability to bond or integrate these new structures [Zha07, Thr09, Hum08]. Driven by the demand for improved integration methods, reliability and performance, innovative solutions are being explored by researchers. One of the developing areas includes insulator formation by CVD polymers for providing integration ease and overall protection from environmental effects.

Over the past couple of years, there have been advances in the vapor phase insulating polymers themselves, particularly in the types of new materials and their possible applications within the electronics industry. This article attempts to provide an understanding of Parylene technology to help address integration, protection and reliability challenges of electronics, medical devices and other related components operating in harsh environments.

1.10.2 Parylene polymers: chemistry and processing

Parylene is the generic name for members of a unique polymer series. The Parylenes (xylylene polymers) have been classified as thermoplastic polymers that are formed on substrate surfaces using vacuum deposition polymerization. The chemistry of Parylene polymers start with the quinonoid hydrocarbon, para xylylene or PX, and its polymer, poly-para xylylene or PPX, which were first reported in 1947 by Michael Szwarc who discovered this polymer accidentally while carrying out experiments to determine the bond energies of toluene and para xylene.

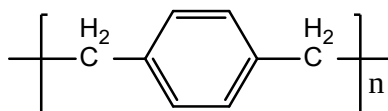


Fig. C6: Poly (p-xylylene) or PPX

Dr. Szwarc postulated the structure of poly (p-xylylene) as shown in Figure C6 and hypothesized that the p-xylylene (PX) is formed by pyrolysis of p-xylene at very low pressure (1 torr) and at temperature ranging from 800-1000°C. Vapor of p-xylene flowing through a heated quartz tube (residence time less than 0.1 second) undergoes homogeneous dehydrogenation yielding a p-xylyl radical and hydrogen atoms. Under heated conditions, the vapor of para xylylene does not polymerize in the gas phase, but spontaneously forms a polymeric film, or coating, on sufficiently cool surfaces exposed to para xylylene vapor. In this process, the monomer is converted directly into a polymer without being a liquid or having any other intermediate involved in the process. Many experiments and observations by researchers established the fact that poly-para xylylene is composed of a sequence of alternating -CH₂CH₂- and p-C₆H₄- units, which further confirmed the identity of para- xylylene and its quinonoid and diradical nature.

In 1949, the extraction of the poly (p-xylylene) film led to the isolation of a by-product of the polymerization, which was identified as a cyclic dimer of p-xylylene and showed that benzene rings in this molecule lie in parallel on above (Figure C7) [Bro49]. At the time of its isolation, only tiny amounts were available to understand its full characteristics.

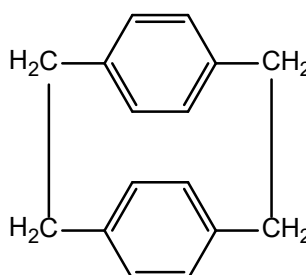


Fig. C7: Cyclic dimer of p-xylylene or di-p-xylylene (DPX) or paracyclophane

In 1951, Cram [Cra51] succeeded in its synthesis by more conventional means and the name “paracyclophane” was suggested for this class of compound. Unfortunately, Cram’s method could not be used for commercial scale production due to a very low yield of 2.1% and very poor conversion efficiency. Efforts to produce this compound in a high yield continued, and in 1960, Pollart discovered a method for producing the di-p-xylylene in yields of 10% or higher and at very high conversion efficiencies. This development inspired research work in number of industrial laboratories around the world to produce poly-p-xylylene polymers.

A breakthrough was marked in 1965 by the experiments of William F. Gorham of Union Carbide with cyclic di-*p*-xylylene or paracyclophane (Figure C7) for the preparation of poly(*p*-xylylene) [Gor65, Gor66, Gor67]. Gorham's work demonstrated that the necessary reactive intermediate could be produced quantitatively in pure form from the cyclic di-*p*-xylylene (a cyclic dimer) under milder conditions than those required for its production from *p*-xylylene. A further advantage of the Gorham process was the absence of gaseous by-products, a disadvantage of the production of *p*-xylylene by all other means then known. Gorham's continued efforts culminated in the issuance of a patent in 1967 showing a commercially interesting method for the production of poly (*p*-xylylene) film and coatings. *p*-xylylene polymer coatings developed by Union Carbide Corporation using the Gorham process are later referred to generically as the Parylenes. Today, the vapor deposition polymerization process, casually known as the Gorham Process, is the commercial Parylene coating process utilized throughout the world.

In the commercial Gorham process [Gor67], the extremely reactive PX is conveniently generated by the thermal cleavage of its stable dimer, cyclic di-*p*-xylylene (DPX), a paracyclophane. In many instances, substituents attached to the paracyclophane framework are carried through the process unchanged, ultimately becoming substituents of the polymer in the coating.

The Gorham process takes place in three distinct steps as outlined in Figure C8, representing a typical Parylene deposition process. Current commercial deposition equipment is also shown in Figure C9 (courtesy by Specialty Coating Systems, Inc.). The first step is the vaporization of the solid dimer at approximately 150°C under vacuum. The second step is the quantitative cleavage (pyrolysis) of the dimer vapor at the two methylene-methylene bonds, at about 680°C, to yield the stable monomeric diradical, *p*-xylylene. Finally, the monomeric vapor enters the room temperature deposition chamber where it spontaneously polymerizes on the substrate. The substrate temperature never rises more than a few degrees above ambient. No liquid phase has ever been isolated, therefore Parylene suffers none of the fluid effects that can cause pooling, flowing, bridging, meniscus or edge-effect flaws. Parylene also contains no solvents, catalysts or plasticizers that can leach or outgas from the coating.

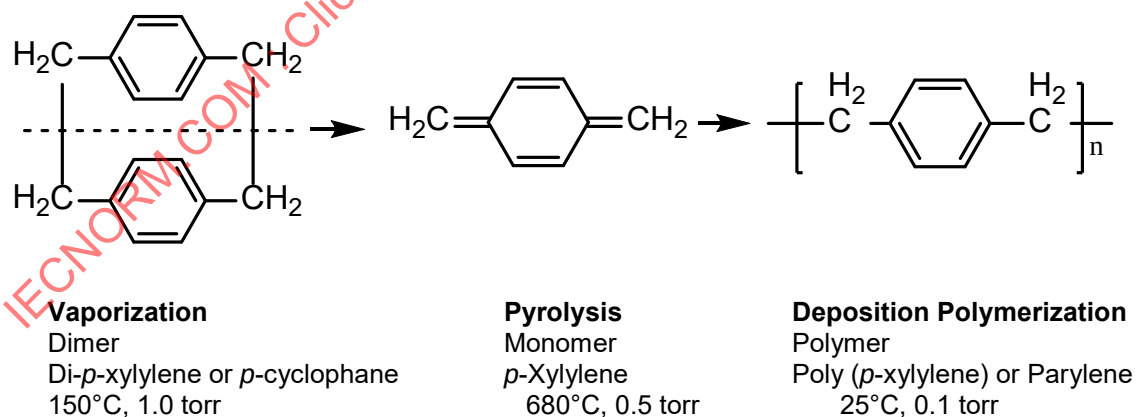


Fig. C8: Parylene vapor deposition polymerization (VDP) process.

The Parylene process has certain similarities with metallizing. Unlike vacuum metallization, however, which is conducted at pressures 10⁻⁵ torr or below, the Parylenes are formed at around 0.1 torr. Under these conditions, the mean free path of the gas molecules in the deposition chamber is in the order of 0.1 cm. As a result, all sides of an object

to be coated are uniformly impinged by the gaseous monomer, providing a high degree of conformability. The principal distinction is that truly conformal Parylene coatings are deposited, even on complex, three-dimensional substrates, including on sharp points and in hidden or recessed areas. Vacuum metallizing, on the other hand, is a line-of-sight coating technology. Whatever areas of the substrate cannot be “seen” by the evaporation source are “shadowed” and remain uncoated.



Fig. C9: A commercial Parylene Deposition System, SCS PDS 2060PC (Photo courtesy of Specialty Coating Systems, Inc.)

Parylene research and development efforts for the past several decades have resulted in many dimer (raw material) variants, primarily by substitution of hydrogen either from aromatic ring positions or from alpha positions of paracyclophane with halogens, organic reactive groups and/or other substituents. Although advancement in substitution chemistry has helped create many Parylene dimer variants, there are three key limitations of Gorham process, in addition to desired polymer performances, that seem to have had significant effects on their commercial success. These limitations are: (i) any substitution or modifications should not decrease the reactivity of the monomer towards polymerization; (ii) the dimer and monomer should perform well in deposition polymerization equipment; and (iii) the feedstock (dimer) from which monomer is generated must be produced at a cost that can be borne by its potential applications. While the Gorham process can be utilized by anyone to produce Parylene polymer coatings, there are several processing parameters and the art of these being carried out impacts the quality and overall performance of Parylene coatings when applied on various substrates. For example, there are significant processing and yield challenges in the processing of fluorinated Parylenes commercially. However, through technological innovation and experience, success has been achieved to apply fluorinated Parylene on a large scale by some while others still face challenges.

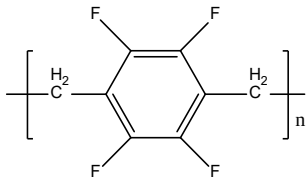
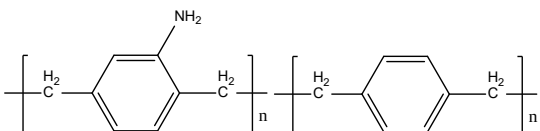
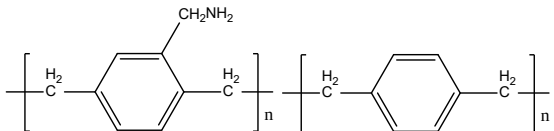
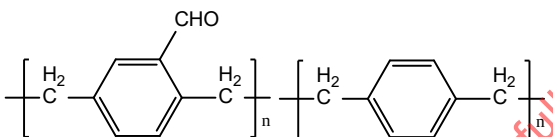
Among the various Parylene variants that were developed or advertised until now, only four of them (Parylene N, Parylene C, Parylene D and Parylene HT) have found wide commercial application and are shown in Table C4 with their commercial or alternatively known names. There are other Parylene types (Table C5) mentioned with their molecular structure in the commercial domain, but their commercial viabilities have either been not established yet or they have very limited potential application. The terms Parylene N, Parylene C, Parylene D, and Parylene HT refer specifically to polymers produced as coatings by the Gorham process using their respective solid state dimers. It is important to note that deposition parameters determine the quality of a polymer coating, so same-structure dimer products may yield different qualities of polymers depending on the pa-

rameters and other factors by which they are applied. Some commercial Parylenes are also available with a fluorescent dye (as a tracer) to facilitate confirmation of their presence on the substrates. In addition, several copolymers of p-xylylenes have been prepared either by simultaneous deposition of the mixture of functionalized paracyclophane derivatives or separately pyrolyzed paracyclophane with different substituents or reactive compounds, but they are limited to academic curiosity. Examples of Parylene containing inorganic substances within its polymeric matrix also exist in academic area. Research and development work continues to create new variants, including surface modified Parylenes to meet future challenges. Recently, a commercial development in the Parylene area was announced, the launch of “microRESIST® ” an antimicrobial Parylene technology. This significant technology, which will be discussed later in this article, combines the benefits of Parylene with antimicrobial properties to effectively eliminate harmful microorganisms on coated devices and components.

Tab. C4: Worldwide commercially available Parylene types

Parylene Type	Name
$\left[\text{H}_2 - \text{C} - \text{C}_6\text{H}_4 - \text{C} - \text{H}_2 \right]_n$	- Parylene N
$\left[\text{H}_2 - \text{C} - \text{C}_6\text{H}_3(\text{Cl}) - \text{C} - \text{H}_2 \right]_n$	- Parylene C
$\left[\text{H}_2 - \text{C} - \text{C}_6\text{H}_2(\text{Cl})_2 - \text{C} - \text{H}_2 \right]_n$	- Parylene D
$\left[\text{F}_2 - \text{C} - \text{C}_6\text{H}_4 - \text{C} - \text{F}_2 \right]_n$	- Parylene HT® - diX SF

Tab. C5: Parylene types with unknown or very limited commercial application

Parylene Type	Name
	- Parylene F - Parylene VT4
	- Parylene A - Amino Parylene
	- Parylene AM - Amino methyl Parylene
	- diX H

1.10.3 Properties of Parylenes

One of the key features of the Parylenes that dominates the decision for their use in many applications is the vapor phase deposition polymerization (VDP) process by which they are applied. VDP provides a room temperature coating process and produces films of uniform thickness, having excellent thickness control, conformality and purity. Parylenes formed by Gorham process, under typical conditions, are highly crystalline polymers. The crystal structure and the morphology of Parylene N (PPX) are well known [Kir86, Iwa73, Iso83]. Parylene exists in two crystalline forms: α and β forms. Parylene (PPX) coating formed by the usual Gorham process shows the α crystalline structure and may change to β form either by heating or annealing or stretching. The transition from β to α , upon cooling, is kinetically hindered, although there is information about such transition. The crystalline phase undergoes further modifications at higher temperatures before reaching its melting point of 420°C; these modifications have not been fully explored. The detailed crystal structures of the α ($a = 592$ pm, $b = 1060$ pm, $c = 655$ pm, $\beta = 134.7^\circ$, for two monomer repeat units per cell) and β ($a = b = 2052$ pm, $c = 655$ pm, $\gamma = 120^\circ$, for 16 monomer repeat units per cell) modifications have been determined. The crystallinity of the Parylenes is normally limited to small sub-micrometer domains, uniformly disposed throughout the continuous amorphous phase. The crystals are oriented such that the molecular chains are parallel to the substrate [Iso83a, Nie67, Mat73].

The typical properties of widely-used commercial Parylenes are discussed below.

1.10.3.1 Physical and Mechanical Properties

Physical and mechanical properties of the Parylenes are summarized in Table 3. Most mechanical properties of the Parylenes are similar to those of other conventional plastics and they vary considerably with aging and annealing. However, Parylenes keep their flexibility even at very low temperatures. Because of their high molecular weight (~500,000) and because the melting temperatures and crystallinity are high, the Parylenes cannot be formed by conventional methods such as extrusion or molding. It has been reported that Parylene N is deposited in a state of compressive stress [Bac87]. The inherent stress is 18 MPa (2300 psi) and is invariant with thickness. This congenital compressive stress can be removed and rendered tensile by a thermal cycle. Solubility in organic or other media, except at temperatures above 175°C, is so low that they cannot be formed by casting.

Impact resistance is high when the Parylene polymers are supported on test panels. Gardner falling ball impact tests on 25.4 µm thick Parylene C coated steel “Q” panels are in the 28.2 N·m range. Wear index values (measured on a Taber® Abraser machine using CS-17 “Calibrase” wheel with 1,000 gram weight) were 22.5 for Parylene C and 8.8 for Parylene N. By comparison, polytetrafluoroethylene is 8.4, high impact polyvinylchloride is 24.4, epoxy is 41.9, and polyurethane is 59.5 [Par14].

1.10.3.2 Electrical Properties

Parylenes are excellent candidates for use in electronics because of their bulk electrical properties. The dielectric constant and dielectric losses are very low and unaffected by moisture absorption. The bulk resistivities are advantageously high because of the purity of the Parylenes, their low moisture absorption, and in particular their freedom from trace ionic impurities. The low dielectric constant for Parylene in the gigahertz frequency range is often of great interest to designers of high frequency devices. Exhibiting the lowest dielectric constant among Parylenes, Parylene HT is particularly suited for these applications. The typical electrical properties of Parylenes are shown in Table C7.

Tab. C6: Parylene Physical and Mechanical Properties

Properties	Method	Parylene N	Parylene C	Parylene D	Parylene HT
Secant (Young's) Modulus (psi)	1, 2	350,000	400,000	380,000	370,000
Tensile Strength (psi)	3	7,000	10,000	11,000	7,500
Yield Strength (psi)	3	6,100	8,000	9,000	5,000
Elongation to Break (%)	3	Up to 250	Up to 200	Up to 200	Up to 200
Yield Elongation (%)	3	2.5	2.9	3.0	2.0
Density (g/cm ³)	4	1.10 – 1.12	1.289	1.418	1.32
Index of Refraction (n _D ²³)	5, 6	1.661	1.639	1.669	1.559
Water Absorption (% after 24 hrs)	7	Less than 0.1	Less than 0.1	Less than 0.1	Less than 0.01
Rockwell Hardness	8	R85	R80	R80	R122
Coefficient of Friction	9				
Static		0.25	0.29	0.33	0.15
Dynamic		0.25	0.29	0.31	0.13
Test Methods: 1. ASTM D 882 (except Parylene HT) 2. ASTM D 5026 (Parylene HT only) 3. ASTM D 882 4. ASTM D 1505 5. Abbe Refractometer (except Parylene HT) 6. ASTM D 542 (Parylene HT only) 7. ASTM D 570 8. ASTM D 785 9. ASTM D 1894					

Tab. C7: Parylene Electrical Properties

Properties	Method	Parylene N	Parylene C	Parylene D	Parylene HT
Dielectric Strength (V/mil)	1	7000	5600	5500	5400
Volume Resistivity (Ohm • cm, 23°C, 50% RH)	2	1.4×10^{17}	8.8×10^{16}	1.2×10^{17}	2.0×10^{17}
Surface Resistivity (Ohms, 23°C, 50% RH)	2	1.0×10^{13}	1.0×10^{14}	1.0×10^{16}	5.0×10^{15}
Dielectric Constant	3				
60 Hz		2.65	3.15	2.84	2.21
1 KHz		2.65	3.10	2.82	2.20
1 MHz		2.65	2.95	2.80	2.17
Dissipation Factor	3				
60 Hz		0.0002	0.020	0.004	<0.0002
1 KHz		0.0002	0.019	0.003	0.0020
1 MHz		0.0006	0.013	0.002	0.0010
Test Methods:					
1. ASTM D 149					
2. ASTM D 257					
3. ASTM D 150					

Many electronics and medical electronic devices are used in critical areas with great demand on reliability. Generally for electronics applications, moisture-insulation resistance tests are carried out in an accelerated manner to evaluate the resistance of conformal coatings to the deleterious effects of high temperature/humidity conditions. Insulation resistance of Parylenes N, C and Parylene HT coated Y-test pattern boards were tested in accordance with MIL-STD-202, Method 302 (test conditions of Temp: 23°C, RH: 50%) and Method 106 (test conditions of Temp: 65°C and RH: 90-95%). This MIL standard is also recognized as meeting the requirements of IPC-CC-830B. Moisture insulation resistance measurements were taken using a megohms bridge at 500 volts DC, with an electrification time of one minute during the 1st, 4th, 7th and 10th cycles at high temperature and humidity. The test consists of 10 cycles (one cycle per day), with each cycle consisting of seven steps. The seven steps range from low temperature, low humidity (23°C, 50% RH) to more severe conditions (65°C, 95% RH). The insulation was again measured upon completion of the moisture resistance test, after a 24-hour stabilization period.

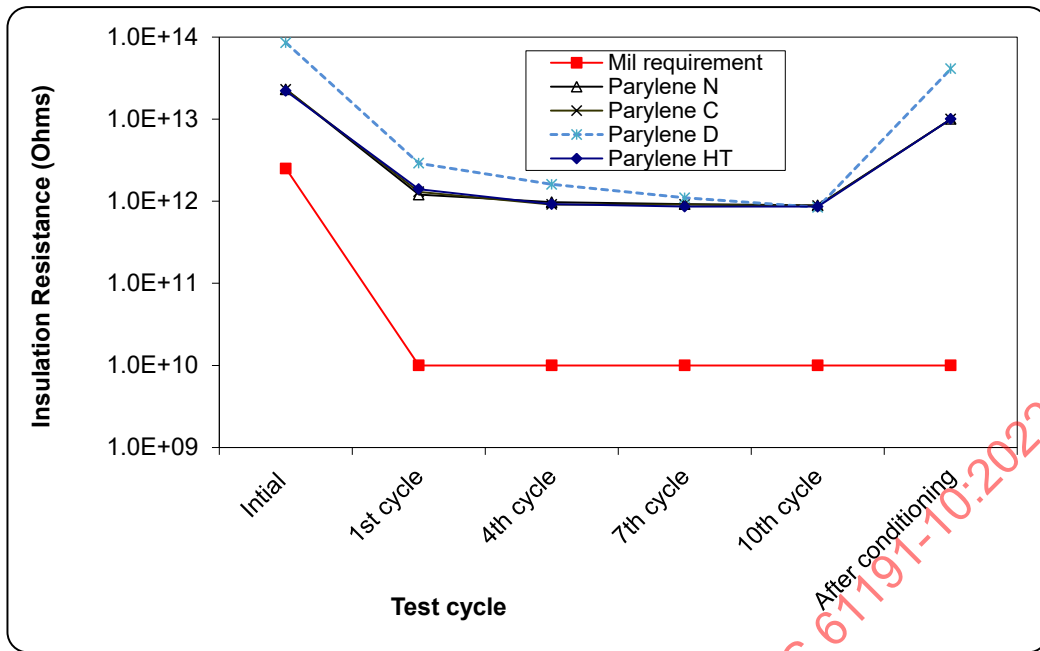


Fig. C10: Moisture insulation resistance of Parylenes

All Parylenes met the MIL requirements for dielectric withstanding voltage at lower thickness (less than 1.0 mil). The tests indicate that Parylenes are capable of providing excellent electrical insulation in many adverse conditions.

A separate study [Rei05] concluded that Parylene C coating with a thickness of 0.05 mm on PCBs was capable of maintaining electrical insulation properties during immersion in PBS solution (phosphate buffer saline, P-3813) at temperatures of 40-80°C for six months.

1.10.3.4 Thermal Properties

General thermal properties are summarized in Table C8.

Tab. C8: *Parylene Thermal Properties*

Properties	Method	Parylene N	Parylene C	Parylene D	Parylene HT
Melting Point (°C)	1	420	290	380	>500
T5 Point (°C) (modulus = 690 MPa)	2, 3	160	125	125	377
T4 Point (°C) (modulus = 70 MPa)	2, 3	>300	240	240	>450
Continuous Service Temperature (°C)	–	60	80	100	350
Short-Term Service Temperature (°C)	–	80	100	120	450
Linear Coefficient of Thermal Expansion at 25°C (ppm)	4	69	35	38	36
Thermal Conductivity at 25°C (W/(m•K))	5, 6	0.126	0.084	–	0.096
Specific Heat at 20°C (J/(g•K))	–	0.837	0.712	–	1.04
Test Methods:					
1. DSC		4. TMA			
2. Taken from Secant modulus-temperature curve (except Parylene HT)		5. ASTM C 177 (except Parylene HT)			
3. ASTM 5026 (Parylene HT only)		6. ASTM 1461 (Parylene HT only)			

Parylenes exhibit changes in mechanical properties with changes in temperature, much like other materials. The oxidative chain scission is the most important mode of degradation for Parylenes. Freestanding Parylenes N, C and D films were exposed to constant elevated temperatures in air-circulating ovens for periods of weeks to months. After exposure, physical properties of the film were analyzed. In the degradation of many polymers, tensile strength is maintained until chain scission has reduced the molecular weight to the point at which entanglement is no longer a factor in determining physical properties. Despite the large variance in tensile strength measurements, the reduction criterion (along with reduction in elongation) allows a reasonable prediction of end of useful life on a log time scale. Although in today's world it may be a matter of scientific debate whether or not to use the Arrhenius extrapolation to predict the end of useful life of any material, a conservative extrapolation of an Arrhenius Plot of failure time (based on reduced elongation and tensile strength) verses temperature is used to determine the ends of useful life for Parylenes N, C and D, and is shown in Figure 7. The data suggest that Parylenes N, C, and D perform in air without significant loss of physical properties for 10 years at 60, 80 and 100°C, respectively.

At different times, freestanding films of Parylene HT, which has higher thermal stability, were also exposed to constant elevated temperatures in air-circulating ovens for periods of weeks to months. After exposure, tensile and elongation properties of the film were analyzed. Based on the failure criterion, which was reduction in tensile strength, an extrapolation of an Arrhenius Plot of failure time verses reciprocal of absolute temperature was developed for Parylene HT and compared with the existing data for Parylene C as shown in Figure C11. This data suggests the following ends of useful life for Parylene HT in comparison with Parylene C.

Parylene Types	150°C	135°C	80°C
Parylene HT	~ 40 yrs.	~ 100 yrs.	>100 yrs.
Parylene C	~24 hours	~70 hours	~10 yrs.

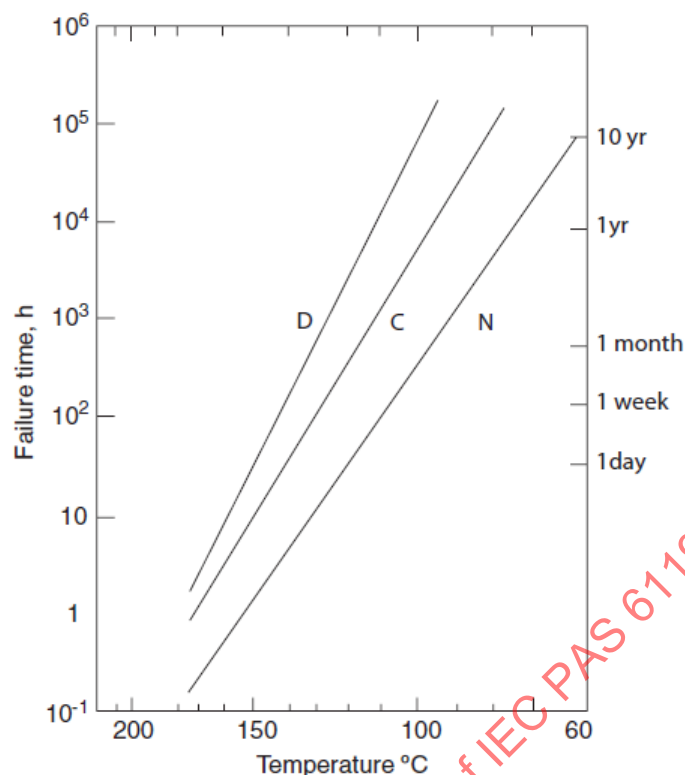


Fig. C11: Useful lifetime of Parylenes N, C, and D as a function of temperature in air (Failure = 50% loss in tensile strength)

Parylene HT has been demonstrated to survive continuous exposure to air for 1,000 hours at 350°C [Xie03]. Clearly, such data can justifiably be made to serve only as a guide for considering the Parylenes for a specific application. Questions of thermal endurance tend to have no clear-cut answers. In situations where performance may be marginal, there is no substitute for retesting under conditions more directly relatable to the application.

The oxidative chain scission is the most important mode of degradation for Parylenes. Significantly, hydrolytic degradation is chemically impossible. Oxidative degradation limits the use of Parylenes at elevated temperatures in many common applications. Figure C12 shows the effect of exposure to elevated temperature in air or in vacuum on elongation to break, an indicator of toughness, or lack of brittleness. The data are given for Parylene C, which suffers substantial change in mechanical properties as the freshly deposited material is annealed. Aging in air at 150°C for ~100 hours causes the elongation to break to drop from its initially very high value to 0, at which point the specimen is mechanically useless. Aging in vacuum at yet higher temperatures (265°C) for a similar length of time gives a stronger, more rigid, stabilized material with 15% elongation at break, the result of annealing.

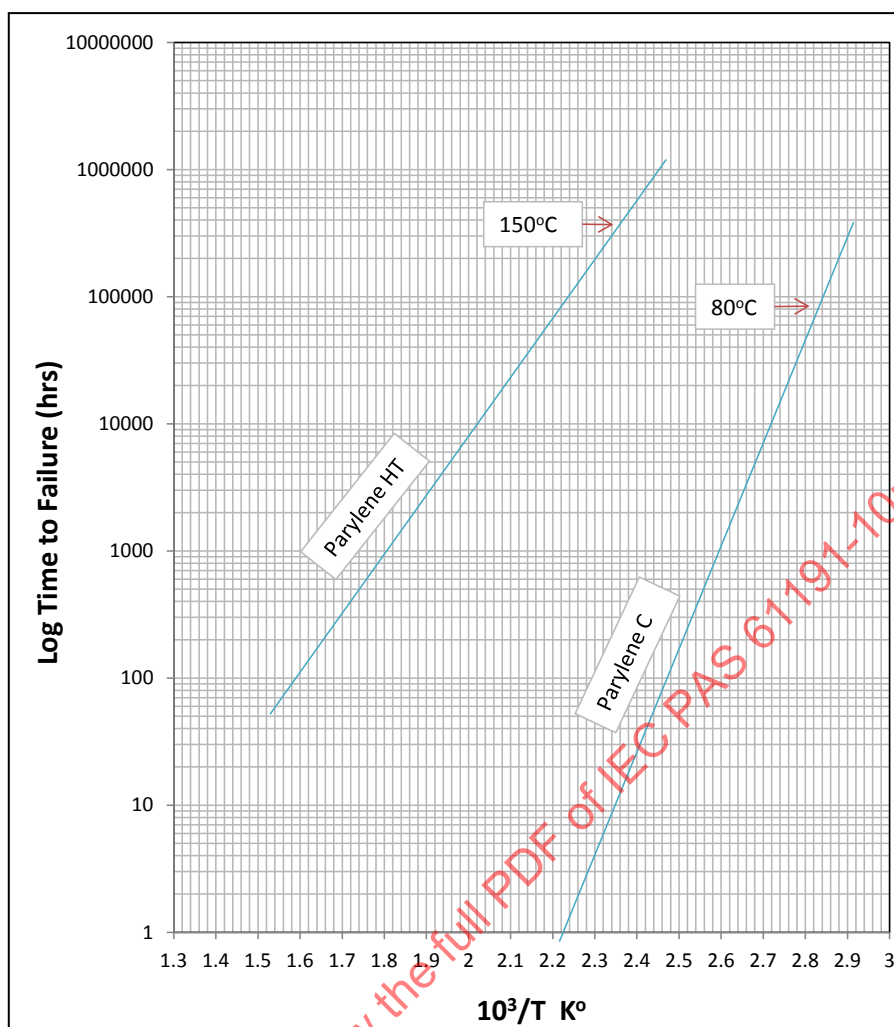


Fig. C12: Useful lifetime of Parylene HT and Parylene C as a function of temperature in air

In oxygen-free atmospheres or in the vacuum of space, the 10 years of continuous service temperature projections exceed 200°C for Parylenes N, C and D (Fig. 10). Conventional antioxidants, incorporated during or after VDP, can extend the life of the Parylenes at elevated temperatures [Pat79, Pat79a, Now80, Bak80]. On the other hand, Parylene HT has ability, without any antioxidants, to resist thermal oxidation up to 450°C both in oxygen and oxygen-free atmospheres. The excellent thermal oxidative stability of Parylene HT in both air and inert environments is due to the stable carbon-fluorine bond in the polymer chain [Kum04].

Another factor in oxidative degradation is ultraviolet radiation exposure. While the oxidation of Parylenes N and C appear to be enhanced by exposure to ultraviolet radiation, Parylene HT has much higher resistance. When exposed to an accelerated UV stability testing per ASTM G154, Parylenes N, C and D film survived less than 100 hours before yellowing or discoloration of the films occurred. Parylene HT film, however, was stable without any change in appearance or other visual properties for more than 2000 hours. The accelerated test was designed for 2000 hours, which roughly can be indicative of about twenty years of UV stability in normal outdoor environment [Kum06]. For the best physical endurance, exposure of the Parylenes to ultraviolet light must be minimized.

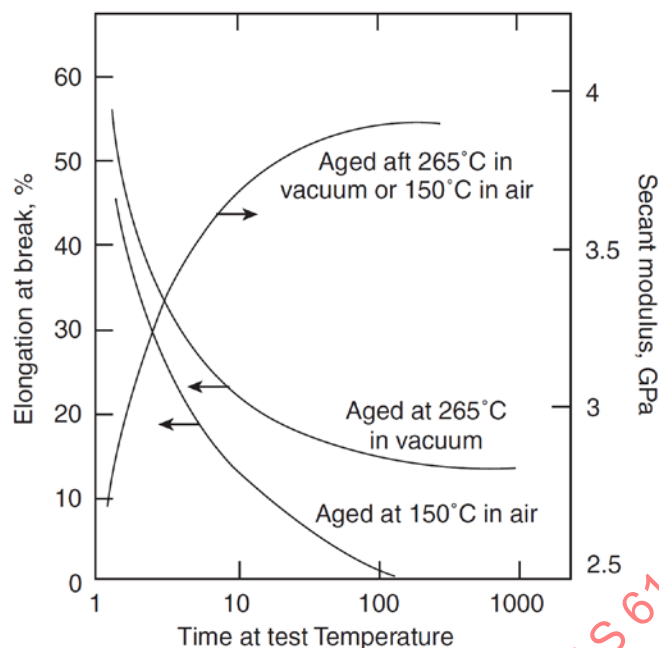


Fig. C13: Effect of temperature on the flexibility of Parylene C in air and vacuum
(To convert GPa to psi, multiply by 145,000)

1.10.3.5 Cryogenic

Unsupported 50.8 μm films of Parylene C can be flexed 180° six times at -200°C before failure occurs. Comparable films of polyethylene, polyethylene terephthalate and polytetrafluoroethylene fail at three, two and one flexes, respectively. Steel panels coated with Parylene C and chilled in liquid nitrogen at -196°C withstood impacts of more than 11.3 N·m in a modified Gardner falling ball impact test. This compares with values of about 28.2 N·m at room temperature. Supported films of Parylene N withstand thermal cycling from room temperature to -269°C without crackling, peeling from substrate, or degrading [Par14].

1.10.3.6 Barrier Properties and Chemical Resistance

Barrier

The barrier properties of the Parylenes are given in Table C9. The bulk barrier properties of Parylenes are among the best of organic polymeric coatings. The Water Vapor Transmission Rate (WVTR) for Parylene C is superior to the most common polymeric materials. Their excellent moisture and chemical barrier attributes are well suited for a variety of applications in medical, electronics, automotive and other areas. Generally applied much thinner than alternate liquid coatings, Parylene provides a pinhole-free barrier to protect against many fluids (e.g., body fluids, automotive liquids, etc.) as well as moisture, chemicals and common gases. Experimental results demonstrated, as shown in Table C10, that Parylene C coating markedly decreased extraction of metals from coated rubber samples. The samples were autoclaved for one hour in one molar hydrochloric acid and the acid extracts were then analyzed for metals known to be present in the rubber samples [Pat89].

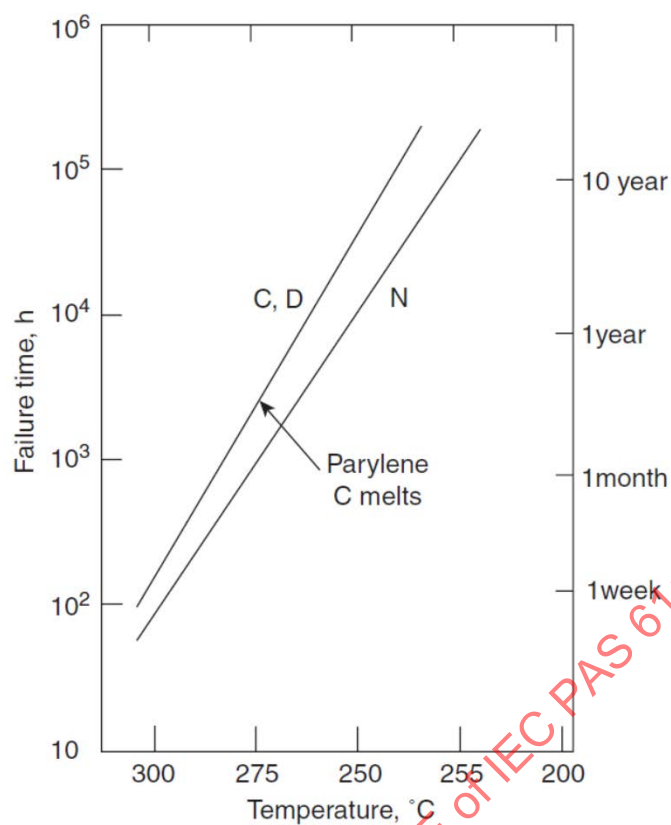


Fig. C14: Long-term effect of aging in vacuum on flexibility of Parylenes at elevated temperature (Failure = 50% loss in tensile strength)

Tab. C9: Parylene Barrier Properties

Polymer	Gas Permeability at 25°C, (cc•mm)/(m ² •day•atm) ^a				Water Vapor Transmission Rate (g•mm)/(m ² •day)
	N ₂	O ₂	CO ₂	H ₂	
Parylene N	3.0	15.4	84.3	212.6	0.59 ^b
Parylene C	0.4	2.8	3.0	43.3	0.08 ^c
Parylene D	1.8	12.6	5.1	94.5	0.09 ^b
Parylene HT	4.8	23.5	95.4	–	0.22 ^d
a. ASTM D 1434 c. ASTM F 1249 (90% RH, 37°C) b. ASTM F 96 (90% RH, 37°C) d. ASTM F 1249 (100% RH, 38°C)					

Tab. C10: The effect of Parylene C coating thickness on extractable metals in rubber specimens [Woo06]

Parylene Thickness (μm)	Calcium (ppm)	Aluminum (ppm)	Zinc (ppm)
0	0.17	4.2	50
0.1	0.15	1.8	35
0.5	0.03	0.1	12
1	<0.002	<0.05	0.2
2	<0.002	<0.05	<0.05

Circuit boards coated with Parylene HT were salt-fog tested by an independent testing facility. The coated boards showed no corrosion or salt deposits after 144 hours of exposure in accordance with ASTM B117-(03) (Figure C15). Boards coated with Parylene C exhibited similar results.

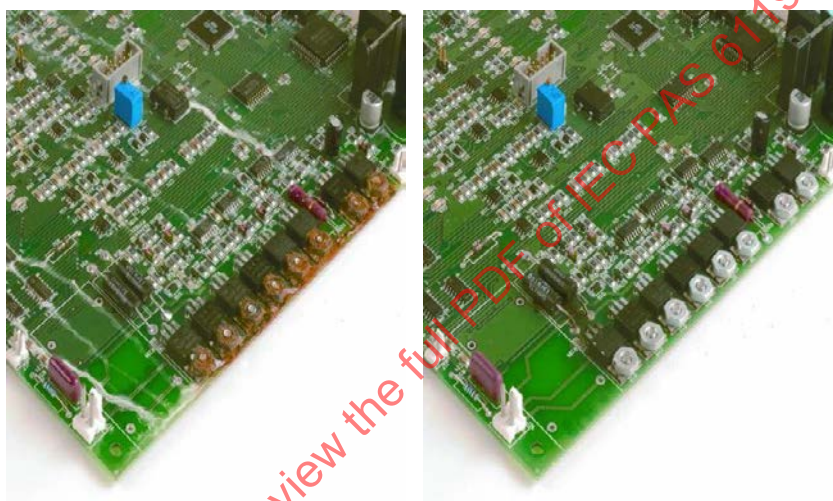


Fig. C15: Uncoated (left) and Parylene HT coated (right) PCB boards after 144 hours salt fog test

Chemical Resistance

The Parylenes resist room temperature chemical attack and are insoluble in all organic solvents up to 150°C. Parylene C can be dissolved in chloro-napthalene at 175°C, and Parylene N softens at the same solvent's boiling point (265°C). Both polymers are resistant to permeation by most solvents. Parylene HT films do not swell significantly with exposure to automotive chemicals and fluids, and there are no perceivable changes in the film's optical or mechanical properties.

At temperatures below the melting of the crystallites, the Parylenes resist all attempts to dissolve them. Although the solvents permeate the continuous amorphous phase, they are virtually excluded from the crystalline domains. Consequently, when a Parylene film is exposed to a solvent, a slight swelling is observed as the solvent invades the amorphous phase. The change in thickness is conveniently and precisely measured by an interference technique. As indicated in Table C11, the best solvents, specifically those chemically most like the polymer (e.g., aromatics such as xylene), cause a swelling of no more than 3%. Table C12 shows swelling data in acids for Parylenes N, C and Parylene HT.

Tab. C11: Parylenes swelling after immersion in solvents at room temperature

Solvent	% Swelling			
	Parylene N	Parylene C	Parylene D	Parylene HT
Dichlorobenzene	0.2	3.0	1.8	nd
Mixed xylenes	1.4	2.3	1.1	nd
Monochlorobenzene	1.1	1.5	1.5	nd
2,4-pentanediene	0.6	1.2	1.4	nd
Trichloroethylene	0.5	0.8	0.8	nd
Acetone	0.3	0.0	0.4	0.0
Pyridine	0.2	0.5	0.5	nd
Isopropyl alcohol	0.3	0.1	0.1	0.0
Freon	0.2	0.2	0.2	nd
Water, deionized	0.0	0.0	0.0	0.0
nd= not determined				

Tab. C12: Parylenes N, C and Parylene HT swelling after immersion in acids

Acids	% Swelling		
	Parylene N	Parylene C	Parylene HT
10% Nitric Acid, RT	0.1	0.1	0.0
10% Nitric Acid at 75°C	0.2	0.1	0.0
70% Nitric Acid, RT	0.2	0.2	0.0
70% Nitric Acid at 75°C	Brittle	1.8	1.2
10% Sulfuric Acid, RT	0.1	0.3	0.0
10% Sulfuric Acid at 75°C	0.2	4.1	0.0
95-98% Sulfuric Acid, RT	0.2	0.4	0.0
95-98% Sulfuric Acid at 75°C	5.3	5.1	2.8

1.10.3.7 Optical Properties and Radiation Resistance

Spectral transmittance

Parylene films are essentially transparent to gamma and x-ray radiation below 10 angstrom wavelengths. Soft X-ray transmission decreases with increasing wavelength, reaching 0.1% at 50 angstrom. The films are opaque to radiation from 10 nm to 240 nm in the UV spectrum. Transmission of nearly 100% is exhibited by Parylenes N, C and Parylene HT from wavelengths of 350 nm in the near UV to 3.3 microns in the IR, where the first absorption occurs [Par99]. Transmission scans of Parylenes N, C and Parylene HT covering 0.25 μ to 2.4 μ are shown in Figures C16 and C17. Such transmission data could not be found for Parylene D.

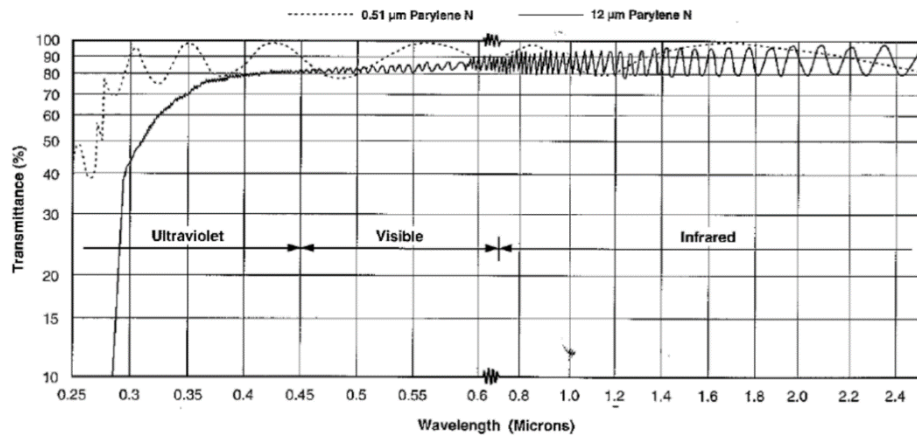


Fig. C16: Transmission spectrum of Parylene N covering 0.25 μ to 2.4 μ

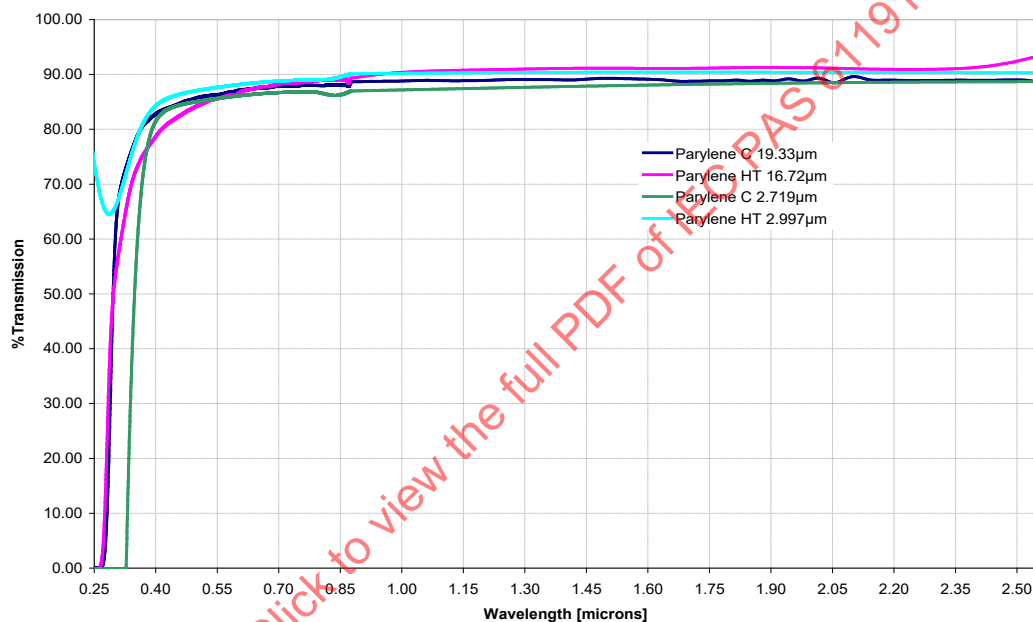


Fig. C17: Transmission spectrum of Parylene C and Parylene HT covering 0.25 μ to 2.5 μ

Mid-IR range

Absorption bands of Parylenes N, C, D and Parylene HT are observed in the 3.2 μ m to 25 μ m range, as a function of the chemical structure of the Parylene polymer molecule. The infrared transmission spectra of Parylenes N, C, D and HT are compared in Figure C18. Infrared spectra can be used to distinguish sample films of the four commercial materials should a practical question of identity arise.

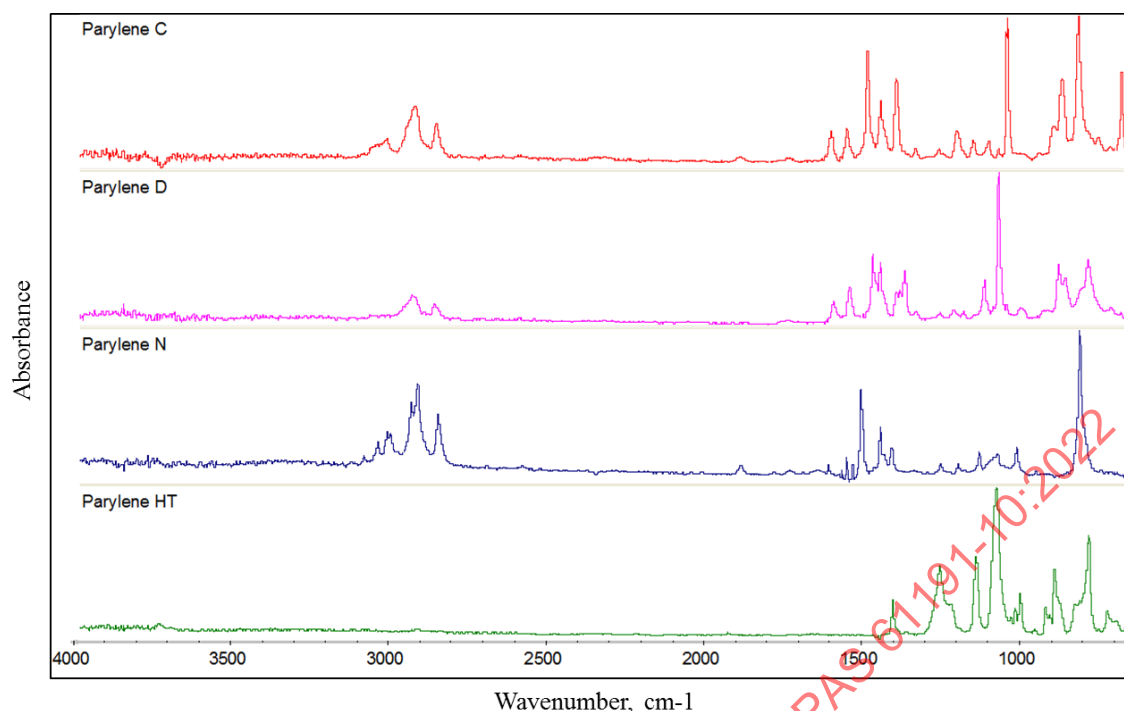


Fig. C18: FT-IR spectrum of Parylenes, covering mid-IR range from 4000-500 cm^{-1} (2.5 – 20 μm)

Mid to near UV range

Parylenes exhibit very little absorption in the visible region and are, therefore, transparent and colorless [Kum08]. Below the 280 nm wavelength, all the Parylenes absorb strongly, as shown in Figure C19.

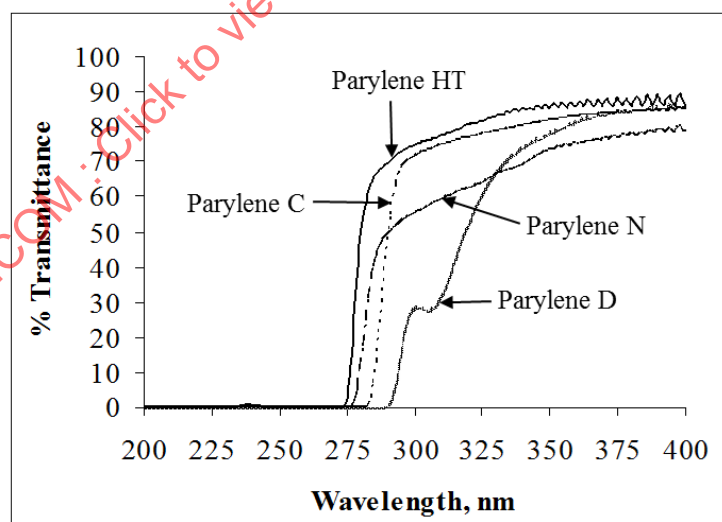


Fig. C19: Ultraviolet spectra of Parylenes N, C, D and Parylene HT

An assessment of possible degradation effects on Parylenes must be made in order to assure extended operation life of sensors, optical windows, LEDs and other display devices operating in direct exposure of solar radiation. Samples of Parylenes N, C and Parylene HT films were exposed to an accelerated UV stability testing per ASTM G154. Parylene films were exposed to radiation from a bank of UVA 340 fluorescent lamps with

Irradiance of 0.77 watts per square meter for 2000 hours. Visual color, chalking, cracking, blistering and flaking were observed on the films after 100, 250, 500, 1000, 1250, 1500 and 2000 hours of UV exposure. Numerical scales (0 -10) are used to depict the degree of exposure effect. The observation results are shown in Figure C20.

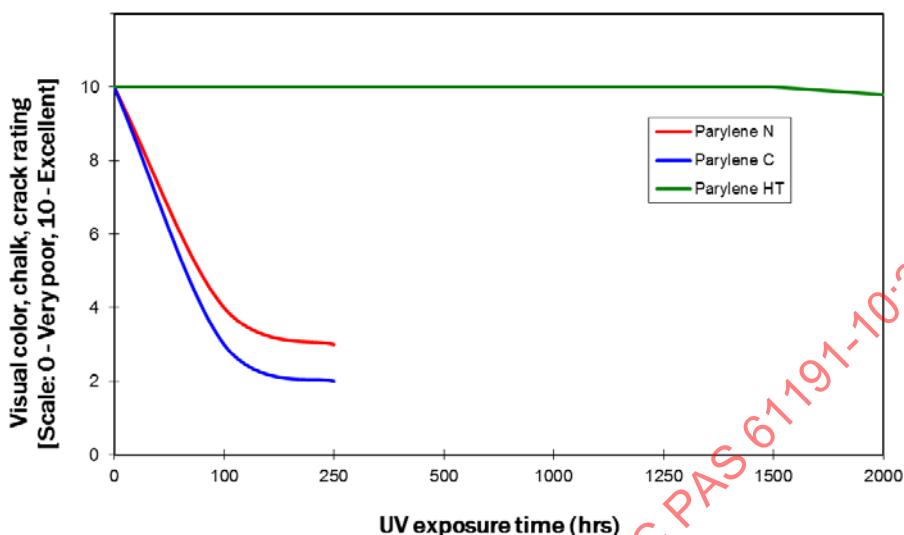


Fig. C20: UV exposure results of Parylene N, C and Parylene HT

Exposure of Parylenes N and C to high intensity UV radiation in air at earth sea-level (ambient atmospheric pressure) causes rather rapid degradation of their physical and optical properties. After 100 hours of exposure, both Parylenes N and C film samples turned yellow (4Y), but there was no chalking, cracking or blistering. However, Parylene HT film was stable without any change in appearance or other visual properties for more than 2000 hours. While the oxidation of Parylenes N and C appears to be enhanced by exposure to ultraviolet radiation, Parylene HT displays much higher resistance.

Refractive index

The refractive indexes for the Parylenes at the sodium D line (589 nm), a visible wavelength that corresponds to a frequency of 510 THz (5.1×10^{14} Hz). With respect to Maxwell relation, the dielectric constants of the Parylenes at the much higher frequency of visible light are close to those observed by conventional means. It seems likely that when reliable gigahertz and terahertz dielectric constant measurements on the Parylenes become available, similar values will be obtained. Index of refraction as a function of wavelength for Parylenes N, C and Parylene HT are shown in Figure 21, however, such data is not available for Parylene D.

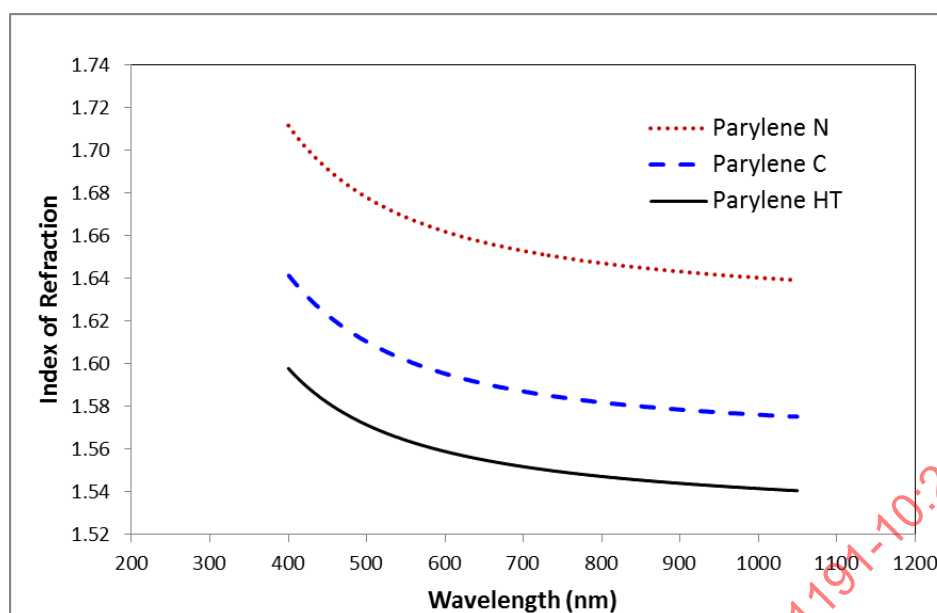


Abb. C21: Parylenes - Index of refraction vs. wavelength (Data courtesy of Filmetrics, Inc)

Radiation resistance

Parylenes N, C, D and Parylene HT films demonstrate a high degree of resistance to degradation by gamma rays in vacuum. Tensile and electrical properties were unchanged after 1000-kGy dosage at a dose rate of 16kGy/hr. Exposure in air leads to rapid embattlement [Iso83].

1.10.3.8 Surface Energy

The surface energies of Parylenes N, C, D and Parylene HT were measured by observing the contact angles for several standard probe liquids. Parylenes N, C and D have surface energies of approximately 45 dyne/cm (i.e., all test liquids having less than 45 dyne/cm surface tension completely wet the as-deposited Parylene surfaces) [Now80a]. The surface energy of Parylene HT is around 25 dyne/cm. Plasma treatments using reactive gases (N_2 , O_2) as well as inert gases (Ar, He) seemed, universally, to lower the contact angle for water, an observation that would imply that such treatments raise the surface energy. Reflectance spectroscopy confirmed the presence of carbonyl in all plasma-treated specimens. Surprisingly, the inert-gas-plasma treatments affected the surface energies of the Parylenes more than the reactive gas plasmas did, as indicated by a water contact angle. However, the surface energies of the plasma-treated specimens universally dropped toward the original value upon standing in air, but stabilized in about one day without recovering the original value. Plasma treatment of Parylene surfaces markedly improves the adhesion of polyurethanes, a result that could be, in part, the result of the surface energy change.

1.10.3.9 Biocompatibility

Parylene polymers are known for their inherent biocompatibility [Loe77, Sta96]. Parylenes N, C and Parylene HT have been tested according to the biological evaluation requirements of ISO-10993 for those tests indicated in Table C13, and successfully passed the tests. Such tests have not yet been performed on Parylene D as it is not used in the medical device and drug industries and its toxicological properties are largely unknown today. Parylenes C, N and Parylene HT are also certified to comply with USP biological testing

requirements for Class VI plastics¹¹ in the categories of acute systemic toxicity, irritation/intracutaneous reactivity and implantation. Certification for ISO-10993 and USP Class VI biological studies can be referenced via the FDA Master File mechanism. Notified Bodies and accredited Third Parties can also reference such data from Parylene coating service providers who maintain such files.

Tab. C13: ISO-10993 Biological Evaluations

Tests	Parylene N	Parylene C	Parylene HT
Cytotoxicity	✓	✓	✓
Sensitization	✓	✓	✓
Intracutaneous Reactivity	✓	✓	✓
Acute Systemic Toxicity	✓	✓	✓
Implantation (2 weeks)	✓	✓	✓
Implantation (7 weeks)	✓	✓	✓
Implantation (26 weeks)	✓	✓	✓
Hemolysis	✓	✓	✓
Pyrogenicity	✓	✓	✓
Prothrombin Time	✓	✓	✓

In vitro tissue culture studies show that human cell types readily proliferate on Parylene C coated surfaces to produce thin, adherent layers of morphologically normal tissue [Kan73]. Culture studies using diploid WI-38 embryonic human lung cells have demonstrated that Parylene C coatings are highly compatible [Kum08]. Successful in vivo growth studies [Nu73] and compatibility of Parylene C with experimental circulatory assist devices have also been reported [Tit80].

1.10.3.10 Tin Whiskers Mitigation

The use of conformal coatings to mitigate the risk of tin whiskers growth has been considered for some time [Ost02, Kad01]. Research work [Woo05, Now08] on the evaluation of conformal coatings as tin whisker mitigators filled several gaps in earlier efforts, and presented evidence that could have positive impact on mitigating tin whisker problems. In 2005, the first phase of the study [Kan73] included the evaluation of six types of conformal coatings. All coatings had different physical properties and the authors assumed that some properties such as Young's modulus, hardness, tensile strength, oxygen permeability and water vapor transmission could have an impact on suppressing the formation and growth of tin whiskers. The assumptions seemed reasonable considering the current knowledge of tin whiskers and some key factors that affect the propensity for formation. The experimental approach included test coupons coated with bright tin over brass, applying six conformal coatings and then subjecting the coated coupons to aging in two stages: 1) 278 days at ambient conditions, which resulted in the formation of nodules, but no significant whisker growth and 2) exposure to 50°C/50% RH for 419 days. The coatings included in the tests were Urethane-Acrylic (three different combinations), Acrylic, Silicone and Parylene C (poly-2-chloro-p-xylylene). It is important to note that except for Silicone and Parylene C, all coatings were applied in two thicknesses - 1 mil thick on one end of the coupon and 4-6 mils thick on the opposite end. The thicknesses of Silicone and Parylene C were 1.5 mils and 0.8-1.0 mil, respectively.

¹¹ Certificate of Compliance, USP Biological Tests, Classification VI, issued to Specialty Coating Systems by NAMSA, Ohio, USA, (1992).

The results of the study demonstrated that the formation of tin whiskers and odd shaped eruptions can be suppressed by the use of conformal coatings. On the other hand, with time, tin whiskers grew under the coatings and, once whiskers growth started, most coatings, particularly thinner ones, were penetrated. The authors did not try to establish any relationship between any of the coatings' properties and their ability to suppress or retard tin whiskers growth. The observations of this study concluded that Parylene C was the most effective and acrylic was the least effective for suppressing tin whiskers and odd shaped eruptions. In addition, it was also concluded that Parylene C will completely and uniformly coat component leads unlike other liquid-type coatings.

A recent study [Mes14] concluded that Parylene C and Parylene C with AdPro Plus® had the best coverage when applied on electronic assemblies and no indication of whisker growth or coating penetration after subjecting the test assemblies to various test conditions, including 85°C/85% RH for 2000 hours. Parylene C with AdPro Plus also provided enhanced adhesion. The objective of this study was to develop an understanding of the key mechanisms by which conformal coatings may provide long-term tin whisker mitigation and nucleation/growth inhibition, and develop or identify conformal coatings that can provide long-term tin whisker mitigation.

Based upon the above studies, it seems that Parylene conformal coatings have potential to help extend the reliability of the electronic components and assemblies by reducing the growth of tin whiskers. Next steps would be to evaluate how long and under what circumstances this would be the case.

1.10.3.11 Improvement in Wire Lead and Bond Strength

Parylenes provide an improvement in hybrid wire lead and bond strength compared to uncoated circuits [Ols85]. For example, a bare 1-mil aluminum wire has a typical bond strength of 3 to 5.5 grams. A 1-mil coating of Parylene C over the wire and bond increases that strength to between 60 and 70 grams.

1.10.3.12 Regulatory Compliance

Widely-used commercial Parylene samples, made available from Specialty Coating Systems, were tested in accordance with the European Restriction on Use of Hazardous Substances in Electrical and Electronic Equipment Directive 2002/95/EC using ASTM D5839. Per test results, Parylenes N, C and Parylene HT are RoHS compliant. Both Parylene N and Parylene HT are halogen-free per IEC-60754-2. Per IPC's expected guidelines, Parylenes N, C and Parylene HT will be in compliance for low halogens.

1.10.3.13 microRESIST® ANTIMICROBIAL PARYLENE TECHNOLOGY

Healthcare providers are continually tasked with improving patient health while reducing the risk of infection. Pathogens that cause healthcare-associated infections (HAIs) pose an ongoing and increasing challenge to hospitals, both in the clinical treatment of patients and in the prevention of cross-transmission of these problematic pathogens [Hid08]. HAIs result in more deaths than AIDS, auto accidents and breast cancer combined in the United States [Saf13]. This has led to an increased interest in antimicrobial protection for devices, including electronics, in continuous contact with patients (e.g., catheters and other medical devices)¹². As a result, manufacturers are looking to antimicrobial coatings that

¹² PR Newswire. Antimicrobial coatings market is expected to reach USD 3.3 Billion globally by 2018: Transparency Market Research, <http://www.prnewswire.com/news-releases/antimicrobial-coatings-market-is-expected-to-reach-usd-33-billion-globally-by-2018-transparency-market-research-186912691.html> (accessed January 22, 2013).

are biocompatible, biostable, inert, non-toxic and can meet FDA compliance guidelines.

Since commercially available Parylenes can meet all the requirements for medical applications except antimicrobial aspects, Specialty Coating Systems developed microRESIST antimicrobial Parylene technology, which can be applied to a variety of medical devices and applications, including catheters, electro-stimulators, endotracheal tubes and other medical devices where antimicrobial properties are critical during a product's use. This commercially-available, significant breakthrough combines the benefits of biocompatible Parylene with antimicrobial properties to effectively eliminate harmful microorganisms on coated medical devices.

Characteristics of microRESIST

Effectiveness

Samples coated with microRESIST were tested for antimicrobial activity according to JIS Z 2801:2010¹³. To determine the microbial log reduction, films containing microRESIST were inoculated with 14 most common microorganisms, and then incubated for 24 hours. All samples protected with microRESIST demonstrated greater than 5 Log reduction after 24 hours.

Sterilization

Two sets of microRESIST treated samples were sterilized – one set using gamma radiation (dose range 10-15kGy (1.0 to 1.5 Mrad)) and the other using Ethylene Oxide (EtO). Samples were then tested for effectiveness against E. coli according to JIS Z 2801. SCS microRESIST, post sterilization, achieved greater than 4 Log reduction against E. coli bacteria.

Dry Film Lubricity

The coefficient of friction (COF) of SCS Parylene coated surfaces (without antimicrobial properties) and SCS microRESIST coated surfaces were tested in accordance with ASTM D 1894-08 at room temperature. Results indicate there is no statistical difference between the samples.

Biocompatibility

Samples protected with microRESIST antimicrobial Parylene technology were subjected to key biocompatibility testing per ISO 10993. Samples met the ISO 10993 requirements for cytotoxicity, sensitization, irritation and implant for 12 and 26 weeks, as shown below:

- Non-cytotoxic per ISO 10993-5,
- Nonirritant and Non-sensitizer per ISO 10993-10,
- Nonirritant after 12-week implantation per ISO 10993-6,
- Nonirritant after 26-week implantation per ISO 10993-6.

1.10.4 Examples of Parylenes applications

Parylenes have been used for protection of various electronics, medical devices and other components for the past several decades and new applications continue to emerge with the advancement of new technologies. Some examples, as highlighted below in Ta-

¹³ JIS Z 2801:2010. Antibacterial products - Test for antibacterial activity and efficacy.

ble C14, demonstrate the use and suitability of Parylenes for enhanced reliability of components in the medical device, electronics, automotive, military and LEDs industries.

Tab. C14: *Examples of Parylenes Applications*

Parylene Application Area	Specific Examples
Electronics Coating Applications	• Printed circuit boards • MEMS wafers • Sensors • Probes / pins • Rotors / stators • Metal components and brackets • Cables • Ferrite cores • Telecommunication devices
Medical Device Coating Applications	• Cardiac assist devices and components • Drug delivery devices – Stents, inhalers (MDI, DPI, nasal) • Cochlear and intraocular implants • Catheters • Neurostimulators • Gastric balloons and cuffs • Endotracheal tubes • Laboratory devices • Printed circuit boards
Automotive Coating Applications	• Mass air temperature and pressure sensors • Emission sensors • Tire Pressure Monitoring Systems • Diesel fuel heaters • O-rings, seals and engine gaskets • Fuel cell and hybrid electronic systems • Engine electronics • MEMS sensors
Military/Aerospace Coating Applications	Military/Commercial • MEMS, sensors • Circuit card assemblies • Power supplies • Backplanes • Elastomeric parts Aerospace • Spacecraft and satellite electronics • Cameras and assemblies • Space Shuttle and International Space Station lab equipment & components

Parylene Application Area	Specific Examples
LEDs Coating Applications	• Video displays • Electronic billboards • Marine lighting • Transportation signage • Outdoor illumination • Vehicle lighting • Commercial refrigeration • Aviation lighting
Antimicrobial Applications	• Urinary catheters • Urological tools • Medical electronics • Any devices that comes in contact with the body or placed into the body

1.10.5 Health and Safety aspects

In a world increasingly conscious of the dangers of contact with chemicals, a process that is conducted within the walls of a vacuum chamber, such as the VDP process for Parylene coatings, offers great advantages. Provided the vacuum pump exhaust is appropriately vented, and suitable caution is observed in cleaning out the cold trap (trace products of the pyrolysis, which may possibly be dangerous, would collect here), the Parylene VDP process has an inherently low potential for operator contact with hazardous chemicals.

To an experienced operator trained in the handling of industrial chemicals, the dimers present little cause for concern in handling or storage. The finished polymer coating presents even less of a health concern. In between the dimer and polymer phases, contact with the reactive monomer is unlikely. In ancillary operations, such as cleaning or adhesion promotion, the operator must observe suitable precautions based on the operation. Before using the process chemicals, operators must read and understand the current Safety Data Sheets, which are available from respective manufacturers.

2 Subdivision according to solvent

Apart from UV-curing systems, solvents or thinners are a main component of the coating material. They are liquid, consist of one or more components and dissolve the binders without chemical reaction. They are added to the coating material during production or before its application in order to adjust its properties, in particular its viscosity. During film formation, they evaporate or, in the case of reactive solvents, become part of the binder.

Typical solvents can be divided into aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, esters, ketones (e.g. acetone) and chlorinated hydrocarbons. The latter have since disappeared from the market because of their ozone-depleting potential.

The situation is completely different with water-dilutable coating materials. With a few exceptions, the water contained in these "water-based coatings" is not a solvent. Water is the dispersant in which the dispersed phase - the binder - is finely distributed as solid particles. Due to the dispersed state, water-dilutable coating materials do not look clear and transparent like a solution, but are milky cloudy. After film formation, however, transparent

coating films are formed.

3 Subdivision by drying and curing mechanism

The processes, reaction sequences and transformations associated with the transition of the applied liquid coating material into the solid film are called curing. The term drying is the same. The use of the term drying in this context should be preferred in view of defined terms such as drying oven, drying time, air drying, etc., although there are tendencies to prefer the term curing. Curing is more commonly referred to when chemical conversions are in the foreground and drying when process engineering requirements are more important. If the protective coatings are subdivided according to their drying or curing mechanism, one can distinguish between the following groups:

- physically drying coating materials,
- oxidatively curing coating materials,
- chemically curing coating materials and
- radiation curing coating materials.

3.1 Physically drying coating materials

The film formation of physically drying coating materials takes place without chemical reactions, only through the evaporation of solvents. In the case of protective coatings, however, a distinction must also be made between two different physical processes. These are on the one hand the physically drying coating materials based on organic solvents and on the other hand the so-called water-dilutable coating materials.

A special case are so-called hotmelts, which are heated above their melting point for application and then cooled to form a film. This melting and solidification step is reversible.

3.1.1 Solvent-dilutable coating materials

These coating materials dry exclusively by evaporation of the organic solvents. With a targeted selection of solvents, these protective coatings are characterized by very fast drying. A major advantage of many purely physically drying coating systems is that the coating film can not only be soldered through at soldering iron temperatures for repair purposes, but can also be removed with the product-specific dilution without the risk of component housings or marking coatings dissolving or damaging. After the repair has been completed, the coating can be reapplied.

3.1.2 Water-dilutable coating materials

Water-dilutable one-component protective coating systems can also be generally counted among the physically drying coating systems. However, they should be mentioned separately here on the one hand because of their different filming mechanism and on the other hand because of their special properties (significantly better chemical resistance than with most conventional solvent-based single-component systems). In one-component insulating and protective coatings, the organic solvents are almost completely substituted by water. They contain special water-dilutable binders that are dispersed exclusively in water. Only a low organic solvent content (< 10%) is necessary for the film formation of the protective coating - this is also referred to as film forming aids.

The cured protective layer is not susceptible to the original solvent, i.e. water, as is the case with conventional, physically drying coating materials. In addition to their excellent dielectric properties and high resistance to moisture under temperature and voltage, the special advantages of waterborne protective coatings include their neutral odor during and after processing, minimal solvent emission, extremely fast drying at room temperature and the absence of special explosion-proof production.

3.2 Oxidatively drying coating materials

These coating systems consist of slightly crosslinked binders dissolved in suitable solvents. Modified alkyd resins are often used as binders, whereby this type of resin can be distinguished between polyurethane (PUR) modified, epoxy (EP) modified and acrylic (AY) modified grades.

What all three variants have in common, however, is the drying process. After the coating has been applied, the solvents first evaporate. The remaining film begins to gel under the influence of atmospheric oxygen. With a further supply of oxygen, the solidification of the film changes from the gel to the solid, dust-dry state and finally leads to complete cross-linking and curing. This type of coating hardening is called oxidative hardening or cross-linking due to the involvement of atmospheric oxygen.

It should be noted that this hardening takes several days and therefore some of the coating properties, such as tracking resistance, dielectric strength, etc. can only be measured after 96 hours or 4 days.

3.3 Chemically curing coating materials

These coating materials include, among others, all two-component or multi-component coatings based on polyurethane and epoxy resins. These coating materials are mixed directly before application from the corresponding components in a certain ratio specified by the coating manufacturer. After mixing, the components react with each other, externally visible by an increase in viscosity. At the end of the pot life, the reaction has progressed to such an extent that the coating is unusable for an application due to its high viscosity.

The limited processing time is therefore the decisive disadvantage of chemically curing multi-component coating systems. For the plant operator, this means that the entire pre-mixed quantity of coating must be processed within the pot life. In order to be able to carry out an almost continuous and economical coating with chemically curing coating systems, preferably coating systems with very long processing times/ pot life, which can amount to approx. 15 hours, should be used. The coating systems are characterized by excellent resistance to numerous chemicals. The film is formed by evaporation or physical drying of the solvents. The chemical reaction of the components with each other runs parallel to this. This evaporation and drying time is shortened by higher temperatures. A higher hardness compared to the coatings cured at room temperature is not achieved.

Moisture-curing coatings can also be classified in the group of chemically curing coating materials. They react with humidity from the ambient atmosphere. This results in coating films with resistances similar to those of two-component coatings. This "humidity curing" is used for polyurethane coatings. They are available both as solvent-based and solvent-free coating systems. Furthermore, this "air humidity hardening" is given with silicone coatings. Here too, both solvent-based and solvent-free coatings are on the market.

Moisture-curing silicone coatings in particular offer a very interesting group of coating ma-

terials. This group of substances are condensation-curing silicone resins which chemically cross-link from the environment while absorbing air humidity and thereby split off an alcohol, which then diffuses out of the film. Silicone protective coatings with this crosslinking mechanism can be formulated solvent-free and are not only of outstanding quality, but also among the most environmentally friendly products, as they show only minimal emissions of volatile organic compounds.

Chemically reactive protective coatings can also include one-component, addition-curing silicone coatings that cure under heat application. They can also be formulated solvent-free and cure at 100 to 120°C.

With addition-crosslinking coating systems, however, it must be taken into account that inhibitions, e.g. by sulfur, polysulphides, polysulfones and other sulfur-containing materials as well as organotin compounds, amines, amides and urethanes, may occur.

3.4 (UV-)radiation-curing coating materials

A very efficient technology for coating is the use of UV-curing coating materials. In the following consideration only the UV-curing coating materials are expressly mentioned, since the electron beam-curing coating materials are not yet of great importance in industrial coating and are not necessarily suitable for electronic assemblies due to the sensitive components.

The most important advantages of a UV coating are listed below:

- With curing times of less than 30 seconds (attainment of manual strength), the assemblies can stay on the belt and thus keep pace with high-speed equipment such as placement machines, wave soldering machines and automated cleaning systems. In addition, immediate handling of the printed circuit boards and removal of the covers are possible.
- Avoidance of bottlenecks in coating, such as those caused by ovens, curing stations and other batch-related activities in connection with solvent-based coatings and varnishes, which are built up in stages.
- Production of UV-curing covers to simplify this step.
- In curing systems with secondary curing, curing by UV light is combined with other mechanisms, such as humidity curing or heat curing, to also cover areas outside of UV radiation (shadow curing).

UV technology, which can be easily automated in plants, reduces costs, especially when compared to the investments required to provide space, time, energy and emission control precautions for older systems. Investments in new systems often pay for themselves after just one year.

The so-called UV protective coatings consist of UV-curable monomers/polymers, e.g. unsaturated polyester resins dissolved in styrene or acrylated monomers/polymers and contain no solvents. The film is formed by completely polymerizing and curing the monomers and polymers under the influence of UV light. This reaction takes place at room temperature. The coating contains so-called radical formers, which decompose under the influence of suitable radiation and trigger polymerization. A decisive disadvantage of these systems are differently polymerized areas after UV-curing of an assembled circuit board due to the shadow effect of the components, which means that any coating under the components does not harden.

This disadvantage of pure UV systems can be avoided if the polymer molecule has a se-

cond crosslinking property independent of UV curing. The so-called TWIN-CURE® system is based on the principle that two different - complementary - chemical curing mechanisms take place during drying. The TWIN-CURE® system undergoes UV drying in the first step and is thus dried in such a way that it can be "traded" without restrictions after a very short time. In a second slower drying step - especially in the shadow areas, i.e. areas in which UV-light-initiated crosslinking is not possible - chemical crosslinking takes place due to the ever-present air humidity. With this cross-linking mechanism, the so-called polyurethane (PUR) curing, the air humidity diffusing into the polymer is "absorbed" and used for polymerization and further curing of the coating in the shadow area. It should be emphasized that the TWIN-CURE® system is not a physical mixture of two different functional resins. The UV-functional group and the isocyanate functionality responsible for shadow curing are located on the same polymer molecule. This double functionality guarantees the highest resistance and quality because no uncrosslinked binders remain in the film as soft resins. This type of combined curing is also found in silicone coatings, where the moisture curing known from silicone coatings is also combined with UV curing.

The so-called CURE-CONTROL system has a dual hardening system in the same way. It is UV-curable and additionally cures in the shadow area under components with moisture from the ambient air. A color indicator contained in the coating material provides information on the degree of curing. The coating material changes its original blue color during UV curing and turns green when cured. In shadow areas it remains blue. Thus it is optically controllable whether the quality of the UV-curing is sufficient at all places. The uniformity of the illumination of the UV lamp or defects of the lamp are also detected immediately. The CURE-CONTROL is temperature resistant up to 125°C and retains its elasticity down to -40°C.

4 Subdivision according to coating thickness

In the past, coating materials were developed using state-of-the-art processes for user equipment, primarily in the two categories of **thin-film and thick-film coatings**, which are defined according to the thickness of the finally cured coating thickness with more or less than 300 µm coating thickness.

Relatively new are **surface modifiers** like e.g. fluoropolymers, which aim at a thickness of only 1 µm with their application process and thus no longer act as a mechanical protection like a barrier, but rather through special physical effects, e.g. changes in certain surface properties. Therefore, not all of the requirements for protective coatings described in Part D below are relevant for these surface modifiers. Due to their very low thickness, these surface modifiers or coatings have the following properties:

- solderable without preparation and therefore easy to repair,
- low refractive index and transparent, so that optical components can also be coated,
- no impairment of the contact surfaces of test points, connectors, switches, potentiometers, etc. (The contacting capability is retained. Therefore, all components can be coated.),
- low mechanical protection,
- absolutely flexible even under continuous bending load,
- no interference with high-frequency circuits.

Thin-film coatings are coating materials that are generally applied to printed circuit boards for total or selective protection. Thick film coatings can be applied as a selective

coating and/or using the "dam&fill" process ("limit wall + backfilling") to provide better protection against vibration and mechanical stress. Thick film coatings are also used for encapsulation of special components or for encapsulation of electronic devices such as sensors.

The climatic conditions under which assemblies are operated are becoming increasingly aggressive and demanding. Thin-film coatings used here are sometimes overtaxed in their protective effect, especially if the assembly becomes dewy. This overload is less due to the lack of performance or quality of the polymers or binders used than to the coating thicknesses generally used at present, with the edge covering of the areas to be protected playing an important role in particular.

According to IPC-2221¹⁴, coating thicknesses of 30 to 130 µm are recommended for conformal coatings based on acrylic, epoxy and urethane resins and 50 to 150 µm for silicone resins.

The coating thickness has a significant influence on the protective effect of coatings. The coating thickness is approximately directly proportional to the migration resistance, i.e. doubling the coating thickness also approximately doubles the migration resistance and thus the protective effect. This makes the solution to the problem seem quite simple: Coating materials on the market are used to apply thicker layers and improve the protective effect. However, this approach has the opposite effect.

If the usual protective coatings are used, the thicker the coatings are applied, the slower they dry. Physically understandable, because the solvent in the wet coating film has to travel a longer distance to leave the coating film. Likewise, with oxidatively drying coating materials, the oxygen must cover longer distances in order to completely harden the coating film. These drying delays are not single linear, i.e. double layer does not correspond to double drying time. The dependence is rather exponential, i.e. double layer corresponds to approx. four times drying time. The time required to achieve the desired final properties, such as adhesion and electrical insulation, becomes significantly longer and is then also more sensitive to fluctuations in coating thickness, which are inevitable on an assembly. Due to solvent retention, these coatings are particularly sensitive to early encapsulation or climate pollution.

A second solution is the **double coating**, which is also often used. In principle, the same statement applies to it. The process times are significantly extended. If the process is not run optimally, there is a risk of wrinkling or "pulling up". In addition, these double coatings should not be regarded as optimal from the point of view of the VOC directive¹⁵, because the purpose of this directive is to record and reduce the consumption of solvents. Possible solutions result from the approach of using coating systems with a higher solid content.

Solvent-free coating materials are a technically and ecologically sensible solution. Their chemical basis is known in principle from casting compounds and casting resins. The boundaries between casting resins and casting compounds and protective coatings are blurred here. The disadvantages of the casting resins and casting compounds are known; they are mainly two-component (2-component) systems with a significantly higher viscosity than the protective coatings and more complex processing due to their 2-component character.

¹⁴ IPC-2221 (May 2003) "Standard on Printed Board Design - Includes Amendment 1"; replaces IPC-D-275 Generic.

¹⁵ **VOC** = Volatile Organic Compound; VOC = Volatile Organic Compound; The VOC Directive was adopted in the 31. BImSchV Point 2.1. into German law within two years.

Four variants of these solvent-free **thick-film protective coatings** are currently in use (see also Fig. C10):

- **1-component PUR protective coating, thermosetting**

This system comes closest to 2 C-casting because the hardener - the isocyanate - is contained in the coating in encapsulated form. During furnace hardening at approx. 120°C, the encapsulation breaks and releases the hardener. These materials can be applied as thick-film protective coating in coating thicknesses of 100 to 3000 µm, or they can be used for casting in the housing. The low glass transition temperature (TG) allows stress-free coating.

- **1-component PUR protective coating, moisture-curing**

This group of substances also contains embedded isocyanate hardeners, but not encapsulated, virtually dissolved in the resin. When air is admitted, the protective coating hardens under absorption of moisture from the air and partly from the printed circuit board. This results in excellent adhesion of the coating. Curing takes place overnight at room temperature; oven drying for 4 to 10 hours accelerates the curing process. The coating thickness is approx. 100 to 1000 µm. The low glass transition temperature keeps the coating elastic down to -50°C.

- **Silicone protective coatings, solvent-free** (see also section 3.3 "Chemically curing coating materials")

They can be either condensation crosslinking (dry with humidity at room temperature) or addition crosslinking (cure with heat of approx. 100 to 120°C). Both produce thick-film coatings, which are particularly recommended for applications with higher temperature loads of up to 200°C.

In the case of thermosetting silicone protective coatings, tests should be preceded by tests for compatibility with the substrate, as substances such as sulfur, amines, etc. inhibit or completely interrupt the curing process. Also to be taken into account is the prevention of contamination by outgassing low molecular weight silicone components.

Coatings with non-silicone coatings show flow disturbances until detachment. Contacts, e.g. in closed housings, can be interrupted. There are also solvent-based silicone protective coatings, which belong to the thick-film protective coatings, but of course not to the solvent-free thick-film coatings.

- **UV-curing coating systems**

These fast-curing coatings are usually based on acrylated polymers that are cured in seconds using UV radiation. Their viscosity range is between 1000 and 4000 mPa/s. In order to also achieve curing in the shadow areas under components, the coating systems are equipped with an additional curing system that reacts with humidity. The two systems on the market are called TWIN-CURE and CURE-CONTROL (described in more detail in chapter 3.4).

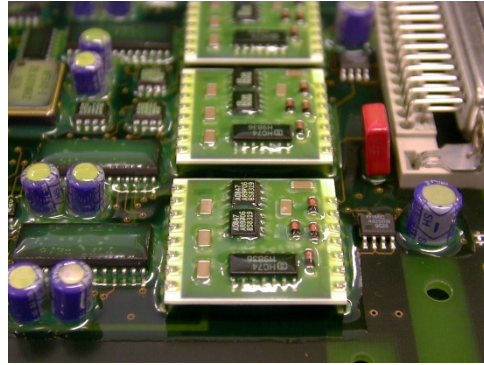
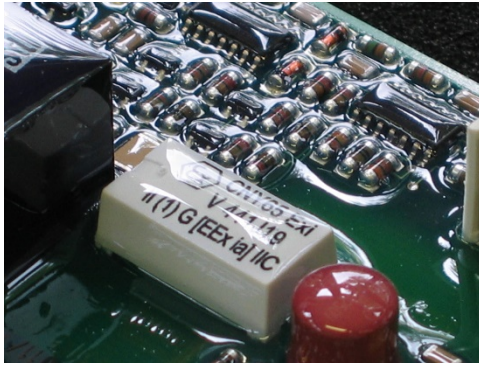


Fig. C22: Examples for a coating with thick-film protective coating

UV coating materials offer an interesting alternative here. The conventional UV-curing coating materials are characterized by the fact that they can be very low viscous, are usually solvent-free and dry particularly quickly. However, they have a considerable disadvantage: UV coating materials only dry in areas where UV radiation reaches the binder directly. In shadow areas, no hardening initially takes place and the coating system remains sticky there and cannot offer the required protective effect. These insufficiently hardened areas not only represent a considerable weakening of the protective effect, they may even lead to the failure of the complete assembly, especially in view of the increased climate loads, i.e. condensation.

In the case of products used in electronics, there is therefore always an indication of additional networking in the so-called shadow areas, i.e. under the components. UV coatings equipped with a combined curing principle offer a sensible technical solution for thick-film coating with the simultaneous ecological advantage of solvent-free application.

FILM PROPERTIES OF PROTECTIVE COATINGS

1 Mechanical properties

- 1.1 Adhesion
- 1.2 Elasticity
- 1.3 Hardness
- 1.4 Further mechanical properties

2 Electrical properties

- 2.1 Insulation and moisture resistance
 - 2.1.1 Water absorption of the coating systems
 - 2.1.2 Water permeation through coating systems
 - 2.1.3 Adhesion of the coating systems
 - 2.1.4 Discussion of the results
 - 2.1.5 Conclusions for the electrical insulation resistance

3 Thermal properties

- 3.1 Stress factors
- 3.2 Thermal mismatch
- 3.3 Fatigue - the Wöhler curve and its consequences
- 3.4 Thermal stress load
- 3.5 Thermal shock resistance
 - 3.5.1 Temperature cycling test
 - 3.5.2 Thermal shock load

4 Condensation

5 Water absorption and water vapor permeability

- 5.1 Requirements
- 5.2 Transport of moisture

6 Thermal resistance

7 Flexibility (modulus of elasticity) and CTE

The requirements for the protective coatings (conformal coatings) can be subdivided as follows:

- Requirements for the liquid protective coating (e.g. viscosity),
- Processing requirements (e.g. drying speed),
- Requirements for mechanical properties,
- Requirements for electrical properties,
- Requirements for thermal properties,
- Requirements for thermal cycling tests and
- Requirements for chemical and physical properties.

The following table lists the properties that influence the processing and above all the respective application.

Tab. D1: Important properties for a protective coating

Mechanical properties	Electrical properties	Thermal properties	Chemical and physical properties.
Bond strength (= adhesion)	Specific resistance	Coefficient of expansion	Water absorption
Tension, compression and bending strength (elasticity)	Surface and insulation resistance	Thermal conductivity	Permeability
Modulus of elasticity (Young's module)	Tracking resistance	Dimensional stability	Chemical resistance
Hardness	Dielectric strength	Glass transition temperature	Resistance to tropical conditions
	Dissipation loss factor	Flammability	Electrolytic Corrosion
	Dielectric constant		Solvent resistance

1 Mechanical properties

In the following, the mechanical properties listed in tab. D1 are described in more detail.

1.1 Adhesion

The adhesion of the protective coating is the interaction of the condition of the surface to be coated and the adhesive power of the protective coating. The used protective coatings, which are essentially responsible for the adhesive power, must be composed suitably to form a continuous film that adheres firmly to the substrate.

Molecular forces (so-called adhesive forces), whose effectiveness is limited to the bordering surfaces, are responsible for the adhesion to a substrate. The adhesion is independent of the coating thickness and for each coating layer capitably determined and an unchangeable quantity. The dry protective coating layer is a continuous solid body consisting of many molecules, which counter fragmentation with a considerable resistance, the so-called cohesion forces.

The correct binding agents (synthetic resins) are matched in a way that the adhesive and cohesion forces of the dry protective layer are in optimum proportion to each other. This composition is the task of the coating manufacturer. Well-matched adhesion and cohesion forces are properties of the protective coating formulation.

If optimum results can only be achieved once with a certain protective coating on a certain substrate, it can be assumed that subsequent adhesion defects on the same substrate are not due to the coating properties but to an insufficiently pretreated, greasy or soiled substrate. However, layers that are too thick can impair adhesion.

1.2 Elasticity

Strictly speaking, this term used for the coating materials as well as for the substrate materials expresses the fact that a deformation (of whatever nature) occurs in the respective material under stress without any time delay, but is just as spontaneously reduced again after the stress path has ceased. If a more or less large amount of deformation remained, the material would have a corresponding degree of plasticity. Elasticity is determined by the quantitative relationship between the action of force and deformation as regulated by Hooke's law¹. Depending on the force applied, either the modulus of elasticity or the shear or rigidity modulus [Zor98] are used as material properties.

For coating materials, however, the term "elasticity" is also used in a different, less sharply defined but more vivid way. Elasticity expresses here that the coating film is not prone to cracking, but shows a certain degree of elasticity. According to DIN EN 971-1, however, the use of the term "elasticity" to describe the ductility of coatings is incorrect.

Electrical assemblies are generally mechanically rigid bodies that are not subject to any discernible changes in shape when in use. Therefore, demands on the elasticity of the coating layer are only made by external influences such as temperature changes, humidity, pressure, vibration and similar. In order to withstand these changing changes in shape, sufficient elasticity is required from the dry protective coating.

Many protective coatings have an elasticity that allows their use even on flexible circuits. The term elasticity is further described in Chapter 7 "Flexibility (modulus of elasticity) and CTE".

1.3 Hardness

In materials science, hardness is the resistance of a material to local external forces. This essentially describes the property of the material zone near the surface. In the case of coating materials, hardness is also meant as that property, but due to the low expansion in thickness, it refers to the entire cross-section of the coating. In order to emphasize their hardness state prevailing in the upper part, we also speak of surface hardness [Zor98].

The hardness of protective coatings - especially the surface hardness, which stands for scratch resistance - is generally considered as of minor importance than the other requirements. If the hardness is too high, it often leads to a lower load capacity under thermal cycling stress.

¹ DIN EN 971-1 (1996-09) "Coatings and paints - Technical terms and definitions for coating materials - Part 1: General Terms", now replaced by DIN EN ISO 4618 2015-1 "Coating Materials - Terms".

1.4 Further mechanical properties

High impact and shock resistance are not expected from protective coatings on electronic assemblies, since the latter are never exposed to those loads during normal use. In general, impact resistance is achieved through optimum balancing of adhesion, elasticity and hardness.

The impact and shock resistance also applies to abrasion. Protective coatings on electronic assemblies are not subject to high abrasion or wear under normal use.

2 Electrical properties

2.1 Insulation and moisture resistance

The number of electronic assemblies used in motor vehicles, telecommunications, building services and toys is constantly increasing. The reliability of the products and devices is essentially determined by the functional reliability of these assemblies. The electronics are increasingly exposed to climatic influences such as moisture and corrosive gases.

Protective electronic coatings are intended to prevent this risk of corrosion damage to electronic assemblies, especially caused by electrochemical migration, and to stabilize the insulation resistance of the circuit carrier during operation in high relative humidity. To assess and improve the reliability of coating protection, it is therefore necessary to know its mode of action and the failure mechanisms. The migration protection is essentially influenced by the adhesion, the stabilization of the insulation resistance by the water absorption behavior of the protective coating [Schw97a, Kai92].

2.1.1 Water absorption of the coating systems

All polymers are more or less permeable to water in its vapor phase [Bag88, Bar94, Gho94]. This also ensures water vapor permeability and absorption of a protective coating. The water absorption reduces the insulation resistance of the coated assemblies [Schw97a]. The lower the degree of curing of the coating systems, the greater the water absorption capacity of incompletely cured coating systems [Tau91].

In operational use, most electronic assemblies are presumably only subjected to short-term, but recurring stress due to condensation or relative humidity above 90 %. The initial phase of long-term measurements of the resistance curve as a function of moisture absorption indicates an initially large drop in resistance (see Fig. D1).

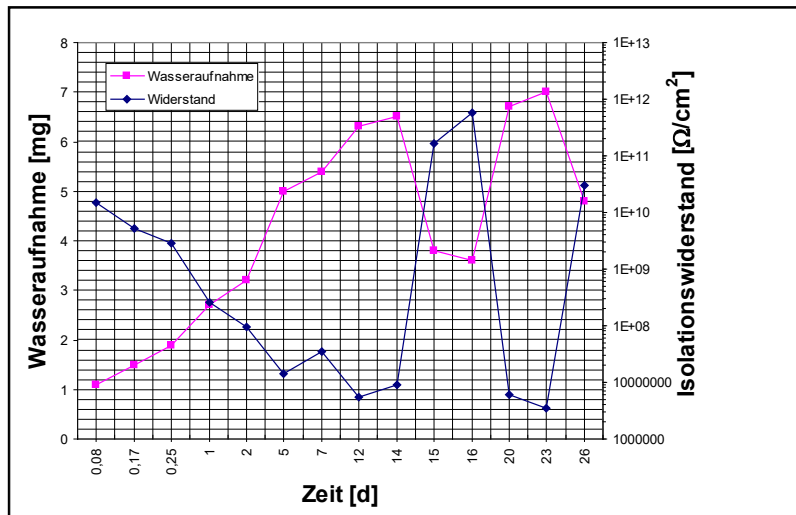


Fig. D1: Time course of the specific resistance as a function of the absorbed water quantity (PUR dip coating cross-linked to FR4, 16 h / 80°C)

Above 5 mg or 4.2 % water absorption, there is no longer any significant reduction in resistance despite further water retention in the system. In the first two hours, the insulation resistance drops below $10 \text{ G}\Omega/\text{cm}^2$, i.e. below $100 \text{ M}\Omega$ on the IPC B25 comb cutout used here, which contains 1809 squares. The sample shows a slight ionic contamination. When compared to highly pure washed test assemblies, uncritical resistance reductions to $10^{14} \text{ }\Omega/\text{cm}^2$ are found there, which also only occur in the course of a few days.

In order to record the water absorption behavior of protective coatings in the first minutes to hours, which determines the insulation resistance, and to exclude the influence of micro gaps in the interface between the protective coating and the assembly, the temporal course of water absorption and release on $75 \times 75 \text{ mm}^2$ protective coating foils was examined (see Fig. D2 and D3).

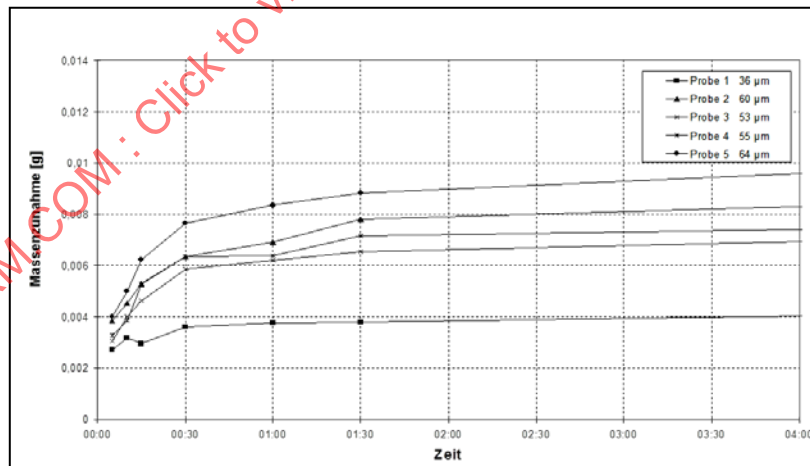


Fig. D2: Time course of water absorption of PUR coatings (16 h / 80°C cross-linked) in dependence of the coating thickness

The logging of the water absorption behavior during the first four hours shows that a "quasi-saturation" is reached within two to three hours (see Fig. D2). Water absorption is very fast in the first few minutes. The film, approx. $60 \text{ }\mu\text{m}$ thick, absorbs approx. 40% of its quasi-saturation in the first five minutes and approx. 80% within 2.25 hours. Drying of the film is about seven times faster than water absorption. The film releases this 80 % within 18 minutes when stored in a room climate (see Fig. D3). This results in a high regenera-

tion potential for the insulation resistance.

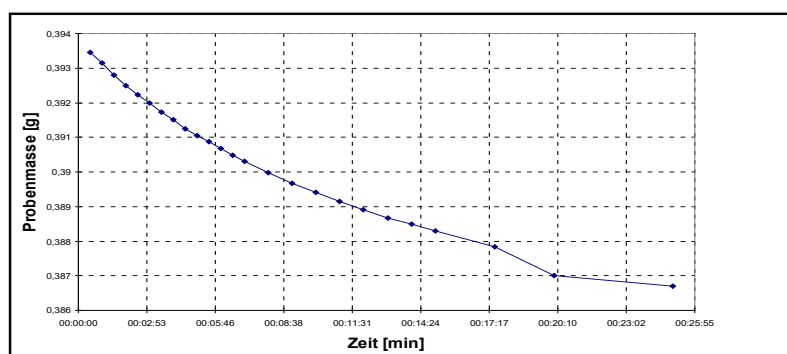


Fig. D3: Time course of the water release of an approx. 60 µm thick PUR coating film (16 h / 80°C cross-linked) in climate 20°C, 55 % rh

The mean values of the quasi-saturation content of the PUR films examined are summarized in the following table, depending on the coating thickness.

Tab. D2: Average value of the quasi-saturation content of PUR films as a function of the coating thickness

Coating thickness [µm]	36	53	55	60	64
Average value of the saturation content [M %]	2.06	2.38	2.29	2.55	2.88
Standard deviation	0.075	0.073	0.333	0.191	0.085
Sample acc. to Fig. D2	1	3	4	2	5

As a result, the water absorption is statistically significantly dependent not only on the degree of curing but also on the thickness of the coating itself. The greater the coating thickness, the greater the relative water absorption. If the curing is supplemented by an upstream vacuum treatment for complete evaporation of the solvent, a value of 1.98 % independent of the coating thickness is obtained.

Comparing this quasi-saturation value of the polyurethane system (PUR), which is independent of the coating thickness, to that of a water-soluble protective coating (AQ) and a so-called raclette film – a wax-based system – the high water absorption of the AQ protective coating is surprising.

Binder basis	PU	AQ	Raclette
Average value of the saturation content [M %]	1.98	11.1	0.049

Resistance measurements according to DIN VDE 303-30 on a test module - equipped with a SO-20 housing, F-SW 26 soldered, uncleaned, covered with raclette foil - showed no change in resistance even after 16 hours of submersion in water.

A high water vapor permeability should not be confused with water absorption. Silicones are mentioned here, for example, despite their high water vapor permeability (Tab. D3) the water absorption over a power of ten is lower than with the usual organic polymers.

² DIN IEC 60093 (VDE 0303-30) (1993-12) could not find "Test methods for electrical insulating materials; specific volume and surface resistivity of solid electrically insulating materials" (IEC 60093:1980); German version HD 429 S1:1983 UK 181.1 Test method for solid insulating materials

This low water absorption shows the advantages of silicone coatings at high humidity and temperature loads. Considerably better electrical values can be maintained here.

Tab. D3: Behavior of some raw materials to water [Lic90]

	Water absorption in %	Water vapor permeability in g/(m ² ·d)
	24 h immersion at RT	37°C, 90% rh, D = 25 µm
Epoxides	0.5 to 1:	20 to 37.2:
Silicones	< 0.3 (usually < 0.1)	594 to 1872:
Polyurethanes	0.6 to 0.8:	66.7 to 134.9:
Polyacrylates	approx. 0.3	550
Polyamides	2.0 to 8.5:	no specification

2.1.2 Water permeation through coating systems

To investigate the barrier effect of the protective systems against diffusion of moisture into unsealed cavities, e.g. under building elements, and against delamination due to hygroscopic impurities, the water vapor permeability of PUR, AQ and raclette films was determined in accordance with DIN 53122-1. All tests were performed at 90 % rh. The water vapor permeability of the PUR protective coating increases exponentially with temperature, as expected due to diffusion laws (see Fig. D4).

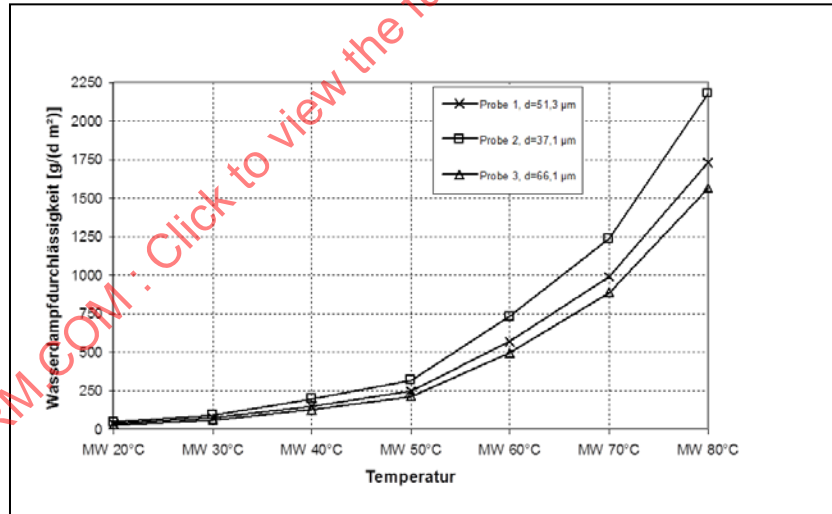


Fig. D4: Water vapor permeability of PU as a function of temperature and film coating thickness (16 h / 80°C cross-linked)

Thinner layers have a lower permeation resistance than thick layers, especially at higher temperatures. At least for PUR-based systems there is a proportionality between water vapor permeability and square root of the coating thickness. This enables a comparison of

³ DIN 53122-1 (2001-08) "Testing of plastic films, elastomer films, paper, cardboard and other sheet materials - Determination of water vapor permeability - Part 1: Gravimetric methods"

⁴ The interplay of diffusion and water absorption is more important than the formation of an aqueous interface or swarm water (accumulation of water, also known as "white tarnishing") in the polymer.

different coating systems independent of the coating thickness (see Fig. D5).

The solvent-based PUR protective coating has a moisture permeation resistance very similar to that of the water-based AQ system. This was to be expected due to the chemical similarity of the binder bases. However, the values of the water vapor permeability of the AQ system scatter much more than those of the solvent-based PUR protective coating do.

Even at room temperature, the wax-based raclette film has a water vapor permeability that is 600 times lower than that of the PUR and AQ protective coating. At 80°C – the upper operating temperature limit specified by the manufacturer – the permeation rate of the 600 µm thick film is approx. 10 g/(d·m²) with very small scattering of the individual measured values.

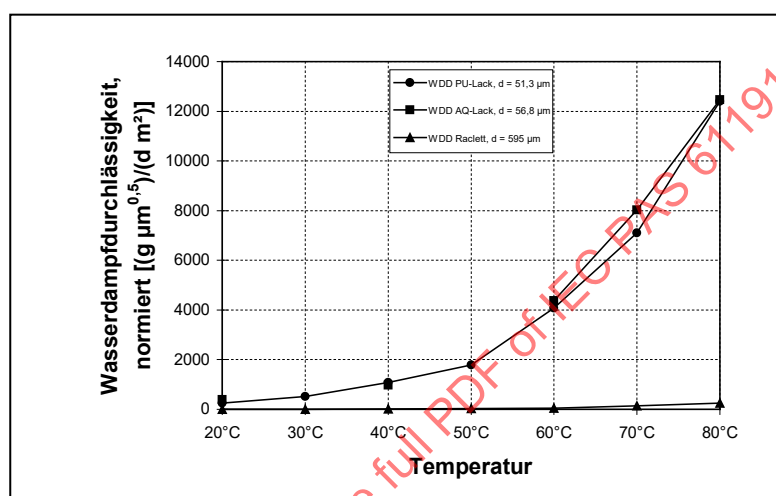


Fig. D5: Comparison of standardized water vapor permeabilities for PUR, AQ and raclette

2.1.3 Adhesion of the coating systems

As electrochemical migration is a corrosion process, the suppression of an activatable boundary layer between coating and substrate is of utmost importance for the protective effect of the coatings. The reliability of this suppression is determined by the bond strength and chemical resistance of the bond between laminate and substrate. These two parameters can be determined via pull-off test according to DIN EN ISO 4624 for basic testing. Unfortunately, the measured value dispersion using this method is up to 30 %.

The adhesion of one PUR, AY and AQ protective coating each to the substrates FR4, tin60lead (SnPb) and copper (Cu) was investigated. The degree of cure, the moisture content and the surface of the SnPb60 substrate were varied. It is pointed out that the curing conditions for the specimen preparation for front tensile tests do not correspond to the curing requirements for assemblies. According to the evaluation of the adhesive strength according to [Fun89] in:

Good adhesion	Pull-off force > 20 MPa
Medium adhesion	5 MPa < Front pull-off force < 15 MPa
Poor adhesion	Pull-off force < 1 MPa

⁵ DIN EN ISO 4624 2016-8 "Coating materials - Tear-off tests to assess the adhesive strength" - previously: DIN EN 24624

The PUR and AY protective coatings have medium adhesion and the AQ protective coating medium to good adhesion when completely cured (see Fig. D6). The follow-up examination shows that in all three protective coatings on copper and FR4 mainly occur cohesion fractures, i.e. separations in the protective coating itself. The adhesive strength thus exceeds the cohesion strength. On tin lead or tin – the standard metallization of electronic assemblies – adhesion cracks occur between the coating and substrate in PUR and AY protective coatings.

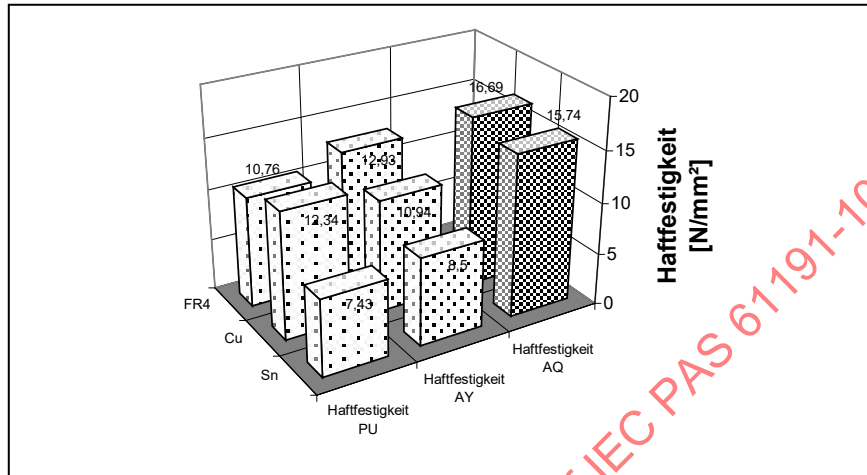


Fig. D6: Adhesion of fully cured samples (4 weeks / 80°C) depending on the type of coating and substrate

Partial curing and thus incomplete crosslinking leads to a reduction in the strength values of all protective coatings (see Fig. D7).

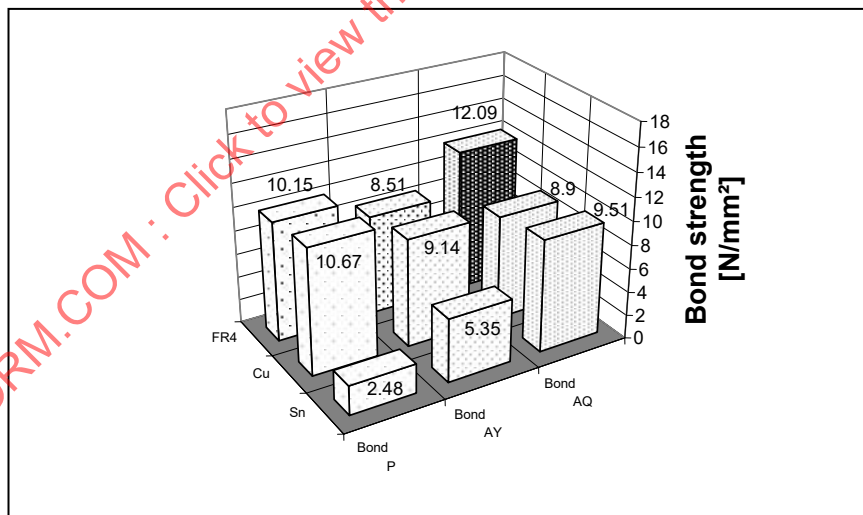


Fig. D7: Bond strength of partially cured samples (2 h / 80°C) depending on the type of coating and substrate

The reexamination of the samples revealed predominantly cohesion fractures in all protective coatings for FR4 and copper. Especially with the AY protective coating, the coating remaining on the substrate side had a sticky consistency. The PUR protective coating failed 100 % on tin as an adhesion failure. The adhesive strength, based on the fully cross-linked state, changed as follows:

(Measured value scattering up to 30 %!)	PUR	AY	AQ
Δ Pull-off force on copper and FR4	90 %	73 %	53 %
Δ Pull-off force on tin	33 %	63 %	61 %

To examine the worst-case the partially cured protective coatings were loaded with different moisture contents in an equilibrium state. This shows that a relative humidity of 55 % does not yet have any influence on the so-called wet coating adhesion (see Fig. D8).

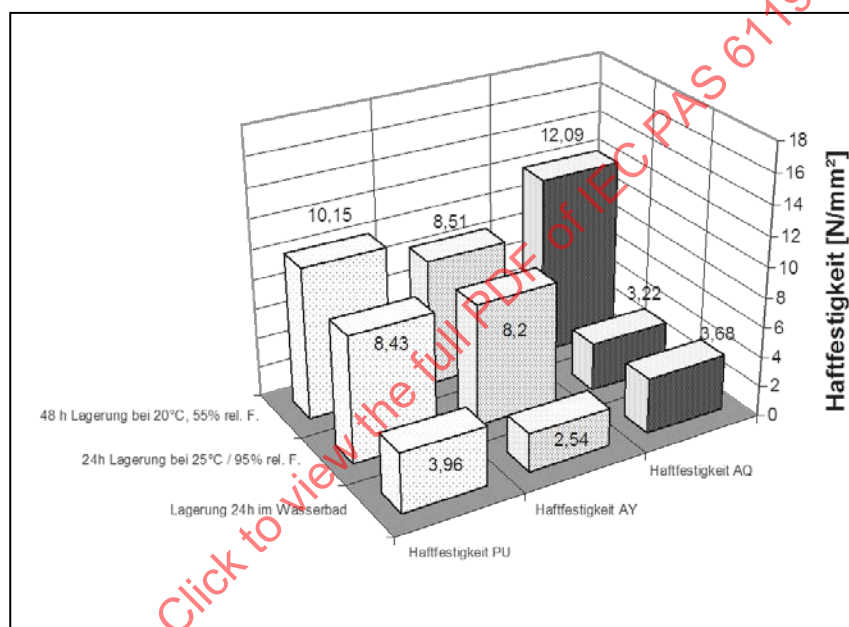


Fig. D8: Bond strength of partially cured samples (2 h / 80°C) on FR4 depending on moisture load and type of coating

A high relative humidity of 95 % does not lead to any significant loss of adhesion with PUR and AY protective coatings. The strength of the AQ protective coating drops by more than 70 %. By setting a water load close to saturation, all coatings drop to approximately the same minimum value.

Since the PUR protective coating showed very low tensile strength on tin, the possibility of surface modification was investigated. Five samples were washed for 5 minutes at 80°C with an aqueous alkaline cleaner before coating and then rinsed in an ultrasonic bath with deionized water. Another five samples were stored at 175°C for one hour after dripping with adipic acid.

Both measures led to an increase in the front tensile test values (see Fig. D9).

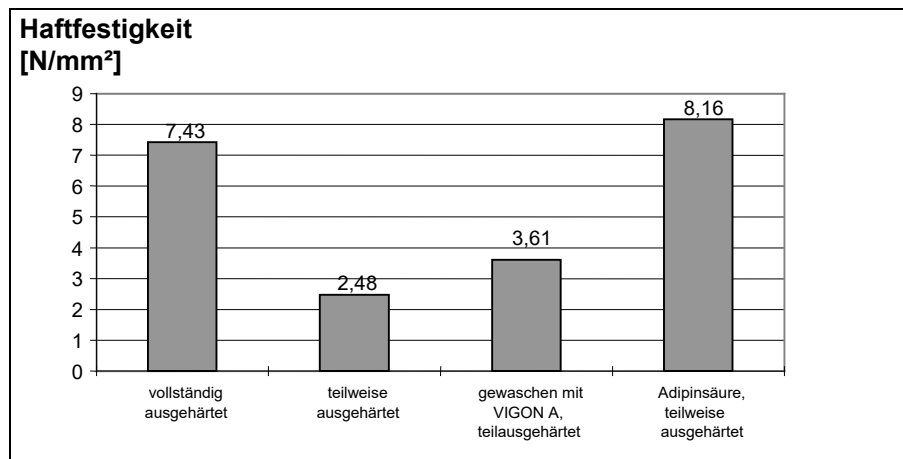


Fig. D9: Influence of surface quality on the adhesion of a PUR protective coating on Sn60Pb

2.1.4 Discussion of the results

The water absorption tests show that a technically relevant influence on the insulation resistance currently only occurs in connection with hygroscopic impurities. Due to the faster water release (approximately seven times faster compared to absorption), the coatings have a high regeneration potential under short-term dewing loads and thus a further safety reserve against shunts due to the reduction of the insulation resistance in addition to the distance to the leakage current limit.

In accordance with earlier differential thermal and X-ray diffractometric tests [Schw97b], the water absorption tests show that a stable state of equilibrium of the PUR protective coating tested is only achieved after curing at 80°C for more than 16 hours. Therefore, it can be assumed that all industrial applications of this coating in the present study correspond to the partially cured state.

In such incompletely cured systems, not only the binder base and the curing parameters time and temperature but also the coating thickness determine the water absorption, since thicker layers require a longer curing time to achieve the same degree of curing [Schw97b]. As a result of the higher water absorption, a greater reduction in resistance would be expected for thicker coatings than for thinner coatings. However, above a certain limit, the insulation resistance does not seem to decrease any further. This indicates a certain fixation of the water molecules, or at least an obstruction of their mobility in the coating polymer. It is conceivable that the protective coating is hindered in its swelling-induced expansion by its application to the substrate surface. In this way, residual compressive stresses are built up which at least partially block the diffusion paths again.

The experiments on water vapor permeability show a proportionality between permeation resistance and square root of the coating thickness. Since the diffusion coefficient of polymers increases with the concentration of the absorbed water, the thinner layers in particular should provide a greater permeation resistance when saturated. The water vapor permeability was measured here at 90% rh just below saturation. As can be seen from the course of water absorption, a water absorption independent of coating thickness and thus degree of cross-linking is to be expected if the coating's water content is below saturation. In this case, the diffusion coefficient does not depend on the coating thickness or the degree of cross-linking. However, since the permeation resistance of the thicker layers, which tend to have a higher water content and a lower degree of cross-linking, increases, this supports the assumption that a mechanism inhibiting the mobility of the water molecules occurs at high load concentrations. Another argument in favor of the blocking hy-

pothesis is that the AQ protective coating has approximately the same permeation resistance as the PUR protective coating, despite absorbing about six times as much water.

An improvement of the protective effect via layer thickening does not seem to make sense, since the permeation resistance of the coatings increases by only 30 % due to layer thickening, but the curing times are extended unfavorably, especially due to accumulations of protective coating (pooling effects).

The front tensile tests on the fully cured protective coatings led to a cohesion failure on FR4, (i.e. an ideally rough surface) and on copper, whose isoelectric behavior is complementary to the PUR protective coating. On tin, the PUR and AY protective coatings fail mainly due to adhesion cracks, as expected based on the results from [Schw97a]. The adhesive strength of the AQ protective coating forms on tin as well as on copper in the same ballpark as on ideally rough FR4. It is thus above its cohesive strength as desired.

An incomplete degree of crosslinking only leads to a weakening of the cohesive strength on substrates to which the protective coatings have a good adhesive strength. Especially with PUR on tin-lead solder, the already weak adhesion is greatly reduced. The superposition of moisture in the partially cured state leads to a drop in the front tensile values. In the case of PUR and AY protective coatings, a relevant drop in the strength values to FR4, i.e. an ideal adhesion primer, only occurs with moisture loads close to saturation. Above 55%rh, the values of the AQ protective coating drop to a minimum level. This corresponds to the expectation of a strong weakening of the cohesion strength, since a solution occurs in the partially cured state of the protective coating due to moisture, i.e. the solvent water.

The treatment of the solder surface with an alkaline cleaning medium increases the poor adhesion of PUR coatings on tin lead. The effect is probably based on a conversion of the isoelectric properties of the tin oxides. The adipic acid treatment led to an increase in roughness of the tin-lead surface, so that the cohesion strength of the coating, as it adjusts to FR4, is almost achieved.

2.1.5 Conclusions for the electrical insulation resistance

The stabilization of insulation resistance by protective coating is provided by a barrier effect between the electrical poles, so that the electroosmotic or electro diffusion mobility of moisture is impeded. In the case of the wax-based system, this goal is achieved through extremely low moisture absorption and permeation rates. It surpasses the coating in its protective effect, especially also in its tolerance against ionic impurities, but due to its thermal stability it can only be used to a limited extent [Schw97b]. In polyurethane systems in particular, in addition to the mechanical barrier effect, the formation of binding forces between the embedded water molecules and the polymer obviously plays an important role. This seems to lower the diffusion coefficient again if it is above a critical moisture concentration. This can be imagined by compressing the diffusion paths.

The protection of the coating systems against electrochemical migration is based on the wet adhesion strength, i.e. the resistance of the bonding forces between coating and metallization against hydrolysis by absorbed water molecules and thus on the suppression of the activability of the metallization for corrosion reactions. Besides an ideally stoichiometric complementary isoelectricity, a roughening of the metallization as described in [Schw97a] has a favorable effect. The AQ protective coating and the wax-based film system have the highest resistance and the greatest tolerance against changing adhesive substrates.

3 Thermal properties

3.1 Stress factors

The stress factor in the processes considered here is the heat energy, characterized by temperature. It causes reversible and/or irreversible changes on/in materials - polymers such as metals. If the temperature is additionally increased for moist materials, the tendency to spontaneous entropy rise increases, i.e. the tendency to irreversible changes.

Lemaire et al. [Lem91] declared in 1991 "the chemical role of water in weathering is far from being understood". Kamal and Saxon [Kam67] emphasize that water can have at least three types of effects that are important in the degradation of polymers:

- physical influences - loss of the bond between the polymer and a substrate or pigment (filler)
- photochemical influences - generation of hydroxyl radicals in combination with sunlight (UV light)
- chemical influences - hydrolysis (splitting) of ester or amide bonds

A fourth influence is given by the possibility of ion formation and the increase of mobility of electric charge carriers. The latter plays a triggering role especially in electrochemical corrosion processes. Other stress factors that affect reliability are listed in [Lie01].

In the automotive sector, the topic of "thermal stress factors" and resulting failures has become increasingly important, not least because more and more electronic assemblies are being installed in automobiles. In addition, these assemblies move ever closer to the aggregates and are thus exposed to increasingly "unfriendly environmental conditions". Automotive manufacturers state temperature gradients from -40°C to the range of $+80^{\circ}\text{C}$ (interior) to $+800^{\circ}\text{C}$ (exhaust gas sensors). This temperature range will certainly not be covered by the "classic" FR4 PCB, but we are talking about a range from -40°C to the $+120^{\circ}\text{C}$ to $+150^{\circ}\text{C}$ range. This temperature load consists of the "external" temperature and the so-called self-heating - which increases more and more with increasing component density. For example, temperature increases from 105°C to 150°C are observed in motor attachments. In particular, the loads at higher temperatures lead to irreversible changes in the sense of the second law (of thermodynamics). Loads due to higher temperatures are summarized in this context under the term "thermal stress load" [Hoc02].

3.2 Thermal mismatch

In addition to the mere thermal load, there is also a mechanical load due to the different coefficients of thermal expansion, especially in the case of material combinations. This is generally referred to as thermal mismatch.

A particularly important consequence results from the modulus of elasticity of the materials under thermal cycling loads. There is always a mismatch of different coefficients of thermal expansion (base material, copper, solder, components, etc.) on an electronic assembly. Different coefficients of thermal expansion lead to stresses during temperature changes, i.e. to different thermal movements.

In a simplified representation, these different temperature expansions and their mechanical consequences - a mechanical stress between these components - can be described as follows:

$$\sigma = E_2 (1/(1-\mu_2)) (\alpha_2 - \alpha_1) \Delta T$$

σ = mechanical tension,

E = modulus of elasticity,

μ = Poisson number (Poisson's ratio),

α = coefficient of thermal expansion,

ΔT = temperature difference.

(for the sake of clarity, the equation is reduced to two substances.)

In addition to the temperature difference and the different coefficients of expansion, the modulus of elasticity in particular plays a decisive role in stress transfer. The higher the modulus of elasticity, the greater the resulting stress. Depending on the material, three or more powers of ten between different materials or moduli of elasticity are possible [Hab97] (for modulus of elasticity see chapter D7).

3.3 Fatigue - the Wöhler curve and its consequences

If the stress amplitude σ , which is necessary for a fatigue break after N cycles, is plotted against N , the so-called Wöhler curve is obtained. It often has a limit value, if one remains below this load limit σ_G , the component is not endangered by fatigue fracture.

Mentioning this Wöhler curve only intends to warn against unnecessarily increasing the temperature deviation, which is proportional to the strain amplitude, in order to derive "more safety" from the tests. In addition, many polymers show insufficient permanent elasticities.

3.4 Thermal stress load

Under thermal stress, polymers undergo more or less pronounced irreversible structural changes. These structural changes lead to changes in mechanical and/or electrical properties.

Especially for electronic assemblies, the thermal stress load should be divided into two categories. The thermal stress caused by the soldering processes should be mentioned first. These thermal loads are significantly higher than the temperature resistance of all components involved, even if only for a short time. These loads and their consequences are explicitly excluded here, since in the event of damage they would be more likely to be

classified as early failures due to material or process defects.

The thermal stress load during the lifetime can also be regarded as thermal aging resistance and differs significantly from the decomposition temperature of a polymer. The thermal aging process of polymers is very different and the aging mechanisms vary with the operating or load conditions. Thermal resistance tests to determine the change in properties are carried out, for example, in accordance with DIN EN 602165.

Typical aging mechanisms - as listed in DIN EN 60216 - are:

- Loss of volatile components, such as low-molecular components, which were present from the very beginning;
- Oxidations; they are accompanied by increasing cross-linking and embrittlement;
- Continuation of molecular polymerization, which often initially leads to an increase in electrical and mechanical strength but later leads to embrittlement;
- Hydrolysis of the polymer by ambient moisture; it can be accelerated drastically by heat;
- Chemical release of low-molecular components formed by the aging process. Such processes can have an autocatalytic effect.

When testing the temperature resistance, various factors must be taken into account that can significantly influence the test results. It is very important whether a polymer or coating system is exposed to damp or dry heat. As a rule, the resistance to moist heat is considerably lower than to dry heat because hydrolytic degradation processes can take place in addition to mere thermal degradation processes.

DIN EN 60216 attempts to simulate the changes in properties of electrical insulation systems under a thermal load. The aim is to determine the so-called temperature index (TI). This describes the temperature at which one or more properties of a system fall below previously defined limit values, e.g. a mass loss of 25 %, a drop in electrical characteristic values to 75 %, etc.

Normally, the temperature index for long-term behavior is specified at 20,000 hours (833 days) and short-term behavior at 5,000 hours (208 days). Since these periods are not practicable for relevant investigations, the aging temperatures are significantly increased and subsequently the values of the failure limit are extrapolated to e.g. 20,000 hours. For this purpose, three temperature ranges are selected, some of which are significantly above the expected temperature index. Now the respective properties are measured cyclically, e.g. 10 cycles per 7 days. The resulting measured values are charted as property changes over time. The mathematical functions can then be approximately determined based on trend lines. This allows calculating the time for the individual test temperatures at which the limit values were undercut. These "downtimes" are now displayed in a second graph, time vs. temperature (see Fig. D10).

⁶ DIN EN 60216-1 (2014-01) "Electrical insulating materials - Properties with regard to long-term thermal behavior - Part 1: Hot storage tests and evaluation of test results" (VDE 0304-21)

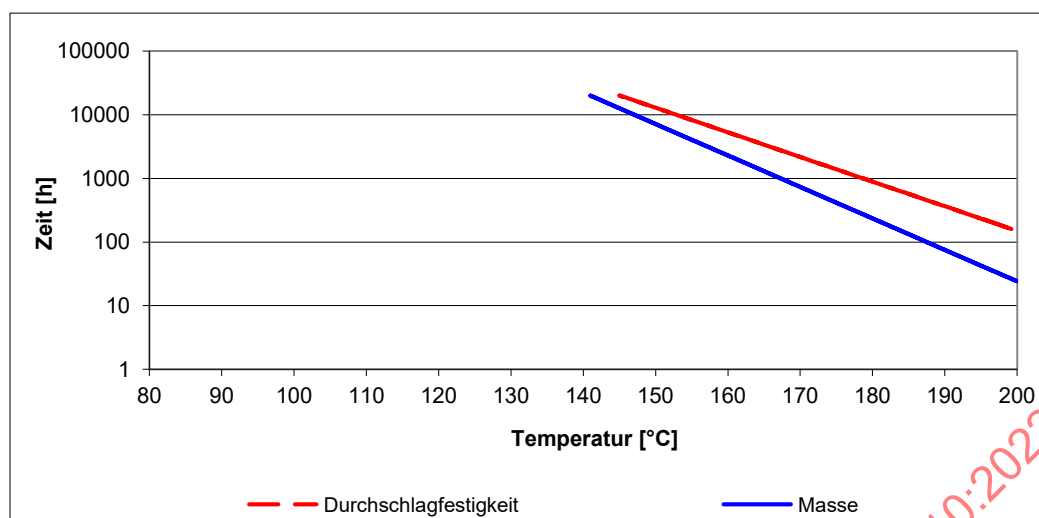


Fig. D10: *Extrapolation of the experimentally determined downtimes to a downtime of 20,000 hours (schematic diagram).*

By combining the individual "failure hours", the calculated failure temperature can now be extrapolated for 20,000 hours. The temperature value thus obtained describes the continuous temperature resistance. Extrapolation to 5000 hours results in the so-called short-term resistance. The accuracy of the straight lines can be determined using a regression factor (coefficient of determination).

3.5 Thermal shock resistance

The appearance of thermal shock resistance is also important. This is the fact that a protective coating system that has been repeatedly cooled and reheated again may be destroyed earlier than the same system that is continuously exposed to the same temperature during the same time. The speed of the temperature change can also be important.

If a protective coating system is exposed to elevated temperatures for a longer period of time, embrittlement, yellowing, loss of gloss, and a change in electrical properties and possibly in adhesive strength usually occur. Especially the change of the electrical properties is paramount to the considerations.

3.5.1 Temperature cycling test

Statements on the cycle capability of printed circuit boards and the so-called TWT (temperature change tests) of printed circuit boards and assemblies are discussed in many working groups; test cycles are defined and applied. The main defect when using these assemblies at high temperatures is the formation of cracks in vias [Hoc01].

Various methods are used to determine thermal shock resistance. Mostly mentioned:

- the "temperature cycle test" (TWT),
- the "Interconnect Stress Test" (IST) and
- the "Thermal Cycle Test with Control Measurements, Four-point Resistance and Temperature with up to 40 Channels" (TCT Comfort 40).

The thermal cycle tests – primarily about the stability of copper sleeves – are linked to electrical detections in the IST and TCT Comfort 40. Degradations in the copper sleeve can thus be read out directly. Here the "simple" TWT is largely obsolete [Bün04].

The situation is different when determining the thermal cycling capability of the coating. Their possible failure lies in embrittlement, cracking and delamination, which are not accessible online for electrical measurement or detection. Here one has to live with the disadvantages of the TWT in the first place, i.e. a determination of the failure time is only possible after certain intervals and must be carried out visually, which is time-consuming.

3.5.2 Thermal shock load

The core issue is the increased demands on the cycle capability of electronic assemblies. The requirements of the automotive industry are the main technology drivers here. The main error when using electronic assemblies in high-temperature applications leads to the question of how solder resist and protective coatings behave under these test criteria.

In addition to these rudimentary IPC requirements, temperature changes in the following gradations became established for corresponding circuits in the automotive sector (various automotive specifications):

-40 / +85°C	200 cycles
-40 / +110°C	up to 500 cycles
-40 / +125°C	up to 500 cycles
-40 / +140°C	up to 1000 cycles
- 0 / +160°C	up to 1000 cycles

The dwell times are between 15 and 30 minutes with a rearrangement time of < 10 s. At the desired high cycle numbers and temperatures, not only mechanical stress and fatigue symptoms but also aging symptoms due to storage at the high temperature are noticeable and are thus included in the load. Findings from the thermal shock tests according to IPC specifications cannot be transferred to the conditions specified here, since after 100 cycles - corresponding to an exposure time of 25 h - aging phenomena due to storage at high temperature are not recorded.

In temperature cycling tests (TWT), the speed of rearrangement is important in addition to the limit temperatures. A distinction is made between so-called "hard" temperature cycling tests with a rearrangement time of < 10 to 30 s - also thermal shock test - and "soft" or slow changes with a repositioning speed of 1 - 3 K/min. A differentiation of the different "hard" and "soft" temperature cycling tests would go beyond the scope of this consideration. In accordance with the findings and agreements of the ZVEI/VdL Ad-hoc Working Group "Cycle capability of printed circuit boards", the "hard" temperature cycling tests were carried out in the following investigations. The test conditions are defined as follows [ON04]:

- Rearrangement temperatures: $T_{\max} = 130 \dots 150^{\circ}\text{C}$; $T_{\min} = -40^{\circ}\text{C}$
- Rearrangement time: < 10 s
- Storage time: 30 min
- Number of cycles: 500 (1000) ... 3000

⁷ ZVEI – Zentralverband Elektrotechnik- und Elektronikindustrie e.V. (www.zvei.de) / VdL – Verband der Leiterplattenindustrie e.V., merged with ZVEI

The driving force for the failures under thermal shock loads is the thermal-mechanical stress build-up due to the different coefficients of thermal expansion [Lie01]:

$$N_f \sim \Delta T^{-1/c}$$

- N_f = Number of cycles until failure
 c = Function of ΔT and frequency (type of temperature change)
 ΔT = temperature difference

In addition to the stresses built up by different coefficients of thermal expansion - which can also lead to failure - fatigue phenomena of materials are also recorded with these test procedures [Ehr99]. From this relationship, it can be deduced that we do not have an acceleration factor as in Arrhenius' thermal degradation.

As described in the hotEL joint project, special attention must be paid to the selection of components. For example, cracks were observed on the first appearance of stable base materials [Pap06].

The effects on solder resists used, their insulation properties, especially under later climatic conditions, are the subject of numerous publications [Sup04c, Sup06c, Sup06f].

Studies of protective coatings show that the thermal cycling tests do not cause failures due to migration or reduction of insulation resistances. However, damage to the coating film by cracks and delamination is possible and, in turn, can then lead to migration and isolation failure [Schw97a].

Residues of solder paste resins in particular often do not form a sustainable basis for a protective coating. Collections of resin residues from the solder pastes show the tendency to discoloration and cracking under thermal shock loads. These can occur under the protective coating, but can also affect the protective coating itself.

Depending on the temperature range, laminate and solder resist must also be carefully selected. Cracks in the substrate usually also destroy the subsequent coating or lead to weak spots under the protective coating. We urgently advise against a protective coating for the repair of such pre-damaged components.

The tests on the thermal shock resistance of protective coatings must usually be carried out on the respective assembly. Besides the basic mechanical properties of the protective coating, the most important influencing variables are:

- Type of geometry (components, assemblies)
- Type and quantity of process residues (flux, solder paste resins, process greases, etc.)
- very complex thermal mismatch
- Coating thickness and coating thickness distribution of the protective coating
- Temperature surge
- Rearrangement time

Statements on the long-term temperature resistance of protective and insulating coatings as well as solder resist coatings are becoming increasingly important. On the one hand, the ambient temperatures under which electronic assemblies are operated are increasing, and on the other hand, the proportion of the temperature load increases significantly due to self-heating over the increasing packing density.

A statement on the long-term temperature resistance of electrical insulating materials can be made by means of an examination in accordance with DIN EN 60216. Depending on the type of polymer, protective coatings based on organic polymers can be used up to 150°C continuous load or 165°C short-term load. Silicone coatings are only indispensable above these temperatures.

The investigations carried out on the long-term temperature load of solder resist masks show that the functional reliability is maintained under this high thermal load. In order to evaluate the functional safety after this exposure time, the electrical properties in particular were examined in more detail. The moisture resistance and insulation resistance in accordance with TM 2.6.3.1 of the IPC-TM-650 showed that no ionic degradation products can form and values of $> 10^8$ Ohm can be maintained even under tougher conditions at 85°C and 85 % rh with 50 V BIAS. The tracking resistance, which is important for insulation, was also maintained at a good level. The solder resists have a very high resistance to thermal shock. Temperature cycling loads of -40°C / +150°C in "hard" alternating – re-arrangement time < 10 s – can be passed. The thermal load during the temperature cycling test can be compared with the corresponding long-term temperature storage.

4 Condensation

The humidity of the atmosphere is often equated with the relative humidity. This is usually a very useful value, but for chemical and physical considerations the absolute humidity is often more meaningful. Here are two definitions:

Relative humidity is the percentage saturation of the air at a given temperature, expressed as a percentage RH⁸ (quotient of the current vapor pressure of the water in the air to the saturation vapor pressure above water).

- At a relative humidity of 50%, the air contains only half the maximum amount of water vapor it could absorb at the appropriate temperature.
- At 100% relative humidity, the air is completely saturated with water vapor.
- If the saturation level of 100 % is exceeded, the excess moisture is reflected as condensation or mist.

Absolute humidity is the total mass of water vapor in one m³ air [g/m³]. This means that when humid air is heated, the relative humidity decreases drastically in some cases, while the absolute humidity in grams of water per cubic meter is maintained. Many physical processes are controlled by this absolute humidity - expressed as partial water vapor pressure.

On the other hand, the dew point is directly coupled to the relative humidity. The dew point describes the temperature of the humid air at which it is saturated with water vapor (100 % RH). If the temperature drops below the dew point, condensation occurs immediately.

At an atmospheric load under normal climatic data, there is always a moisture load. The coating of the assembly is balanced with the water vapor (water vapor partial pressure) of the atmosphere. Since no polymer is impermeable to water vapor, a certain proportion of water is always present in the polymer. This water is dissolved or stored in the polymer. With increasing temperature and/or increasing humidity, more water can accumulate in the polymer. In these cases, the balance "water dissolved in the polymer" to the vapor pressure of the water in the air is the decisive driving force. The situation is different with

⁸ RH = rh = Relative humidity

condensation, where osmotic processes dominate.

The ISO 9223 Corrosivity Classification can be used to evaluate these climatic conditions with regard to relative humidity. This describes a "Time of Wetness", the average time in a given climate during which the relative humidity has a value of >80 %. At large, even in our temperate latitudes a humidity of >80 % RH can be expected for up to 2500 hours or 100 days or more.

The physical effects of (air) moisture on polymers and thus also on electrical assemblies are to be divided into adsorbed moisture (water) and absorbed moisture (water).

An adsorption of water is an accumulation of water on a metal or plastic surface and, for example, can lead to a reduction in surface resistance. However, the insulation inside the material is not affected; it is only changed by the absorption (of water). Absorption describes the physical absorption of a substance into another substance.

In practical moisture loads, e.g. of electrical assemblies, both phenomena occur next to each other. Even "dry" surfaces already have a moisture film. Here, of course, the question arises: How dry are dry surfaces? This question can be answered for example with a scanning tunneling microscope [Fre99]. In very dry atmospheres of less than 50 % RH, a "water film" of approx. 10 nm forms - more in the form of drops or islands. A film of this thickness can already interact with hygroscopic, i.e. water-attracting impurities on the film surface. From approx. 50 % RH the water film thickness increases drastically and can reach coating thicknesses of more than 60 nm.

With extremely hydrophilic metal surfaces - e.g. with formed metal oxide layers, adsorption starts much more strongly, with 50 % RH already reaching 80 nm and rapid growth to more than 100 nm is possible. With over 50 % RH a closed water film has formed on the metal surface! For coatings of more than 10 nm, "normal" water properties can be assumed, i.e. dissolution processes of salts on the surface can begin and ionic processes can take place [Luc73]⁹. There is always a latent risk of condensation at humidity levels above 80 % RH. The dew point can be overstepped by a little temperature drop of only 2 to 3 degree. Contamination can significantly reduce the dew point, e.g. in case of NaCl contamination the dew point is already 75 % rh. This is called relative critical humidity. Relative critical humidity is the combination of temperature and relative humidity at which a substance begins to absorb moisture from the atmosphere. It is a material constant [Teg98].

Particular attention must be paid to the interaction between protective coating and, for example, solder paste residues, especially during condensation. With an assembly coating, contaminations on the printed circuit board are incorporated into the protective coating film. Depending on the degree of contamination, the protective effect may deteriorate drastically. Here, the exposure to condensing moisture is much more sensitive than, for example, a load with high humidity. Test combs with very good moisture insulation values of > 500 MΩ at 85°C / 85 % rh can show drops in resistance to a few kΩ and corrosion failures due to migration within a few hours/days with condensing moisture. Here, the possibility of assembly cleaning must be considered.

Fig. D11 shows an exemplary mixture of an acrylic resin lacquer with a typical solder paste resin. A very unfavorable resin ratio of 50:50 was deliberately chosen. There are no flux residues and/or corresponding tin or lead soaps from the solder activation in the mixture. This mixture clearly shows the difference of the physical load and its results at high humidity load (85°C/85 % rh) and at condensation (40°C/100 % rh).

⁹ See also: IPC-HDBK-830 Guidelines for Design, Selection, & Application of Conformal Coatings, (2002).

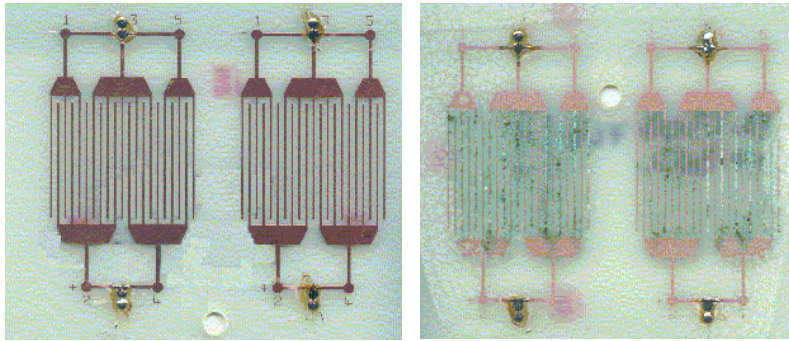


Fig. D11: Exemplary mixture of an acrylic resin coating with a typical solder paste resin under high humidity load (85°C/85 % RH) (left) and condensation (40°C/100 % RH) ¹⁰ (Work drawing Lackwerke Peters GmbH + Co KG)

While the mixture is still resistant to migration at high humidity, a massive migration can be observed during condensation. The processes taking place with the two load types are not comparable.

5 Water absorption and water vapor permeability

5.1 Requirements

Protective coatings and thick-film coatings are insulating materials such as glass, ceramics, which act as insulators due to their property values in the sense of DIN VDE 0110. Only materials with a volume resistivity $>10^{10}$ Ohm·cm are considered. They must be largely impervious to electrons. This primary requirement is fulfilled by various materials and accordingly insulating materials or compounds can be composed of very different types of natural resins, plastics, synthetic resins and various additives such as plasticizers, pigments and fillers. Insulation systems based on plastics and synthetic resins are used almost exclusively for applications as protective coating, potting compound or coating compound for assembled printed circuit boards.

A generalized requirement for an electronic assembly is that the functional reliability is guaranteed in the event of a moisture load - considering various climatic conditions. Certain restrictions regarding resistance to certain substances - in particular to water - must be taken into account here. In the following, the basics of exposure to moisture are examined in more detail.

At an atmospheric load under normal climates, there is always a moisture load. All polymers on an electrical assembly are in equilibrium with the water vapor of the atmosphere. Organic polymers exhibit - depending on their chemical composition and structure - a behavior between hydrophobic (water-repellent) and hydrophilic (water attracting). As a rule, hydrophobic behavior is aimed for. The polymeric substances, which by microscopic observation prove to be naturally pore-free, absorb water through a sorption process. When polymers are exposed to water or water vapor, this penetrates into the polymer. Physically this means that processes such as absorption, diffusion, osmosis or electro osmosis take place.

¹⁰ To show the corrosion more clearly, a copper comb was chosen because of the colored corrosion products.

¹¹ Now DIN EN 60664-3 (2017-11) "Insulation coordination for electrical equipment in low-voltage systems - Part 3: Use of coatings, pouring or encapsulation to protect against contamination".

Since no polymer is impermeable to water vapor, a given proportion of water is always dissolved in the polymer. With increasing temperature and increasing humidity, more water can accumulate in the polymer or even in the polymer/substrate interfaces. This effect can be noticeable in SMD components through the so-called popcorn effect in soldering processes.

The insulating effect of a coating depends primarily on the extent to which it can be affected by moisture. Two different processes have to be considered here. On the one hand, polymers show a permeability of water molecules and on the other hand a water absorption into the polymer.

Molecules or atoms of gases and liquids move and mix due to their thermal movement. In a static resting liquid, each molecule "migrates" on average about 1 cm per day. The distance of one cm corresponds to about 10 space changes per second. This phenomenon is also known as Brownian molecular movement. In polymers, these space-changing processes take place at a speed that is reduced by a factor of 100 or more.

This permeability of polymers in itself is not an absolute exclusion criterion for use as an insulating material, provided that the diffusing moisture cannot accumulate either in the polymer-substrate interface or in the polymer. This provides important information for the analysis of the substrate. Contamination with electrically conductive components, e.g. salts (hand perspiration), can certainly weaken the interface by forming islands of moisture.

The situation is different with the water embedded in the polymer. The amount of water absorbed is determined both by the number of polar groups in the polymer backbone and by the density of cross-linking. Diffusion tests show that this motility depends not only on temperature, but also on the amount of water already dissolved in the polymer. If the polymer contains little water (few polar groups), few water molecules with little interaction move relatively freely in the matrix. The diffusion coefficient has a relatively high value. With increasing water content (many polar groups), the water molecules accumulate in "clusters". The interactions increase and the mobility and thus the diffusion coefficient decreases. If the simple storage of water molecules - isolated from each other - is rather uncritical, the formation of clusters or water-filled interfaces is very problematic. In these clusters, electrical charges can be transported very easily, which is reflected in a sharp drop in insulation resistance.

The knowledge of the general permeability of water molecules through a polymer film also draws attention to the substrate, the substrate to be coated. Moisture-sensitive contaminations and weak points already present here cannot be isolated and made perfectly harmless. Water-soluble components are a potential weak point. A reliable statement about the actual protective effect of a coating can only be made in connection with a load on the assembly as close as possible to the process.

In physics, these outlined regularities are called heterogeneous equilibria. The water dissolved or accumulated in the polymer is in equilibrium with the gas/vapor phase outside the polymer. Each aqueous solution has a characteristic vapor pressure and all processes are designed to balance vapor pressures. This orientation towards vapor pressure means that certain surface contaminations with salts are only activated at characteristic relative humidities. Sodium and potassium chloride are only activated at $> \sim 70\%$ rh, but their carbonates at $\sim 40\%$ rh and the acetates at $< 20\%$ rh. These corresponding humidities are also referred to as "Critical Relative Humidity" (CRH). The expected humidity load of the assembly is therefore a "key load" which also determines the coating.

DIN EN ISO 9223 also help in this estimation. There, the "corrosion potential" of the atmosphere is classified into the "time of wetness" - which is decisive for our consideration here - and the exposure to air pollution (chloride and sulfur dioxide content). Classification according to t_1 and t_2 interiors with and without climate control - a time load of up to max. 250 h, this corresponds to max. 3 % per year - of over 80 % rh is assumed. Experience shows that electronic assemblies perform their function under this load even without a protective coating. Outdoor operation in temperate zones with up to 5500 h over 80 % rh – this complies with 60% of the year – is already a considerable burden on the electronic assembly and a protective coating is certainly appropriate.

5.2 Transport of moisture

The transport of moisture (water) from the vapor phase (atmosphere) into and through a coating film at different climatic conditions is called permeation. The process of the passage of a substance through a body can be described in the following steps:

- adsorption of the permeating substance on a body surface,
- solution in the body,
- diffusion through the body (towards decreasing concentration).

In idealized behavior, this dependence is described by the Henry equation:

$$c = S \cdot p$$

c is the concentration of the sorbed substances, S is the solubility/sorption constant of the polymer and p is the partial vapor pressure of the sorbed substance in the vapor space. In the case of the air humidity load, this is the vapor pressure of the water in the air, which is related to the relative humidity as follows:

$$p = rh \cdot p_s(T)/100$$

with rh = relative humidity in percentage, $p_s(T)$ the saturation vapor pressure of water in air at temperature T . As a result, it is not the relative humidity that is the driving parameter, but the actual vapor pressure of the water in the atmosphere. At 35°C / 90% rh there is a water vapor pressure of approx. 51 Pa, at 65°C one of 225 Pa and at 85°C / 85 % rh one of about 491 Pa. At "room conditions", it is only around 16 Pa.

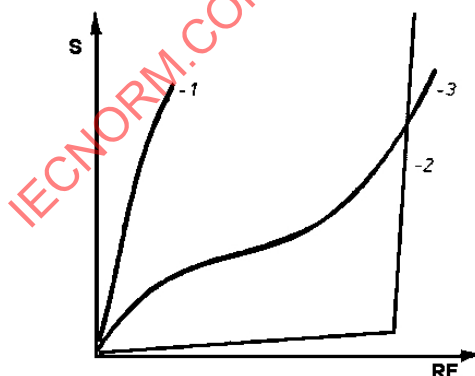


Fig. D12: Sorption isotherm S as a relationship between the water content of the substance and the relative humidity rh of the ambient air at constant temperature.
(1 - highly hygroscopic; 2 - salts; 3 - polymers with low water absorption)

¹² DIN EN ISO 9223 (2012-05) "Corrosion of metals and alloys; Corrosiveness of atmospheres; Classification".

The solubility/sorption constant is a material constant of the coating material, which can be influenced though by washing and dissolution processes on the assembly. Incorporated substances, especially ionic impurities (e.g. tin or lead soaps), but also polar foreign resins from solder paste residues can increase this material constant and thus cause an increased moisture absorption - combined with a further decrease in insulation resistance.

6 Thermal resistance

Heat conduction is an energy transport via atomic and molecular interactions at unequal temperature distribution. The empirically developed equation of heat conduction goes back to *Fourier* and *Biot* and reads:

$$q = - \lambda \text{ degree } T$$

where q is the heat flux density and degree T is the temperature gradient. The minus sign indicates that the heat flow is contrary to the temperature gradient. The proportionality factor is called thermal conductivity coefficient with the unit $\text{Wm}^{-1}\text{K}^{-1}$. Generally speaking, thermal conductivity is a function of location, time, pressure, density, physical state, chemical composition and temperature. However, under these experimental boundary conditions, it is primarily dependent on the chemical composition of the substance and its physical state. For the stationary state of a shift, the required solution function is then:

$$\lambda = \frac{Q}{t} \frac{d}{A (T_1 - T_2)}$$

with Q = heat quantity ($Q/t = q$), t = time, d = coating thickness, A = measuring surface and $T_1 - T_2$ = temperature difference.

From this, the thermal resistance can be defined according to the electrical analogy. The thermal resistance of a body decreases with increasing thermal conductivity (λ) and larger contact area (A) and increases with increasing thickness (l).

$$R_L = \frac{l}{\lambda \cdot A}$$

The ability to conduct heat - the thermal conductivity - is a specific property of a material. Metals have the best thermal conductivity, followed by inorganic solids. This is followed by organic solids and liquids. Gases have the worst thermal conductivity. Some numerical values are listed in Table D4.

Tab D4: Thermal conductivity of various materials

	λ in $\text{Wm}^{-1}\text{K}^{-1}$
Tin, aluminum, copper	64, 200, 400
Air	Approx. 0.02 - 0.03
Polymers (unfilled)	Approx. 0.2 - 0.4
Polymers (insulating filled)	1 - 10

For protective coatings, an average thermal conductivity of $\sim 0.3 \text{ Wm}^{-1}\text{K}^{-1}$ can be assumed. For coating thicknesses of 20 to 40 μm , i.e. 20 to $40 \cdot 10^{-6} \text{ m}$, this thermal resistance can be neglected in the calculations, since the largest resistances determine the current or heat flow in a series connection in accordance with an electrical circuit.

A limiting factor for a heat transport is the maximum amount of heat to be transferred to the environment. Heat can be transferred or released from the heated body through two principles. On the one hand, this is possible via the heat radiation and on the other hand via the heat emission to the surrounding air. There are two types of heat transfer to the surrounding air: free and forced convection.

The maximum amount of heat that can be transferred via these processes depends on various parameters and is difficult to calculate in detail.

7 Flexibility (modulus of elasticity) and CTE

The modulus of elasticity plays a particularly important role in thermal shock loads. A mismatch of different coefficients of thermal expansion (base material, copper, solder, components) is found on an assembled module. Different coefficients of thermal expansion lead to stresses during temperature changes, i.e. to thermal movements. One remembers the former click-click on the railway rails, based on the "expansion joints" common at that time.

In a simplified description, these different temperature expansions and their mechanical consequences - a mechanical stress between the components - can be described as follows:

$$\sigma = E_2 (1/\nu_2) (\alpha_2 - \alpha_1) \Delta T$$

Here σ stands for the mechanical stress, E is the modulus of elasticity, ν is the Poisson number (Poisson's ratio), α_1 , α_2 for the two coefficients of thermal expansion and ΔT is the temperature difference. Simplified, the consideration - for the sake of a better overview - is reduced to two substances.

The modulus of elasticity is a measure of the stiffness of the material, of its resistance to deformation. The higher the modulus of elasticity, the more stress must be applied during deformation. Examples: steel approx. 200,000 MPa, lead 18,000 MPa, epoxy resins 3,000 to 5,000 MPa, polyurethane resins 1,000 to 2,500 MPa, silicone resins approx. 2 MPa)

These basic considerations are obligatory for protective coatings and casting compounds. In the worst case, misjudgments lead to demolition of components and thus to the immediate failure of the assembly. As a rule, there are no direct component failures with the protective coatings. The force that occurs under thermal cycling loads with "too hard" protective coatings is more likely to lead to cracking in the protective coating film. The occurring mechanical stress exceeds the tensile strength of the protective coating film, which tends to tear due to the lower coating thickness compared to casting compounds and cannot transfer the forces to the components. The cracks in the protective coatings in turn only lead to faulty currents and failures when exposed to moisture (e.g. condensation).

Even with thick-film coatings, it is less likely that the components will be destroyed, but rather that cracks will form in the film. The decisive factor for the stability of the system under a thermal cycling load is the resulting stress from the formula shown.

The "driving force" is the temperature difference. Small temperature differences in the application (e.g. from 10 to 40°C) also result in only small mechanical stresses. If, on the other hand, the assembly experiences temperature changes, e.g. from -40 to +100°C, the temperature difference of 140°C leads to noticeable mechanical forces. Experience shows that the low temperatures here tend to cause problems with thermally induced stresses. This is also explained by the modulus of elasticity. The modulus of elasticity itself is also temperature-dependent and increases at low temperatures, the polymer "freezes". The increase in modulus of elasticity is particularly large if the glass transition temperature is undershot. This is another advantage of silicone protective coatings. Due to the high segment motility, the glass transition temperature is extremely low ($< -40^{\circ}\text{C}$) compared to other polymers and the increase in modulus of elasticity at low temperatures is very low.

Small differences in the coefficients of thermal expansion also reduce the stresses induced by the temperature differences. However, it is very difficult to bring polymers with a coefficient of thermal expansion of usually $100 - 250 \times 10^{-6}\text{K}^{-1}$ to a value of approx. $20 \times 10^{-6}\text{K}^{-1}$ and below (corresponding to base material (FR 4) or metals).

A core parameter for reducing the mechanical stress is the modulus of elasticity, which is directly proportional to the stress. This shows that silicone protective coatings with an elastic modulus of approx. 2 MPa can reduce the mechanical stresses caused by thermal stress by a factor of 1000 compared to epoxy resins or polyurethanes. The very low modulus of elasticity of silicone coating materials (protective coatings and casting compounds) promises excellent properties, especially at high thermal cycling loads up to -40°C (in some cases up to -65°C). This statement applies not only to silicone protective coatings, but also to silicone casting compounds and silicone gels, which are characterized by the lowest possible modulus of elasticity.

Epoxy resins and polyurethane resins can be elasticized in a wide range - without, however, achieving the moduli of elasticity of silicone resins. However, in this case the water absorption of the polymer generally increases.

INFLUENCE OF THE ASSEMBLY ON THE PROTECTIVE COATING

- 1 Base material**
- 2 Component and circuit board layout**
- 3 Solder resist**
- 4 Soldering materials and soldering process**
 - 4.1 Flux types
 - 4.2 Composition of No-Clean fluxes
 - 4.2.1 Solvents
 - 4.2.2 Activators
 - 4.2.3 Auxiliary ingredients
 - 4.2.4 Resins
 - 4.3 Residues from the soldering process
 - 4.3.1 "No-Clean" rosin residues
 - 4.3.2 Water-soluble residues
 - 4.3.3 Resin residues from synthetic pastes
 - 4.4 Detection of residues
- 5 Drying parameters**
- 6 Keeping areas clear and exposing areas**

1 Base material

The base materials used to manufacture the printed circuit board play a significant role in determining the electrical, mechanical and thermal properties and, last but not least, the expected costs of the assembly to be manufactured. The selection of the right base material is therefore essential. Glass and epoxy laminates are still the most commonly used in Europe. However, it turns out that the well-known standard FR4 material will no longer be able to meet all requirements in the future. For this purpose, new base materials are offered that are optimized for special requirements such as thermal management, HDI technologies and halogen-free operation. Laminates with improved high-frequency properties are also available.

As it is well known, there are different base materials, most of which are coated with solder resist, which differ not only in price but also in their properties. For example, the use of FR4 laminate instead of FR2 material can significantly reduce or avoid electrochemical corrosion because the epoxy fiberglass laminate absorbs less water than the FR2 material. This interaction of course also has an influence on a possible protective effect through a protective coating.

In Tab. E1 some electrical properties with typical measured values for some common base material types are shown in the lower performance spectrum.

	FR-2	FR-3	FR-4
	Surface resistance		
after storage in moist heat	10,000 MΩ	100,000 MΩ	1,000,000 MΩ
in increased temperature	100 MΩ	1,000 MΩ	10,000 MΩ
	Specific volume resistance		
after storage in moist heat	50,000 MΩ cm	100,000,000 MΩ cm	5,000,000 MΩ cm
in increased temperature	1,000 MΩ cm	10,000 MΩ cm	500,000 MΩ cm

Tab. E1: Electrical properties for common base materials¹

2 Component and circuit board layout

All single parts of the assembly, from the circuit board, all different manufacturing processes and manufacturing materials and finally the housing, will have an influence on the climatic resistance of the final electronic product. On the circuit board, the distances between voltage and current and the insulators between them determine the sensitivity. The design and requirement of areas which need to be coated are based on these conditions.

Due to an unfavorable component geometry, condensing humidity cannot flow off and remains on the assembly as a "puddle". This high water load in the long term is difficult to be covered by any protective coating. The installation position of the electronic has a high influence on the durability. Vertical arrangement of an assembly has the advantage over horizontal installation, as condensing water can drain off better. All reliability tests should therefore always be carried out not only in the installation position but also in the corresponding housing, as this will change the water condensing characteristics, too.

¹ Source: VDE/VDI TRAINING SHEETS FOR PRINTED CIRCUIT BOARD PRODUCTION
VDE/VDI 3711, Sheet 2, "Rigid, rigid-flexible, flexible and multilayer materials; characteristics, base materials for printed circuit boards / multilayer".

For the protective coating itself, the equipment has a very large influence. The selection of the components to be equipped is already decisive for the coating process that can be used. IC skirting, for example, can be sealed or open from the bottom side. It is a difference in price of only a few cents, but this simple fact defines the safety distance to this component to be kept free of coating during application. Very often using sealed components for just a few cents more can save a lot of money and time for proper masking or choosing a cheaper conformal coating process. If a component is described as "washable" it can be coated too, if chemical resistance to the used solvents is given.

Only if the process of protective coating is already taken into account during the phase of the development and layout of the final board design, it can be carried out reliable, repeatable and at predictable costs. Any infringement makes protection more difficult and more expensive. Ideally, the assembly is designed with regard to a process to be used.

Examples:

- In vertical immersion, coating-free components and areas all are aligned along one edge of the assembly, that the immersion level can be approached undisturbed.
- For selective (cup) dipping, distances between the coating and the coating-free area are selected in such a way that the cup can intervene between them without any problems.
- If a selective, coordinate controlled application (spraying, casting, jetting, dispensing) is selected, bigger components are placed in distant, defined position to avoid collision with the application head.

General distance rules are difficult to define. Not only the components and the protective coating determine the necessary gap between the coating surface and the coating-free area, but also possible conductor paths, the cleanliness level of the surface, the type of coating drying or curing, the coating process, etc. The basic principle of the largest possible distance always helps to facilitate the coating process. The same applies if a transition or tolerance zone is created in addition to the coating area and the coating prohibition area. Very often a traffic light system is used to define areas in the specific drawings:

Green: Area must be coated

Orange: Area can be coated or contaminated with coating, but there is no need to coat this area

Red: Area must be free from any coating

Printed circuit boards are provided with vias and both larger and smaller fixing or mounting holes. These holes represent a special challenge for the coating process with liquid protective lacquer when they are located in the coating area. Holes of any diameter direct open the path of the coating to the opposite side. This results in missing coating on the coated side and second, it can lead to unwanted coating on the opposite side. If Vias have to be coated, it is recommended to plug them. Mounting holes and other holes should not be inside or close to the coating area. Otherwise they might be masked.

3 Solder resist

In the original definition according to VDI/VDE standard 3710, Sheet 4², solder resists/solder resist masks are a permanent solder mask print that covers the areas of a printed circuit board that are not to be soldered during subsequent soldering processes.

² VDI/VDE Standard 3710, Sheet 4 (1993-06) "Production of Printed Circuit Boards; Printing Processes" inactive

This definition must be extended today. In addition to resistance to liquid soldering tin, the avoidance of bridging during wave soldering and the physical protection of the printed circuit board, compatibility with a wide variety of preservation processes (Hot Air Levelling (HAL), chemical Ni/Au (ENiG), chemical tin (CSN), etc.) is required today. Also excellent dielectric properties even under the harshest climatic conditions, as well as compatibility with a wide variety of chip adhesives, protective coatings and other materials is required.

Since the solder mask remains on the PCB, it must also fulfill its insulating and protective function during the entire lifetime of an electrical assembly. Therefore, solder resist masks have to meet the same high requirements as base materials and components.

Solder resists can be divided into two groups. With conventional screen printing coatings, the solder resist pattern is created by printing with a screen stencil. With using the photostructurable solder resists (LPiSM = liquid photoimageable solder mask), the printed circuit boards are coated *planar* in horizontal or double-sided vertical screen printing or in curtain coating and all common spraying processes. The non-conductive pattern is created during the subsequent exposure and development process. With this method, significantly better resolutions can be achieved. The different solder resists on the market also differ in their composition and the binder systems used, and thus also in their quality. The photostructurable solder resists are of the highest performance level as they are usually used for PCBs for SMT assemblies.

Various international, national and company-specific standards define the requirements for solder resist and suitable tests of their properties. The IPC (Institute for Interconnecting and Packaging Electronic Circuits) standard with the current issue IPC-SM-840C³ is a globally recognized standard for the qualification of solder resists. It has been incorporated into German and other international standards in key areas.

The IPC-SM-840C distinguishes between classes T ("Telecommunication") and H ("High Reliability"):

- Class T includes computers, telecommunication equipment, advanced industrial electronics, etc. Class T solder resist masks are suitable for high performance commercial and industrial products where high performance is required but the interruption of performance is not life threatening.
- Class H includes equipment where continuous power is required and stand-still/failure cannot be tolerated, e.g. in life-supporting electronics. Class H solder resist masks are suitable for areas where a high level of safety and continuous operation is required.

The basic requirements of a solder resist mask with regard to environmental exposure are, on the one hand, protection of the copper in the conductor pattern against electrocorrosion and electromigration and, on the other hand, retention of the insulation properties. Classical insulation requirements result from the IPC-SM-840 C, which requires at 65°C and 90 % r.H. minimum insulation values of 500 MOhm. Electromigration tests are performed at 85°C and 85% r.H. for 500 h or 168 h.

Weaknesses in the applied solder resists - insufficient cross-linking, mechanical injuries - cannot be remedied by a protective coating, since the cross-linking density and chemical resistance of protective coatings - even under optimal processing conditions - are still lower than those of solder resist coatings.

³ IPC-SM-840C "Qualification and Performance of Permanent Solder Mask" (Properties and Requirements for Permanent Solder Masks)

Therefore the adhesion on the solder resist is no measure for the quality of a protective coating. Rather, the adhesion must be checked for the critical points that are actually to be protected. These are primarily the solder joints and component leads. At these points, the remaining flux residues in particular have an influence on adhesion and wetting properties of the protective coating.

4 Soldering materials and soldering process

A soldering process with not proper set parameters can leave disproportionately large and uneven quantities of flux on the PCB. Possible causes are e.g. too high flux application, inadequate soldering process or unfavorably designed solder masks. Not optimum setting for the wave and therefore a not proper flow of the liquid tin on the PCB will also leave more residues. These higher amounts of residues have a direct influence on the electrochemical stability and adhesion of protective coatings.

A solder paste consists mainly of a flux and a solder powder. After re-melting (=re-flow), residues of the flux remain at or around the soldering joint. The chemical composition and physical properties of these residues determine their further treatment before a protective coating is applied onto the printed circuit board.

Flux buildup together with water, which diffuses through the protective coating layer, forms a system of low electrical conductivity, which can lead to electrochemical corrosion on the printed circuit board underneath the protective coating layer. Whether this effect occurs depends on the design of the PCB, e.g. the potential differences between adjacent conductors, the distance and the mounting position, but also on the expected load parameters. Here, condensation on the assembly must be regarded as critical.

Above all, immersion baths must be protected against the introduction of conductive buildup. The solvents in the protective coating can wash off flux residues that accumulate in the dipping tank. If cleaning is necessary before the protective coating can be tested under conditions as close to practice as possible (e.g. with operating voltage, power loss, installation position) by means of climatic tests. Optimum results will be achieved only by applying adequate cleaning processes before the protective coating process.

It is very difficult to determine the position and concentration of the remaining fluxes, as modern no-clean fluxes are hardly visible. By means of a special process (see chapter F6), it is possible to make no-clean fluxes visible in a simple manner by means of a color reaction.

4.1 Flux types

Different solder paste and flux standards make a rough classification of the ingredients of the different fluxes possible. In general, the standards describe the corrosion behavior of the residues.

Tab. E2: Division of flux in accordance with **JIS-Z-3284**

Division of Flux	Component		
	Main Component	Active Component	Containing Fluoride
Resin	Modified Resin	1. No addition 2. Halogen salt of amine 3. Organic acid 4. Amine organic acid salt	F (containing) N (not containing)
	Synthesized Resin		
Organic	Water base Substance		
	Solvent base Substance		
Inorganic	Watersoluble Substance	a. Ammonium halide b. Zinc halide c. Tin halide d. Phosphoric acid e. Hydrohalogenic acid	
	Nonwatersoluble Substance		

Tab. E2 shows the JIS-Z standard for solder pastes. The DIN EN 29454-1 provides a similar classification.

In the industry the classification according to IPC-J-STD-004B (largely identical to EN 61190-1-1) is commonly used. This specification describes the respective flux with three letters and a number:

Base: RO(sin) - RE(sin) - OR(ganic) - IN(organic)

Activity L(ow) - M(oderate) - H(igh)

Halide content < 0,05 % (500 ppm) 0 (Yes) - 1(No)

All combinations are possible, e.g. ROL0, REM1 or ORL0.

J-STD004B and DIN EN 61190-1⁴ describe the level of effectiveness of fluxes and residues. However, it does not describe in any way what influence the residues have on a protective coating.

Two large groups of solder pastes are widely known on the market today. Solder pastes with water-washable residue and the wide range of No-Clean solder pastes. The first group of solder pastes (respectively their fluxes) must be washed, as both the fluxes and the residues are highly hygroscopic and would lead to severe corrosion if remaining on the assembly. These fluxes will therefore no longer be considered in the following. In principle, clean surfaces are required for an ideal protective coating. In order to save the time and cost-intensive washing process, NoClean fluxes were developed with the objective that coating can be applied on their residues without prior cleaning. In this case, it is important to know something about the type of flux residues and their effects.

⁴ DIN EN 61190-1: Connecting materials for electronic assemblies - Part 1-1: Requirements for soft solder fluxes for high-quality connections in electronic assembly (IEC 61190-1-1:2002); German version EN 61190-1-1:2003)

⁵ J-STD004B, Requirements for Soldering Fluxes, December 2008, www.ipc.org

4.2 Composition of No-Clean fluxes

The typical components of NoClean fluxes are:

- solvents (alcohols, esters, ethers etc.),
- resins (rosin, acrylate resins, synthetic resins),
- activators (carboxylic acids, amines, organic halide compounds) and
- additives (thickeners, dispersants).

The main components of fluxes are resins and solvents. The quantities of activators can vary greatly. Halide-free fluxes usually have more activators than fluxes containing halides. A typical composition of a No-Clean flux and the corresponding solder paste is shown in Fig. E1.

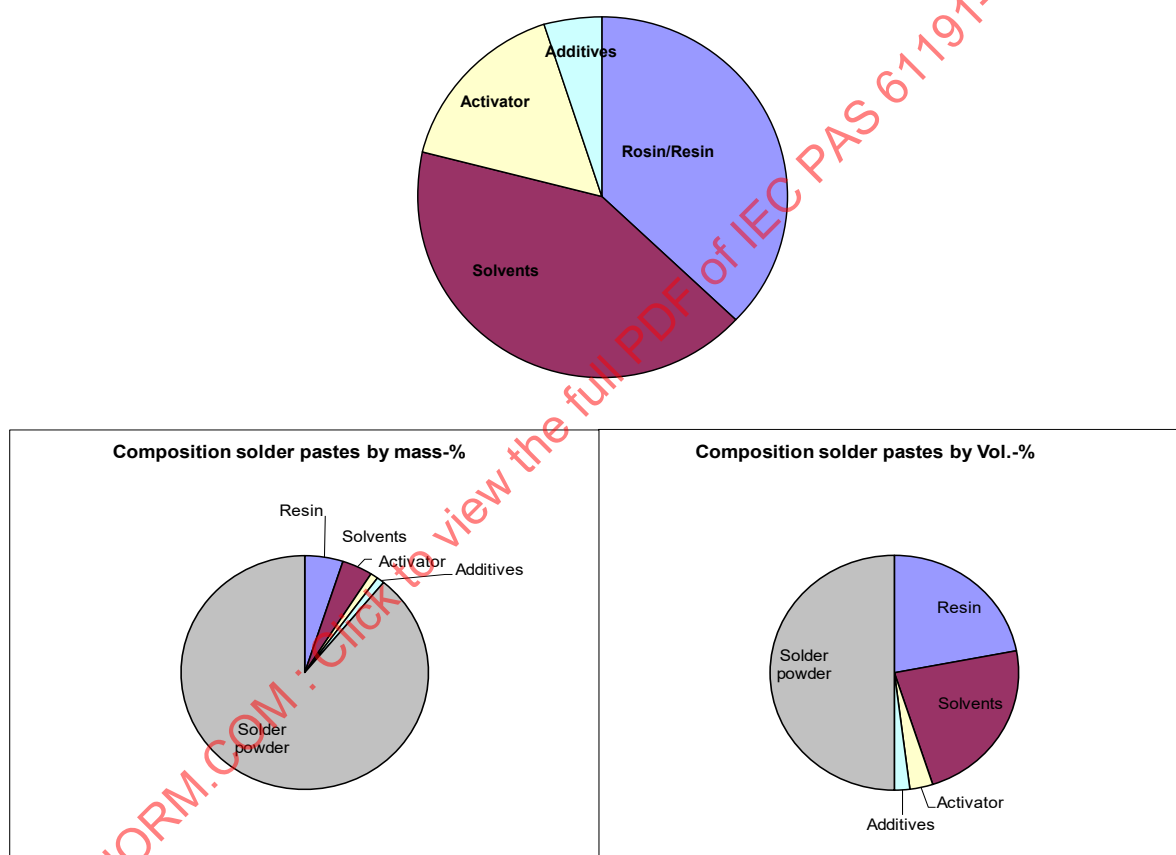


Fig. E1: Typical composition of No-Clean fluxes for solder pastes (above in volume proportions) and the associated solder paste (below left in weight proportions and in volume proportions, below right)

Since the solder and the flux have a very different density, the distribution of volume in the solder paste has changed accordingly. After the reflow process, the re-flowed solder and flux residues are present. Most of these residues are rosin or resin.

4.2.1 Solvents

After resins, solvents make up the largest proportion of a flux in terms of quantity. The task of the solvents is to solve the resin and the activators. The solvents also determine

the application properties such as printing or dispensing, as well as the drying behavior of the solder pastes during reflow. The solvents are not necessary for soldering. A mixture of low and high boiling solvents is almost always used. These can be: monohydric and polyhydric alcohols, glycols, esters, ethers, aliphatic, and much more. Regardless of the boiling point, the solvents are selected that they are easily to evaporate during reflow or pre-heat so that no significant amounts remain in the residue. TGA measurements of various solvents for lead-free NoClean solder pastes have shown that the total amount of solvent does not completely evaporate. It was proven that some solvent residues remain at normal reflow temperatures.

In practice, it has been shown that the residues are often still sticky for hours, especially with short temperature profiles. In these cases, solvents are still temporarily retained by the resin. With increasing time, however, they evaporate, so that the stickiness of the residues disappears. If the residues are still sticky, check whether this affects the reliability of the protective coating. Sticky residues could dissolve better in the protective coating than non-sticky residues.

4.2.2 Activators

Activators are substances in fluxes that significantly improve the wetting behavior of solders. The rosin should be mentioned first. Rosin provides the greatest activation in almost all fluxes due to their high number of acid groups. Other activators can be, for example: dicarboxylic acids, organic halide compounds (bromides and chlorides), amines and alkanolamines.

Carboxylic acids and amine compounds play the most important role as halide and halogen free compounds. A huge selection of carboxylic acids is available. Many of the useful dicarboxylic acids are described in the literature, such as adipic acid. Modern fluxes contain a mixture of coordinated carboxylic acids, each of which requires a slightly different effective temperature to start reacting with the oxide layers. The decomposition or effective temperatures are somewhere between 100 and 220°C. The amount of carboxylic acids with a low rate of decomposition, such as adipic acid, is always used in such amounts, that only a few traces are left after soldering. Modern fluxes also use other carboxylic acids with a higher rate of decomposition.

In numerous analyses of the residues (circuit board and furnace), traces of organic acids could at best be found. Residues of water-soluble carboxylic acids deteriorate the surface resistance, also in combination with a protective coating. An influence on the reliability of the protective coating can be largely excluded (no cracking).

A similar statement can be made of the amine compounds. Although significant amounts of the compounds are found in the furnace residues, they are not detectable at the soldering joint. The halide compounds are usually thermally very stable and can be detected in the residues with appropriate analytical effort. However, the amount of solder paste used is so small that their quantities in the residue tend to be in the ppm range. An influence on the reliability of the protective coating is rather unlikely, but cannot be definitively excluded. The results of individual investigations indicate indirect damage to the coating layer caused by corrosion of the underside of the conductor path by halide containing residues.

4.2.3 Auxiliary materials

Chemically neutral auxiliary materials are used in the fluxes, for example to simplify the mixing of the solder paste or to improve the application properties of the solder pastes. Additives for better miscibility are added in very small quantities and are no longer detect-

able in the residue. The used rheological additives to improve the printing or dispensing application are almost always thermally stable compounds (waxes) which also remain in the residue.

Studies had shown that these waxes practically do not evaporate within the usual soldering temperatures. These substances usually have a melting point between 50°C and 120°C, which does not change even after multiple melting. In addition, these materials exhibit very good adhesion to the printed circuit board material and the usual metallization.

The waxes run very strongly to thin films. In tests with different types of protective coatings, only a PU coating shrank slightly. No cracks were found in any of the coatings. The tests have shown time and again that these types of fabrics can be coated very well and also exhibit very good adhesion to a wide variety of protective coatings. It could be shown that residues consisting mainly of such substances have little or no effect on the reliability of the protective coating.

4.2.4 Resins

The resins make up the most important and largest proportion in a No-Clean flux. Different resin types are used which differ in their physical and chemical properties. The natural rosins are the most widespread and have been in use for a long time. There are numerous variants available, which differ all by their origin and purity slightly. They all have in common that they have a similar acid number and a melting range of about 75 to 85°C. They are often used in older formulations for the lead containing alloys, but also in halide free compositions as a minor part of the resins.

A general property of "natural" rosins is that they change little chemically and physically after reflow process. Storage temperatures above or close to the melting temperatures of the resins cause oxidation (brown coloration) and embrittlement of the resins.

The residues of natural rosin usually show a poor surface resistance at temperatures above the melting point (<100 MOhm). This property can also have a negative influence on the surface resistance of the protective coating. The flux residues based on natural rosins form thin residue layers covering larger areas around the components and solder joints.

Another group are the partially polymerized rosins. Their degree of polymerization is between 20 and 80 %. Compared to natural, untreated rosin, these resins have a higher melting range between 80°C and 90°C. During reflow process, these resins continue to polymerize and increase their melting range, which can then reach 100°C or higher.

This property is used to ensure a high surface resistance (>1000 MOhm) even at temperatures >80°C. This also has a positive effect on the protective coating. However, the partially polymerized rosins also tend to be highly brittle and have reduced adhesion to the surface of the printed circuit board - compared to natural rosin. Very often cracks can be formed inside the residues after cooling.

Acrylic resins play a rather subordinate role. Their melting range is usually similar to that of partially polymerized rosin resins, but they are less brittle and have better adhesion to the printed circuit board. Coated residues of acrylate resins are usually crack-free even after shock storage, but the surfaces are often no longer homogeneous.

Furthermore, other resin systems, for example epoxy resins, are used, which, however,

play virtually no role in practice. They are not discussed here.

4.3 Residues from the soldering process

From the point of view of the compatibility of the residues with the "conformal coating", the residues of the solder pastes can be classified as follows:

- "No clean" rosin residue,
- water-soluble residues,
- synthetic resin residues,
- Residues of reactive epoxy resin solder pastes.

The reflow process also has a considerable influence on surface quality and coating ability. In reflow conditions - also with solder pastes - various chemicals may start outgassing. These gases will condense as deposits in colder areas of the reflow equipment. These residues are applied evenly to the assembly during the reflow process, for example.

A detailed description of experiments to investigate the influence of residues from the soldering process on the protective coating is contained in [Schm07]. The results are summarized below.

4.3.1 "No-Clean" rosin residues

The fluxes of the so-called No-Clean solder pastes consist of dissolved rosin or chemically modified rosin and activators such as carboxylic acids and amines in a high-boiling solvent. After the soldering process, the solvent has evaporated and leaves solid residues at the soldering joint, which does not have to be removed to ensure electrical reliability. The high surface resistance can be achieved with help of the water-repellent nature of the solid rosin, which has a softening point of 80 to 85°C. Below this temperature, the ionic activator residues are effectively encapsulated against moisture with the rosin. Below the softening point, natural rosin is brittle and can break into small pieces over time, which can lead to flaws if a protective coating was applied to it.

Rosin based residues can be optimized to reduced cracking by adding plasticizers and thus becoming better compatible with the protective coating. However, there is a risk of outgassing of the plasticizers over time. However, there are some No -Clean rosin based solder pastes on the market, whose residues are compatible with some protective coatings.

4.3.2 Water-soluble residues

The flux of solder pastes with water-soluble residues consists mainly of semi-solid polyalcohol ethers and activators such as carboxylic acids and amines. Suitable rheological properties are achieved by adding solvents and thixotropic agents. The residues are hygroscopic and corrosive and must be washed off. After the printed circuit board has been washed and dried, the coating can be applied.

4.3.3 Resin residues from synthetic pastes

For years, there have been efforts to replace the natural product rosin or derivatives of this natural product with a synthetic resin. The advantage of a synthetic resin over rosin would be a consistency in the quality of the raw materials, as they are independent of harvest conditions and geographical locations. However, finding a replacement for rosin is a very complicated task.

The suitability of rosin as a flux carrier for solder pastes lies in its solubility in many high-boiling solvents, in the activating effect of Abietic acid, the high electrical resistance below the softening point of 80 - 85°C and the good encapsulation of the corrosive activator residues after the soldering process. It is very difficult to find a synthetic resin with all these properties. Since some years, many solder pastes are on the market, which contain bigger quantities of synthetic resins. Advantages are described as a higher consistency, higher temperature resistance and transparent, clear and minor amounts of residues. There are also some disadvantages: Normally this group refers to the "No-Clean" range of solder pastes, but if for any reason cleaning needs to be done, it is much more difficult. Due to the advantage of higher melting range, they show better compatibility with protective coating at elevated operating temperatures. The coatings become less prone to crack over elevated thermal shock testing.

4.4 Detection of residues

It is very difficult to determine the position and concentration of the remaining flux residues, as the modern No-Clean fluxes are hardly visible. The Zestron® flux test (see chapter F6) offers the possibility for an easy visualization of remaining No-Clean fluxes by a color reaction.

The Zestron flux test visibly detects the activators of fluxes through a color reaction. The test thus supplements the ion equivalent tests (ionic contamination) by making critical flux residues visible that cannot be detected or dissolved in the used water-alcohol mixtures. It also provides information about the local distribution of impurities and enables an improved evaluation of the reliability of electronic assemblies.

5 Drying parameters

A protective coating can only fulfill the requirements and achieve full chemical and physical properties after full cure. Some coating materials require up to 31 days reaching optimum properties. These optimum properties are normally not required after application before testing the assembly, but for evaluation of coating materials it might be important to maintain this time. For this reason, it is important to check the drying and curing parameters for each type of protective coating and assembly, which needs to be coated.

As it is well known, coating with thin-film coatings according to the mission statement "a lot helps a lot!" leads to a significantly poorer coating quality, if not to an even faster failure than without protective coating.

Thick layers of coating interfere with the ability of solvent evaporation on one hand. On the second hand they reduce the oxygen or moisture uptake (depending on the curing mechanism of the coating). As both processes take place simultaneously, a state is reached very quickly in which the upper layer is completely cross-linked and the lower layer is still sticky and remain uncured for up to years. Such a coating tends to absorb more water and

accelerate corrosion, especially in the presence of flux residues.

Too fast start of forced drying immediately after coating exacerbates the problem, as the surface is very quickly "sealed" and the correctly cross-linked coating becomes thinner and thinner. The risk of forming bubbles in the coating film is increasing too, if a "flash-off" area for evaporation of the bigger parts of the solvents for some minutes is not available between coating and curing processes.

Particularly when coating assemblies with different components and geometries, accumulations of coating can occur, e.g. at the base of high components or between very closely spaced components. It may even be necessary to optimize the coating process if a modification of the drying/curing parameters does not lead to success. Double coating can be one option.

Conclusion: Only if the entire manufacturing and processing process is critically considered and optimized, a protective coated electronic assembly can be obtained, which retains its functionality under the required conditions for as long a service life as possible.

6 Keeping areas clear and exposing areas

Some parts of electrical assemblies must remain uncoated. These areas can be for example

- SMD connectors, THT connectors, contact areas for testing
- Structures that are damaged by coating (e.g. light emitting diodes, relays, mechanical components, cut-outs, etc.),
- surfaces which need to be treated with following connection methods

Keeping areas free from coating can be achieved as follows:

- by simply not coating during selective coating processes
- by applying metallic or plastic covers before coating and removing these covers after coating (at the risk of delamination at the crack edges up to partial lifting when removing the covers)
- by application of masking materials like tapes or dots made out of plastic, which is chemically resistant to the coating and its solvents.
- by application of liquid or gel masking materials, air or UV curing. These will create a dam and protect the areas, which need to be protected.
- by avoiding coating flow run-off (by closing PCB through-holes, keeping the coated assembly levelled, preventing lateral run-off and applying mechanical boundaries)
- by removing the coating after the coating process

In special cases, it might be required to remove the coating. The reasons for this can be the necessity to exchange, install or remove components on the assembled PCB or to contact the electrical test points on the PCB again. Additionally the coating tools needs be cleaned from coating buildup, too.

Possible processes are the use of chemical coating removers, compressed air guns, brushes, mechanical abrasive blasting processes or thermal treatments. During selection the right method always take care, that only the protective coating will be removed. The solder resist should remain unattacked on the assembly. Coating removal should be pos-

sible both selectively and over a wide area. The stripping process should continue to be non-destructive, among other things so that the assembly remains electrically perfect. After the coating has been removed, it should be possible to apply the coating again. A detailed description of coating stripping and rework can be found in section K of this guide.

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SUBSTRATE AND PRETREATMENT PRIOR TO THE PROTECTIVE COATING

- 1 Requirements for the cleaning of assemblies**
- 2 Decision on cleaning**
- 3 Purity requirements**
- 4 Minimum surface purity before protective coating**
- 5 Measurement and analysis of ionic impurities**
- 6 Detection of critical impurities**
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1 Requirements for the cleaning of assemblies

Cleaning before protective coating allows optimum adhesion of protective coatings. In particular, crosslinking toxins, such as those produced during soldering, are safely removed during cleaning. In addition to standardized testing of the ion equivalent, it is therefore important to check for crosslinking toxins in particular for the verification of the purity of components to be coated. In addition to the increase in reliability, one or more cleaning steps planned in advance also offer advantages in terms of total costs compared to no-clean production.

2 Decision on cleaning

The demand for the cleaning of electronic assemblies has been increasing steadily for several years. At the same time, after more than ten years of field experience with no-clean processes, an increasing number of field failures can be observed, especially in coated or encapsulated assemblies. Furthermore, the increased use of power-connecting, controlling and securing assemblies in the market has drastically increased the requirements for these high-voltage assemblies with regard to dielectric strength and aging resistance. Manufacturers of assemblies with increased requirements in terms of climatic and long-term resistance should therefore ask themselves whether they want to take the potential risks of no-clean production.

No-clean technology has proven itself for many production purposes and will continue to play a dominant role in the future. During the last ten years, however, a lot of experience has been gained and many manufacturers of coated assemblies have returned for cleaning in the meantime. Since cleaning technologies have also undergone significant further development in terms of costs, process windows, material compatibility and occupational safety, clean and no-clean technologies should be compared critically.

Cleaning is the same as coating or protective coating. Introduced at a later date, it is unnecessarily expensive and the freedom in the optimal process selection is severely limited. Repairing is always more expensive than taking cleaning into account right from the start in development and design. This path is also riskier, as the decision to clean is usually taken due to customer pressure. This should not be allowed to happen in the current competitive situation. However, if the cleaning philosophy is implemented consistently, there is great potential for cost savings from procurement through design to production.

3 Purity requirements

Traditionally, the result of cleaning processes is optically evaluated according to IPC-A-610D¹. For this purpose, optical magnifications, usually ten times, are used in the production of electronic assemblies. However, mould release agents, grease layers or many fluxes leave behind visually invisible thin residue films depending on the process. Even unsuitable cleaning processes can leave behind invisible adsorption films. These residues impair the possible protective coating and the adhesion of protective coating compounds (Fig. F1 and Tab. F1).

¹ IPC-A-610D (February 2005): "Acceptability of Electronic Assemblies"; by the Fachverband Elektronik Design e.V. (FED; www.fed.de), the IPC-A-610D "Acceptance Criteria for Electronic Assemblies", also published in German translation, contains a comprehensive compilation of visual and textual visual inspection - quality - acceptance criteria, which are mainly used after the completion of the assembly.

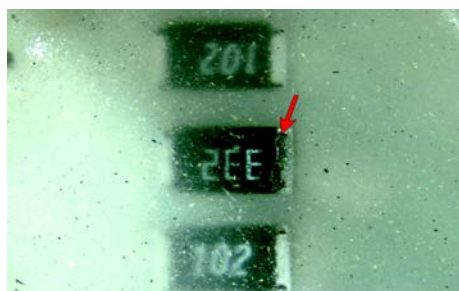


Fig. F1: Example of infiltration of a protective coating compound due to insufficient adhesion due to electrochemical migration

Tab. F1: Contaminants and their effects

Contaminants	Effects
Resin residues from flux / solder pastes	Leads to insufficient adhesion and delamination in case of thermal cycling of protective coating compounds.
Activator residues from fluxes/brazing pastes	Unfavorable for adhesion with most protective coating compounds. Danger of delamination, hygroscopic.
Organotin compounds (reaction product of flux and solder)	Blocks the crosslinking reaction of silicones. This results in a lack of adhesion. The protective coating is infiltrated.
Sulfur and ammonium compounds (may be contained in flux/solder paste)	Blocks the crosslinking reaction with many protective coating compounds. This results in a lack of adhesion. The protective coating is infiltrated.
Mold release agent on/at components	Prevent correct wetting by the protective coating compound and give germination points for delamination or infiltration of the protective coating.
Oligomeric components of substrates and solder resists (faulty processing)	Results in a film with a release agent effect.

This therefore requires the definition of function-oriented evaluation criteria to characterize the result for cleaning prior to protective coating. In addition to the improved evaluation of process reliability, which can be documented in accordance with DIN ISO 9001:2008 2015, such evaluation criteria also enable more efficient cost optimization of the cleaning process, since quantifiable safety and reserves of the cleaning process are now visible.

4 Minimum surface purity before protective coating

In principle, the minimum purity for coating processes is based on the established standard J-STD-001D², which is considered the most important industry standard for the purity qualification of assemblies. The following procedures are necessary for a complete qualification:

² J-STD-001D (February 2005): "Joint Industry Standard - Requirements for Soldered Electrical and Electronic Assemblies"; by the Fachverband Elektronik Design e.V. (FED; www.fed.de) published in German translation J-STD-001D "Requirements for soldered electrical and electronic assemblies" describes the practical requirements for the solution of electrical and electronic assemblies as well as for the organization of the soldering process. The directive is practically the globally recognized standard and is also briefly classified as the basic directive on soldering.

- Optical qualification by microscope at 20 or 40 times magnification (according to IPC-A-610D)
- Qualification of resin purity ($< 40 \mu\text{g}/\text{cm}^2$ for Class 3 assemblies)
- Ionic contamination measurement ($< 0.4 \text{ NaCl Eq. } \mu\text{g}/\text{cm}^2$)
- Detection of other organic impurities (cross-linking toxins, activator residues)
- SIR measurement³ after or during air conditioning storage
- Determination of surface tension ($> 40 \text{ mN/m}$)

5 Measurement and analysis of ionic impurities

Ionic pollution, expressed in sodium chloride equivalent V_{NaCl} , is currently used to assess the working climate safety of electronic assemblies⁴. It is usually performed in accordance with IPC Test Method 650⁵ with a 75% or 50% 2-propanol water solution (see Fig. F2). The geometries and surfaces of the assembled components on the printed circuit boards are generally not taken into account when determining the surfaces. The measured values of the ion equivalent are guide values. To determine statistical values, a number of 3 to 5 measurements of the same assemblies is recommended. The evaluation is based on the standard J-STD-001D⁶. If the sodium chloride equivalents caused by the residues of various fluxes are compared with the failure rate due to migration in the climate test, a small V_{NaCl} value must be classified as a necessary but not sufficient condition for protection against electrochemical migration in coated and uncoated assemblies.

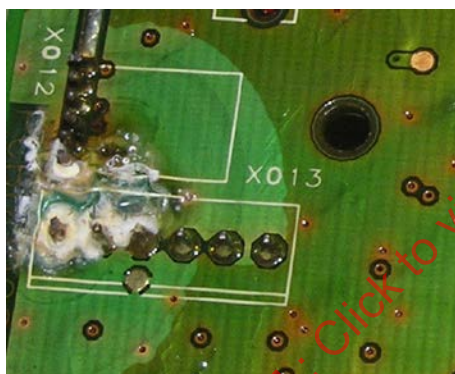


Fig. F2: Delamination and cracking of the protective coating

It must be taken into account that the ion equivalent is an integral measured variable and thus does not adequately describe the situation typical for the reflow process with local accumulations of impurities. A small ion equivalent is a necessary prerequisite, especially for the purity characterization of surfaces prior to protective coating. Hygroscopic contamination usually leads to delamination of the protective coating and thus to its failure within a few years. In addition, the J-STD-001D standard requires proof that the surface is organic-free.

³ SIR = Surface Insulation Resistance; measurement of surface resistance; described in IPC-TM-650 (see footnote 5) or in DIN/VDE 0303-/30.

⁴ A large ion equivalent indicates a large amount of hygroscopic impurities. These usually lead to delamination of the protective coating and thus to its failure within a few years (Fig. 5-03).

⁵ IPC-TM-650 (August 1997): "Test Methods Manual"

⁶ IPC J-STD 001C (as of March 2000): "Joint Industry Standard - Requirements for Soldered Electrical and Electronic Assemblies", together with IPC-S-815 (as of December 1987) "General Requirements for Soldering Electronic Interconnections" was replaced by J-STD-001D (as of February 2005) "Requirements for Soldered Electrical and Electronic Assemblies".

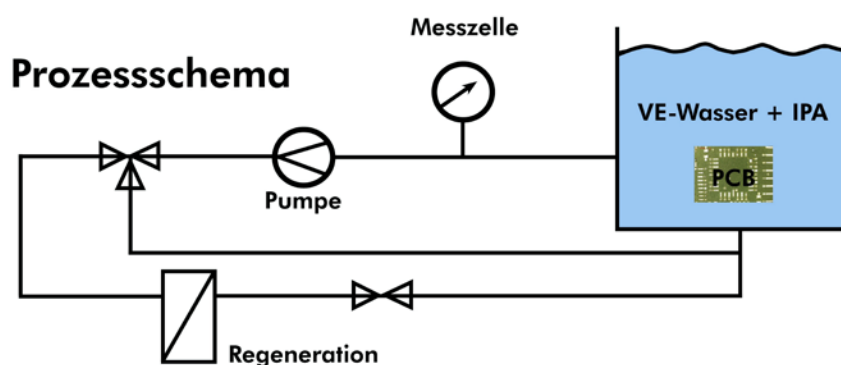


Fig. F3: Scheme for the determination of the ion equivalent by the contaminometer method

6 Detection of critical impurities

Especially with no-clean fluxes, very thin, often optically unrecognizable films form, which cannot be detected sufficiently reliably even when measuring residual ionic contamination (expressed in sodium chloride equivalent to V_{NaCl}) and cannot be detected cost-effectively using charge contrast methods (see Fig. F4) in a scanning electron microscope or HPLC.



Fig. F4: Comparison of optical and electrical purity through charge contrast display

In the meantime, there are fast and easy-to-use coloring methods (e.g. Zestron[®] Flux Test) that use a paint reaction to selectively detect organic acids as activators in fluxes (see Fig. F5). They thus make it possible not only to detect activator residues from fluxes, but also to make their distribution visible. The test reacts specifically to organic acids, i.e. to activator residues of fluxes. Resin residues can also be detected by another method (e.g. Zestron[®] resin test), which is also based on a selective paint reaction.

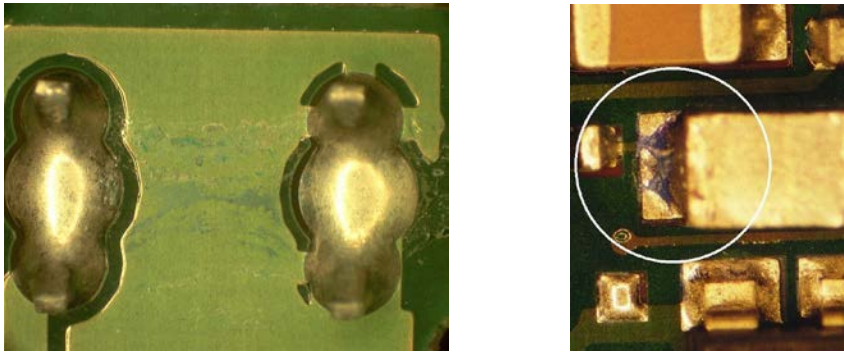


Fig. F5: Creepage current path (left) or flux residues (right) visibly displayed by means of the Zestron® Flux Test

6.1 ZESTRON® Flux Test

The ZESTRON® Flux test detects the activators of the fluxes very well through a paint reaction and thus provides information on the local distribution of impurities.

Advantages:

- Easy to perform test procedure
- Better evaluation of the (climatic) reliability of assemblies
- More meaningful than ion equivalent, even critical flux residues are made visible

Implementation:

- Applying the ZESTRON® Flux Test to the assembly
- Rinsing with distilled water
- Drying of the assembly with dryer and oil-free
- Optical evaluation

6.2 ZESTRON® Resin Test

The ZESTRON® resin test visibly detects the local distribution of resin residues on assemblies by temporary staining. Critical resin residues that lead to poor adhesion of the protective coating compound and delamination effects can thus still be located in production and removed by a cleaning step. This ensures that the critical resin content of $< 40 \mu\text{g}/\text{cm}^2$ required by J-STD-001D is maintained.

The test thus complements the ion equivalence measurement (detection of saline residues) and the ZESTRON® Flux test (detection of activators/acids).

Advantages:

- Quick and easy to use, no long instruction necessary
- No complex test device necessary, therefore
 - No space required
 - Very low investment costs
 - Mobile and location-independent use
- Random sample inspection possible during ongoing production
- Low cost per tested part

Implementation:

- Applying the ZESTRON® Resin Test Indicator to the assembly
- Rinsing with distilled water
- Drying of the assembly with dry and oil-free compressed air
- Optical evaluation

6.3 SIR measurement

The SIR measurement³ serves to prove the insulation effect of the surface. A high insulation effect guarantees that electrical signals on the assembly are not distorted. Flux residues or conductive impurities can lead to leakage current bridges and thus to malfunctions. SIR measurement involves storing a comb structure in a climatic chamber and measuring the surface resistance between the individual comb structures. This allows the surface resistance of the assemblies to be determined after soldering.

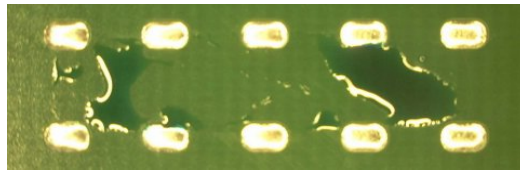
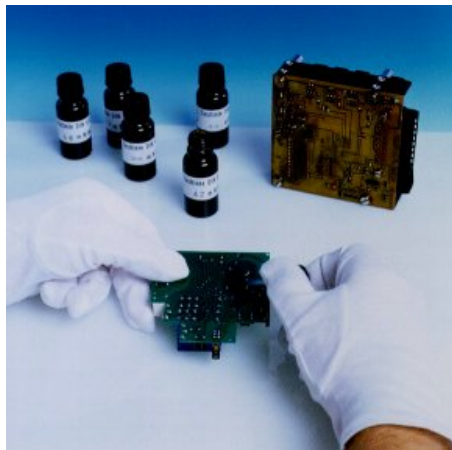
The methods presented guarantee reliable detection of the different impurities. Nevertheless, the integration of a cleaning process is often necessary in order to meet all production limits required by J-STD-001D. This should not only remove impurities, but also positively influence the adhesion of the protective coating compound, so that the risk of subsequent cracking and delamination is minimized.

6.4 Surface tension

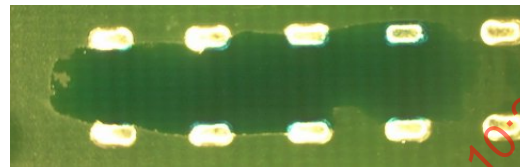
The surface tension is the decisive factor as to whether sufficient wetting by the protective coating compound is possible. Test inks are used to detect thin films of resin residues, unsuitable solder resist masks and mold release agent residues. Critical residues that lead to poor adhesion of the protective coating compound and delamination effects can thus be detected and removed by a cleaning step. Good wetting and reliable adhesion of the protective coating compound is guaranteed from a surface tension of more than 40 mN/m.

To determine the surface tension using test inks, 2 ink strokes of approx. 1 cm length are applied to each test specimen. The surface tension is determined by the iteration between the smallest value at which the test ink just flows apart and the maximum value at which the ink just contracts within 10 s (see Fig. F6). The accuracy is approx. 3 mN/m. It should be noted that from surface tensions greater than 40 mN/m the values can be very strong-

ly influenced by the composition of the test ink. Therefore, the use of the same inks is recommended for reproductive tests.



Poor wetting = Impure surface



Good wetting = Clean surface

Fig. F6: Determination of surface tension using test inks

6.5 Technical cleanliness

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7 Implementation of the cleaning processes

7.1 Cleaning types

The simplest way to clean electronic assemblies is manual cleaning. Solvents or alcohols are mainly used, which are applied to the assembly with a brush or a brush. The residues are then wiped away. The surface is more or less optically clean, especially when the residues are evenly distributed. However, good adhesion of the protective coating compound can only rarely be achieved.

Much more reliable is the mechanical cleaning of the components. The advantage lies in a defined, reproducible process or cleaning result. The optimum coordination of cleaning mechanics and chemistry plays a major role in the selection of a suitable cleaning process. By varying the supporting mechanics such as spraying, pressure flooding or ultrasound, the process can be adapted to the respective requirements of geometry, material sensitivities and residues to be cleaned off. The optimum combination of mechanics and cleaning medium ensures the desired efficient flux removal on the assembly.

7.2 Cleaning systems

The cleaning systems can basically be divided into organic solvents, aqueous alkaline surfactant cleaners and water-based, surfactant-free microphase cleaners (MPC[®] cleaners).

The advantages of organic solvents are their good cleaning performance and their wide process window. Their disadvantages are often their high VOC content and their flammability, which requires their use in an explosion-proof cleaning system. Due to the economic, ecological and safety-related advantages of water-based systems, organic solvents are becoming less and less important.

Conventional surfactant cleaners have the essential advantage that they do not have a flash point and generally have a low VOC value. The main disadvantages of cleaning assemblies with surfactant cleaners are the cleaning principle itself. With conventional surfactant cleaners, the cleaning agents are permanently bonded to the impurities. Due to the permanent binding of the surfactants to the impurities, active agents are depleted. The resulting bath loading limit can only be counteracted by re-dosing or a complete bath change. This results in high costs for the cleaning medium, the work involved, the disposal and the removal of the used cleaner. At the same time, surfactants adhere to the substrate surface. These can lead to problems in downstream processes, such as encapsulation.

Tab. F02: Comparison of different cleaning systems

Cleaning agent	Benefits	Please note
Organic solvent	Removal of various impurities possible	- High VOC value - Combustible - Explosion-protected systems necessary
Aqueous alkaline cleaners (surfactant cleaners)	- Low to no VOC values - Non-combustible	- Short bath service life - Disposal of large quantities of cleaning agents necessary - Residue-free drying difficult (leads to problems with the adhesion of the protective coating)
Water-based microphase cleaners	- Low to no VOC values - Removal of various impurities possible - Non-combustible	Agitation of the cleaner must be selected to suit the process (pressure flooding, spraying, ultrasound)
HFE-based cleaners	- Removal of various impurities possible - Limited VOC value - Non-combustible - Residue-free drying	- Material compatibility - Energy consumption

7.3 Microphase Cleaner

Microphase cleaners (MPC) combine the advantages of surfactant cleaners and solvents without accepting their disadvantages. Such a cleaner is composed of a mixture of water and highly active ingredients. The effect of heat and/or agitation forms a phase mixture with an emulsion-like appearance. This is capable of removing all organic and inorganic impurities that arise in electronics production from surfaces.

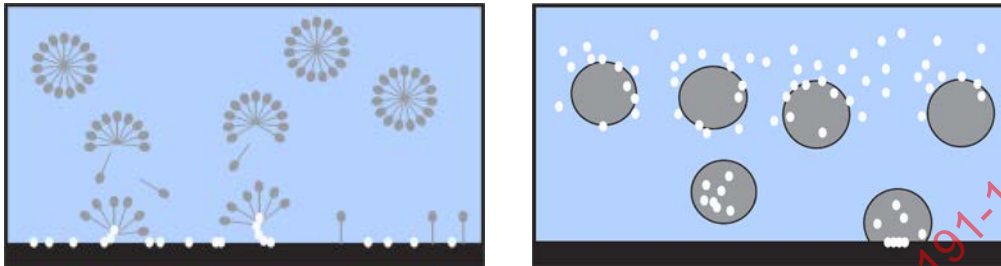


Fig. F7: Comparison of the cleaning effect of surfactant (left) and MPC® cleaners (right)

The cleaner serves as a transfer medium for removing dirt from the substrate surface into the filters. The impurities do not dissolve. The dirt particles removed by the microphases are stabilized at the phase boundary and released again by the cleaner in the filter (see Fig. F7).

With conventional surfactant cleaners, the active ingredients are permanently bound to the impurities. At the same time, surfactants adhere to the substrate surface. These can cause problems in downstream processes such as protective coating.

Due to this property, the dirt particles from the cleaning bath can be filtered more efficiently than from solvents or surfactant cleaners. Microphase cleaners do not deplete active ingredients and, unlike surfactant cleaners, are self-regenerating. This results in very long bath service lives. Their service life is limited only by the design of the filtration (Fig. F8).

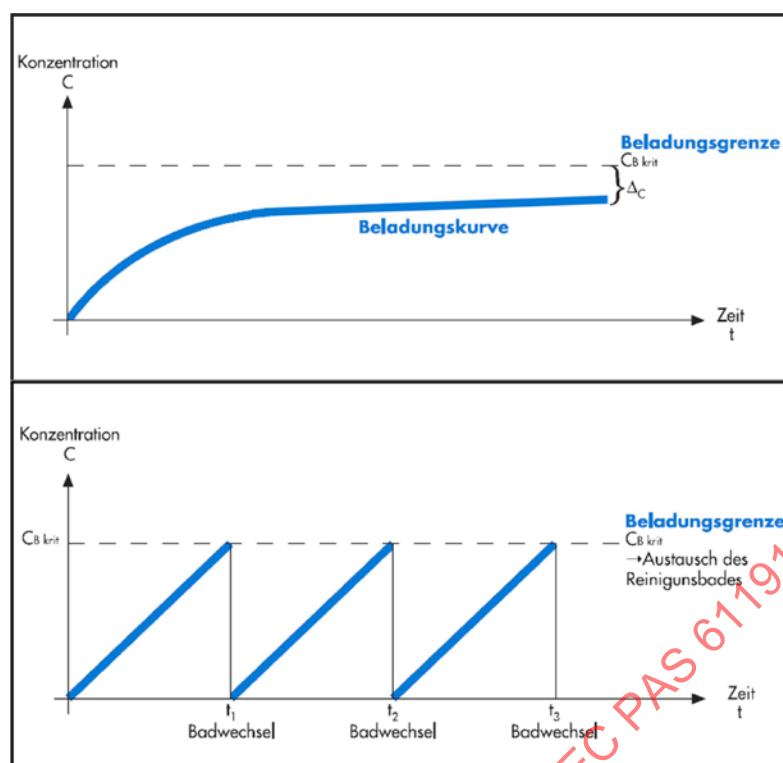


Fig. F8: Comparison of bath service life of surfactant cleaners (bottom) and MPC® cleaners (top)

The following advantages result from the significantly extended bath life:

- The critical load limit is not reached. This guarantees additional process reliability for the user.
- The long service life of the cleaner results in low consumption. The costs for changing the bath as well as for the disposal and transport of the cleaning media are significantly reduced.
- Due to the surfactant- and solids-free formulation of the MPC® technology, no residues remain on the substrate surface. This results in a high level of process reliability during the subsequent coating process.

The combination of cleaning and verification of cleanliness provides comprehensive support for the production of assemblies. It enables cost-optimized problem solutions and thus makes a decisive contribution to process reliability and ultimately to the operational reliability of the manufactured assemblies. Today, the user is increasingly looking for the support of specialists who are intensively involved in solving special cleaning problems. The implementation of a cleaning process is increasingly based on a joint cooperation with the supplier of cleaning media and systems. It must always be oriented to the individual requirements of the customer.

APPLICATION METHODS FOR CONFORMAL COATINGS

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1 Subdivision of the application methods

Conformal coatings can be applied by brushing, spraying, dipping or with automatic, selective coating systems. The PCB's can be coated over their entire surface or selectively.

The high packaging density of printed circuit boards is known to lead to ever smaller distances between the coating area and the non-coating area. These narrow distances, in combination with coating-sensitive components, make the application of conformal coating difficult. In some cases, the coating cannot be applied as desired.

Before selecting the best application method for the user, it must be clarified which specifications and boundary conditions will have to be fulfilled. Of high importance is the required production capacity, the need for selective coating, the degree of automation and possible contract manufacturing.

The following general overview (Tab. G1) of the coating methods indicates which different coating methods are available to apply conformal coating. There are many different application methods available, since the individual requirements for the application of conformal coating can vary a lot.

Tab. G1: Overview of application methods for conformal coatings

Entire Area	Vertical	→ Dipping/flooding		
	Atomized	→ Spraying		
	Airless	→ Spraying		
	Curtain coating	→ Select Coat® *		
Selective	Painting	→ Manual brush application		
	Curtain coating	→ Select Coat® *		
	Non-contact, selective jetting	→ Precise Coat® *		
	Spraying	→ Requires masking of critical components	Airless	
			Air-assisted	
			Stream-Coat® **	
	Dipping/flooding		Horizontal dipping	
			Form cup flooding	→ Static (various ventilation techniques)
				→ Dynamic (Milli-Coat® **)
				→ Static-dynamic

Registered trademark of Nordson Corp.; ** Registered trademark of KC-Produkte GmbH

Conversely, this means that not one single method can satisfy all requirements. Even if all different methods would be available to the user, the fulfillment of the specific protection requirements for PCB's that are difficult to coat may only be possible with additional measures accompanying the process.

In certain situations, atomized spraying methods can reach their limits earlier, because these processes usually require greater distances to critical components in order to prevent splashes and prevent coating in no-coat areas.

If there is a too narrow gap between the coating area and critical components, sealing can be carried out with high viscous materials. Such pasty materials can be used to seal microswitches, sockets or other non-wash-tight component connections. These and other additional protective measures can be applied manually or automatically, but require additional effort.

The greater the distances are that have to be maintained in certain processes, for example to keep contacts free of coating, the more additional work like re-coating of those components that cannot be coated, might be necessary. In this respect, special attention should be paid to the selection of the coating method, to make sure that it is meeting the application requirements.

The following table is listing the advantages and disadvantages of the most popular coating methods. The different application methods will be discussed in more detail on the following pages.

Tab. G2: Application methods for conformal coatings including advantages and disadvantages

Procedure	Benefits	Disadvantages
Brushing	• high availability • suitable for repairs • suitable for 2-C coatings • cannot be automated • allows for selective application	• uneven coating thickness • bottom side of the component remains uncoated • might present health issues for operator • does require extraction to protect operator • poor quality control and poor repeatability • very labor intensive
Atomized spraying	• high availability • can be automated	• overspray, no exact edge definition possible • uneven coating • bottom side of the component remains uncoated • does require high cleaning effort for cabin, tools etc. • effective extraction or separation system required
Dip coating	• simultaneous coating of top and bottom side • coating also under components • no overspray • can be automated • even coating • rational manufacture	• PCB must allow to be completely dipped into coating • open tank with solvent atmosphere on the surface • residues on the boards are causing for contamination of the tank • Not possible for every layout

Procedure	Benefits	Disadvantages
Selective flood-dip coating	selective coating possible	- requires the use of special tools - open coating tank with solvent atmosphere on the surface - residues on the boards are causing for contamination of the tank
Selective curtain coating using the SelectCoat® process	- no masking required - allows for selective or complete coating - reduced fluid consumption uniform coating application - rational manufacturing, high degree of automation - powerful process controls are available - closed fluid system - very flexible, since operation is software based - no additional toolings required	- top and bottom coating requires inverter - no coating under the components
Selective coating with Precise Coat® non-contact jetting	- allows for extremely selective application - reduced fluid consumption allows for selective or complete coating - uniform coating application - rational manufacturing, high degree of automation - powerful process controls are available - closed fluid system - very flexible, since operation is software based - no additional toolings required	

2 Application by brush

One of the first application processes for conformal coating was the manual brush-coating process. The coating is applied manually by an operator to the corresponding areas of the assembly using a brush (see Fig. G1). The result is mainly dependent on the skill of the operator and for this reason subject to considerable fluctuations. Due to the complex and manual work, this process can only be used for extremely small quantities and relatively low-quality requirements.

The advantages of the brush/coating application are the very low investment costs for the "processing materials", the excellent suitability for repair work, the suitability for the application of 2-component coatings and the possibility for a selective application.

During processing the brush should be dry, especially in case of moisture-curing coating materials. Generally, all conformal coatings can be applied with a brush, slow-drying ones are better than quick-drying ones, because the conformal coating dries on the bristles and

stiffens them. This coating process is mainly used for coating small surfaces, small quantities and repair work. For larger areas and quantities from approx. 50 pieces and up the time-consuming process is too expensive. The extraction of the solvent vapours is absolutely necessary for this application.

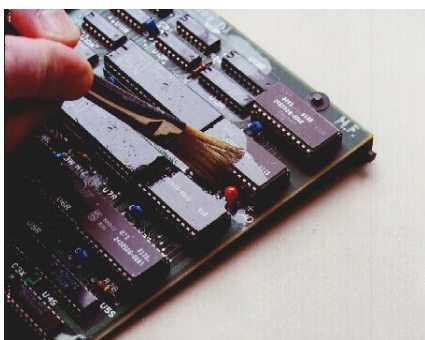


Fig. G1: Manual coating with brush

Because this method does not allow for repeatable results, the lack for automation, work-physiological concerns and the fact that top and bottom side cannot be coated in one step, the application possibilities of this process have severe limitations. Initially used in a larger scale, meanwhile this process does no longer play a role in modern electronics production.

3 Application by spray cans

As an alternative to manual coating with a brush, manual application of the conformal coating with a spray can has also developed at the same time. The one-component, solvent-based coating materials are filled ready for use in an appropriate spray can. The high internal pressure atomizes the liquid conformal coating and is applied as a fine mist. The spray can is moved over the assembly by the operator in a more or less even movement. This allows coating of much larger areas compared to the brush application.

The high amount of overspray does not allow for a selective application with precise edge definition. All areas which have to remain uncoated like connectors, contacts and mechanical components, have to be masked to prevent that they will be affected by the coating fluid. Similar to other manual processes, no repeatable result can be guaranteed. In addition, the relative high cost for the aerosol cans have a negative effect. For these reasons, today this method does also no longer play an important role and is only used to a limited extent in exceptional cases.

4 Application by spraying

Atomized spraying: this process, developed for general coating technology, is using compressed air for atomizing of the coating and creating a fine spray mist (see Fig. G2). The spray gun is either moved manually over the assembly to be coated, or the assembly is conveyed through a spray booth in which one or more stationary spray guns are mounted and spray the assembly from different positions.



Fig. G2: Coating by spray process

In this case, the usual manual spray gun is replaced by an automatic spray gun, which is applying the coating from different positions onto the part to achieve a uniform result. Other systems are using stationary spray guns and the parts are passing underneath the fixed nozzle.

Airless spraying: similar to air-assisted spraying, high-pressure pumps are atomizing the coating fluid into fine droplets of coating. Due to the high fluid pressure, no additional atomizing air is required. The advantage of this process is that less mixture of solvent with air is created and less extraction volume is sufficient.

The high amount of overspray does not allow for a selective application with precise edge definition. All areas which have to remain uncoated like connectors, contacts and mechanical components have to be masked to prevent that they will be affected by the coating fluid. After the coating has dried, these masks have to be removed again. As a result, the previously intact coating layer is torn open again and there is a risk of moisture penetrating at these interfaces.

Although the investment costs in this case are relatively low, high material loss due to overspray, uneven coating layers and a high cleaning effort of the tools and the spray booth must be expected. In addition, effective extraction and an appropriate separation system for the coating mist that occurs must be provided (especially with solvent-based coatings).

5 Application by dipping processes

It is helpful to describe the different processing techniques with appropriate nomenclature. Therefore, a difference has to be made between the dipping process where the assemblies are immersed into the static tank and the flood process where the part is static and the fluid level is elevated to flood the assembly. Furthermore, the assembly can be positioned horizontally or vertically.

In dipping systems, the complete assembly is immersed into a tank filled with the coating fluid to completely coat the surface of the circuit. This can be done manually or automatically. Since several assemblies can be dipped simultaneously, a high throughput and, depending on the concept, a high degree of automation can be achieved.

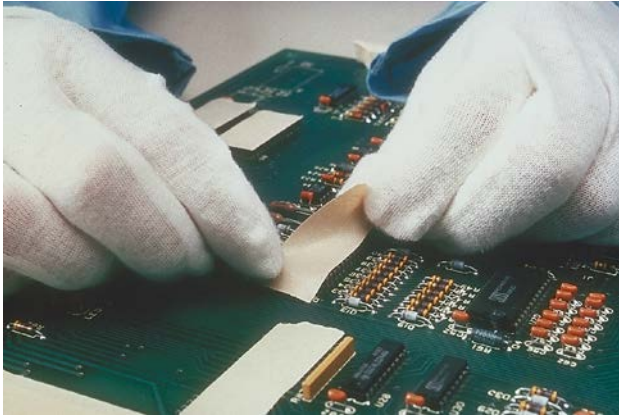


Fig. G3: Manual masking

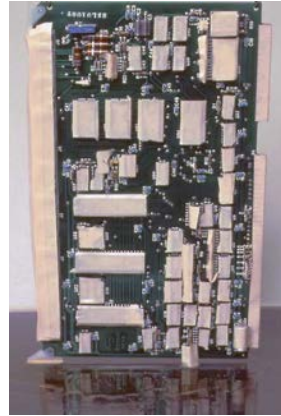


Fig. G4: The board is dipped into the tank.

However, a partial coating is not possible with this process. All areas which have to remain uncoated like connectors, contacts and mechanical components have to be masked (see Fig. G3) to prevent that they will be affected by the coating fluid. After the coating has dried, these masks have to be removed again. As a result, the previously intact coating layer is torn open again and there is a risk of moisture penetrating at these interfaces.

Masking of contact surfaces before and after the coating can be dispensed with in the case of very thin coatings which do not impair the contactability, e.g. very thin fluoropolymer coatings.

In order to ensure the best possible wetting of the assembly, the coating material must be adjusted to a certain viscosity and both the immersion and the immersion speed in the dipping bath must be very precisely maintained in order to prevent air entrapment, especially under larger components.

However, volatile components (solvents) of the coating fluid evaporate because of the large open surface of the dipping tank, causing a change in viscosity. This change is affecting the flow and wetting behavior and the coating quality. It has to be noted that during the dipping process (conductive) residues will be washed off the surface of the assembly and will continuously contaminate the dipping tank. This contamination will have a negative impact on important properties of the coating fluid and the protective function cannot be fully guaranteed.

5.1 Vertical dipping

Assemblies can be dipped manually or automated. Smaller assemblies and small series are possible with manual loading and unloading of the assembly. Because a large surface area is coated in a short time, the assembly must be placed into an extraction cabin to remove the solvent vapors during drying.

When processing larger assemblies, the dive in and retract speed must be selected depending on the viscosity of the conformal coating in such a way that all components will be completely flooded and no runners, dripping edges are formed on components and/or assembly edges during processing. A slight tilting of the assembly can reduce the drip edges. The rule of thumb for thin film coating fluids with a viscosity of 35+/-5 sec (DIN cup 4) is using a dive in speed of approx. 40mm/sec and a retract speed of approx. 1 to 3mm/sec.

Particular attention must be paid to the high risk of contamination of the coating material

when dipping. This negative characteristic is described in Chapter H3 "Contamination". The same processing parameters apply to vertical flooding. Often flooding represents the cheaper alternative, because the fixture holding the assembly does not have to be moved.

Inline dipping machines can coat up to 1000 pieces per hour on both sides. The part handling of the dipping machine is depended on the part itself and how the part will be presented. Using a robot can be an elegant solution, since it can be used for both dipping the part and hold it afterwards so excess fluid can drip off the part. Ideally part handling should already be discussed during the design phase, because the dipping process leaves only very little space to hold that part, or this reason very often connectors are used.

5.2 Horizontal dipping

One possibility of dipping assemblies without coating components is horizontal dipping. For this purpose, the assembly is dipped into the coating tank only to such an extent that the coating material only floods the component side by approx. 2 to 3 mm. Critical components are placed onto a socket so that the fluid level does not touch them. Once part is removed from the dipping tank it has to be held under a slight angle, so that fluid can run off without damaging the socket, then the part can be put in a vertical position so all excess fluid can drip off the part. The horizontal dipping process allows for precise positioning of the parts to prevent forming a "wave" during dipping.

6 Flood method application

6.1 Form cup flooding

Form cup coating has been used for the first time in 1986 by the company KC-Produkte and has been continuously developed from then on. The assembly to be coated is placed on a product specific tooling, called "form cup". The coating material in the form cup is applied to the assembly in the area of the outer contour of the forming cup. Generally, three methods of forming cup coating are used (see Fig. G5):

- o Static cup flooding
- o Dynamic cup flooding (Milli-Coat®)
- o Static-dynamic shape cup flooding

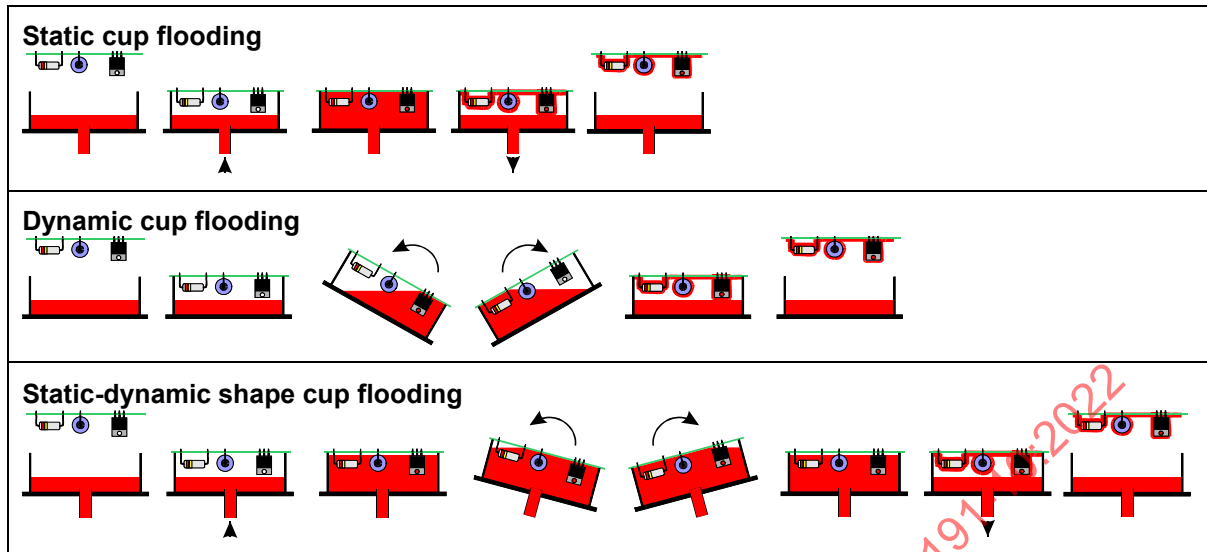


Fig. G5: Schematic representation of the cup flooding process

6.1.1 Static cup flooding

At the beginning, an assembly is mounted onto the horizontally arranged form cup. The liquid level in the form cup is then raised and the space between the assembly and liquid level is simultaneously vented until the coating material has completely wetted the assembly above it. After the liquid level has been lowered, the assembly can be removed, turned and dried.

The assembly usually lies loosely on the form cup. The liquid level is lowered very slowly so that no excessive amount of coating material is produced on the coated bottom side of the assembly during the lowering process. Especially with large assemblies with angled coating geometries, the way in which the space between the assembly and liquid level is ventilated is essential. Coating defects will occur if entrapped air cannot be vented and this air bubble is preventing that the fluid is wetting the part.

If the coating material flows back into the tank via the rim of the form cup to support ventilation, the coating material is enriched with air (bubbles, foam) and irreversibly damaged. However, some suppliers have a ventilation method that does not require the coating material to return to the tank. This technology can be integrated particularly well into automatic processes. It can be used for thin-film coating fluids and other well flowing coating materials.

6.1.2 Dynamic cup flooding (Milli-Coat®)

In this process the part is placed onto the form cup and a fixture is pressing it down, then the form cup with the part is turned twice by 110° . The coating material flows completely over the components and surfaces in the area of the form cup. Due to capillary action fluid can even wet surfaces underneath components. After turning back to the initial position, excess coating material drips back into the form cup. The adjustable drip-off time determines the amount of coating material or the resulting coating thickness of the coating. The coating process is significantly shorter than with static cup coating. Integration into an inline process requires more complex handling than with static cup coating.

In this coating process, no coating material runs back into the reservoir, because the constant air volume between the liquid level and the assembly does not require ventilation. Coating limits of one millimeter can be realized.

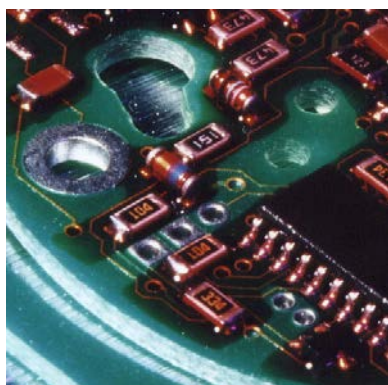


Fig. G6: Coating with the Milli-Coat[®] process

The more precisely the coating process can apply the coating material, the less rework is required and the better the quality of the coating. Form cup processes allow a high precision of the coating result. Therefore, the latest method of form cup coating is the subject of the following considerations.

6.1.3 Static-dynamic cup flooding

The name shows that it is a "hybrid" between the dynamic and static form cup flooding. It is an application method which combines the advantages of the two previous methods.



Fig. G7: Selective form cup coating machine

The form cup is filled with coating material till a few millimeters below the upper edge of the form cup. The assembly is placed onto the form cup using locating pins and spring-loaded fixtures. This complete unit consisting of spring-loaded fixtures, the assembly and the form cup is tilted approx. 15 to 30° to both sides so that the coating material floods the entire area within the form cup fast and without bubbles. Then the fluid level is slowly lowered to remove excess coating material from the assembly. This prevents dripping. The coated side of the assembly is turned upwards and dried. This coating process allows for relative precise edge definition and can be used for both thin-film and thick-film coatings.

Static-dynamic flooding can easily be automated, since the entire coating unit can be mounted between the conveyor belts. There is no open material overflow or return to the reservoir, because, similar to the Milli-Coat® process the venting takes place while the assembly is connected. Since the coating is created due to the tilting action, higher viscosity coating fluids can be processed compared to static cup flooding where the result depends a lot on the flow behavior of the coating fluid.

6.2 Form cup

6.2.1 Coating contour precision

The final precision of the coating is depending a lot on the precision of the form cup. A special manufacturing process allows for a repeatable dimensional accuracy of the contour of the cup walls with a tolerance of only 0.2 mm. Even if, for example, there is a gap of only 0.5 mm between the component to be coated and the plug not to be coated, there is sufficient space for a 0.3 mm thick cup wall. This allows to coat the component and keep the plug uncoated. Using a spring-loaded fixture to press the assembly against the form cup is contributing to the precision of the coating.

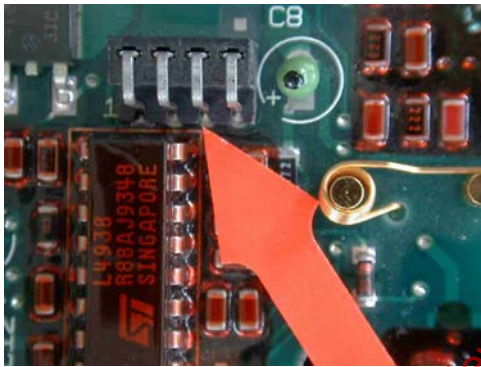


Fig. G8: Accuracy of the form cup coating

6.2.2 Quality of the coating

All surfaces and components in the form cup are completely coated during static-dynamic form cup flooding at least in the same quality compared to vertical dip coating. In order to achieve the required coating thickness during vertical dipping, a second coating pass might be required. Using form cup flooding one cycle might be sufficient since the board will dry in a horizontal position. Using thickfilm coatings or two-component coating fluids can also improve the overall performance because they can provide higher resistivity against humidity.

Vertical or horizontal hybrid assemblies can be coated together in a single operation.

6.2.3 Throughput for form cup coating

The capacity of the form cup coating machine can be configured according to the requirements, as it depends primarily on the number of form cups used in a single operation. Different coating systems can offer more or less space to allow parallel -coating of multiple assemblies.

For example, about 8 assemblies (euroboard format) per minute or 480 pieces per hour can selectively be coated on one side. The system takes about 10 minutes to set up and about 10 to 15 minutes to remove and clean the cups.

6.2.4 Appearance of a form cup

The form cup is made of tinned sheet steel. Its walls are soldered flat to the floor and have a tolerance of only 2/10 mm. It is mounted in the coating system with a few screws. For static form cup flooding and static-dynamic form cup flooding, the form cups are equipped with hose connections for the supply of coating material. In case of the dynamic Milli-Coat® method, fluid is filled into the open cup from above. Locating pins position the assembly very precisely onto the form cup. Assemblies of identical size with different population, can often be coated then same form cup. The form cups are available at the machine manufacturer.



Fig. G9: Illustration form cup

The form cups can be cleaned either with suitable organic cleaning agents or with water-based cleaners. Cleaning systems are available for both methods.

6.2.5 Summary

There still is no universal coating method which can process all assemblies and all coating materials satisfactorily. Development will have to continue on the system side in order to meet the requirements of future assemblies. However, the new static-dynamic coating process opens up further possibilities for the user of high-quality protective coating of electrical assemblies.

7 Application by spray process

New on the market are further spraying processes that can apply the coating material without the formation of spray mist, although they work with air support (see Fig. G10). The protective coating is applied with little accompanying air. The air only has the task of keeping or distributing the coating stream in its desired form. No spray mist and no coating splashes are produced.

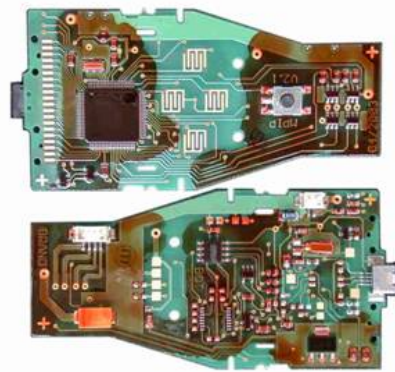


Fig. G10: *Spraying a thick-film coating with Stream-Coat® (left) and assembly sprayed with thin-film protective coating (right)*

The results of the spray and dispensing technology (Stream-Coat®) developed in recent years show that the coating can also be applied behind component legs and, to a limited extent, under components.

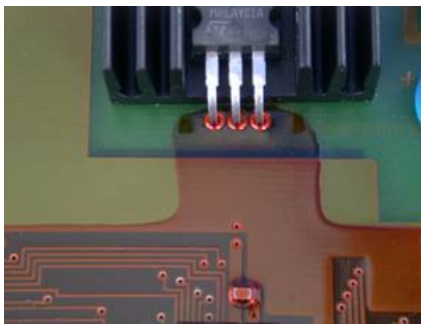


Fig. G11: *Power transistor with all-round coated terminals*

An essential feature is the slim round nozzle with a diameter of approx. 4.5mm, which can access between high components. The coating pattern is mist and splash-free. Thick-film protective lacquers can also be applied with this nozzle. One nozzle can be used alternately for spraying and dispensing. For example, component edges can be coated with a material bead without pressure immediately after coating with the same nozzle in order to obtain special protection.



Fig. G12: *Selective spraying system SSC 500 with Stream-Coat® technology, left batch with rack, right inline*

8 Automatic and selective coating process

With selective coating, it is possible to coat only certain, precisely defined areas of a printed circuit board and to keep other areas free in a controlled manner. This eliminates cost- and labor-intensive masking operations which are required with conventional coating methods (e.g. manual masking of connectors). Alternatively, the assemblies can also be coated completely, if required. Since this process is software-based, no additional tools or resources are required aids. This technology allows to use a complete system solution which has been developed for this particular application.

The compact coating system (see Fig. G13) consists of the following components which are designed to work perfectly together:

- a special filmcoating applicator,
- heated, recirculating fluid system,
- a multi-axis robot to move the applicator,
- the integrated system controls and
- the EasyCoat coating software.

This process enables the user for the first time to completely control and monitor the entire coating process.



Fig. G13: Coating system for the SelectCoat® process

8.1 SelectCoat® process, theory of operation

The coating applicator with the special CrossCut nozzle creates an exactly defined fan pattern (see Fig. G14). Different nozzle sizes allow to match the flow rate, coating thickness and application width to the individual application requirements.

An essential part of this process is that the coating material can be applied without overspray and with exact edge definition. Contrary to conventional coating processes, in which

the coating material is atomized by compressed air and overspray cannot be avoided, the SelectCoat process uses airless technology, which can prevent overspray

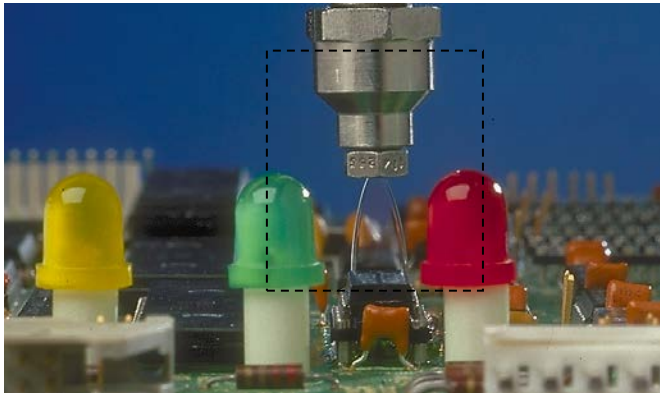


Fig. G14: Closed fan pattern

The special coating applicator can be opened and closed within a few milliseconds, allowing for programmable interruptions within the coating sequence. The coating applicator is moved over the PCB by a multi-axis robot and applies a uniform and closed coating film to the previously defined areas of the assembly. The coating speed of the robot can be programmed between 0 and 1.000 mm/s. The high coating speed provides an extremely high throughput and correspondingly short coating cycle times. Due to the programmable opening and closing of the applicator, specific interruptions of the coating film can be programmed at any position of the printed circuit board in order to not coat certain areas. Since the coating material is only applied to the areas which have to be coated, manual masking, unmasking and cleaning work required with conventional methods, can be eliminated

8.2 Closed and recirculating fluid system

The entire fluid system is designed as a closed and recirculating system. Since the fluid system is closed, no volatile components can evaporate, which would have a negative impact on the coating result. In addition, an integrated heater with PID¹ temperature control provides a consistent viscosity of the coating fluid even during fluctuations of the ambient temperature. These precautions are providing the necessary, consistent process parameters which are required to achieve a repeatable coating result.

Since all relevant process parameters can be adjusted to the individual application requirements, all conventional conformal coatings, like acrylates, urethanes, epoxides, silicones and also solvent-free or UV-curing products can be processed with the SelectCoat[®] process. Depending on the exact configuration of the entire system, the coating applicator can cover an area of up to 515 x 525 mm. This allows that both very large assemblies and multi-up carriers can be processed easily and conveniently in a single operation.

¹ PID - Proportional-Integral-Differential Control; enables fast derivative action, targeted approach close to the setpoint and final precise correction of the control difference

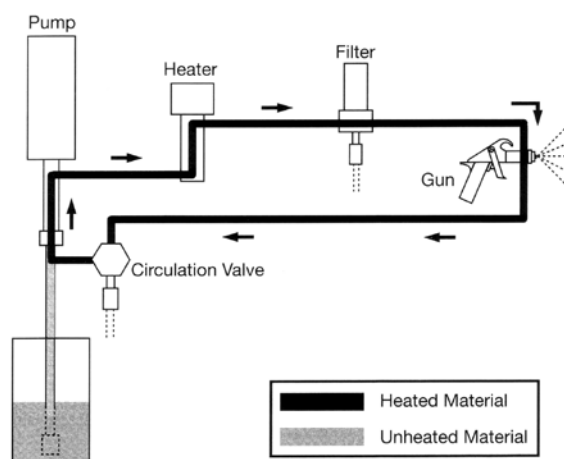


Fig. G15: Closed and recirculating fluid system

8.3 Software for the coating system

An essential part of this complete solution is the special software. The functions of the robot and the coating applicator are precisely linked by pre-programmed coating commands. Since this software is menu-driven, no special knowledge is required for programming. This makes it easy and convenient to create a separate coating program for each assembly. The system can be equipped with an automatic camera system for simple and convenient programming. This also allows to detect board fiducials to match the position of the coating program with the actual position of the assembly. For graphical programming an image of the assembly can be acquired with that camera system to create the coating programs offline.

The SelectCoat® process allows to apply the coating material directly to the assembly depending on the actual surface structure. Once coating programs have been created, they are stored in the computer and can be executed as required.

The system control ensures that the coating results of this process can be achieved as often, repeatable and precisely positioned as required. Since the coating material is applied selectively and without overspray, the material utilization is over 95 percent.

8.4 Process control

To ensure that the coating width is within the specified tolerance during production and to record important process data, the shape of the fan pattern can optionally be monitored with closed loop control. The width of the fan pattern is measured at selectable intervals with a laser and - if necessary - automatically re-adjusted to ensure consistent and repeatable results. The generated data will automatically be saved with date and time in a log file. This applies to all other relevant process data, too. The software allows to configure which data will be saved in the log file.

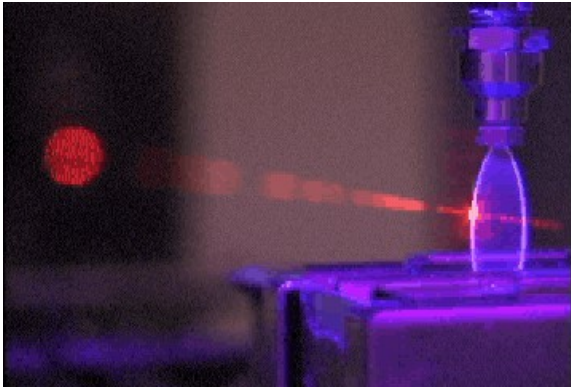


Fig. G16: Automatic monitoring of the fan pattern with laser

This automatic data logging ensures that the current requirements for traceability and statistical process control are fully met. A complete proof of quality can be maintained over the entire production period and it is possible to evaluate the data statistically if required.

8.5 The Coating platform

The described components are completely integrated into the SelectCoat workcell. With the compact, free-standing system, the operator only has to place the parts into the system and start the coating process with the push of a button. Then the part can be removed again and can be deposited for drying. Additional safety devices ensure that the system can only be operated when the doors are closed and the extraction is activated. The monitoring of the exhaust air within the system ensures that no critical solvent concentrations can occur. This is one reason why the system can be operated directly within the existing production and no additional explosion-protected areas have to be set up.

In-line systems are available to ensure a continuous production process (see Fig. G17). In this case, the entire coating system – including board handling and curing oven – is operating fully automatic and equipped with width-adjustable edge-handling conveyors. In order to achieve optimum results and short throughput times, a special technology is used for drying. The combination of infrared and convection ensures a consistent and even curing of the coating film. Multiple independently controlled temperature zones, allow for an optimum temperature profile and can avoid unnecessary high thermal loads. A cooling zone at the exit of the curing module ensures that the coated and cured boards can be conveyed to the next production step without any problems.



Fig. G17: Complete in-line production

In combination with an inverter, the in-line system can automatically coat top and bottom side of the boards. The digital inputs and outputs of the system allow to link certain functions or conditions with other production processes in order to achieve optimum coordination of the overall process.

8.6 Non-contact jetting with the PreciseCoat® technology (pulse width modulation)

8.6.1 Process description

Completely new possibilities for the application of different coating materials result from the use of pulse width modulated jetting valves. Conventional (needle) valves are turned on at the beginning of each coating sequence, moved at constant speed and turned off at the end of the coating sequence. There is no possibility to vary the flow rate or the coating thickness during that sequence.

Pulse width modulated applicators (see Fig. G18) allow to divide each coating sequence into small segments. The applicator is triggered with an adjustable frequency, causing it to open and close every x milliseconds. With each actuation of the applicator, a small quantity of the coating fluid is jetted onto the surface of the substrate as an exactly defined dot, comparable to the operation of an inkjet printer.

This operation is making a very important difference to needle dispensing: the jetting application is **non-contact**. Although a short needle is used to guide the coating fluid, the gap between needle and substrate is much larger and the dot flies from the needle to the substrate (Fig. G19). The dot volume of a single "shot" can be adjusted within a certain range depending on the properties of the coating fluid.

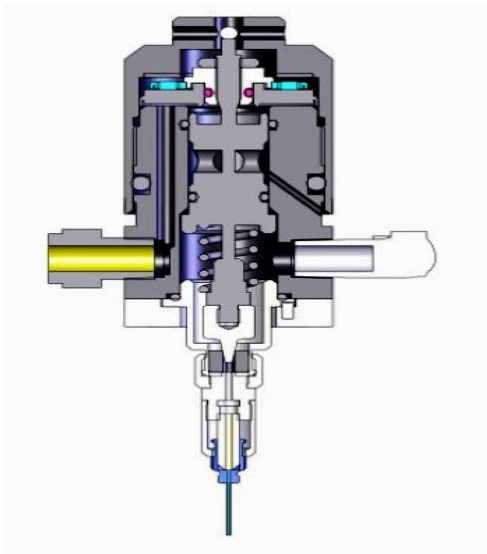


Fig. G18: Sectional drawing of SC-400 jet valve with pulse width modulation

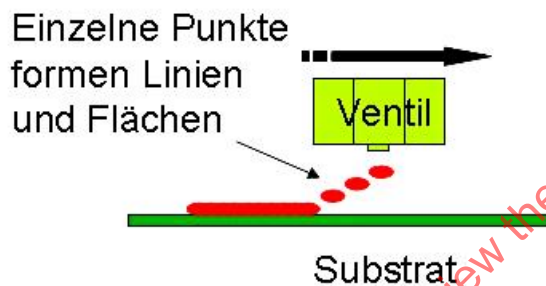


Fig. G19: Frequency modulated jetting

The flexibility for the application is considerably increased using pulse width modulation and the different control options. It is possible to move the applicator to a fixed position of the assembly and apply individual small dots to the previously defined areas of the PCB to achieve maximum selectivity. For example, coating of a single SMD component. Depending on the number of pulses, dot size and coating thickness can be adjusted to the requirements. This technology allows for an extremely selective coating, even if the requirements might be difficult (see Fig. G20).

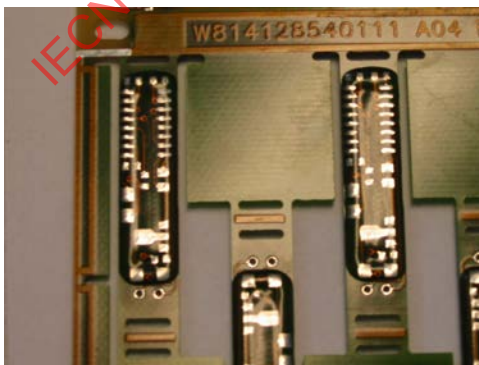


Fig. G20: Selectively coated assemblies using pulse width modulation

On the other hand, even complex geometries, lines or large areas can be coated at high speed using higher frequency. In this case, the applicator moves at a consistent speed and is triggered at the previously programmed frequency. Individual dots are jetted continuously according to the coating program. The dot diameter and dot-to-dot spacing can be programmed in the coating software so that the individual dots touch each other and are creating a homogeneous and uniform layer (Fig. G19).

8.6.2 How to achieve different coating thicknesses

At the beginning, the basic settings are determined depending on the coating requirements and the coating fluid to be processed. These include the mechanical adjustment of the applicator, the selection of the correct needle diameter, and adjustment of the fluid pressure. Since the application is non-contact, there is always a certain gap between needle and PCB, the jetting of the fluid is independent of the surface tension.

By changing the jetting frequency or changing the coating speed, the coating thickness can directly be influenced using the software of the coating system. If a low frequency is used (a few cycles per second), the flow rate is also low and a correspondingly low coating thickness is applied. As the valve frequency increases, the flow rate will also increase and the coating thickness will increase. Important to know: in the software both the jetting frequency and the coating speed can be adjusted to match the actual requirements. In this context, it is particularly important that non-contact jetting with this applicator allows to operate with a relatively large gap between the needle and the surface of the product. For this reason, very thick layers can be applied without having the risk that the needle is touching the fluid on the board, which might cause for stringing or contamination.

Compared to traditional coating processes, pulse-width-modulated jetting applicators do not only offer a significant improvement in quality but also greater flexibility for the production. Reduced operating costs, improved material utilization and, of course, the available process controls are the premises to achieve an efficient and production-safe application. Since a programmable robot is used for the coating process, multiple coating programs can be created and saved in the computer. Later on the coating programs only have to be loaded and then they can be executed as often and repeatable as required. The cost for repair, rework or failure of wrong coated boards can be enormous. For this reason, it is very important to examine the available technologies in detail, because the most suitable process can achieve significant cost reductions caused by defects.

9 Application using dispensing valves

In various areas of electronics production, liquid or pasty media are applied precisely and with repeatable accuracy using dispensing valves. This includes applications like dispensing of SMD adhesive², solder paste, underfill or potting material. A dispensing valve attached to a robot will be moved according to dispensing program. The valve with a dispensing needle can apply either dots (without motion) or lines (in motion) onto the substrate (see Fig. G21).

However, two items are of great importance when dispensing conformal coatings: conventional dispensing valves usually apply a too high film thickness, which is almost impossible to be cured completely and presenting the risk for insufficient protection. In addition, larger areas of a PCB can only be covered by applying a large number of parallel beads, which takes a lot of time and is also causing for an too high coating thickness.

² SMD - Surface Mount Device; adhesives used for fixing electronic components on circuit boards.



Fig. G21: Needle dispensing process

For these reasons, dispensing systems are hardly used at all for the application of conformal coatings.

An exception is the dispensing of sealing compounds to prevent the penetration of conformal coating into certain components. In this case, before the conformal coating process a bead of a higher-viscosity sealing compound is dispensed around the component to be sealed to prevent that coating fluid can penetrate into that component. The application of this "dam" is usually done using an automatic dispenser.

10 Application via vacuum process

Parylene coating materials cannot be melted, casted or sprayed. Due to their insolubility, they cannot be applied by dipping or spraying, but only by a vacuum process (see Chapter C1.9).

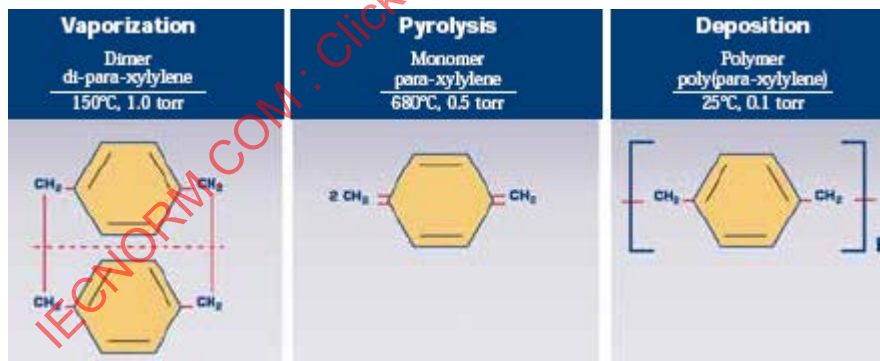
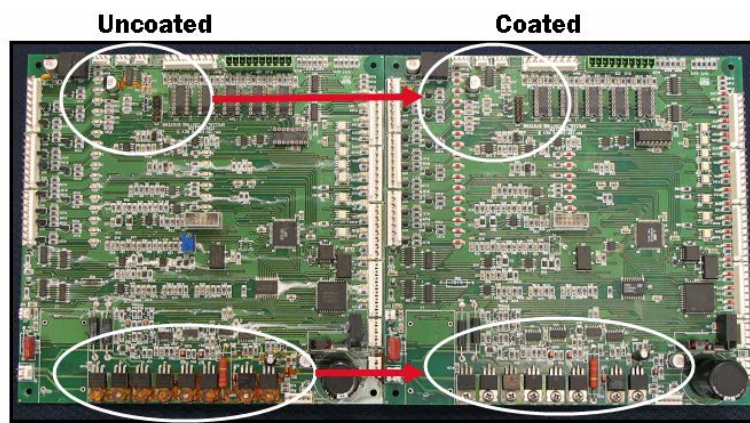


Fig. G22: Parylene Vapor Deposition Polymerization (VDP) using the example of Parylene N.

The solid crystalline dimer Di-Para-Xylylen is sublimated (vaporized) at approx. 13.33 Pa (1.36 mmWS) and 150°C. This sublimate is the basis to generate the reactive gaseous monomer para-xylylen by pyrolysis at approx. 680°C and 6.66 Pa (0.68 mm wc). This monomer is fed into the coating chamber at room temperature, where it is immediately polymerizing as poly-para-xylylene on the surfaces (of the electronic assemblies). In this dry process, a pinhole-free polymer layer is created that is meeting the contour of the part and can access even very small openings. The layer is transparent and not visible to the naked eye (Fig. G23). Like all three-dimensional crosslinked polymers, it is considered

insoluble and infusible.



PCB boards with Parylene HT® after 144 hours salt fog test in accordance with ASTM B117-(03)

Fig. G23: Example of a parylene coating on electronic assemblies

Because there is no liquid phase, even edges of components are covered with a uniform layer. During this process the substrate temperature is rising only very little, above room temperature, the max. will be approx. 50°C. The substrates to be coated do not have to meet any special requirements apart from being resistant against vacuum. There are no solvents, catalysts or softener involved in this process. Since the process is running at room temperature, there is no thermal or physical stress for the substrate (e.g. by curing).

The electrical insulation capability of $>200 \text{ V}/\mu\text{m}$ provides a strong protection against ESD and disruptive discharge in high-voltage applications. Parylenes do also have a very low dielectric constant when applied as a coating.

HANDLING PROTECTIVE COATINGS DURING PROCESSING

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1 Requirements for coating rooms and equipment

1.1 Overview and definition

Coating materials are prepared, mixed, applied and dried for subsequent processing in coating rooms and coating facilities. The coating materials used may contain solvents, be flammable and therefore cause fire and explosion hazards.

Liquid flammable coatings have a flash point. The flash point is the lowest temperature at which vapors develop from a liquid in such quantities that a flammable mixture can form together with the ambient air. Depending on the flash point, a distinction is made between the following classes:

- extremely flammable (flash point below 0°C, boiling point at most 35°C), formerly hazard class A I according to VbF
- highly flammable (flash point between 0°C and less than 21°C), formerly hazard class A I according to VbF
- flammable (flash point at least 21°C, at most 55°C), formerly hazard class A II according to VbF

Regardless of the height of their flash point, flammable liquid coating materials are always flammable in a finely divided state (formation of aerosols, e.g. as spray mist). For safety reasons, this is particularly important for air-assisted spraying processes, as a very large proportion of spray mist is inevitable and the risk of ignition is correspondingly high.

There are coating materials that can cause damage to health if the air limit value in the ambient air is exceeded. In this context, special attention must be paid to the air routing within the respective coating system in order to be able to reliably comply with the applicable limit values during operation.

The processing (provision, preparation, application, drying) of highly or easily inflammable coating materials may only take place in separate rooms. These rooms are regarded as rooms at risk of fire. Unless the respective plant is designed for its intended use and can rule out the formation of an ignitable gas mixture by the process used (e.g. casting process without air support) and additional technical equipment (extraction monitoring, air flow). This must be checked in each individual case and proven accordingly.

1.2 Explosion-protected areas

Special requirements apply to pure coating rooms and separate areas, including fire protection, explosion protection and operation. In rooms with a fire hazard, e.g. coating rooms or separate areas, the operator must determine the areas with an explosion hazard.

These potentially explosive atmospheres are divided into the following zones according to the probability of the occurrence of hazardous explosive atmospheres:

- Zone 0: An Area in which an explosive atmosphere consisting of a mixture of flammable substances in the form of gas, steam or mist with air is present continuously, for long periods or frequently.
- Zone 1: An area in which an explosive atmosphere consisting of a mixture of flammable substances in the form of gas, vapor or mist with air is likely to occur occasionally during normal operation.
- Zone 2: An area in which an explosive atmosphere is not expected to occur as a mixture of flammable substances in the form of gas, steam or mist with air during normal operation, but only for a short time if it does occur.

Potentially explosive areas are always considered to be flammable areas at the same time. In addition to fire protection measures, the following additional requirements must be met in potentially explosive atmospheres: Floors must be electrostatically conductive. In hazardous areas, the leakage resistance of the floor, including the floor covering, must not exceed 10⁸ ohms. The use of objects or equipment made of insulating materials in potentially explosive atmospheres must be avoided. If objects or equipment made of conductive or dissipative materials cannot be used, measures must be taken against dangerous charges. Possible measures are e.g. conductive or dissipative coatings, conductive threads in textiles, surface limitations or even safe organisational measures.

1.3 Storage of coating materials

Liquid highly flammable, highly flammable and flammable coating materials (e.g. coatings, solvents) - formerly hazard classes A I, A II and B according to VbF - must be stored in special rooms. Potentially explosive areas are always considered to be flammable areas at the same time. In addition to fire protection measures, the following additional requirements must be met in potentially explosive atmospheres: Floors must be electrostatically conductive. In potentially explosive areas, the leakage resistance of the floor, including the floor covering, must not exceed 10⁸ ohms.

The use of objects or equipment made of insulating materials in potentially explosive atmospheres must be avoided. If objects or equipment made of conductive or dissipative materials cannot be used, measures must be taken against dangerous charges. Possible measures are e.g. conductive or dissipative coatings, conductive threads in textiles, surface limitations or even safe organizational measures.

1.3 Storage of coating materials

Liquid highly flammable, highly flammable and flammable coating materials (e.g. coatings, solvents) - formerly hazard classes A I, A II and B according to VbF - must be stored in special rooms. However, in coating rooms and separate areas, a maximum quantity corresponding to the requirements of a work shift may be provided. Flammable liquids may only be stored in shatterproof and sealed containers (e.g. metal containers). Flammable liquids can also be stored in safety cabinets that have been type-tested according to DIN EN 14470¹. The storage rooms must be adequately ventilated and illuminated. The ventilation must be effective near the ground, as many solvents are heavier than the ambient air and therefore sink downwards. The ventilation system must ensure a constant air exchange rate of at least five times an hour.

¹ DIN EN 14470-1: Fire-resistant storage cabinets - Part 1: Safety cabinets for flammable liquids

1.4 Mixing and staging areas

With regard to structural measures and labeling, the same requirements apply as to coating storages. If only coating materials, solvents or similar materials with a flash point sufficiently above the processing temperature (at least 5 K for pure solvents or at least 15 K for solvent mixtures) are processed, an explosion is not to be expected. If coating materials, solvents, etc. with a flash point not sufficiently above the processing temperature are processed, the following potentially explosive zones (see 1.2) must be defined. In rooms in which coating materials, solvents, etc. are partly filled from open containers, mixed, decanted or pumped over:

- with natural ventilation: 1 m around the processing point zone 1, another 2 m zone 2,
- for technical ventilation: 1 m around the processing point zone 1, another 1 m zone 2,
- for extraction at the processing point: 0.5 m around the processing point zone 2.

1.5 Coating equipment

Coating equipment is understood, for example: Spray walls, stands and cabins, flooding systems and dipping tanks.

Spray-coating work may only be carried out in work areas which are provided with technical ventilation. Spray booths or spray stands are suitable. According to BGR 231² and BGIA/LASI-ALMA recommendation³, however, suitable respiratory protection must always be worn to protect against aerosols and organic vapors. Respiratory protection can only be dispensed with completely at spray stands under certain conditions.

Spraying walls or organizational measures are also suitable for manual spraying with a small amount of coating (less than 0.5 kg per working shift). Organizational measures are e.g. temporal or spatial separation of spraying work and other work or effective natural ventilation. Coating equipment in which water-based coatings are used must be corrosion-resistant.

In addition, the dipping containers for flammable coating materials must be equipped with one of the following devices:

- a cover that can be closed safely in the event of fire,
- a cover that closes automatically in the event of a fire,
- an extinguishing device which can be triggered manually from a safe distance, or
- an automatic extinguishing device.

² BGR231: Employer's liability insurance association rules: Protective measures concept for spray coating work - Coating aerosols

³ BGIA – Berufsgenossenschaftliches Institut für Arbeitsschutz; LASI – Länderausschuss für Arbeitsschutz und Sicherheitstechnik; ALMA – Arbeitskreis der Ländermessenstellen für chemischen Arbeitsschutz

1.6 Extraction and ventilation in rooms and areas

Rooms and areas in which coating materials are processed (e.g. coating rooms, separate areas, evaporation rooms/places, mixing and preparation rooms) must be ventilated. This must be designed in such a way that

- a dangerous explosive atmosphere is prevented and
- the air limit values of gases, vapors and mists produced are maintained.

As a rule, this can only be achieved by suitable technical ventilation (air exchange by fans). The following measures have proven effective for effective technical ventilation: Supply air in the upper area and extraction in the lower area of the room as well as transverse flow through the spraying area/room. If supply air or exhaust air filters are used, they must not be easily flammable.

Spraying walls, stands, cabins and other equipment (e.g. spraying robots) for spraying and spraying coating materials must be equipped with suitable extraction devices which effectively prevent spray and spray mist from escaping from the working area. Otherwise, the technical ventilation (extraction) for new systems must be designed in such a way that operation of the system is only possible with effective extraction. The air discharged into the atmosphere must not contain more than 3 mg of coating solids per m^3 of exhaust air (TA-Luft value⁴).

On automatic coating systems, the extraction system must remain effective even after the application device has been shut down as long as the formation of hazardous explosive atmospheres by solvent vapor-air mixtures is to be expected. If the defined minimum exhaust air volume flow rate is not reached, an automatic application device must be stopped and the further supply of coating materials must be prevented. This can be done, for example, by means of flow monitors in the exhaust air volume flow. However, monitoring the motor of the suction device alone is not sufficient.

Dipping containers with a surface area of more than $0,25 \text{ m}^2$ for coating materials with a flash point $< 40^\circ\text{C}$ or which are heated above their flash point during operation must be equipped with a suction device. This can be achieved, for example, by means of a suction wall on one long side of the dipping container and low-pulse supply air from the opposite side.

1.7 Evaporation and drying rooms or areas

With regard to structural measures and markings, the requirements for rooms and structural installations, electrical and non-electrical devices as well as components with regard to fire protection and explosion protection must be observed.

Technical ventilation is required in drying rooms (not coating dryers to DIN EN 1539⁵). The electrical and non-electrical equipment and components must at least meet the requirements for operation in Zone 2.

⁴ TA-Luft: First general administrative regulation of the Federal Immission Control Act (Technical Instructions for Air Pollution Control - TA Luft; July 2002)

⁵ DIN EN 1539: Dryers and furnaces in which flammable substances are released

1.8 Processing of UV-curing coating systems

In UV technology, the liquid coating film is cured by ultraviolet rays. This curing takes place very quickly, usually within a few seconds. As a rule, photoinitiators are used to start the polymerization process. Other components of UV coatings can be pigments or additives. Normally UV coatings are solvent-free and therefore non-flammable. During the processing of UV coatings, however, hazards can arise which are determined by the chemical composition of the coating material, the application technique used and the type of curing of the coating. These significant hazards and the most important protective measures are listed in the following Table. H1.

Tab. H1: Hazards and protective measures when handling UV-curing coating systems

Hazard	Safety measures
Contact with or inhalation of UV coatings or aerosols and solvents as mist or liquid (especially in spraying processes)	Avoidance or reduction of coating aerosols by suitable coating technology (e.g. dip coating, low-mist coating or casting processes), use of suitable technical ventilation
Inhalation of ozone	Detection of the ozone by suitable technical ventilation, no return of the extracted air into the work area, installation of suitable equipment (e.g. filters) before discharge into the environment
Exposure to UV light	Avoidance of emissions of hazardous radiation into the working area through suitable screening, locking of accesses and openings of UV drying systems, regular inspection of seals and covers during maintenance.

1.9 Operation

Coating work is only permitted with sufficiently effective ventilation. The personnel employed must be informed about the working methods. The concentration of pollutants and the proportion of overspray (coating aerosols) should be reduced as far as possible. Combustible coating materials in coating rooms and separate areas may only be provided in the quantity required for the progress of the work – at most in accordance with the requirements of a working shift – and if possible only in the original containers. Larger quantities must be stored in separate coating stores. Vessels, packages and containers used at the workplace must be labeled in accordance with the Hazardous Substances Ordinance and should always be kept covered. Empty containers should be removed from the work rooms daily.

Dipping tanks must be covered after completion of the work in order to avoid evaporation of solvents. Objects that can be dangerously charged, e.g. workpiece supports or conductive containers, should be earthed to establish equipotential bonding.

Deposited coatings and residues should be removed from the coating systems and their surroundings at appropriate intervals. Cleaning can be facilitated, for example, by applying peelable lacquer or attaching paper covers beforehand. Dissolved deposits and cleaning rags etc. should be collected in lockable, non-combustible containers and removed daily from the processing rooms. This applies in particular to rags soaked with drying coatings or solvents.

Work involving a risk of ignition, e.g. work with flying sparks (grinding), fire work (cutting, welding) and work with spark-cracking machines and tools may only be carried out in rooms with a risk of fire (e.g. coating rooms) and in areas with a risk of fire and explosion

(e.g. coating areas in production rooms) if the operator has granted written permission and special safety measures have been taken.

1.10 Rules and regulations

Further information and essential requirements for the safe construction and operation of coating rooms and coating equipment can be found in the following documents, among others:

Laws, regulations, technical rules:

- Equipment and Product Safety Act (GPSG)
- Industrial Code (GewO)
- Building regulations of the federal states
- Workplace Ordinance (ArbStättV) with Workplace Guidelines (ASR)
- Industrial Safety Regulation (BetrSichV)
- Ordinance on Hazardous Substances (GefStoffV)
- Technical Rules for Flammable Liquids (TRbF)
- Technical Instructions on Air Pollution Control (TA Luft)
- TRBS 2152 Dangerous explosive atmospheres - Basics

European standards:

- DIN EN 1127-1 Explosive atmospheres - Explosion protection
- EN 1539 Dryers / ovens where flammable substances are released
- EN 1953 Spraying and spraying equipment for coating materials
- EN 12581 Dipping coating systems and electrophoretic coating systems for organic liquid coating materials

Accident prevention regulations:

- BGV A3 (previously VBG 4) Electrical systems and equipment

2 Monitoring processing parameters

The same applies to thin-film protective coatings as to thick-film protective coatings: The protective coating should be homogeneous, without flow disturbances, bubble-free, without visible soiling or streaks, especially without detachment from the assembly. Contacts must remain absolutely free of coating and masking agent residues. Hardening must not be inhibited.

For physical reasons, but unfortunately hardly feasible, evenly thick protective coatings are desirable. The coating thickness should be between 30 and 60 µm for thin-film protective coatings, for thick-film protective coatings it usually starts at 100 µm and in the maximum case passes to the encapsulation covering the component at several millimeters.

In order to meet these requirements, several parameters of the protective coatings must be matched and monitored to the respective processing techniques used (spraying, dip-

ping, dispensing, etc.). The compatibility of fluxes and solder resist coatings with the protective coating must also be checked. The prerequisite for reproducible coating application is an assembly surface that is free of contamination and does not interfere with the flow or even cause delamination. This usually means that the assembly must be cleaned before coating.

To maintain a reproducibly good coating quality, the following parameters must be taken into account: Viscosity, contamination, purity of the assembly. To achieve this, the following basic recommendations must be observed, which are largely independent of the protective coating system used.

2.1 Viscosity and flow time

In principle, a check of the viscosity of the protective coating is recommended both for incoming goods inspection and for process monitoring. Due to its easy handling, the measurement of the run-out time with dip cups (see Fig. H1) is used by many protective coating processors as a standard test method for determining the viscosity of coatings in production and incoming goods inspection. Strictly speaking, this measurement method can only be used to determine the flow time perfectly for Newtonian liquids (i.e. systems that do not exhibit thixotropy), but it does provide values with sufficient accuracy for production.

However, it should be noted that there are differences in the test methods with regard to the flow cups used. Thus, flow cups show completely different flow times even with the same nozzle diameter. These differences lie in different volumes and different flow geometries.

Up to now, the flow time according to DIN 53211⁶ was specified as standard. However, this standard was already withdrawn in 1996. It was replaced by the international standard DIN EN ISO 2431⁷ with the title "Determination of flow time by use of flow cups".



Fig. H1: Dip cups according to the DIN or ISO standard

Since measurement according to DIN is still established in practice with many protective coating processors, we continue to find the DIN specification in technical data sheets and delivery certificates. At the same time, the flow times according to ISO are often specified,

⁶ DIN 53211 (valid until 1996-05) "Paints, varnishes and similar coating materials; determination of flow time by use of DIN cups". New Din EN ISO 2431

⁷ DIN EN ISO 2431 (2012-03 Coating materials - Determination of flow time by use of flow cups

so that both values will often be available at first⁸.

The ISO cup can be purchased in the laboratory equipment trade (e.g. Byk Gardner). The software "Viskosoftware" from Erichsen Testing Equipment (www.erichsen.de) is recommended for simple conversion of the viscosity values of standardized flow cups.

2.2 Flow time and temperature influences

The flow behavior and the viscosity of a protective coating change depending on the temperature. For this reason, it must be ensured that the measurements are carried out at the same initial temperature. Otherwise, the results cannot be compared. The viscosity data usually refer to the measurement at a temperature of 20°C according to DIN 53211.

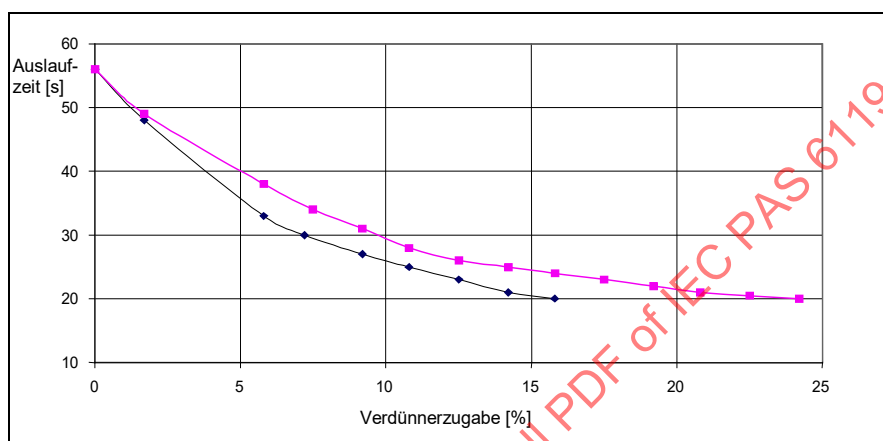


Fig. H2: Viscosity as a function of thinner addition (20°C, 4 mm flow cup, DIN 53211))

2.3 Viscosity and temperature

Depending on the application method, the processing viscosity of thin-film coatings should correspond to a flow time of 35 ± 5 seconds⁹, measured with a 4 mm flow cup (according to DIN 53211), irrespective of the coating temperature. Usually the processing temperature is between 20 and 30°C.

Compressed air spraying process: Application viscosity and temperature should be similar to the brush application. The air pressure used for spraying should be 2.5 to 4 bar using a spray nozzle diameter of 0.8 - 1.5 mm.

Dip coating process: When applying protective coatings using the dip coating process, the flow time should be 25 ± 5 seconds, measured with a 4 mm outlet cup (according to DIN 53211), irrespective of the processing temperature.

The pleasant possibility of correcting viscosity by adding thinner also has its turn side. What happens if the coating is first carried out at 30°C, sampled and approved, but then has to be coated at 20°C? Thinner is added so that the solid content is reduced and with it the coating thickness is also reduced. It is therefore recommended to strive for the average coating thickness of the specified thickness tolerance during sampling in order to

⁸ DIN and ISO cups differ in the volume and size of the outlet bore.

⁹ When determining the viscosity of a coating, the time it takes for the coating to flow out through the bore of the measuring cup is measured.

have room for temperature-related corrections.

When processing thick-film protective coatings, the viscosity is measured either with the DIN or ISO cup, or more elaborately with a viscometer. The latter provides additional information on the thixotropy of the protective coating, which is particularly important for thick-film protective coatings. Thixotropic protective coatings provide better edge protection and more precise adherence to the coating geometry for selective coatings because they do not run into areas free of paint after coating.

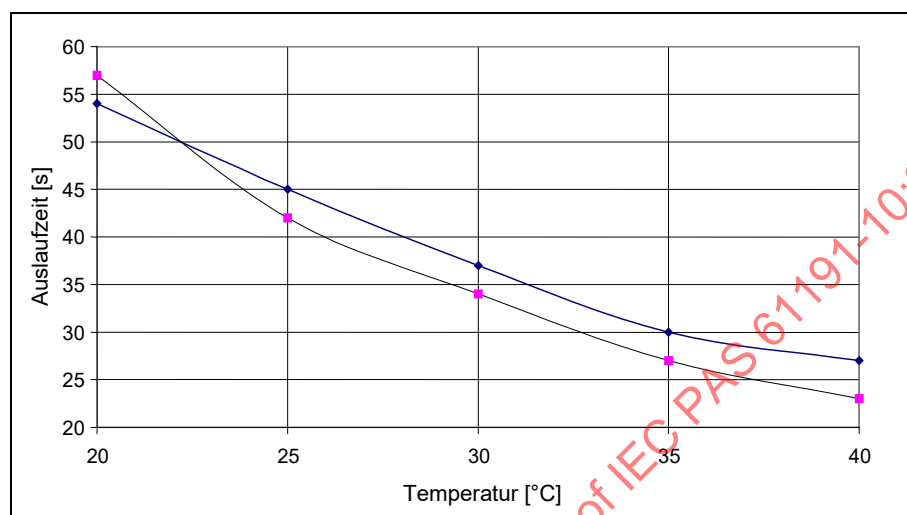


Fig. H3: Viscosity as a function of temperature (4 mm outlet cup, 20°C)

Temperature fluctuations have a greater effect on thick-film protective coatings than on thin-film protective coatings. Because they are usually solvent-free, the viscosity can only be varied by changing the processing temperature. The thick-film protective coatings benefit from the insensitivity to fluctuations in coating thickness, because this is still far above the thickness of thin-film protective coatings in the event of deviations.

20 to 30°C should be preferred as processing temperature for protective coatings. For an even and complete wetting of the flat assembly, the following dipping parameters have proven themselves:

- Lower the board at 1-5 mm/sec (faster speed if few components on the board)
- Hold for 15 seconds - air bubbles to escape
- Raise at 1-3 mm/sec until the board is above liquid
- Tilt board at 45° - hold about 45 seconds to drain

If possible, the circuit boards should be tilted at an angle of 60° and rotated slightly at the same time. The resulting flow tip prevents droplet residue at the edge of the circuit board. Subsequent drying can take place both at room temperature and much faster at 80°C.

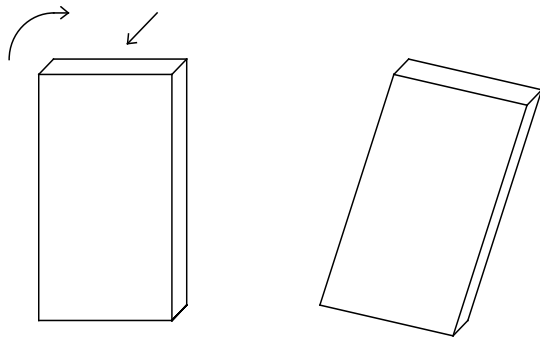


Fig. H4: *Dripping of printed circuit boards after dipping (tilted and rotated at an angle of 60°)*

If a protective coating is applied at too low a temperature ($< 20^{\circ}\text{C}$), the drying of the protective coating may be extremely prolonged until it is tack-free / non-sticky; furthermore, the viscosity increases to such an extent that the coating material is very difficult to apply or can only be used at very low temperatures. so much thinner must be added that, as described above, the coating drying time is extended or the solid content is reduced to such an extent that the protective coating cover is too thin.

Too high temperatures ($> 30^{\circ}\text{C}$) cause a strong drop in viscosity and possibly too fast drying, so that the coating material no longer has sufficient flow properties or film formation starts too quickly.

The recommended temperature range of 20 to 30°C offers balanced processing properties of the protective coatings, whereby temperatures close to 20°C naturally favor the course of the coating material at the expense of the drying speed, whereas temperatures close to or up to 30°C result in rapid drying with limited flow properties.

3 Contamination

Most thin-film protective coatings have a drying mechanism based on the fact that solvents evaporate from the coating and chemical curing begins in parallel with evaporation. Chemical curing is achieved by absorbing oxygen or hydrogen from the air.

This process of absorption of air, called contamination, also takes place everywhere in the coating plant where protective coating forms large surfaces; especially in vertical dipping. This effect can be reduced but not prevented by gassing the system with inert gas. The protective coating manufacturer therefore recommends that the protective coating bath be renewed from time to time.

Why renew? Because the evaporated solvent is replaced by continuous addition of thinner, but at the same time the thickening with solvent resulting from the chemical reaction (polymerization) is reduced. This results in an accumulation of already polymerized coating and an accumulation of solvents in the protective coating stock, while the proportion of the original coating material is reduced.

After seven weeks, tests on a dipping system showed a reduction in the volume resistance of the applied coating by a power of ten without any change in the protective coating.

In the "milli coat" cup process, the components are selectively dipped and horizontally dried, which allows higher coating layers to be achieved than in vertical dipping. Any flowable coating, conventional thin-film coating or thick-film coating can be processed.

The contamination of the coating is only a fraction of that of vertical dipping and can be neglected.

4 Maintenance of dipping systems

Because dipping systems usually have to cope with large numbers of assemblies, they have a correspondingly large dipping tank filled with coating material. A pump system continuously conveys it from the storage tank into the dipping tank, where it flows back into the storage tank via an overflow edge.

Maintenance of dipping systems primarily means cleaning encrusted components at all points where the coating comes into contact with ambient air. Cleaning media are mainly flammable, organic solvents. This must be taken into account when planning the site.

The time intervals of maintenance are influenced by the factors:

- Drying and curing properties of the coating material;
- Entry of dirt particles;
- equipment of the plant (nitrogen, valves, pump) and
- dwell time between the coating phases.

Coating materials that dry purely physically can be cleaned in suitable solvents even when completely cured due to their re-solubility.

Protective coatings which have physical and chemical or exclusively chemical drying mechanisms can only be removed in cured condition with great effort using destructive cleaners. Due to continuous contamination with ambient air, chemical hardening causes agglomerates to form, which sink in the bath or accumulate at flow-calmed points.

The cleaning of cured water-based coating materials is particularly laborious, especially because of their good solvent resistance. Solvent-resistant 1C-PUR protective coatings can be cleaned with similar effort.

In addition, all protective coatings have a more or less pronounced tendency towards skin formation, which occurs in flow-calmed areas of the immersion bath and must be removed at regular intervals if necessary.

If electronic components are dipped without prior cleaning, there is a risk that the agents used during the assembly process may enter the surface. This includes fluxes, greases, solder balls, dust etc. and in the worst case the storage container for the coating material is contaminated with silicone adhesives.

Depending on the design of the type of pumps, valves, hoses and bath heating, the maintenance intervals of the system vary. An extension of the intervals is achieved by applying inert gas to the immersion bath. With smaller assemblies, this effect is more effective because large assemblies introduce more ambient air.

The dipping tank should be protected from contamination. If the dipping system is not used, the dipping tank should be covered or closed. The printed circuit boards to be coated in the dipping process should be as clean as possible. In addition, auxiliary equipment must be cleaned regularly.

Finally, the dipping tank should be completely cleaned after a few months, depending on

the consumption of coating material. With a very low consumption of protective coating, it may be necessary to regularly replace the coating material with fresh material.

The dwell time between the coating processes has a considerable influence. Here, the rule "less use, less wear", does not apply, but rather the contrary. Solvents evaporate in the bath and through hoses, so that the coating material thickens. Chemical hardening begins and thickens the coating even more. This forces the hose lines to be cleaned or even replaced, even if the system is not used very often.

In general, the maintenance interval depends on the factors mentioned above, therefore no time specifications are possible. In order not to have to accept any quality losses, it is recommended to take coating samples at monthly intervals and to dry them according to the data sheet in order to check the volume resistance, if possible also after moisture storage.

In general, the maintenance requirement for all coating systems is higher during downtimes than during operation. When using chemically drying coatings, hoses must generally be replaced after long downtimes.

All systems require special effort if UV-curable coatings with moisture curing are used. The hydrogen penetrates the commercially available hoses and causes the coating to gel or harden. It is advisable to obtain information from the coating manufacturer or an experienced service provider.

The cleaning of spraying equipment is well known and is therefore not mentioned.

5 Aging of protective coatings

It is not only the natural aging of the protective coating with its special formula, but also the permanent soiling, which increases with the operating hours, which makes it necessary to completely replace the protective coating from time to time. The following factors make this exchange necessary.

5.1 Coating aging

Coating aging occurs due to the increasing polymerization of the coating resins, especially in coating container with open surfaces. It is accelerated by solvent evaporation as well as by the pumping over and the constant new contact of all coating particles on the surface with the oxygen of the air. Another acceleration factor is the coating temperature: Rising temperatures, e.g. above 22°C, reduce the viscosity, but also accelerate the reaction speed of coating hardening! The fact that the coating already ages in closed delivery containers can be seen from the minimum usability date specified there. This must be taken into account if the coating system is not refilled until the end of the latter date.

5.2 Dust and dirt absorption

Today, protective coatings in dip coating plants are usually used with a solvent content of between 55 and 75 %. This solvent content is used for both coating and cleaning during dip coating. In fact, the cleaning effect of solvents - usually mixtures - is a desired effect, since for many years assemblies have only rarely been cleaned before protective coating. It is also no secret that the contamination on the assemblies is sometimes considerable. Washed off dust and dirt are taken up in the dip tank and fed to separators and filters in the coating circuit. In settling chambers, non-floatable particles are separated at a very

low horizontal flow velocity and collect on the floor, e.g. in the coating reservoir. Floating dirt particles as well as air bubbles are prevented from re-entering the circuit by baffles. The bottom of the dipping tank and the bottom of the coating reservoir must therefore be cleaned of the sunk sludge at regular intervals.

5.3 Solubilizing substances not related to coating

The high solvent contents clean the assembly surfaces not only by rinsing, but also by dissolving substances foreign to the lacquer, e.g. residues of soldering aids, soluble adhesive and other resin residues. These are absorbed by the protective coating in dissolved or solid form.

Permanent absorption of these substances leads to a constant saturation and they thus simultaneously become part of the coating and the protective layer. At some point, a concentration of these foreign coating substances is achieved which impairs the protective properties of the coating on the assembly. At this point at the latest, the coating volume in the coating circuit must be replaced urgently. The dissolving of substances foreign to lacquer - just like the coating aging - cannot be stopped by filters.

5.4 Service life extension

The best measure against coating aging is the permanent coating circulation exchange through coating consumption and refilling of "fresh" coating. Outside operating hours it is recommended to cover open coating containers. The oxygen in the air is trapped under the lid. It is not displaced by the evaporating solvents, because solvent vapor diffuses in every free (gas) space as if it were alone there, a limitation of this diffusion is only possible by saturation. Flushing with nitrogen is able to largely displace the low oxygen content of the air. However, solvent evaporation in 100 % nitrogen takes place just as intensively as in only 79 %. If not circulated, skin formation takes place, as the solvent concentration decreases on the free surface and the remaining resin grows together to form a skin. Pumping over (to avoid skin formation) leads the coating permanently to the free surfaces and increases the temperature. A limitation can be achieved here possibly by cooling.

Dust and dirt can only be prevented from entering the protective coating if the components are cleaned before coating. Dipping in solvent protection coatings with high solvent contents largely replaces the cleaning process with the disadvantage that the dirt is introduced into the separators and filters of the coating circuit.

Where assemblies are not cleaned and not dipped, the coating is applied over the dirty surfaces of the electronics and incorporated during the film formation for (assembly) lifetime.

6 Environmental protection with regard to protective coating

The responsible treatment of our environment is one of the central tasks of all companies. Extensive regulations and laws exist for the handling and disposal of contaminated wastewater and all types of waste. The noise hazard caused by sound sources in the working area is regulated by BGV B3 "Noise" (formerly VBG 121). If noise immissions outside the operational environment, namely into the environment, are to be assessed, the Sixth General Administrative Regulation of the Federal Immission Control Act, the TA-Lärm, "Technical Instructions for Protection against Noise", must be consulted. The following comments deal exclusively with emissions into the atmosphere.

Emissions are generated wherever coating processes are carried out. Volatiles released during coating processes include not only organic solvents as thinners, but also additives of all kinds from paints, casting compounds and other coating materials.

6.1 Regulations and laws for air pollution control

The legal basis for air pollution control is the law on protection against harmful environmental influences caused by air pollution, noise, vibrations and similar processes (Federal Immission Control Act - "BImSchG").

Among other things, this BImSchG contains the regulations for the construction and operation of plants that generate emissions into the atmosphere; it authorizes the issuance of emission protection ordinances and administrative regulations. The so-called "EU Solvents Directive" deals with the handling of all solvents, regardless of how they end up in the atmosphere.

The BImSchG makes a fundamental distinction between installation requiring a permit and those not requiring a permit.

6.1.1 Installations requiring approval

BImSchG, §4 contains the basis for the determination of installations requiring approval. According to the 4th BImSchV, all installations producing ≥ 25 kg/h of organic compounds are subject to approval. Further contents of this BImSchG are of no interest in connection with the protective coating of electronics, as it is assumed not to advance into emission ranges of ≥ 25 kg/h in the foreseeable future. The annual emission limit for the permit requirement is 15 t/a. Related to an operating time of 230 d/a and 2-shift operation with 14 h/d, a limit emission of 4.65 kg/h is obtained.

6.1.2 Installations not requiring approval

BImSchG, §22 obliges the operator of installations not requiring approval to erect and operate them in such a way so that

- harmful environmental impacts are prevented that can be avoided in accordance with the state of the art,
- unavoidable harmful effects on the environment are kept to a minimum according to the state of the art, and
- waste resulting from the operation of the plant is properly disposed of.

Installations not subject to authorization must also be notified to the authority.

6.2 EU Solvents Directive (VOC Directive)

6.2.1 General information

On 11 March 1999, the Council of the European Union adopted Directive 1999/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations.

Thresholds and limits for solvent emissions have been set for various applications such as vehicle and wood coating, coil coating and many others. For systems for coating electronic assemblies, the values of field of activity No. 8 apply: "Other coatings, including metal, plastic, textile, fabric, film and paper coatings".

This Directive should be transposed into national law by the end of 2001 by each EU Member State. In principle, the transposition of 1999/13/EC into national law could be tightened up. Germany has made use of this option - other member states have adopted the VOC Directive into national law without amendment.

The German implementation is elaborated in the 31st BImSchV: "31st Ordinance on the Implementation of the Federal Immission Control Act (Ordinance on the Limitation of Emissions of Volatile Organic Compounds from the Use of Organic Solvents in Certain Installations)".

It is not the purpose of this presentation to reflect this important regulation; only the limit values for field of activity No. 8 are given below. This field of activity includes:

"...any activity in which metal or plastic surfaces, including bulky goods such as ships or aircraft, are coated, including the application of release agents or rubber coatings".

Table 2 enclosed contains the original text of the Regulation for field of activity No. 8.

Installations with an annual consumption of less than 5 tonnes do not fall within the scope of the Regulation and the limit values need not be complied with. However, these installations must also be reported to the authority. Existing installations must have been registered or approved by 31 October 2005 at the latest and comply with the monitoring and compliance requirements of the Regulation since 31 October 2007.

6.2.2 Solvent balance (31.BImSchV, Annex V)

According to the regulation, each consumer of organic solvents must prepare the so-called solvent balance. It serves the following purposes

- Knowledge of the actual consumption and thus the total emissions over 12 months (not the consumption values from capacity data of plants). The result shall be compared with the thresholds in Table 2.
- Determination of future reduction options.
- Provision of information for the public on solvent consumption, solvent emissions and compliance with regulations.

Areas based on the thresholds in field of activity No. 8:

- Annual consumption < 5 t: the consumer falls outside the scope of the Directive, the limit values need not be complied with.
- Annual consumption ≥ 5 however < 15 t: the consumer falls within the scope of the regulation, the limit values must be observed, a solvent balance according to the regulation is mandatory. If the limit values of so-called "captured emissions" and/or "fugitive emissions" are exceeded, action must be taken with the help of the reduction plan.

6.2.3 Reduction plan (31. BImSchV, Annex IV)

The plant operator shall submit a reduction plan to the competent authority. The plan aims to reduce the average content of total solvents used and/or to increase the efficiency of the solids in order to reduce the total emissions from the plant to a certain percentage of the annual reference emissions, the so-called target emission, within a certain timeframe. The measures leading to emission reduction are left to the plant operator.

A table has been defined for the execution of the reduction plan in the 31. BImSchV. If the procedure set out in this table proves inappropriate, the competent authority may allow an operator of an installation to use any alternative plan which it considers to comply satisfactorily with the principles set out in the regulation. If low-solvent or solvent-free substitutes are still under development, the plant operator must be granted an extension of the deadline for implementing an emission reduction plan. The availability of substitutes must be guaranteed at all times.

Just as the dates for compliance with the maximum total allowable emissions are laid down in the regulation for both new and existing installations, this also applies to the emission reduction measures to be implemented in accordance with the reduction plan.

6.3 Technical Instructions (TA) air

The "Technical Instructions for Air" is the "First General Administrative Regulation for the Federal Emission Protection Act" (technical instructions for keeping the air clean - TA Luft). It refers to § 48 BImSchG and is a general administrative regulation. It applies to the measurement and monitoring of emissions from installations subject to authorization in accordance with 31. BImSchV. The latest version of the TA-Luft was adopted on 24 July 2002.

6.4 Hazardous substances in the workplace

Permissible diffuse emissions for certain pollutants whose use at workplaces is unavoidable are regulated by the TLV value. The TLV value is "the highest permissible concentration of a working substance as gas, vapor or suspended matter in the air at the workplace, which, according to the current state of knowledge, does not generally impair the health of employees, even in the case of repeated and long-term exposure, usually 8 hours daily, but with an average weekly working time of 40 hours (in 4-shift operation 42 hours per week on average of four consecutive weeks) and does not unreasonably affect their health.

The permissible TLV values for the hazardous substance to be used can be found in the valid TLV value list. This list of TLV values, i.e. "Technical Rules for Hazardous Substances TRGS 900", is published at regular intervals by the Federal Minister of Labor and Social Affairs. The vapors and gases present at the workplace are generally not discharged in the exhaust air pipes of the process systems. They appear in the solvent balance as diffuse emissions.

6.5 Summary

According to the agreement, this compilation of environmental protection regulations deals with the field of activity No. 8 in which the protective coating of electronic assemblies is contained. Afterwards, the plant operator has to make the following decisions in sequence:

1. Requires approval or not according to BImSchG, § 4.

According to the current state of the art, the result is: Not subject to authorization, procedure for the construction and operation of plants in accordance with BImSchG, § 22.

2. Determination of the annual consumption of solvents and comparison with the 31. BImSchV.

Consumption is below the threshold value of 5 t: The annex shall not be subject to the provisions of this Regulation.

Consumption in the range ≥ 5 and < 15 t: The limit values of the 31. BImSchV must be observed, the solvent balance and reduction plan must be drawn up.

Consumption > 15 t/a: According to the current state of the art in the protective coating of electronic assemblies unlikely, possibly as an isolated case.

For the long-term reduction in the area under consideration, energy-intensive exhaust gas cleaning systems with their known side effects will not be used with an increase in coating activities, but preferably "cold" processes and/or low-solvent and solvent-free coating systems. The latter are under development and testing.

6.6 Literature

- TA Luft 2002, joint ministerial journal of 30.7.2002
(GMBI. 2002) Issue 25-29, pp. 511-605, available from Carl Heymanns Verlag KG, Luxemburger Straße 449, 50939 Cologne (Tel. 0221-943730) or from the Internet with address: www.bmu.TA-Luft
- EU Solvents Directive: EUR-Lex: EUR-Lex:Applicable Community law document 399L0013
- 31. BImSchV, www.juris.de, pp. 1 to 39
- Solvents in the metal industry - Guide to accounting, limit values and reduction plan in accordance with 31. BImSchV for operators of degreasing and coating plants; VDMA 2002, available from VDMA, Technology and Environment, Lyoner Straße 18, 60528 Frankfurt, tel. 069-6603-1612

AVOIDANCE OF TYPICAL ERRORS DURING PROTECTIVE COATING

- 1 Application of too high coating thicknesses**
- 2 Double coating**
- 3 Early hermetic casing of coated circuit boards**
- 4 Avoidance of defects in the protective coating**
- 5 Typical fault patterns in the protective coating**
 - 5.1 Chemical causes of error patterns
 - 5.2 Process-related causes of error patterns
 - 5.3 Flow defects

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If the protective coating process of assembled modules is inadequate, various fault patterns can occur which impair the protective effect or generate additional failure patterns.

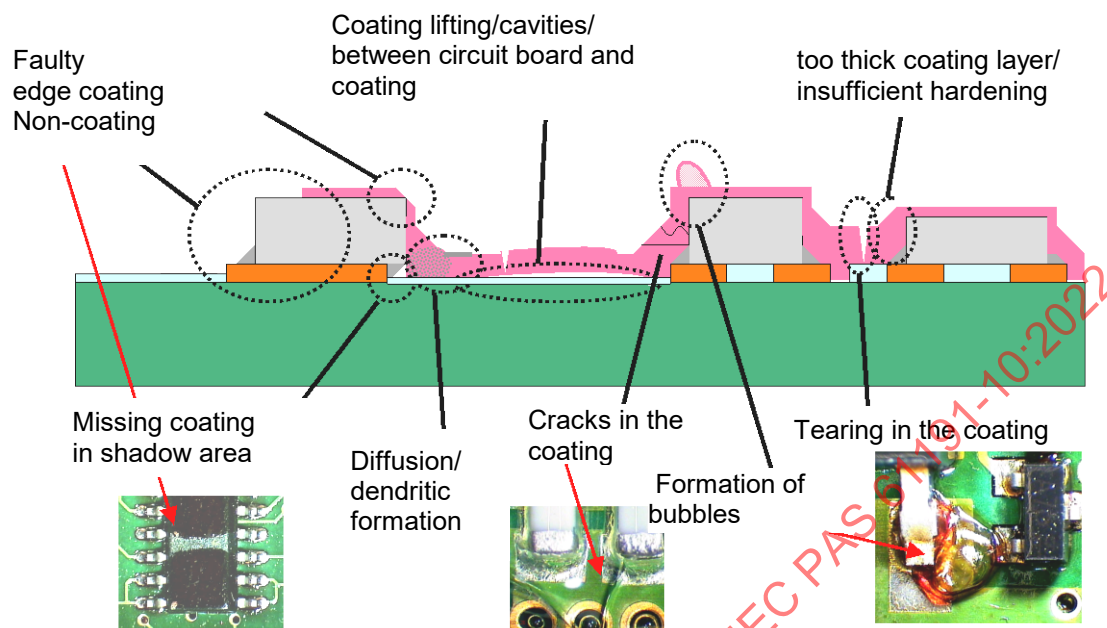


Fig. I1: Incorrect execution of protective coatings

1 Application of too high coating thicknesses

In the case of protective coating of printed circuit boards with thin-film coatings, the rule "a lot helps a lot" is fundamentally wrong! The thicker the layers of protective coating, the slower they dry. Any residual solvents still present can lead to negative phenomena after installation in the devices, one of which is the odor nuisance for the user.

On the other hand, the oxidative drying described above takes considerably longer with thick protective coatings, so that the desired properties, such as adhesion and electrical insulation, especially under the influence of moisture, are significantly deteriorated. There is a particular risk of excessive coating thicknesses in the "brushing" and "spraying" application processes.

Completely contrary aspects apply to thick-film protective coatings. This is where "a lot helps a lot" applies, provided the protective coating is flexible at low temperatures and shows good adhesion to the substrate. In this case, the coating thickness can be several millimeters. The same applies to UV-curable thick-film protective coatings as to moisture-curing thick-film protective coatings.

2 Double coating

In general, the same applies to a double coating as was already mentioned for too high coating layers with thin-film protective coatings. The second coating can usually be applied either shortly after the first (between the wet and sticky state of the protective coating) or after at least two days of drying at room temperature. Under no circumstances should the second coating be applied between the drying phases described, as there is otherwise a risk of "wrinkling".

Due to the high coating thicknesses, thick-film protective coatings do not require a double coating.

3 Early hermetic casing of coated circuit boards

While the tack-free quality of a protective coating is often achieved after just one to two hours of storage at room temperature, oxidatively curing protective coating systems in particular require two to three days for complete hardening/crosslinking at room temperature, depending on the coating thickness applied. According to DIN 46449¹, air-drying protective coatings can only be tested for dielectric strength, tracking resistance, etc. after 96 hours at the earliest.

It should therefore take a few days to dry at room temperature before coated circuit boards are encapsulated. After hermetic encapsulation, the oxidatively curing protective coatings in particular have no possibility of completing crosslinking due to the lack of atmospheric oxygen. The drying process can be accelerated by forced drying of the coated printed circuit boards for 6 to 8 hours at 60 to 80°C, whereby sufficient oxygen supply must be ensured.

4 Avoidance of defects in the protective coating

In order to enable or simplify a complete control of the coating, colorless settings of the protective coatings as well as colored versions that create a clear contrast to the substrate are available. In the case of colorless protective coatings, special fluorescent additives allow easy control of the coating under UV light. Further details can be found in the respective leaflets.

5 Typical fault patterns in the protective coating

5.1 Chemical causes of error patterns

One of the most common defect patterns are flow disturbances of the protective coating in the form of coating-free areas. This is usually caused by soiling of the component surface with oils or greases, which leads to a significantly reduced surface tension. The applied protective coating tries to leave this altered surface and forms a spherical shape on it, resulting in defects in adjacent areas. If there is also silicone on the assembly, this effect is further intensified. This means that within a few minutes coating-free areas can be created over a large area or the housings of the ICs can become completely coating-free.

With partial coatings, this phenomenon has the further very unpleasant side effect that the displaced protective coating runs into critical areas free of coating, e.g. beyond insertion edges in plug sockets or microswitches etc.

This effect of the coating-free areas occurs with all protective coatings, but especially with water-thinnable coatings, which react extremely sensitively because of their own high surface tension. However, washing such contaminated components before coating involves the risk of contamination of the entire bath and requires special solutions.

The following table lists individual error types with chemical causes and possible remedial

¹ DIN 46449 (1970-04) "Insulating varnishes and insulating resin materials for electrical purposes; finishing varnishes, test methods".

measures.

Tab. 11: Types of faults in the protective coating based on chemical causes

Error type	Cause	Possible remedy
Flow defect (see chpt. I 5.3)	• Silicone release agent for IC housings; • Cream for fingerprints; • Greases, oils, process-related; • Silicone soldering aids; • Silicone adhesive for component mounting; • Conductive adhesive; • Solder resist incompletely cured or equipped with non-stick additives.	• Plasma cleaning/activation; • Manual, selective cleaning with IPA and brush; • If possible, then clean in an installation with aqueous cleaner; • Maintain positive process parameters once; no coating change; maintain curing parameters.
Destroyed coating	<i>Flux residues or even unreacted flux accumulations do not only lead to disturbance of the lacquer image, but to destruction of the lacquer and thus to protection. Even worse is the formation of dendrites, which form as soon as moisture penetrates and current is present. The destroyed coating layer is permeable to moisture like a sponge and thus accelerates the process. Often flux collects on larger pads, where it is apparently prevented from evaporating.</i>	
Bubble formation in the coating	• Moisture in the assembly or in the ambient air; • Flux reinforces the process; • Influence of the system and the viscosity of the coating.	• Dry the assembly; • Eliminate air access to the system; • Regulate viscosity.
Lack of adhesion, dissolution	• Moisture in the assembly and bubbles between the assembly and the coating; • Flux reinforces the process. <i>All influences listed under "Flow defects" lead to a reduction in adhesion. Unfortunately, this only becomes apparent after the coating has completely cured or during operation of the assembly.</i>	• Plasma cleaning/activation; • Drying, cleaning and drying the assembly • Manual, selective cleaning with IPA and brush; • If possible, then clean in an installation with aqueous cleaner; • Maintain positive process parameters once; no coating change; maintain curing parameters.
Barcode unreadable	• Washing process; coating solvent	• Use washable ink.
Surface of solder side contaminated with flux	• Assembly not cleaned.	• Aqueous cleaning.
Formation of a wrinkled skin	• Coating application too thick; • Second coating; • Coating-repellent substrate; • Drying too fast.	• Thinner application or more thinning of coating; • Extend intermediate drying; • Extend RT drying.
Formation of spun threads	• Quick-drying coatings; • Acrylic coatings.	• Add dilution up to 150 %; • Reduce the atomizing air as much as possible; • Reduce nozzle spacing.
Crystallization, inhibition, wrinkling	• Incompatibilities between coating and substrate; • Chemical reaction of the EP coating with flux.	• Aqueous cleaning.

Error type	Cause	Possible remedy
Lack of adhesion of silicone coating	The presence of inhibiting substances on the assembly, for example sulfur from rubber gloves.	- Plasma cleaning/activation; - Sulfur-free gloves.
Lack of adhesion of thermosetting 1K-PUR coatings	The presence of inhibiting substances on the assembly, e.g. solder resist.	- Plasma cleaning/activation; - Change solder resist.
Bubble formation on component	- Heating during the drying process. Displacement of the air bubble under components by capillaries; - Chemical reaction with flux; - application error.	
Interruption of switching contact, failure	Grease in the switch dissolves with manual brush cleaning of the solder side with IPA, distributes itself and occupies contact surface.	Do not immerse the assembly completely, but brush off the solder side wet and then rinse it in such a way that the switch remains dry.
Cracking on the component	Relay or LED housings made of PS or PMMA are attacked by various solvents and detergents.	- Component made of resistant materials; - Solvent-free thick-film coatings.
Cracking of device plugs	Cleaning, defective material.	Plug made of suitable material.

5.2 Process-related causes of error patterns

In addition to the chemical causes for the occurrence of defects during coating, process-related causes must also be taken into account. Often the errors that occur are a combination of both, which means that remedial measures do not take effect immediately. The following table tries to show individual error types with process-related causes and possible remedial measures.

Tab. I2: Types of faults in the protective coating based on process-related causes

Error type	Cause	Possible remedy
Coating outside the coating limit	Flow of the coating by lowering the viscosity in the drying oven.	- Increase pre-drying time; - Avoid thermosetting coatings.
Coater after drying 5 h, 60°C	Coating tanks under component not fully dried.	- Reduce gap distance; - Increase drying time; - Change coating type.
One-sided accumulation of coating	Coating flow due to inclined bearing after coating the solder side.	Plan the insertion edge for storage in the magazine.
Critical component coated	Insufficient distance to coating surface.	- Use of wash-tight components; - Planning layout; - Sealing with pasty coating bead.
Oblique components hinder the coating process	Soldering process.	Soldering aids.
Solder balls on the assembly interfere Sealing of the form cup	Soldering process.	Change soldering process parameters.

Error type	Cause	Possible remedy
Sealing of the coating form cups disturbed (housing does not fit onto the assembly)	Adhesive residues from bonding capacitors and other components.	Use low-viscosity 1-component adhesive instead of hot-melt or pasty synthetic resin adhesive (e.g. PUR Adhesive 1810).
Dirt particles on the assembly	Soldering process, transport packaging, handling, etc. <i>Particles only become clearly visible after the coating has dried and reduce the quality, especially when conductive particles are involved.</i>	Blowing off with compressed air distributes the dirt particles in the environment. Terminate the cause. Wash before coating.
Unwanted coating of a coating-free area	- Layout design; - Application method too imprecise; - Flow defect due to contamination.	Adapt the layout to the specifications of the system builder.
Moving parts too close to the coating limit	Layout design.	- Change layout; - Soldering aid.
Too small distance between component and later mounted housing	Layout design.	Change layout.
Coating of critical components	- Open vias; - Press-fit holes; - Application procedure. <i>On the component side, drop-shaped elevations form when the soldering side is coated, which causes leaking components to coat upon contact.</i>	- Close vias; - Dispense holes with 1K pasty lacquer.
Drop in resistance during functional climate test	Open vias with voltage potential under components when using AQ coatings because of their conductivity in uncured condition.	Use a different coating system
Scratches, bent or damaged components	- Packaging defective; - Equipping error.	- Timely planning of packaging; - Improvement of the final inspection before coating; - Change equipment.
Coating runs into plug	Coating runs in sharp corners by capillary force up to several cm along the corner. <i>The connector must be sealed thinly to the assembly.</i>	- Add exactly the quantity required for sealing - Connector cannot be sealed all around with 1-component pasty coating due to coating thickness and effort.
Barcode unreadable	- Washing process of the assembly; - Influence of the coating.	Solvent-resistant ink

For illustration, some typical error images are shown in Fig. I2.

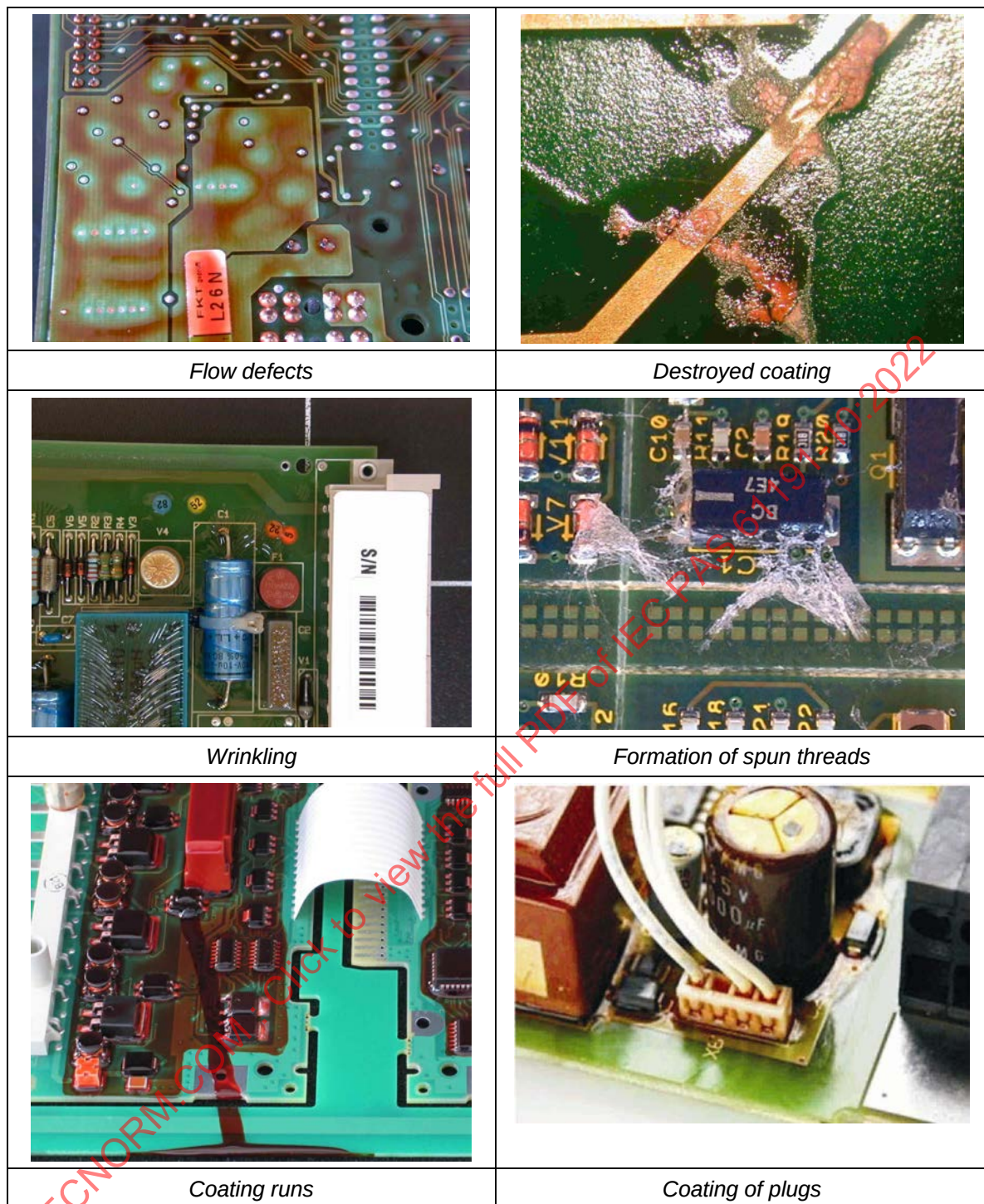


Fig. 12: *Examples of typical error patterns*

As further information for the process sequence of the protective coating should be observed:

- Inclined storage of selectively coated assemblies leads to subsequent running of the protective coating. The result can be an unwanted coating of critical components such as plug sockets, switches, etc;
- Immediate exposure of the freshly coated assemblies to draughts can cause orange peel skin;

- To prevent the formation of air bubbles in the protective coating by thermal expansion of the air under the component, the protective coating must either be dried immediately after coating in the drying oven or it must be dried at room temperature until the skin is hard enough to prevent bubbles;
- Protective coating containers must be closed tightly immediately after use, especially with thick-film protective coatings, because these react quickly with ambient air;
- Rapid immersion during vertical immersion leads to coating runners. Parallel immersion and hanging also because the protective coating accumulates behind component surfaces and runs off with a delay;
- Water-based coating materials must not freeze because of damage to the protective coating.

The small insight into the subject of defect patterns provided in the previous chapter is intended to sensitize the assemblers who protect their electronic assemblies by means of coating. Many of the fault patterns shown can be reduced or prevented in the run-up to planning by appropriate measures (for example the determination of the distance between the coating surface and the critical components, the selection of the suitable protective coating, the suitable equipment, the question of cleaning open through-plated holes, etc.). The timely conduct of discussions with specialists, protective coating manufacturers, plant constructors or service providers in order to avoid errors while taking experience into account helps to save time and costs.

5.3 Flow defects

Electronic assemblies undergo a multitude of production processes during which they come into contact with chemical substances. These leave behind impurities which can often lead to leveling problems with protective coatings or encapsulation. A flow defect occurs when the protective coating does not remain in the liquid state at the applied locations, but is removed from them and accumulates in heaps elsewhere. The reason lies in the different surface energies of both materials. The wettability with protective coating or casting compound is greatly minimized in contaminated areas.

Common causes:

- Flux residues (resins or activators),
- Grease (fingerprints from hand cream),
- Salts (tin salts or fingerprints),
- Release agents (silicone, Teflon^{TM2} on IC housings),
- Silicone-based bonding,
- Solder resist (non-polar, finely filled),
- Print material (oligomeric components),
- Other causes.

Especially injection molded components show strong dewetting on their surface. These

² Eine Marke von: The Chemours Company FC, LLC, Wilmington Del., US

result from mold release agents used in the overmolding process. The release agents are implemented in the housing parts, which is why cleaning does not usually bring any improvement.

The same applies to adhesion problems caused by non-polar, e.g. finely filled solder resist and oligomeric components that diffuse out of the base material and are hardly detectable on the print surface.

Test/measurement:

The contact angle measurement can be used to determine in the laboratory before coating whether the protective coating and substrate will have a wetting problem or how good the wetting actually takes place. Comparative inks of defined surface energy are used for this purpose.

Remedial measures:

In case of contamination, especially from the soldering process, cleaning the assembly in wet chemical baths can help. In the process, the interfering foreign substances are removed primarily by means of ultrasound. The cleaned substrate can then build up adhesive forces for protective coating. The assembly must be washable. However, cleaning does not always lead to success and must always be tested beforehand.

The soldering issues "no-clean" and "lead-free", which have been much discussed in the past, have often brought about an aggravation rather than an improvement in the situation. The contaminants from these modern processes have become more aggressive and more difficult to remove.

A frequently used method for the removal of progression disorders is the manual reworking of the removed areas. This however is not recommended without some criticism as the defects indicate the existence of foreign materials. Overcoating includes these and accepts possible failures under the protective coating.

If the flow problems are caused by silicone adhesive used for fixing, only a change of material, e.g. to silicone-free PU or hot melt adhesives, can help.

TESTING METHODS FOR THE PROTECTIVE COATING

1 General verification of the protective coating

2 Methods for testing climate resistance

2.1 Water immersion test

2.1.1 Execution

2.1.2 Evaluation for uncoated assemblies

2.1.3 Evaluation for coated assemblies

2.2 Coating Reliability Test (CoRe Test)

2.2.1 Application

2.2.2 Implementation and results

2.2.3 Evaluation

2.3 Climate-cycle test

2.4 Condensation water test

3 Methods for testing coating results

3.1 Coating adhesion

3.2 Coating thickness

3.3 Special features for surface modifications

4 Methods for testing and designing the drying of protective coatings by thermal analysis

4.1 Problem definition

4.2 Procedure

4.2.1 Measuring principle

4.2.2 Evaluation

4.2.3 Sample preparation

4.3 Application examples

4.3.1 Influence of the thermal stability of solder resist masks on solder bead adhesion

4.3.2 Curing behavior of protective coatings

4.3.3 Thermal resistance