



BSI Standards Publication

Printed board assemblies

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

National foreword

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PUBLICLY AVAILABLE SPECIFICATION



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

INTERNATIONAL
ELECTROTECHNICAL
COMMISSION

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PRINTED BOARD ASSEMBLIES –**Part 10: Application and utilization of protective coatings for electronic assemblies**

FOREWORD

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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:

This PAS was approved for publication by the P-members of the committee concerned as indicated in the following document

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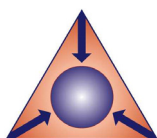
for the

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”



GfKORR – Gesellschaft für Korrosionsschutz e.V.

CONTENT

Part A INTRODUCTION

Part B 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

Part C CLASSIFICATION OF 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
 - 1.7 UV acrylic hybrids
 - 1.8 Thixotropic protective coatings
 - 1.9 ORMOCER[®]s
 - 1.10 Parylenes
- 2 Subdivision according to solvent
- 3 Subdivision by drying and curing mechanism
 - 3.1 Physically drying coating materials
 - 3.2 Oxidatively drying coating materials
 - 3.3 Chemically curing coating materials
 - 3.4 (UV-)radiation-curing coating materials
- 4 Subdivision according to coating thickness

Part D 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
- 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
- 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

Part E 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 NoClean fluxes
 - 4.3 Residues from the soldering process
 - 4.4 Detection of residues
- 5 Drying parameters
- 6 Keeping areas clear and exposing areas

Part F SUBSTRATE AND PRETREATMENT OF PROTECTIVE COATINGS

- 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
 - 6.1 ZESTRON® Flux Test
 - 6.2 ZESTRON® Resin Test
 - 6.3 SIR measurement
 - 6.4 Surface tension
 - 6.5 Technical cleanliness
- 7 Implementation of the cleaning processes
 - 7.1 Cleaning types
 - 7.2 Cleaning systems
 - 7.3 Microphase Cleaner
- 8 Optimization of the cleaning processes

Part G APPLICATION METHODS FOR PROTECTIVE COATINGS

- 1 Subdivision of the application procedures
- 2 Application by brush or brush method
- 3 Application by spray cans
- 4 Application by spraying
- 5 Application by dipping processes
 - 5.1 Vertical dipping
 - 5.2 Horizontal dipping
- 6 Flood method application
 - 6.1 Form cup flooding
 - 6.2 Form cup
- 7 Application by spray process
- 8 Automatic and selective coating in the casting process
 - 8.1 How the SelectCoat® process works
 - 8.2 Closed and circulating coating supply
 - 8.3 Software for the coating system
 - 8.4 Process control
 - 8.5 Coating system
 - 8.6 Non-contact jetting with the PreciseCoat® technology

- 9 Application via dispensing procedure
- 10 Application via vacuum process

Part H HANDLING PROTECTIVE COATINGS DURING PROCESSING

- 1 Requirements for coating rooms and equipment
 - 1.1 Overview and definition
 - 1.2 Explosion-protected areas
 - 1.3 Storage of coating materials
 - 1.4 Mixing and staging areas
 - 1.5 Coating equipment
 - 1.6 Extraction and ventilation in rooms and areas
 - 1.7 Evaporation and drying rooms or areas
 - 1.8 Processing of UV-curing coating systems
 - 1.9 Operation
 - 1.10 Rules and regulations
- 2 Monitoring processing parameters
 - 2.1 Viscosity and flow time
 - 2.2 Flow time and temperature influences
 - 2.3 Viscosity and temperature
- 3 Contamination
- 4 Maintenance of dipping systems
- 5 Aging of protective coatings
 - 5.1 Coating aging
 - 5.2 Dust and dirt absorption
 - 5.3 Solubilizing substances not related to coating
 - 5.4 Service life extension
- 6 Environmental protection with regard to protective coating
 - 6.1 Regulations and laws for air pollution control
 - 6.2 EU Solvents Directive (VOC Directive)
 - 6.3 Technical instructions (TA) air
 - 6.4 Hazardous substances in the workplace
 - 6.5 Summary
 - 6.6 Literature

Part I AVOIDANCE OF TYPICAL ERRORS DURING PROTECTIVE COATING

- 1 Application of too high coating thicknesses
- 2 Double coating
- 3 Early hermetic capsules 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

Part J TESTING METHODS FOR PROTECTIVE COATING

- 1 General verification of the protective coating
- 2 Methods for testing climate resistance
 - 2.1 Water immersion test
 - 2.2 Coating Reliability Test (CoRe Test)
 - 2.3 Climate-cycle test
 - 2.4 Condensation water test
- 3 Method for testing coating result
 - 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
 - 4.3 Application examples

Part K REPAIR OF COATED ASSEMBLIES

- 1.1 Stripping of assemblies
 - 1.1 Chemical coating stripping
 - 1.2 Mechanical coating stripping
- 2 Soldering through of coatings
- 3 Repair coating

PART L BIBLIOGRAPHY

PART M LIST OF AUTHORS

PART N COMPARISON OF THE GUIDELINE WITH THE IPC MANUAL

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 paths. 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

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.

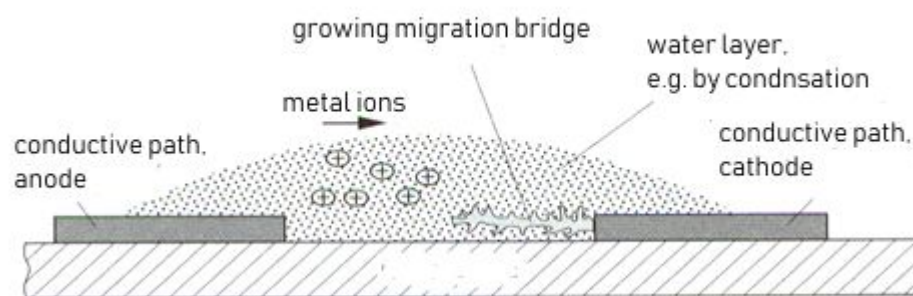


Fig. B1: Model of the development of a water-related electrical disturbance:
 (a) There is charge transport in the liquid medium water
 (b) Metal ion transport to the cathode can cause dendrite growth, i.e. metallic and oxidic material deposits are formed

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.

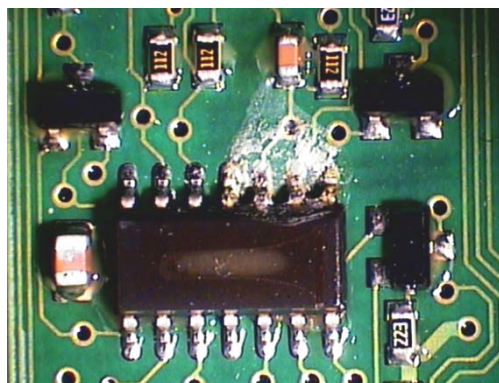


Fig. B2: Possible fault pattern on an assembly after electrical operation with clear condensation (white-colored area shows a large accumulation of corrosion products)

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.

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
 - 1.6.2 Crosslinking systems and product groups
- 1.7 UV acrylic hybrids
- 1.8 Thixotropic protective coatings
- 1.9 ORMOCER[®]s
 - 1.9.1 Material class
 - 1.9.2 Properties
 - 1.9.3 Application in microelectronics
- 1.10 Parylenes
 - 1.10.1 Introduction
 - 1.10.2 Parylene polymers: chemistry and processing
 - 1.10.3 Properties of Parylenes
 - 1.10.4 Examples of Parylenes applications
 - 1.10.5 Health and Safety aspects

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 diallylphtalate. 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: $\text{R-NCO} + \text{H}_2\text{O} \rightarrow \text{R-NH-COOH}$ (unstable carbamic acid) $\rightarrow \text{CO}_2$ (gas) + R-NH_2 (amine intermediate) followed by: $\text{R-NH}_2 + \text{OCN-R}'$ (further isocyanate molecule) $\rightarrow \text{R-NH-CO-NH-R}'$ (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.

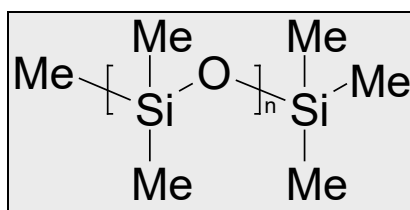


*Fig. C1: Bond ratios / polymer structure of silicones (dimethylpolysiloxane).
(The number $n+1$ of Me_2SiO groups describes the degree of polymerization)*

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-

ow 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.

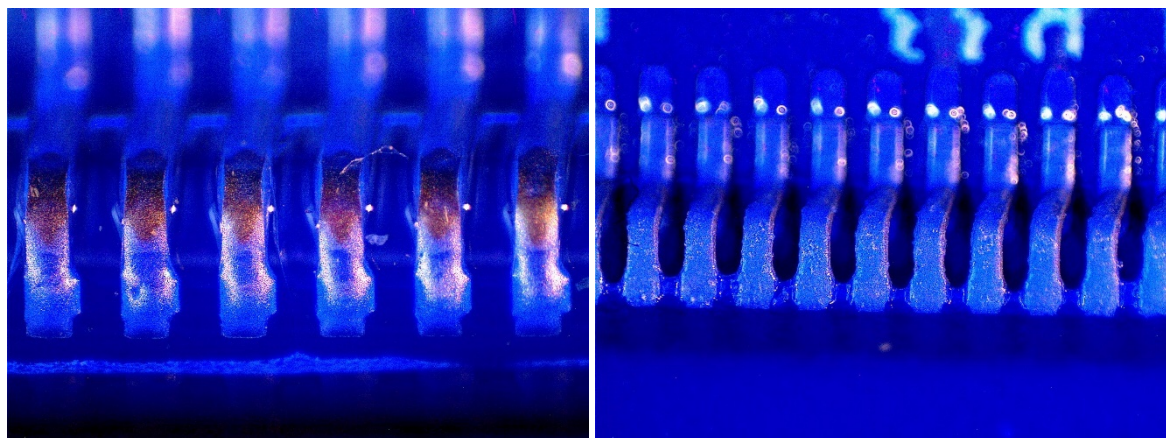
In the coating processing industry, the pseudoplastic and thixotropic flow properties are often used to apply high coating film thicknesses with low tendency to run off on vertical surfaces.

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.

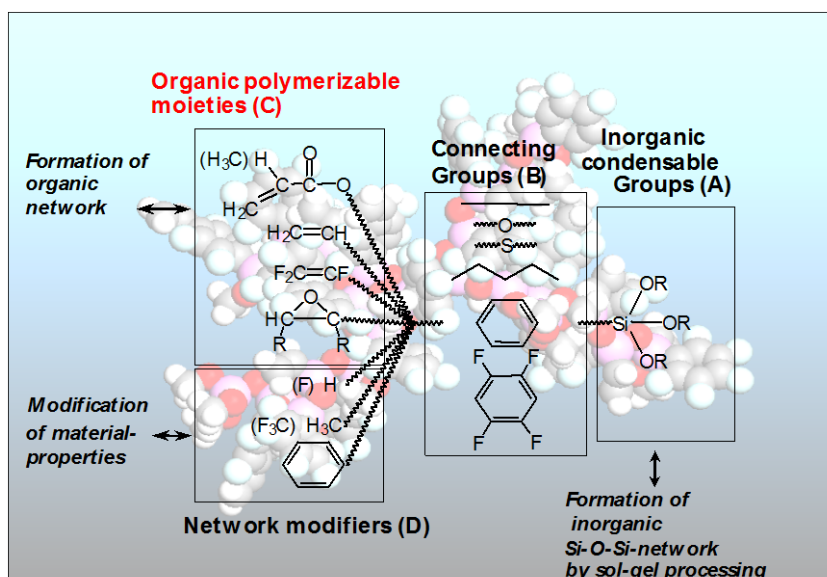


Fig. C2: Schematic drawing of typical starting products (alkoxysilanes) for the production of ORMOCER[®]s, e.g. for (micro-)electronics⁸

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.

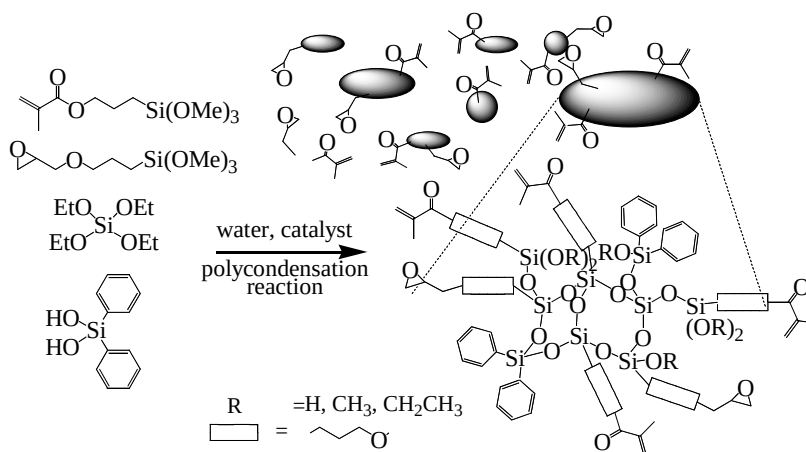


Fig. C3: General scheme of ORMOCER[®]A-synthesis for (dielectric) passivation⁹

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.

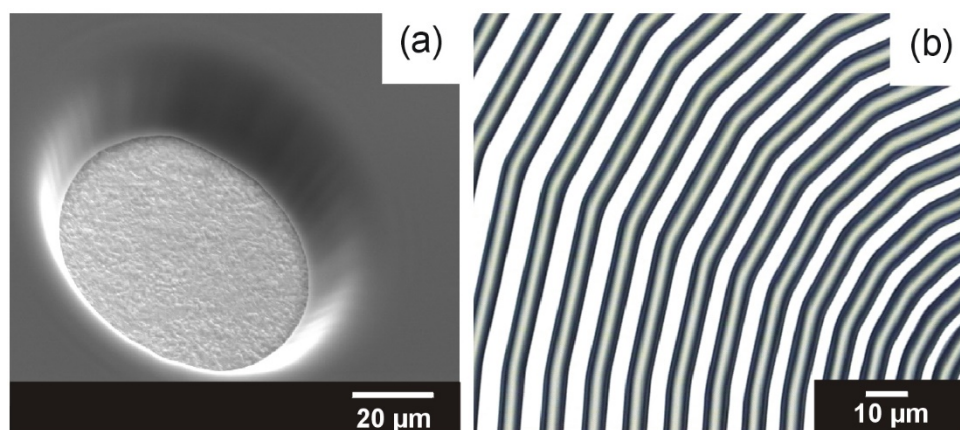


Fig. C4: (a) SEM image of a through-hole in ORMOCER®A on a Ti/Cu/Ti metallization layer; (b) Light microscope image of dielectric-passivated Guard rings (dark) in Si detectors on an Si/SiO₂ substrate (light). The layers were applied by centrifugation

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°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.

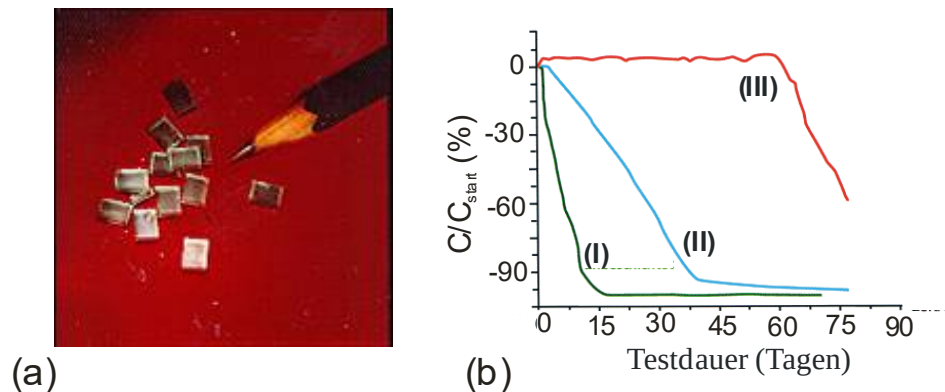


Fig. C5: (a) passivated thin film capacitors; (b) change in capacitance of uncoated (I), conventionally encapsulated (II) and ORMOCER®A coated (III) thin film capacitors depending on the test duration. The test conditions were 95 °C / 100 % relative humidity

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 µm) 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 µm 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.

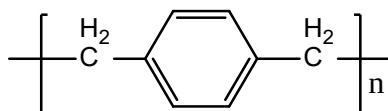


Fig. C6: Poly (p-xylylene) or PPX

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.

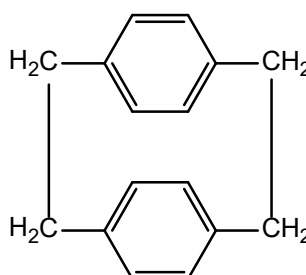


Fig. C7: Cyclic dimer of p-xylylene or di-p-xylylene (DPX) or paracyclophane

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.

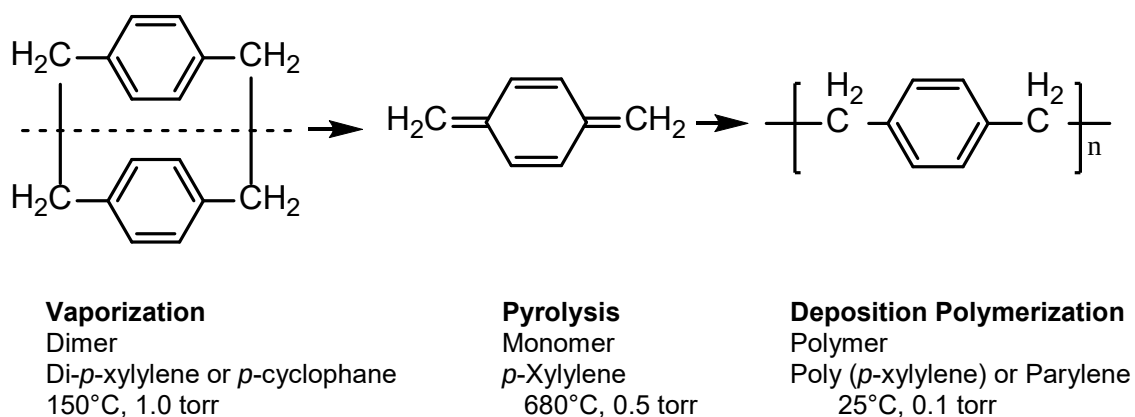


Fig. C8: Parylene vapor deposition polymerization (VDP) process.

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.



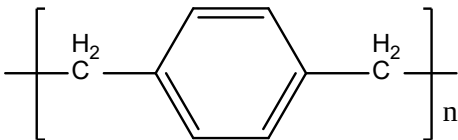
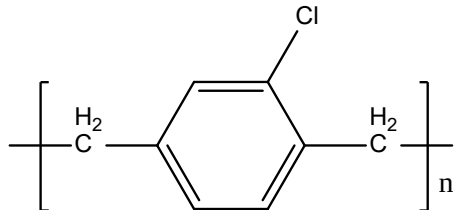
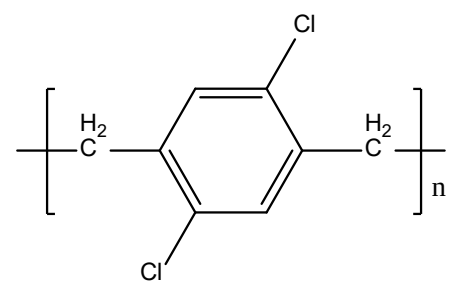
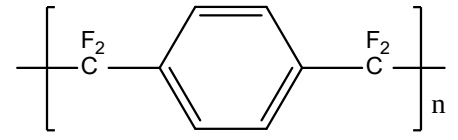
Fig. C9: A commercial Parylene Deposition System, SCS PDS 2060PC (Photo courtesy of Specialty Coating Systems, Inc.)

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.

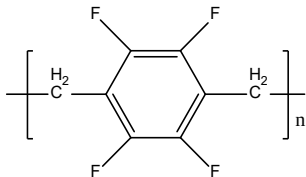
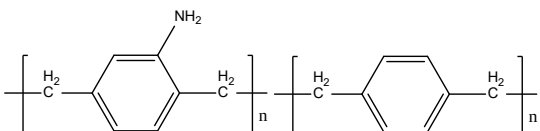
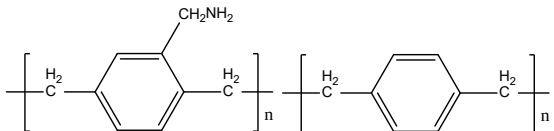
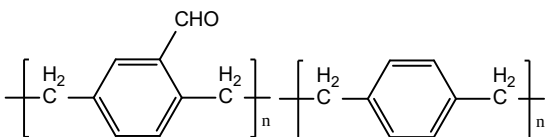
Among the various Parylene variants that were developed or advertised until now, only four of them (Parylene N, Parylene C, Parylene D and Parylene HT) have found wide commercial application and are shown in Table C4 with their commercial or alternatively known names. There are other Parylene types (Table 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
	- Parylene N
	- Parylene C
	- Parylene D
	- 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.

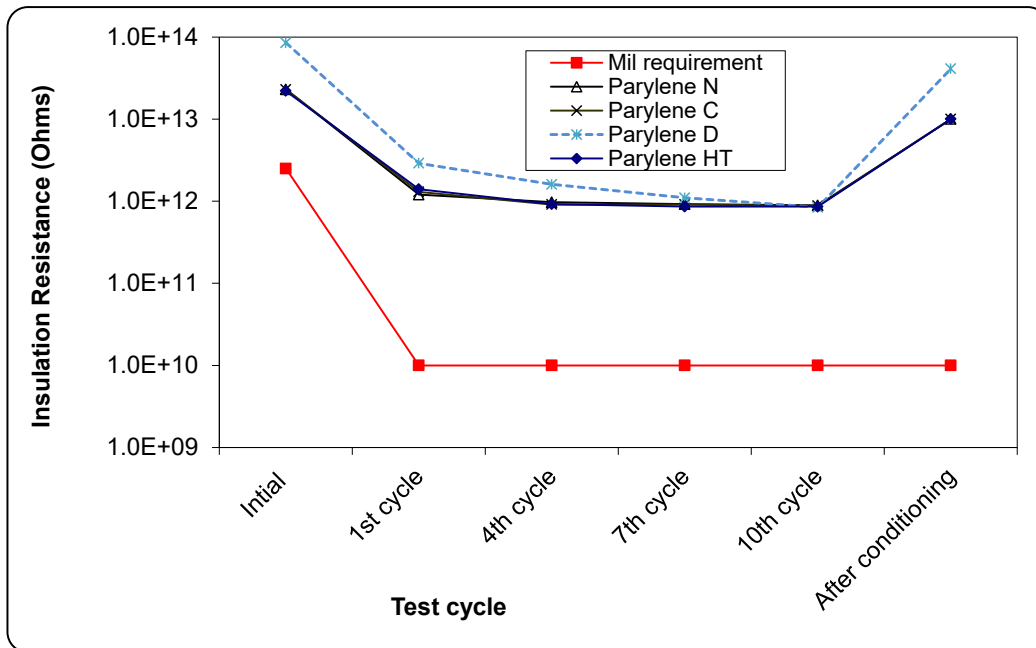


Fig. C10: Moisture insulation resistance of Parylenes

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.

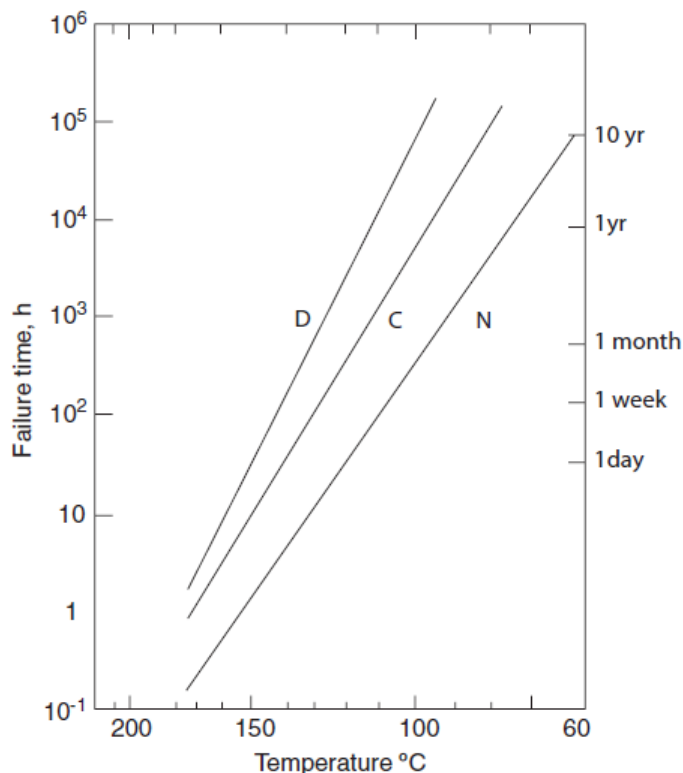


Fig. C11: Useful lifetime of Parylenes N, C, and D as a function of temperature in air (Failure = 50% loss in tensile strength)

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.