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# THE PLASMA PRETREATMENT OF PLASTICS

## The plasma pretreatment of plastics

### 1. Introduction

A method of obtaining adherent compound structures which is more environment-friendly and operationally safe than conventional processes is the use of low-temperature plasmas. By contrast with conventional methods, these open up new possibilities for pretreatment as a means of promoting adhesion.

- Grease, oil, wax and even silicones can be removed leaving no residues whatsoever.
- Plastic surfaces can be roughened without harming the material or the use of aggressive chemical baths.
- The wetting capability of homopolar plastics with adhesives, paints, printing inks, etc. can be radically improved.
- Poorly defined surfaces can be given a very fine coating of primer.

In the process, the workpieces undergoing treatment are exposed for a few seconds or minutes to a "cold" plasma which is produced in a vacuum chamber by applying an electrical voltage to the respective process gas. The gaseous phase of the process is easy to monitor and control, and even workpieces of extremely complicated shapes can be treated.

Since the reaction medium is heavily diluted, only relatively small quantities of chemicals are used, normally non-hazardous gases such as oxygen, argon, helium, ethylene or tetrafluoromethane. Furthermore, since these are used in sealed chambers, no hazardous gases or fumes are produced at the workstation.

By selecting the appropriate gas and adjusting the plant parameters accordingly, processes can be tailor-made to meet the specific application of the user. Some examples, taken mainly from the electrical and automotive industries, which describe the plasma process and its economical incorporation in the production sequence are given below.

## 2. Improving adhesion by plasma treatment

A number of different plasma processes are used, depending on the application concerned, i.e.

a) To remove coatings which reduce adherence in the form of e.g. oil, grease, wax (e.g. mould releasing agents on plastic components), silicones or tensides, oxidising gases are generally used such as oxygen or mixtures of oxygen and tetrafluoromethane; inert gases are generally used for parts which are sensitive to oxidation/13/.

b) Plastic surfaces can be roughened with argon or oxidising plasmas (in the case of a partially crystalline polymer structure), thereby markedly increasing the contact areas/15/. Process duration: 8 - 20 mins.

c) The physical stabilisation of the contact surface can be achieved on certain plastics, e.g. polyethylene, by cross-linking the individual polymer chains by treatment with inert gas plasmas/15/. Process duration: 20-60 mins.

d) As a consequence of the low surface tension of many types of plastic, such as PP, PEEK, EPDM, PE, PBTP, LCP and silicone rubber, their wettability with adhesives is inadequate. With oxidising plasmas, it is possible for polar chemical functional groups, such as -OH, -C=O, -COOR, to be fixed on the surface, thus achieving the optimum surface tension for bonding purposes /13/. The surface tension can be determined by means of wetting angle measurement, a wetting balance or, quite simply, by applying testing inks. Process duration: from a few seconds to 3 mins.

e) Finally, materials with surface characteristics which are difficult to define, e.g. recycled plastics, can be given a reliably adherent coating of plasma polymer having a defined surface tension (as an adherent agent). Duration of process: 2 - 5 mins.

### 3.1 Roughening of plastic surfaces

If the above-mentioned etching process is carried out on partial-crystalline plastics for a prolonged period and with a high degree of intensity, the surface becomes roughened, since the amorphous areas are removed more rapidly than the crystalline areas /15/. Alternatively, all types of plastic can be roughened with inert gas plasmas, e.g. argon, provided the conditions are such that the surface can be bombarded with ions which are sufficiently high in energy, e.g. in special ion etching plants.

#### Case study No. 1:

After a 10-minute period of treatment in a plasma plant, plastic bushes possess an adherent surface and are sealed with rubber, with an extremely low reject rate. As a result, the user was provided with an acceptable alternative to the previous process of immersion in a glazing bath, typically containing chromic or chromosulphuric acid, which had been banned because of the environmental problems it caused.

#### Case study No. 2:

Plastic components for indicating instruments can be given matt, non-reflective surfaces with plasma treatment lasting 15 minutes.

### 3.2 "Activation" of plastic surfaces / 23, 24, 25/

The surfaces of many industry-related plastics such as polyethylene, polypropylene, polybutylene-terephthalate, EPDM (ethylene-propylene-diene-terpolymer), PEEK (polyaryletherketone) and LCP (liquid crystal polymer) are homopolar to the extent that they cannot be satisfactorily wetted with paints (particularly water diluted), printing inks or adhesives. By plasma treatment with gases containing oxygen or nitrogen, polarchemical functional groups can be fixed on the plastic surface.

The mechanism should correspond to an incomplete oxidation of the polymers, whereby hydrogen atoms are replaced by OH-, -C=O, O=C-O- or -NH, -NH<sub>2</sub>-groups and similar, without causing the disintegration of the carbon atom chains. This imposes a need for the process to be controlled with care, in order to achieve the necessary polarity (or wettability) of the surface for the application concerned, while avoiding the formation of short-chain surface coatings, arising from "over-activation", which impair adhesion. As a rule, however, a sufficiently large process window to ensure dependable production, identified by the parameters of pressure, output and duration of treatment, can be defined. At all events, care must be taken to ensure that the plasma treated parts are "active" in the truest sense of the word on leaving the reactor. The characteristic of polarity (wettability with polar liquids) changes markedly in the course of time from a few days to a few months.

Usually, polarity diminishes with increasing storage time, which may be due to a variety of causes. During storage, it is possible for homopolar coatings to form on the surface e.g. through contamination from the surroundings (oil mist, softening agents from packaging films or diesel soot from forklift trucks) or through the migration of active constituents from the interior of the plastic to the surface. In addition, it is suspected that the polar chemical functional groups, at least to some extent, migrate towards the interior of the plastic through the movement of the polymer chains and are thus lost as adhesion-promoting agents.

In certain cases, an increase in wettability has even been observed /26/, probably due to the retrospective oxidation of the surface coating of the plastic through the reaction of the oxygen in the air with residual reactive centres (e.g. radical points).

It is therefore advisable to carry out the plasma activation immediately before the application of paint, foam rubber or adhesive.

#### Case study No. 1:

Interior motor vehicle components made of polypropylene are pretreated for painting by means of oxygen plasma for a period of two minutes in a continuous-flow plant. The throughput rate of the specially designed tandem-type installation is matched to the painting robots arranged downstream. Two pallets leave the plant every two minutes (see Fig. 2).

#### Case study No. 2:

Polycarbonate reflector components are treated in the same plant with O<sub>2</sub> plasma for a period of six minutes. As a result, the adhesion of the metallised aluminium as a reflective coating is radically improved.

Case study No. 3:

The housings for accelerator output sensors, made of PBTP, are pretreated in a small, simple tubular reactor before the application of adhesive. So far, it has been possible to save 1500 kg of CFCs a year.

Case study No. 4:

The housings for capacitors, relays and switches are subjected to six minutes of oxygen plasma treatment in a large bulk goods plant (capacity 60 litres) prior to being sealed with epoxy resin and/or printing (see Fig. 3).

Case study No. 5:

Cavities in large polyethylene mouldings are internally activated with an oxygen plasma before being filled with foam, in order to ensure that the foam adheres properly.

Case study No. 6:

Vehicle bumper claddings made of PP/EPDM are pretreated for painting in a large process chamber, with a capacity of four cubic metres, with an oxygen plasma for a period of 30 seconds. Output from the plant is around 80 units an hour.

Case study No. 7:

Toy components made of ABS are prepared for painting with water-based paints with O<sub>2</sub> plasma for a period of five minutes. As a result, the subsequent processing required to avoid stress cracks, which is necessary with solvent based paints, was eliminated.

### 3.3 Precoating by plasma polymerisation

Macromolecular coatings deposited by low-temperature plasmas, known as "plasma polymers" (by common usage although somewhat misleading), possess a number of fascinating characteristics, i.e.

1. They can consist of almost any organic substance which can be transferred in the gaseous phase, including even those which cannot be polymerised by conventional methods, e.g. methane, benzene and even ferrocene, hexamethyldisiloxane, etc.
2. Irrespective of the process conditions, the deposited coatings are usually highly cross-linked (and are therefore insoluble), swell only a little or not at all and usually constitute excellent diffusion barriers.
3. By comparison with conventionally produced polymers, plasma polymers are exceptionally thermally stable.
4. Very fine (e.g. in the area of 10 nm), pinhole-free coatings can be applied to substrates of any shape. The thickness of the coating can easily be adjusted by varying the duration of the coating process.
5. In general, the coatings exhibit excellent adherence on most substrate materials, provided the process is properly controlled.

In the light of these noteworthy characteristics, plasma polymers and their production have been intensively researched in the last twenty years /27/.

At present, the following processes are of particular interest for the pretreatment of plastics.

#### 3.3.1 Plasma polymerisation of adhesion-enhancing coatings /27/.

This process represents an interesting alternative to plasma activation, since it permits the production of surfaces with clearly defined, reproducible wetting characteristics, irrespective of the basic material. As a result, even materials which are difficult to define, such as recycled materials, can be pretreated by a standard process to improve adhesion.

It has proved possible to demonstrate that, provided suitable process gases and parameters are chosen, even in large-capacity installations, an extremely high degree of wettability with water can be achieved (although the wetting angle with water can no longer be measured as a result of spread), which is of particular interest from the aspect of water-based paints.

Parts at risk from corrosion, e.g. metal components, can be passivated with a plasma polymer coating immediately after fine cleaning with plasma, then stored for the subsequent application of paints, foam coating or adhesive without any problems.

Case study:

Polypropylene materials of widely varying compositions, and polyethylene, can be "primed" with a plasma polymer coating, which is deposited in two minutes, in such a way as to permit the fault-free application of adhesives, paints or foam coatings.

### **3.3.2 Plasma deposits of conductive coatings**

As a rule, plasma polymers provide excellent insulation, with the result that, as long ago as the seventies, investigations were made into their suitability as dielectrics for capacitors /29/. It is only very recently that the production of electrically conductive plasma polymer coatings has been reported /30, 31, 32/. This is a new field and the related processes are by no means fully developed. Nevertheless, there is every reason to believe that the application of conductive coatings of this type will eventually play a significant role in the electrostatic painting of plastic components.

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