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Dr. Gupta Verlag

61. Jahrgang, November 2008
GFKUED 2 61 (11) 681-748 (2008)
ISSN 0176-1625

Dr. Gupta Verlag, Postfach 10 41 25, 40852 Ratingen
G 4637 Postvertriebsstück

11| 2008

In-line Plasma Treatment of Plastics

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Since 1995 Plasmatreat, which today is a globally operating company, has focused its activities on the development of atmospheric-pressure plasma processes. Openair technology is protected internationally by patents and is employed in almost all fields of industrial production. Without any use of chemicals environmentally friendly, innovative and low-cost surface treatments have been implemented. Materials such as plastics, metals, glass or ceramics are efficiently and effectively cleaned, activated or coated in-line by means of Openair plasma. A brilliant visual appearance after painting, optimum adhesion in plastic joints and high anticorrosive protection in the

1. Introduction

A key technology for the future is the cleaning and activation of the surfaces of materials by means of atmospheric-pressure plasma. The in-line process not only fulfils the growing demands on the adhesive bonding and painting of plastic parts, but also is more economically efficient and more environmentally friendly than many other processes. Whether the product in question is a mobile phone housing or light switch, a mud guard or display, industry must meet steadily rising demands for quality, design and environmental protection and is expending ever more effort on improving its adhesive bonding and painting processes. A decisive factor in all of this is the best possible precleaning and activation of the surfaces to be treated. Pretreatment processes range from ionizing or flame treatment through wet-chemical methods, power wash and the use of primers to mechanical cleaning with ostrich feathers. Despite the expense incurred in these activities the level of waste in production caused by particles of dust is often well over 10 %. Static charges on surfaces, slight but unacceptable remnants of fine dust in deep-seated areas and pollution of the environment are the most common problems in said processes.

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Paper presented at the DKG Trade Conference, 2008
17-18 June 2008, Fulda
Deutsche Kautschuk-Gesellschaft (German Rubber Association) e.V., Frankfurt
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2. Lasting solution

To ensure reliable and durable adhesion of bonded joints and an immaculate visual appearance of coats of paint on plastics a good pretreatment process is absolutely essential. The patented Openair plasma technology developed by Plasmatreat, Steinhagen, as early as 1995 completely eliminates the problems referred to above and replaces environmentally dubious and high-cost cleaning processes. It is equally suitable both for the microfine cleaning of surfaces and for improving adhesion. The systems based on a jet principle operate at atmospheric pressure and with the aid of an arc ignited in the jet and the operating gas, air, generate a plasma which flows at zero potential on to the product to be treated. It contains particles which are sufficiently excited to initiate selective effects on the surface.

3. Plasma – the 4th state of matter

Plasma is the name given to matter at a high, unstable energy level. Energy is input via the solid, liquid and gaseous states of matter. If by means of electric discharge additional energy is fed into gaseous matter electronically excited states are produced. When this occurs electrons can leave their atomic shells and chemical bonds may be broken. This results in the formation of free electrons, ions and molecular fragments, i.e. plasma is produced. To date, however, it has scarcely been possible to use this state at normal pressure due to its instability.

Fig. 1 To ensure an immaculate visual appearance high-grade mobile phone housings are pretreated with plasma prior to painting. The rotary Openair jet achieves operating widths of up to 130 mm. (Photo: Plasmatreat)

Only the process developed by Plasmatreat made its use under atmospheric pressure industrially applicable. By developing and employing special jets it became possible for the first time to use this hitherto scarcely industrially exploited state of matter in production processes, and what's more in-line also in production lines.

4. Electrically neutral plasma beam

The technology is environmentally friendly. The jets are driven solely by air, or if need be with a desired process gas also, and by high voltage. A particular feature is that the emergent plasma beam is electrically neutral and as a result possible applications are greatly extended and simplified. Its intensity is so high that when fixed single jets are employed treatment speeds of several 100 m/min can be achieved. Depending on the power of the plasma jet a single plasma beam can be up to 50 mm long and have a treatment width of 25 mm. The plasma source is moved at a distance of 10 to 40 mm from the surface and at a speed of 6 to 600 m/min relative to the surface of the material being treated depending on the treatment power required.

By using rotary plasma jets an operating width of up to as much as 130 mm per jet at treatment speeds of up to 40 m/min can even be achieved. Apart from the single jets whole rotary systems are also available for pretreating relatively large surface areas. Depending on the application they contain a number of plasma generators which rotate at very high speed. Depending on the diameter and arrangement of the plasma jets areas up to 2,000 mm wide can be treated in a single pass. The typical rise in temperature of a plastic surface during treatment amounts in this case to $\Delta T < 20$ °C.

Plastic surfaces are often chemically unreactive since their long polymer chains exhibit low surface tension and have no or only few functional groups. As a result they undergo adhesive bonding only with difficulty. The ions and free electrons in the plasma beam insert nitrogen and oxygen atoms into the surface of the polymer and functional groups such as –OH and –NH are formed.

The effects of the process on the surface of the material are set out below.

- Activation: It activates the surface by selective oxidation processes and increases the surface tension by a significant factor. Thus, values of up to 72 mN/m are possible on many plastics.
- Discharge: Technically a plasma state is designated as an electrically conducting gas. When the zero-potential plasma beam strikes the surface electric charge carriers on the statically charged workpiece can flow away to earth. In this way static discharge of the surface ensues.
- Cleaning: The plasma flowing at almost the speed of sound brings about the ultrafine cleaning of metals, plastics, ceramics and glass.
- Coating: By adding a precursor selective nanocoatings can be applied in-line. This allows individual tailoring of surfaces according to the requirements of the later properties of the product.

"Overall activation of the surface takes place which has a very positive effect on adhesion", declares the Managing Partner Dipl.-Ing. Christian Buske. "Due to the process of discharging surfaces our plasma system affords cleaning effects that by far surpass those of conventional systems." Here the user exploits the high electrostatic discharge effect of a free plasma beam. This effect is given further positive impetus by the very high speed at which the plasma flows out as a result of which loosely adhering particles are also effectively removed from the surface. From the economic point of view it should be noted that the user can always integrate the jet systems employed "in-line", that is to say integrate them directly into new or already existing production lines.

Fig. 2 Fine Openair jets bring about ultrafine cleaning, high activation and selective nanocoating even when surface geometries are extremely small (Photo: Plasmatreat)

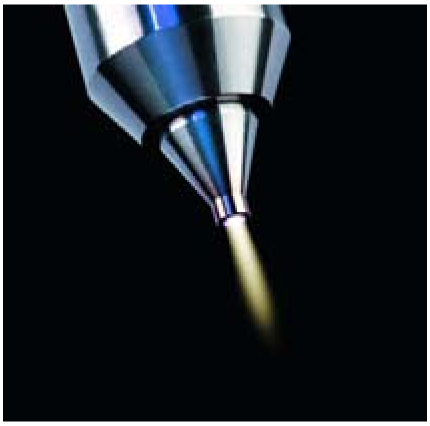
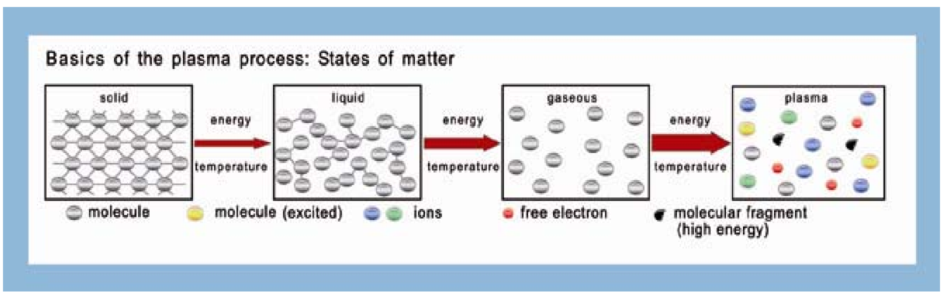


Fig. 3 States of matter (Diagram: Plasmatreat)



5. Environmentally friendly improvement of adhesion

Precision pretreatment and ultrafine cleaning of bonding surfaces by means of atmospheric-pressure plasma allows both the use of modern solvent-free UV adhesives as well as water-based systems. According to Christian Buske, "In this way polycarbonate windows, for example, can be glued into place in the housing shells of mobile phones using solvent-free UV adhesives". The decisive advantage of the technology consists in that hitherto incompatible substrates can be made to stick to one another so that water-based or often even UV-based adhesives adhere to highly adhesive-resistant surfaces, such as nonpolar plastics. Additional pretreatment by means of chemical primers or brushing and rinsing surfaces can be dispensed with completely. As a result emissions of VOCs (volatile organic chemicals) can be avoided from the outset. Treatment is extremely uniform and can be monitored by a process control system.

Fig. 4 Abrasion-resistant imprints are required especially in the food industry. The plasma ensures optimum adhesion properties (Photo: Plasmatreat)

6. Applications

6.1 Plasma in the injection moulding process

Target technologies for the plasma treatment described here include two-component injection moulding as well as preceding and following processes such as painting, adhesive bonding, imprinting and coating surfaces. The process allows the production at low cost of structural components in rigid-flexible composites. To obtain strong joints between normally uncombinable plastics plasma pretreatment can be used to replace expensive ABS/PS, for example, by the lower cost structural component polypropylene (PP) in rigid-flexible composites involving TPU (thermoplastic polyurethanes). The process has equally great potential for fine cleaning and improving adhesion in multicomponent technology for plastic-plastic and plastic-metal composites. It is employed for both thermoplastic-thermoplastic and thermoset applications (thermoplastic-LSR, TP-rubber).

Pretreatment by means of atmospheric-pressure plasma not only allows the joining of incompatible materials, but also process reliability is optimized and high demands for quality are met. The achievable level of adhesion is increased, the effect of processing parameters related to adhesion is lower and the joining of standard materials is improved.

6.2 Pretreatment prior to structural bonding of plastic- car body subassemblies

In bodywork, for reasons of weight saving, individual subassemblies are now no longer manufactured from sheet steel or aluminium, but rather from high-performance plastics. In doing this as part of the assembly process for a subassembly, such as an inner mud guard, for example, single parts are bonded to one another in the course of an automatic joining process. The ability of a plastic to bond well depends essentially on its surface tension which should be greater than that of the adhesive. This is frequently not the case, however, so that a suitable surface pretreatment becomes necessary. Secure adhesion of a two-pack polyurethane adhesive to SMC or PPO (e.g. Noryl) is achieved by pretreatment with plasma which cleans the surface to the limit of detectability and additionally activates it.

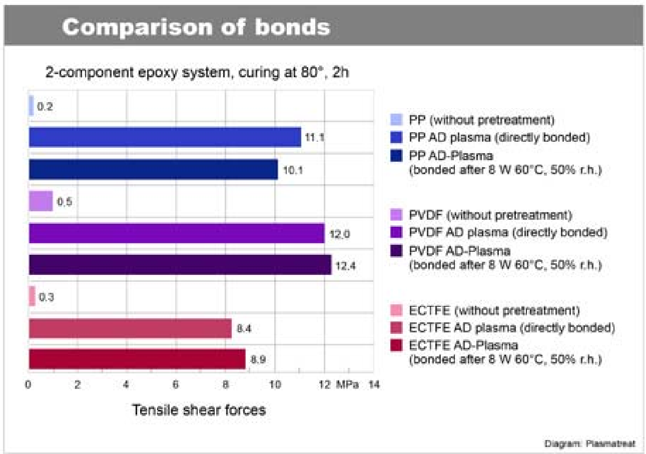


Fig. 5 Tensile shear strengths of plastic joints. (Graphic: Plasmatreat)

Conventional methods of preparing SMC surfaces - such as sanding down or cleaning with acetone - are not only replaced by plasma treatment, but also bonding results are surpassed. After assembly the high-performance thermoplastic and thermoset parts fulfil all requirements with regard to lightweight construction, passive safety, mechanical properties and a first class surface finish. Here, Openair technology can be used as a pretreatment process both for the adhesive bonding as well as for the painting of these subassemblies, as is the case, for example, in vehicles made by BMW and Rolls Royce.

6.3 Bonding of elastomers

For the “Golf IV” Volkswagen developed an additional bonded door seal for preventing wind noise. This self-adhesive seal made from a thermoplastic elastomer (TPE), which as a non-polar material has a very low surface energy, was to be additionally fixed at the ends by means of adhesion points composed of a MS polymer adhesive. To improve the adhesion of the adhesive the elastomer has to be pretreated. The conventional method is the manual application of primer, a process that today is hardly used any more at Volkswagen. A solvent-free system was sought. After comparing different corona and plasma systems, with particular value being attached to great process latitude, VW chose Plasmatreat’s in-line technique.

Michael Steege, former specialist consultant for adhesives and sealants in process engineering at Volkswagen AG, explains the reasons, “When these seals are pretreated with Openair plasma directly prior to the application of adhesive this process replaces several working steps. Due to the highly effective pretreatment not only the otherwise essential precleaning of the bonding surfaces but also the application of solvent-based primer just before bonding is rendered unnecessary. The positive consequence for Volkswagen is that the pot life of a primer no longer need be taken into account. There were no longer any emissions of solvent, nor any logistical pressures in supply. In addition, the Plasmatreat process has the great advantage of reproducibility when the system parameters are precisely monitored.

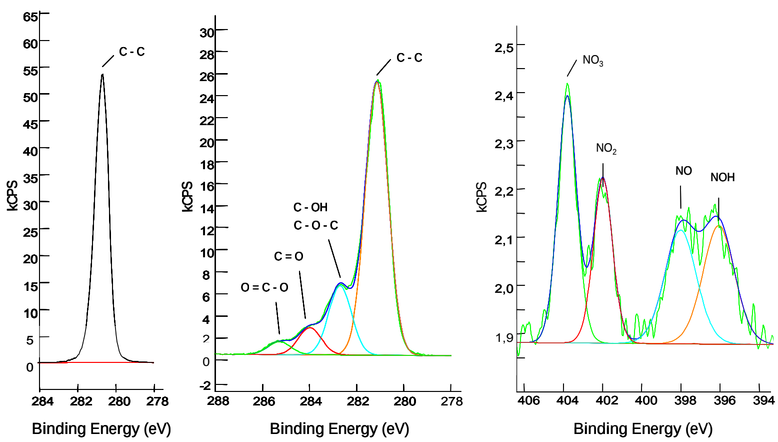
6.4 Plasma prior to painting

The more technologies are in conformity with one another the more common it is that all that counts in the buying decision of the end customer is appearance. Design elements and flawless surfaces become ever more frequently the sole distinguishing features. Switches with laser-etched symbols, high-gloss decorative trim and covers, display windows with a scratchproof coat of paint and glittering fascias, ventilator grilles or handles on glove

Fig. 6 Multicomponent medical technology: The plasma-treated metal insert is subsequently encapsulated in plastic in the injection moulding process. (Photo: Gira)

Fig. 7 Brilliant surfaces are achieved in automotive engineering by pretreatment with atmospheric-pressure plasma prior to painting (Photo: Plasmatreat).

Fig. 8 XPS analysis (X-ray photoelectron spectroscopy) of an untreated polypropylene and on treated with Openair plasma (Diagram: Fraunhofer IFAM)
Diagram 1: PP, untreated (surface energy 27 mN/m)
Diagrams 2 and 3: PP treated with Openair plasma (surface energy up to 72 mN/m)



compartments – even the plastic parts in the interiors of automobiles today are provided with the most expensive coats of paint.

Another example is the painting of mobile phone housings. Today the highest standards are imposed on the surface: the appearance of the paint must be absolutely flawless and the overall appearance must on no account be affected by contaminants. Even a scarcely visible grain of dust on the surface of the housing before painting results after painting in an unsightly uneven area which customers generally will not accept. Electrostatic effects are the principal cause here for the adhesion of dust. Well-known suppliers to the mobile phone industry in China, South Korea and Finland responded to this a long time ago. For these suppliers Plasmatreat had great success in installing units for cleaning mobile phone housings which allow extremely efficient cleaning in-line. Immediately prior to painting several rotating plasma generators clean the plastic surfaces with high efficiency. In this way it was possible to reduce the wastage rate for the users from 12 % to less than 5 %.

6.5 Dispensing with primers in automotive engineering

For three years now a large American automobile manufacturer has also been benefiting from this technology in the pretreatment of plastic surfaces. High demand for its vehicles combined with the highest demands on multilayer painting gave rise to bottlenecks in the stoving ovens.

A vehicle part typically has to pass through many stations during the painting process. A typical plastic part is given a coating of primer-adhesion promoter, one to eight coats of paint and finally a clear coat. Stoving ovens, however, have limited capacity. Most manufacturers have only one paint line and stoving oven in a facility. Accordingly, a part will pass though the same oven four to nine times. Any way a manufacturer can increase capacity without adding significant capital expenditure, such as the procurement of an additional oven, allows significant cost savings. One fewer pass through the painting process eliminates the cost of primer, the associated labour costs and reduces the fixed costs of the oven.

In certain vehicles, however, it is not feasible to retain the same visual appearance of a surface while reducing the number of decorative coatings used. However, with the aid of the atmospheric-pressure plasma treatment described here the primer can be dispensed with completely even in this case. This results in a 25 % reduction in the number of passes through the stoving oven and hence in a significant increase in oven capacity.
Other pretreatment processes considered by the manufacturer such as corona or flame treatment methods were dropped on account of the conductivity of the parts, the possibility of thermal damage and on grounds of safety. These risks are completely precluded when atmospheric-pressure plasma is used.

6.6 Metallisation of plastics

The technology is of interest for the metallisation of plastics in two respects. On the one hand, the adhesion of the sputtered metal layers is significantly improved by the uniform conditioning of the surface since adhering organic residues and particles are completely removed. On the other hand, however, it is possible to remove an already deposited layer selectively by means of a sharply focused plasma beam and relatively low treatment speeds. The improvement in quality achievable by cleaning is frequently accompanied by a reduction in defective products of over 10 %.

7. Summary

The applications described here make clear that scarcely any bounds are set to the versatility of the pretreatment method now used in practically all sectors of industry. The Openair system is capable without restriction of in-line integration and is compatible with robots. Its decisive advantages include primarily the reliability and quality of the process in production operations. Thus, the high requirements well known in this respect can be fully met. Equally welcome are the simplicity of integration into process workflows and the higher economic efficiency in comparison with traditional methods – and all this goes hand in hand with outstanding environmental compatibility. *Inès*