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Automation Systems & Intelligent Solutions

Surface Functionalisation of Three-dimensional Plastic Parts

Robot-controlled functionalisation by electron treatment

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Abstract

Plastic parts made of non-polar polymers (e.g. polypropylene) are used in various applications. Before printing, coating and bonding, reliable surface activation is required to ensure sufficient wetting of the surface as well as to avoid adhesion problems and adhesion fractures.

In the automotive industry, flame treatment is the method of surface activation, as it works continuously as well as is easy-to-use and cost-effective. During the surface activation, polymer degradation may also occur, affecting adhesion and leading to cohesive fractures in the non-polar polymer to be activated.

The operation of compact low-energy electron emitters on an industrial robot enables an environmentally friendly reproducible and long-term stable functionalisation of three-dimensional (3D) plastic parts.

Compared to flame treatment, the energy consumption and CO_2 emissions can be significantly reduced, which leads to cost reductions and increased sustainability for the operator.

An economical and high-quality functionalisation of complex three-dimensional plastic parts requires the use of efficient area emitters in combination with 3D-capable finger emitters. The additional running costs amount to approximately 0.10 €/m².

Content

1. Standardised facilities that are not standard

The ASIS GmbH, headquartered in Landshut near Munich, is a system provider for automated systems in surface technology. The internationally positioned company exports from four locations in Germany and a subsidiary near Shanghai to over 30 countries worldwide.

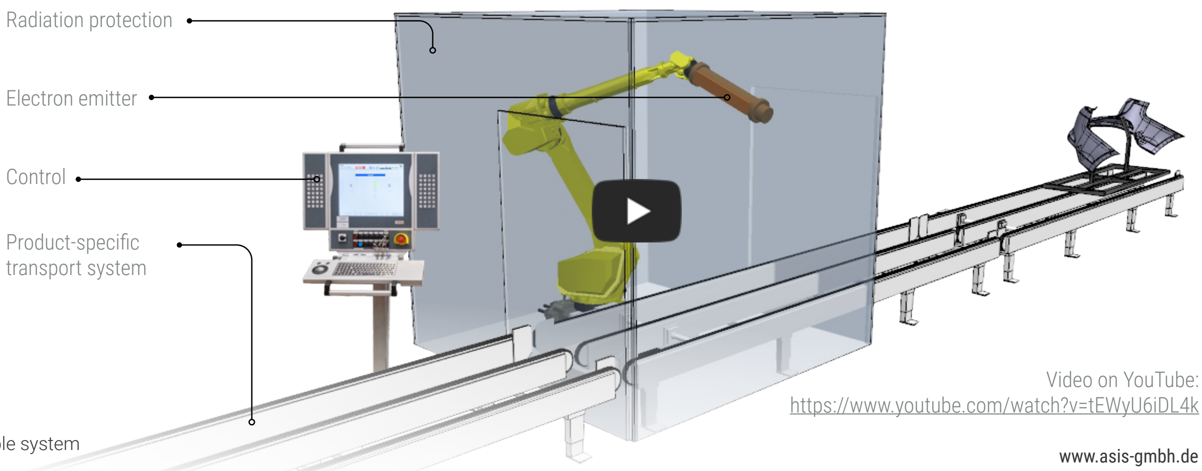
The range of services includes turnkey systems for wet paint or enamel coating, systems for quality control, surface treatment and electron treatment, wet paint application technology and process automation technology.

A dedicated digital simulation site develops material flow simulations, offline robot programming and feasibility studies.

ASIS in numbers

- Founded: 01.05.1998
- CEO: Hans-Jürgen Multhammer
- Quality assurance: ISO 9001
- Inform. assurance: TISAX
- Export countries: > 30 worldwide

Complete solutions in the area of inline electron beam technology for surface functionalization of complex three-dimensional plastic parts are the newest business field. These industrial facilities consist of compact electron emitters as well as a product-specific transport, control and radiation protection system (see Fig. 1 video).



Video on YouTube:
https://www.youtube.com/watch?v=tEWyU6iDL4k

Fig. 1: Example system

2. Physical process for surface functionalisation

Plastic parts made of non-polar polymers (e.g. polypropylene) have a low surface energy, which leads to adhesion problems as a result of insufficient wetting, e.g. during printing, coating and bonding. In the run-up to these processes, reliable surface activation is required to ensure sufficient wetting of the surface, especially in the case of lacquer structures without adhesion promoters, as well as to avoid adhesion problems and adhesion fractures. The degree of surface activation depends on the ratio of the surface energy of the plastic part and the surface tension of the lacquer, adhesive or ink.

Challenges:

- Non-polar plastic parts have a low surface energy
- Adhesion problems during printing, coating or bonding without prior activation
- Flame treatment requires a lot of energy, has high CO_2-emissions, has a high temperature influence and leads sometimes to non-uniform activation
- Handling of highly explosive fuel gases (methane, butane, propane)

Solution:

- Precise energy input by electron treatment for uniform, repeatable and long-term stable surface functionalisation
- Simultaneously higher product speeds, lower temperature input and higher sustainability

Before the activation step, adhering plastic additives, particles or release agents have to be removed, e.g. by CO_2-snow jet cleaning, plasma treatment or steam cleaning [1], in order to prevent the formation of local adhesion weak points.

In the activation step, additional surface polarities (mostly oxygen-containing polar groups) are generated to increase the surface energy of the plastic part and to ensure the formation of intermolecular interactions, e.g. with the lacquer, for optimum wetting.

In the absence of reactive and polar groups on the surface of the plastic part, the adhesion is based only on the weak non-covalent Van der Waals interactions (interaction of temporary dipoles). This means that high adhesion strength requires the formation of further physical interactions and/or chemical (covalent and/or ionic) bonds.

It should be noted that the adhesive strength is influenced by polymer degradation during activation and can possibly lead to a cohesive fracture in the edge layer of the activated plastic part (e.g. polypropylene).

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Fig. 2: Robot-controlled flame treatment of three-dimensional plastic parts

Flame treatment is the method of choice when plastic parts have to be activated in the automotive industry [2].

This easy-to-use, cost-effective and mostly robot-controlled process (Fig. 2) allows a reproducible continuous process in air atmosphere.

Alternative activation processes are atmospheric pressure plasma activation, gas phase fluorination, corona [1, 3] and electron treatment [4].

The functionalisation of plastic surfaces requires energy, e.g. for short-term surface heating and/or the generation of reactive species for the subsequent generation of polar groups (e.g. carbonyl (C=O), carboxy and hydroxyl groups [2]) (Fig. 3, 4).

Flame treatment:

- Formation of reactive species
- Reaction with polymer molecules
- Enhanced temperature
- Short-term stable functionalisation

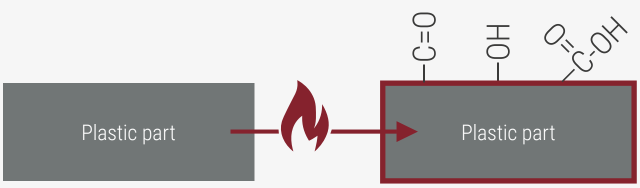

Fig. 3: Principle of flame treatment

Electron treatment:

- Formation of air plasma
- Reaction with polymer radicals
- Minimum temperature increase
- Long-term stable funcionalisation

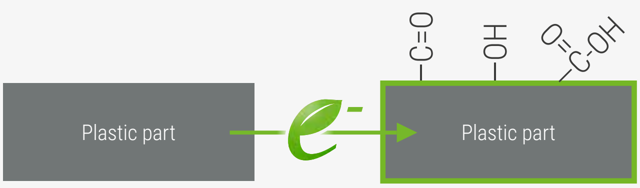

Fig. 4: Principle of electron treatment

Flame treatment uses an oxidising gas flame for the surface activation. The excess of oxygen is required for the generation of oxygen-containing polar groups on the surface of the plastic part.

The main disadvantages are the use of explosive fuel gases (e.g. methane, butane, propane), the high temperature influence and sometimes the non-uniform surface functionalisation, especially for plastic parts with complex 3D geometry.

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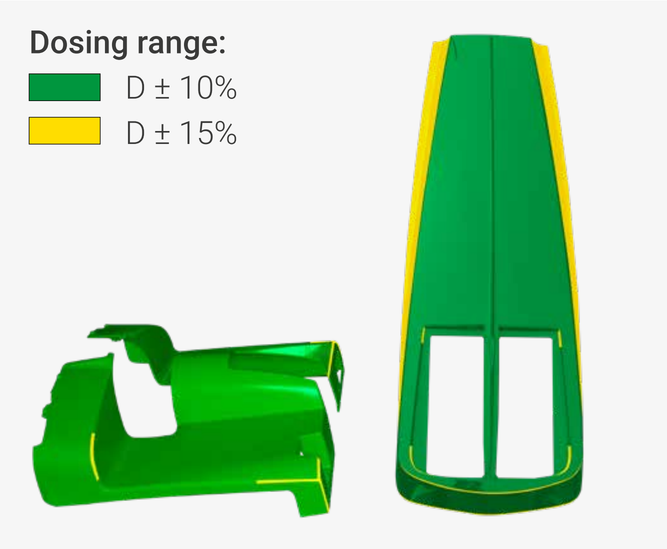

Fig. 5: Surface dose distribution on three-dimensional plastic parts [6]

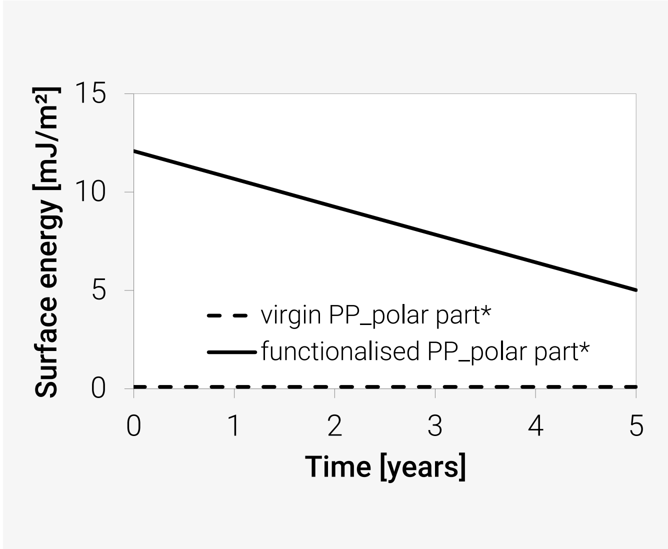

Fig. 6: Polar part of surface energy after an electron treatment as function of storage time [7]

This is where the new concept comes in. The electron treatment can provide an alternative here, as it enables uniform (Fig. 5) and reproducible surface functionalisation with a low temperature increase.

In addition, electron treatment produces long-term stable surface functionalisation (Fig. 6) at higher product speeds.

This mostly unknown physical process offers a high potential for a sustainable and environmentally friendly functionalisation of three-dimensional plastic parts.

Compared to flame treatment, energy consumption and CO_2-emissions can be significantly reduced, which leads to cost reductions and increased sustainability for the operator.

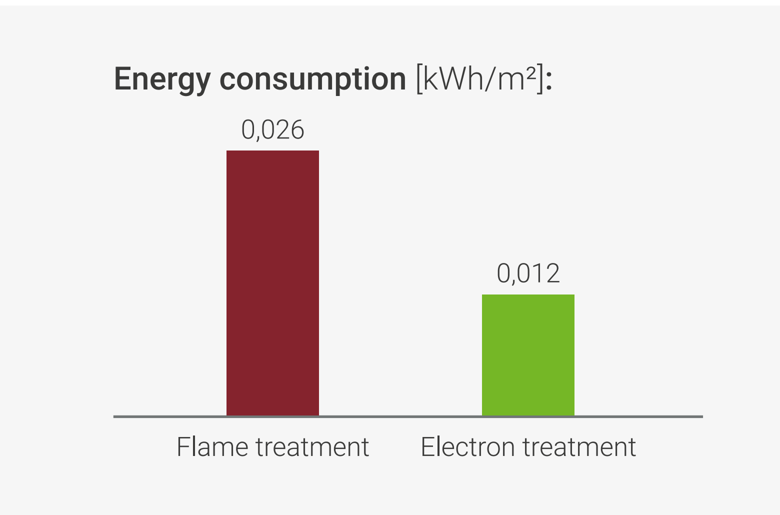

Table 1: Energy consumption for flame and electron treatment

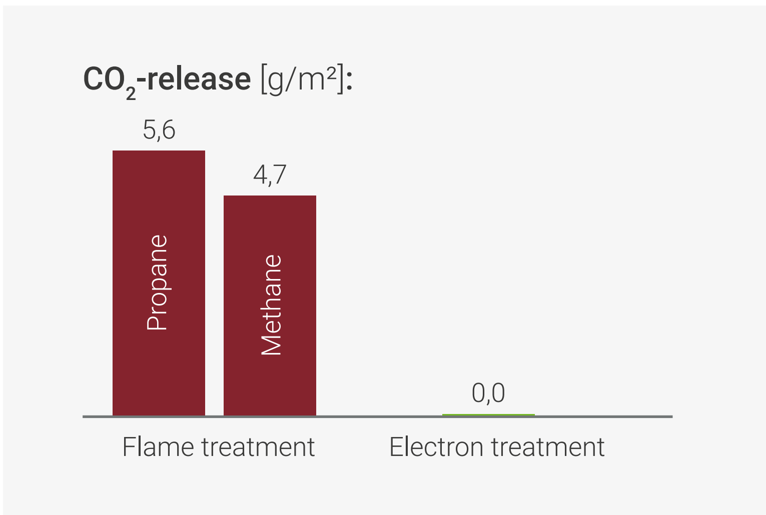

Table 2: CO_2-release for flame and electron treatment

3. Precise process control

In the sustainable and highly productive functionalisation by electron treatment, the use of chemical reaction initiators and additives is not required, since the electrons transfer their kinetic energy in several interactions to the atoms and molecules of the air (plasma generation) and the plastic parts to be activated.

At the end of the energy transfer process in the plastic part, covalent bonds are broken and polymer radicals are formed (see Fig. 7).

These react with the bi-radical oxygen, for example, and lead to the formation of various oxygen-containing polar groups.

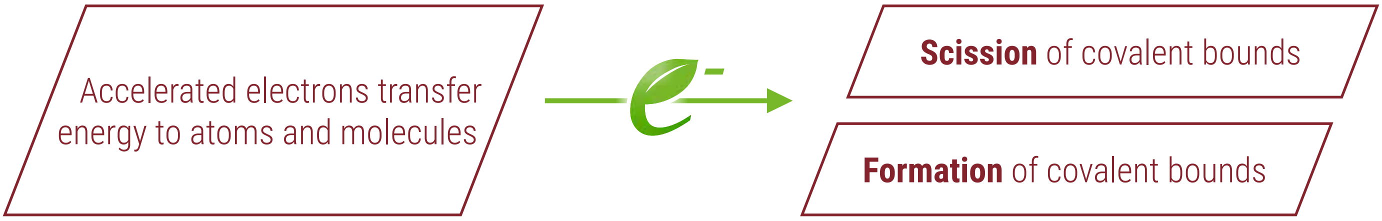

Fig. 7: Basic mechanisms of the interaction of accelerated electrons

The polymer radicals are the starting point of complex chemical reactions leading to a change in the chemical structure and altered chemical, mechanical and thermal properties of the plastic parts.

A customised functionalisation can be achieved by the purposive selection of the process parameters acceleration voltage, dose, dose rate and beam current.

Furthermore, the process parameters depend on the material composition of the plastic part to be surface functionalised (e.g. pigments, fillers, additives) and the chemical environment during the electron treatment.

The chemical environment includes the gas atmosphere, humidity and temperature during electron treatment. An overview of electron induced chemical reactions is shown in figure 8.

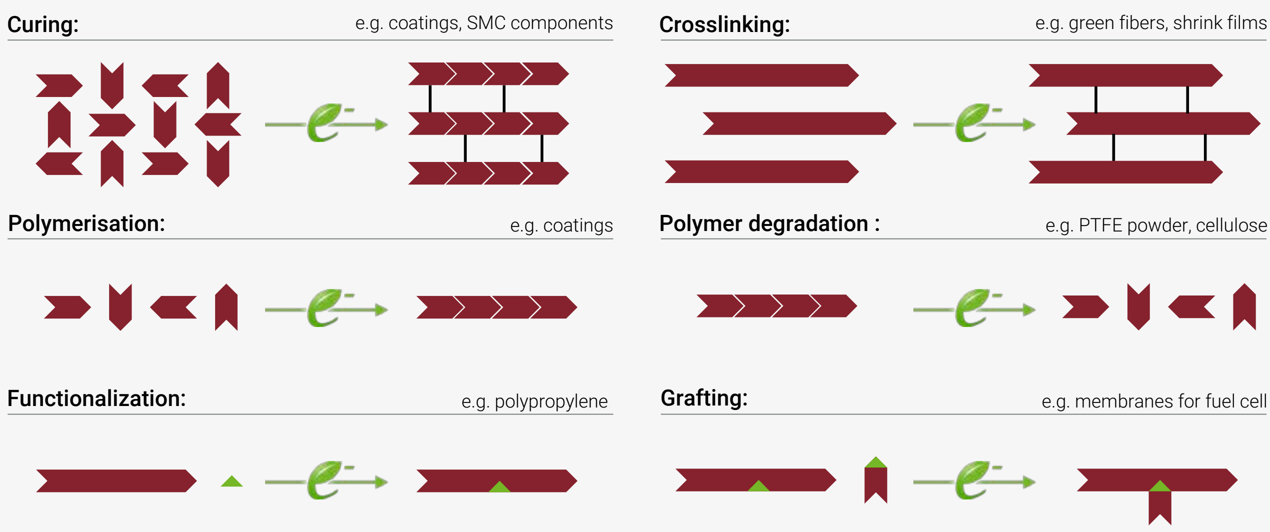

Abb. 8: Overview of electron-induced chemical reactions

The dose characterises the energy absorbed per mass and controls the number of radicals generated per polymer molecule and thus the intensity of the desired functionalisation. The unit of the dose is Gray (abbreviation: Gy). Depending on the composition of plastic part, a dose in the range of 5 kGy to 50 kGy is required for the functionalisation.

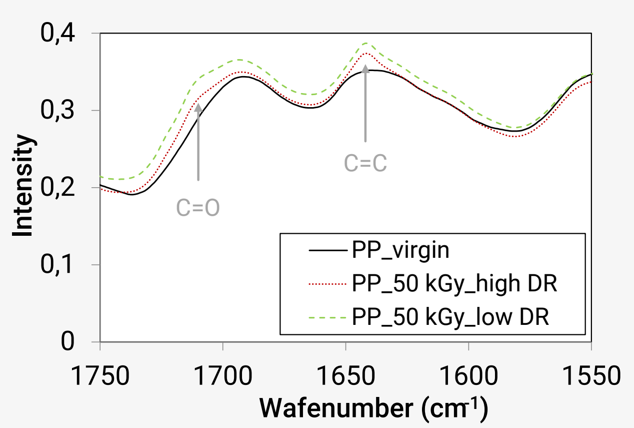

Abb. 9: Influence of dose rate (DR) on the generation of functional groups

The dose rate during electron treatment describes the dose absorbed per time. Thus, it controls the radical generation rate and influences all time-dependent processes during the non-thermal functionalisation, such as reaction kinetics, reaction with atmospheric oxygen (Fig. 9) and temperature increase on the plastic surface.

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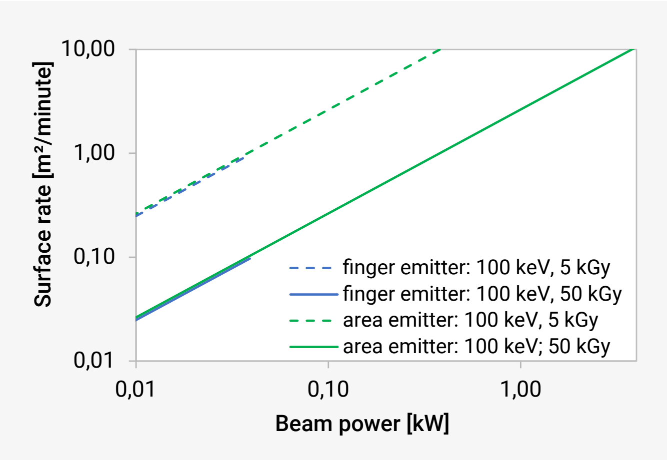

Fig. 10: Surface rate as function of beam power

The acceleration voltage determines the spatial energy input into the edge layer to be functionalised and must be adapted to the corresponding task in order to minimise the energy input into the plastic part and undesired substrate damage as well as to optimise the energy efficiency of the functionalisation.

The beam current controls the temporal energy input into the edge layer to be activated and thus the dose rate or surface rate (Fig. 10).

4. Compact facility design

The availability of maintenance-free, compact, low-energy electron emitters allows their coupling with an industrial robot and thus the functionalisation of three-dimensional plastic parts as well as the integration into the production process (Fig. 11)

These facilities are characterised by low costs, short service times as well as high energy efficiency, high surface rate and long service life.

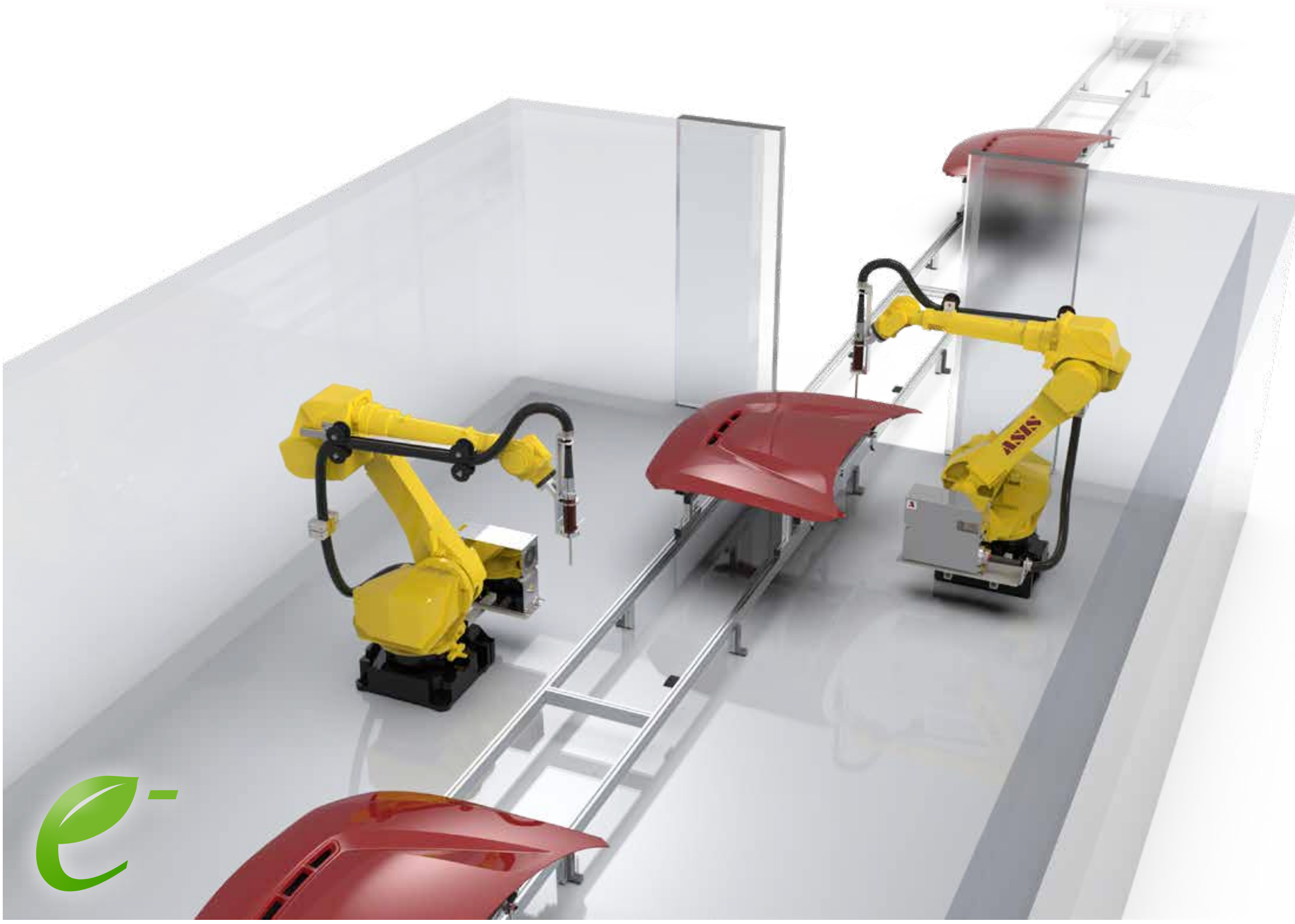

Fig. 11: Robot-controlled functionalisation of three-dimensional plastic parts by electron treatment

5. Surface functionalisation by electron treatment

Surface functionalisation by electron treatment enables the formation of oxygen-containing polar groups on the polymer surfaces without the use of additional chemical additives or additional gases.

The weak air plasma induced by electrons and the polymer radicals generated in the edge layer of the plastic part lead to the formation of long-term stable oxygen-containing polar groups.

Advantages:

- Higher surface energies
- Long-term stable functionalisation
- No use of highly explosive fuel gases
- Low temperature process
- Significant reduction of energy consumption (by ~ 55 %) compared to flame treatment
- No additional emission of CO_2 (reduction of 4.7 ... 5.6 g/m²)
- High throughput

Disadvantages:

- Higher investment costs
- Additional shielding against X-ray and bremsstrahlung

Based on the component-specific CAD data and the calibration parameters of the electron emitter used (spatial dose rate distribution), the modification paths for complex three-dimensional plastic parts are calculated with a special programming tool to ensure their uniform and reproducible functionalisation.

The new process leads to reproducible long-term stable surface energies as well as lower energy consumption and CO_2 emission.

Modern compact low-energy electron emitters use linear cathodes (area emitters) and point cathodes (finger emitters) as well as a single-stage acceleration, so that no scanner is needed for the out fanning of the beam.

The vacuum system required to generate free electrons is sealed off in the beam exit direction by a thin electron beam exit window (usually titanium foil). When leaving the vacuum system, the low-energy electrons release a part of their kinetic energy in the electron beam exit window and heat it up. In an 11 µm thick titanium foil, 40 % of the electron energy (at 100 keV) is absorbed.

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Excessive operating temperatures of the electron beam exit window lead to fatigue and later to mechanical failure. In the interest of a long lifetime, the area-specific beam power is limited. Thus, the maximum beam power of compact electron emitters is also dependent on the area of the electron beam exit window. The required 3D capability of a compact electron emitter decreases with increasing area of the electron beam exit window and beam power of the electron emitter.

An economic modification of three-dimensional plastic parts requires the use of efficient area emitters in combination with a 3D-capable finger emitter (see Fig. 12).

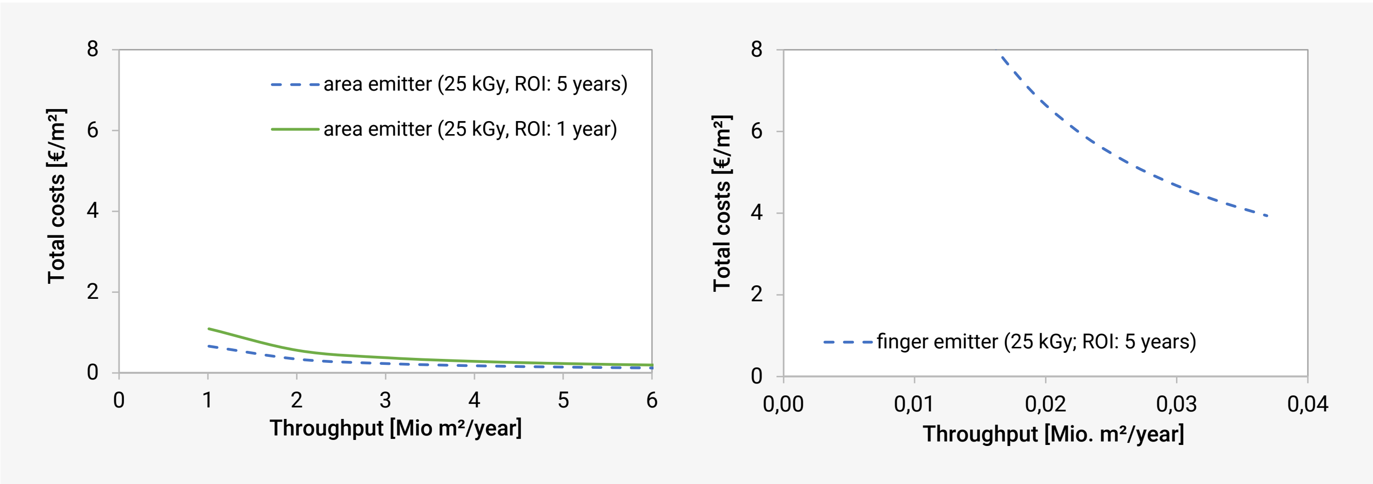

Fig. 12: Additional total costs at 100 keV electron energy for an area (left) and a finger emitter (right).

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6. Summary

The coupling of low-energy compact electron emitters with an industrial robot enables the functionalisation of three-dimensional plastic parts.

This non-thermal functionalisation method produces reproducible, uniform and long-term stable surface energies at low energy consumption and no CO_2-emission.

An economical functionalisation of complex three-dimensional plastic parts requires the use of efficient area emitters in combination with 3D-capable finger emitters.

The total costs of the electron treatment including investment (ROI: 1 year), energy and maintenance costs are less than 0.30 € per m², if more than 4 million m² of surface have to be functionalised annually.

At this annual throughput, the CO_2 and energy savings amount to at least 18.6 t and 56 MWh, respectively.

7. Contact

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