



FLUOR TECHNIK SYSTEM GMBH

*Small
Fluorination
Booklet*



» Why surface pre-treatment?

Plastics have many advantages:

- They are light.
- They do not rust.
- They can be produced at a low cost.
- They are easy to model.

This is why ever more plastics are being used.

Important selection criteria for plastics are:

- Mechanical properties
- Thermal properties
- Processability
- Price

When a suitable material has been found, it is often the case that the surface does not meet requirements made of it. This is particularly true for the low-cost polyolefines PE and PP.

The surface is the sole material property which can be changed without affecting other properties.

This means that surface pre-treatment is often an alternative to costly material searches or indeed the only option for achieving set targets.

For many applications, fluorination has proved to be the best form of pre-treatment.

Examples are:

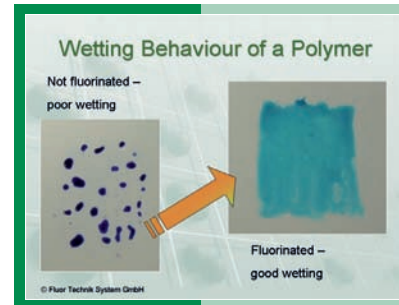
- Decorating (painting and printing)
- Sticking (flocking and laminating)
- Achievement of preset friction coefficients
- Minimisation of diffusion and permeation

The surface properties achieved through fluorination are stable over a long period of time. Fluorination has been employed successfully in many areas:

- Packaging
- Medical systems
- Construction
- Air and space travel
- Automotive industry
- Textiles
- Electrical systems

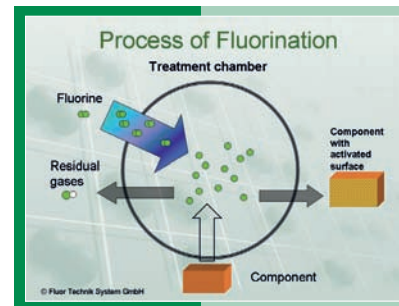
Fluorination

In the fluorination process, the surface of the plastic parts to be treated is exposed to a fluorine mixture. Due to its



high reactivity, fluorine causes the required surface changes. It does not need to be encouraged through additional energy. This makes the process very simple and safe to monitor.

Process



The material is brought into the treatment chamber. A fluorine/nitrogen mixture with a ratio of 10:90 flows in the required concentration into the chamber. The contact time between

the gas mixture and the material surface is freely selectable. Then, the treatment chamber is purged several times with air and the treated material can be removed.

All the relevant process parameters such as:

- Concentration
- Treatment time
- Temperature

are controlled automatically.

» *Tailor-made surfaces*

Fluorination has proved itself to be a very effective form of surface pre-treatment. It gives surfaces:

- Improved wettability
- Adhesivity
- Suitable friction coefficients
- Barrier properties

The following limits can be given for surface properties:

Non-wettable \longleftrightarrow Completely wettable

Anti-adhesive \longleftrightarrow Adhesive

Sticky \leftarrow Blunt \rightarrow Low-friction

These properties are the result of the surface energy, the polarity of the surface and the hardness of the material.

Often, when selecting materials, the mechanical and thermal properties are at the heart of the decision. When a material has been found, the surface does not always meet the necessary requirements.

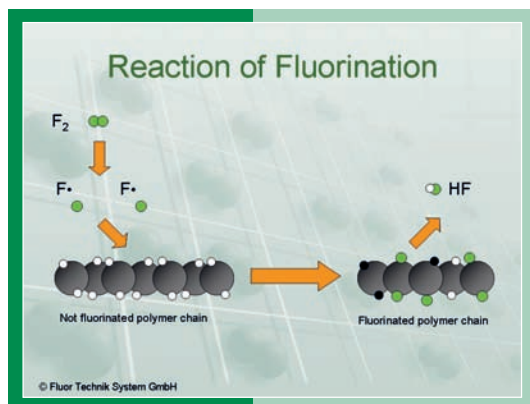
Fluorination makes it possible to change the surface properties without influencing the mechanical and thermal properties.

Special requirements placed on surfaces are:

- Gluable
- Printable
- Paintable
- Wettable
- Defined friction values
- Minimisation of diffusion and permeation

The fluorination process is suitable for all plastics. Homogeneity is guaranteed during treatment.

This method, which is beneficial to the product, is impressive on account of its highest possible safety, environmental protection and economic viability.



Reaction:

During fluorination of plastics, the hydrogen atoms are slowly substituted with fluorine atoms.

The quantity of substituted atoms can be controlled by the process controller. It is also decisive in the level of surface effects achieved.

Through targeted reaction control, it is possible to turn partially-fluorinated carbon atoms into almost perfluorinated atoms.

The penetration depth of the fluorine atoms into the substrate is at a molecular level. This can be measured in Angström units. In this way, it is possible to make targeted changes to the surface properties, without having any effect on the basic properties.

The binding energy of the carbon-fluorine compound is extremely high, meaning the fluorination cannot be reversed.

The binding energy of the fluorine atom with an electronegativity of 4.0 means that the bond is strongly polarised. The resulting dipole moment means that there is a sharp increase in the polar component of the surface energy.

» Offline method

Gas phase fluorination involves an inline or offline process depending on the product.

Three-dimensional formed parts are treated offline in a vacuum process. In doing so, the surface properties, such as surface tension, permeation and sliding properties, are influenced.

Used as a dry method, the latest technological knowledge and process optimisations are implemented to provide:

- High environmental compatibility
- Treatment which is beneficial to the product
- Improved economic application

In the process, a 10:90 mixture of fluorine and nitrogen is employed. In the vacuum chamber, the fluorine mixture is diluted down to the concentration designed for the product.

An important factor for the mixing process is that a concentration profile is used over the treatment cycle.

Decisive for the treatment of the plastic parts is also that the homogeneity in the chamber is guaranteed at all times during the process, i.e. that both temperature and concentration compensation occur.

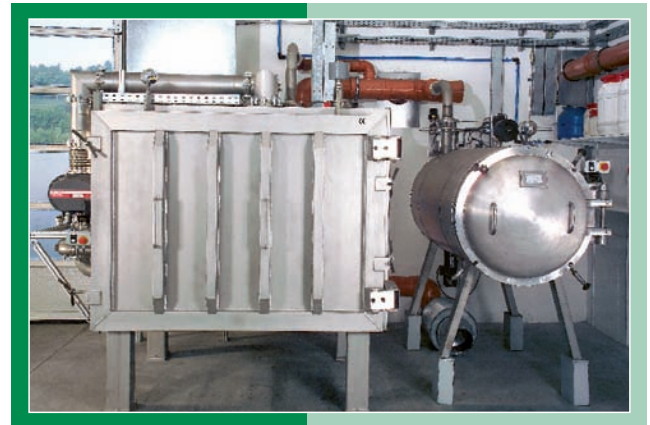
The length of treatment and the corresponding concentration profile are agreed with the customer for the product and are then verified in preliminary experiments.

The appropriate sets of parameters are then saved to the PLC controller as a recipe, so that it can be replicated at any time.

After multiple vacuum pumping and aeration cycles, the chamber can be opened without there being any risk.



PLC controller



Offline system

» *Inline method*

In the inline method, it is possible to fluorinate web material continuously.

Films, textiles and even foams of different material backgrounds can be fluorinated in this way.

The maximum width and thickness of the material are limited by the system being used. The length of the material is solely limited by the winding unit being used.

Fluorination can achieve special effects as regards polarity and long term stability, which could not be achieved using alternative methods.

The material is fed into the treatment chamber through a roller system. In the interior of the treatment chamber, the fluorine concentration required for the product and the application is fed in.

The fluorine concentration is monitored using an optical measurement in the UV range. A valve system increases or reduces the fluorine mixture according to the measurement.

The active length of the treatment chamber and the travel speed are used to specify the treatment time.

After an additional roller system with a purge zone, the material is removed and wound up.

Application:

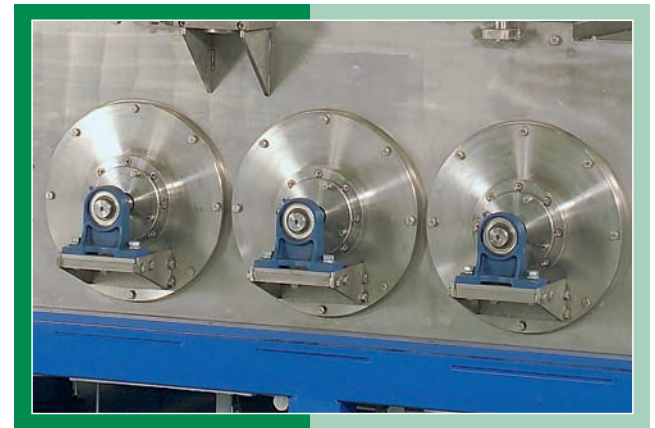
Hydrophilising of reeled film and web type material before coating, gluing or painting

such as:

- Foams
- Technical textiles
- Woven textiles
- Profiles



Inline system



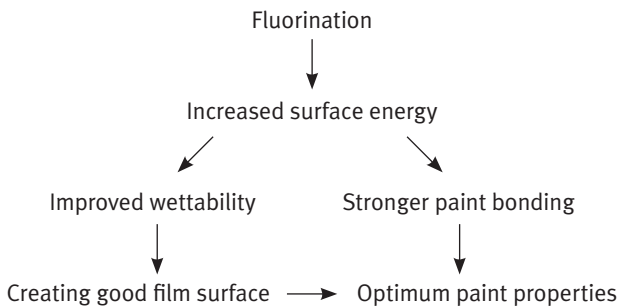
Inline system in detail

» *Painting*

During painting, there are three variables which have the most influence on the paint quality of the finished component:

- Wettability
- Film formation
- Adhesion

Fluorination influences all three of these properties in a positive way.



Cost savings can be achieved through:

- Savings in primer costs
- Use of water-based paints
- Use of low-cost painting systems
- Savings in paint layers

Even with complex geometries, fluorination gives absolutely even pre-treatment results.

Undercuts, recesses and wraparounds are treated homogeneously.

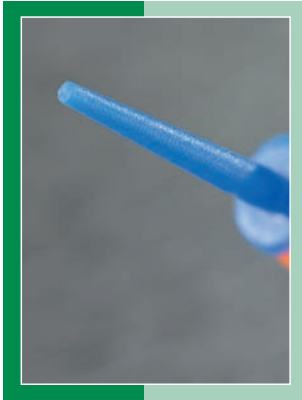
This leads to a consistently high painting quality, right into the rearmost corner of the component.



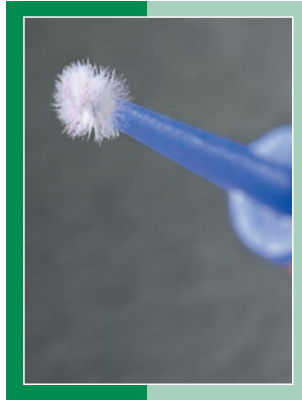
Raw part



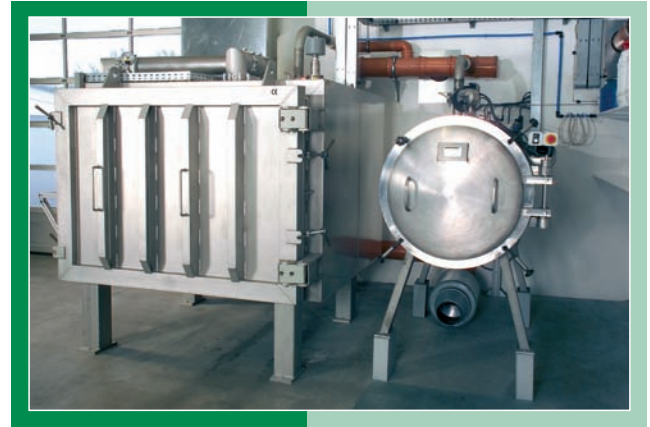
Painted part



Raw part



Flocked part



Vacuum reactors

» Flocking

Flocking of parts is, in the wider sense of the term, a gluing operation, which requires very high adhesion forces.

The adhesive is applied to either the whole substrate or to part of it. In an electrical field, the flock attaches itself to the surface so that the flock is vertical. Depending on the purpose of the operation, the flock may consist of various different, small fibres, such as polyamide, viscose, polyester, etc. After drying and fixing, the flock is permanently bonded to the substrate.

The thing which all these applications have in common is the superb adhesion of the adhesive to the substrate.

Insufficient adhesive power on the surface of plastics can be significantly improved through fluorination.

Areas of application:

- Friction reduction:
 - e.g. Panes of glass in the automotive industry run in
 - Flocked sealing profiles
 - Bendable shafts as actuating links
 - Guides for sunroofs
- Seals:
 - e.g. Window guide profiles
 - Dust seals
- Noise reduction:
 - e.g. Flocked glove boxes
 - Dashboard panelling
 - Boot panelling



Sticky materials



Sliding materials

» *Minimising sliding friction*

Many components from elastomers, e.g. NBR, EPDM or other natural rubber types tend towards stickiness, due to their surface properties.

The blunt and yet freely-adhesive surface of these components greatly reduces their installability.

In addition, with many formed parts, creaking sounds occur as the breakaway forces between the rubber and the frictional partner must be overcome.

Intensive fluorination of these components under certain circumstances means that many fluorine atoms are stored in the surface. This can lead to a considerable reduction of sliding friction.

Increased roughness of the elastomer surface can provide this effect with additional impetus.

This surface effect means that the rubber properties are not affected and remain stable over a long period of time.

Investigations using a scanning electron microscope have made it possible to make statements on the penetration depth of the fluorine and the surface topography. The recordings have confirmed that the penetration depth increases during the holding time.

The environmentally-friendly fluorination process can replace the lubricants and additive migrating on the surface. The possible savings in rubber recipes mean that fluorination is a highly economic alternative.

The latest experiments and results show that even silicones show considerable improvements as regards to minimisation of friction values.



Gas circulation

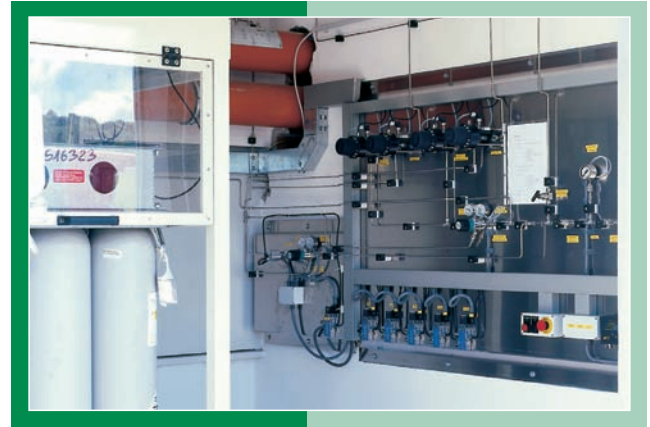
» Permeation barrier

Plastics are naturally permeable to certain gases and liquids.

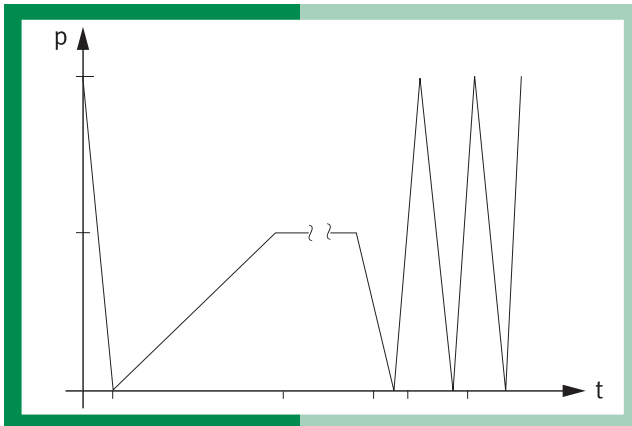
For this reason, the contents of a plastic container will evaporate over time. This process is known as permeation.

Particularly susceptible to this are containers for unpolarised short-chained solvents and benzines. This can be noticed starting with a light odour and then leading to a massive loss in weight.

This permeation can be reduced through strong fluorination. Typically, plastic fuel containers for automotive use are fluorinated to minimise the permeation of benzine.



Fluorine supply



Process sequence pressure versus time

This type of fluorination forms barrier layers which have other beneficial effects.

Typically, it is also possible to limit the migration of softening agents and other additives in elastomers.

This prevents too many softening agents from diffusing on the surface and thus embrittling the plastic.

In addition, it is possible to minimise softening agent migration in PVC.

These barrier layers also provide special protection for the surface. The chemical resistance to acids and alkalis is improved.

» QM System

For a properly functioning QM system, the following steps are required:

1. Defined parameter sets

These are specified together with the customer, their product and their application in the sampling phase.

These parameter sets are later saved to the PLC controller as a recipe.

2. Defined process

The process during fluorination is fully automated. Deviations are detected by the PLC and are then signalled and reported.

3. Documentation

The process is fully documented. Deviations of actual values from the set target values are recorded.

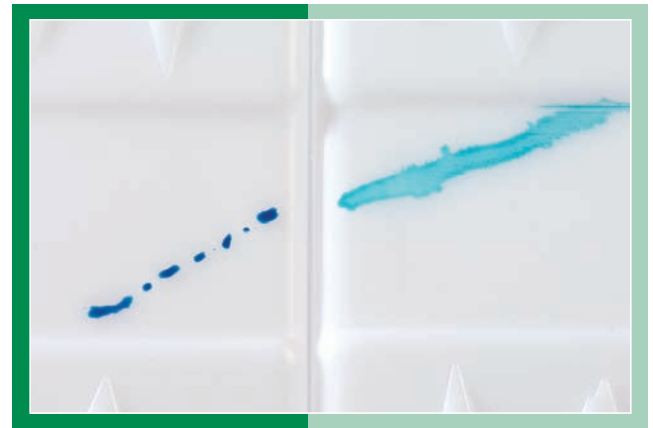
4. Measurement of the surface tension

The surface tension can be measured using either a wetting angle measuring unit or with test inks according to DIN ISO 8296.

Measurement using test ink is a more rapid and more straightforward test directly on the system. Often, this is a more low-cost alternative to laboratory measuring systems.

We are certified to DIN EN ISO 9001:2000 by the TÜV CERT certification office of the Hessen Technical Surveillance Association:

Certificate no. 73 100 145



Measurement of surface effects

» Workplace protection

Fluorine is the element in our periodic table capable of the most reaction. Therefore, fluorine is toxic and corrosive.

Naturally, fluorine only occurs in a bonded state, for example as fluorspar (CaF_2). To obtain the fluorine, hydrogen fluoride is subjected to electrolysis (HF).

The processing of fluorine and fluorine mixtures is subject to statutory and liability insurance regulations, which can vary from country to country.

In our systems, only fluorine mixtures of F_2/N_2 10/90, i.e. 10 % fluorine in 90 % nitrogen are used. There are approved valves and pressure reducers for these mixtures.

Storage of F_2/N_2 mixtures has been the state-of-the-art for many years. For reasons of safety, the appropriate supplier companies can provide detailed data on the F_2/N_2 mixtures in high pressure cylinders.

A detailed risk analysis has meant that the gas supply area has been made separate. It is separated off from the working area of the machine operator.

All the valves in lines carrying fluorine are provided in redundant, i.e. double versions. Should there be a leakage, then a second valve is always available.

Personal protective equipment and appropriate training for employees are prescribed.

The maximum workplace concentration value for fluorine is 0.1 ppm. This value is continually measured and evaluated. Should the value exceed this level, then there is an immediate alarm and the fluorine supply is interrupted automatically.



Maximum workplace concentration measurement



Maximum workplace concentration measurement

» Environmental protection

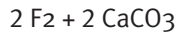
The regulations for the operation of fluorine systems are clearly defined in the TA Air (Chapter 3.1.6., Class II).

The maximum permitted concentration in the outflow air may not exceed the current limit value of 3mg/m³ HF.

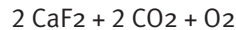
For this, the outflow air of the vacuum pump and the fluorine supply is led over a calcium carbonate absorber.

In the absorber, the remaining gas containing fluorine is led over a bed of calcium carbonate gravel (CaCO₃).

On passing through the lime bed, calcium fluoride (CaF₂), also called fluorspar, is produced with the following formula:



reacts to form



Calcium fluoride (CaF₂) is a naturally occurring and non-toxic mineral with very low water solubility.

The calcium carbonate absorbers are always designed so, that the current and future limit values of the TA Air are complied with.

A check of the outflow air is possible at any time from a maintenance platform using the measurement points attached to the chimney.



Calcium carbonate absorber



Maintenance platform

» *Fluorination of plastics*

Your benefits:

- **Long term stability**
The surface effects achieved are stable for months, even years, depending on the material.
- **Smooth and Even**
The even distribution of the gas in the treatment chamber means that any exposed surface is pre-treated in a way which is absolutely identical.
- **Geometry-independent**
Even deep grooves, undercuts or interior areas are evenly pre-treated.
- **Reproducible**
The fully-automated process means that very good reproduction results are possible.

» *Contact us!*

We can help you to solve your problems through qualified consultation and tailor-made solutions from individual items to mass production.

We look forward to positive, mutual co-operation.

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