Off-line fluorination

Modern process and plant technology from Messer Griesheim

Fluorination is used to make specific modifications to the surface properties of plastics such as wettability and permeation resistance. It is a process that has been used in the automotive industry for more than ten years now as a way of reducing the permeation of fuel vapors from the tanks of motor vehicles.

The variant known as in-line fluorination, however, is suitable only for blow moldings, whereas the off-line fluorination process described in this article can be used on both blow moldings and injection-molded plastics components. This opens up the possibility of using fluorination for a wider range of applications.

Messer Griesheim offers a new generation of off-line fluorination plants suitable for fluorinating containers and accessories with widely differing geometries and volumes. This new development is notable for its great flexibility and high level of automation. Fields of use include the fluorination of PE heating oil tanks (Fig. 1) and containers for agrochemicals, as well as the preparation of plastics components for painting.

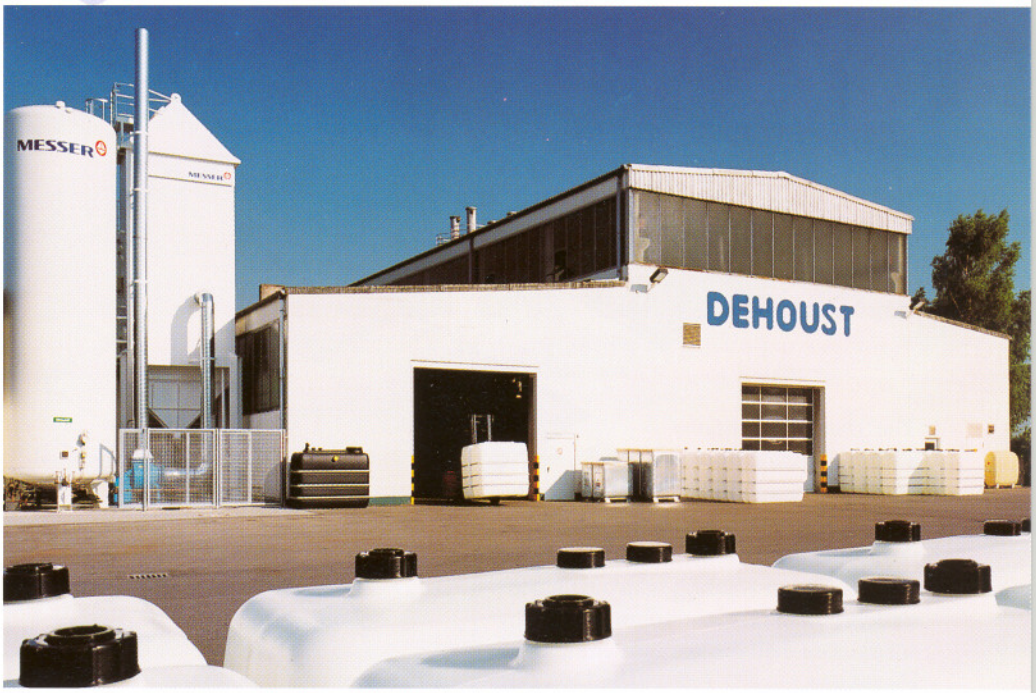

Fig. 1 The Dehoust Company uses off-line fluorination in the treatment of polyethylene heating oil tanks *(93.00.74.a)*

Principle of the off-line fluorination process

As a further development of the fluorination process, Messer Griesheim's off-line fluorination can be used to treat containers and accessories in a wide variety of geometries and volumes. The range of vessels treatable by off-line fluorination extends from small containers with capacities of 50 ml to large containers holding 4,000 liters. Fig. 2 is a block chart for an off-line fluorination plant in which the plastics components are treated in a vacuum chamber.

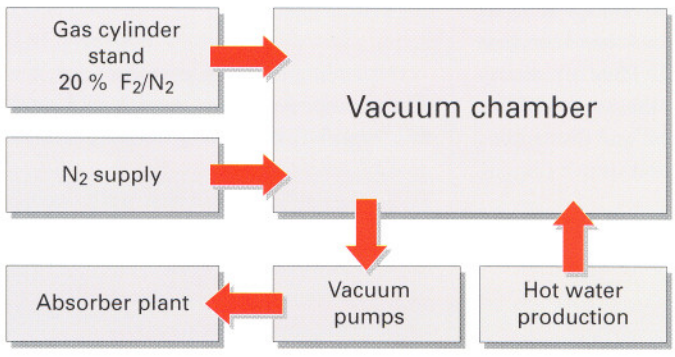

Fig. 2 Block chart for an off-line fluorination plant *(e.G.90.90.62.p)*

The vacuum chambers can be constructed with volumes ranging from less than 1 m^3 to more than 30 m^3.

Before the actual fluorination process the components are conditioned in the vacuum chamber. The conditioning treatment currently in use employs nitrogen or a hydrogen-nitrogen mixture. Its purpose is to free both the surface of the plastics components and also the vacuum chamber of not only moisture but also the oxygen that impairs the formation of a barrier layer.

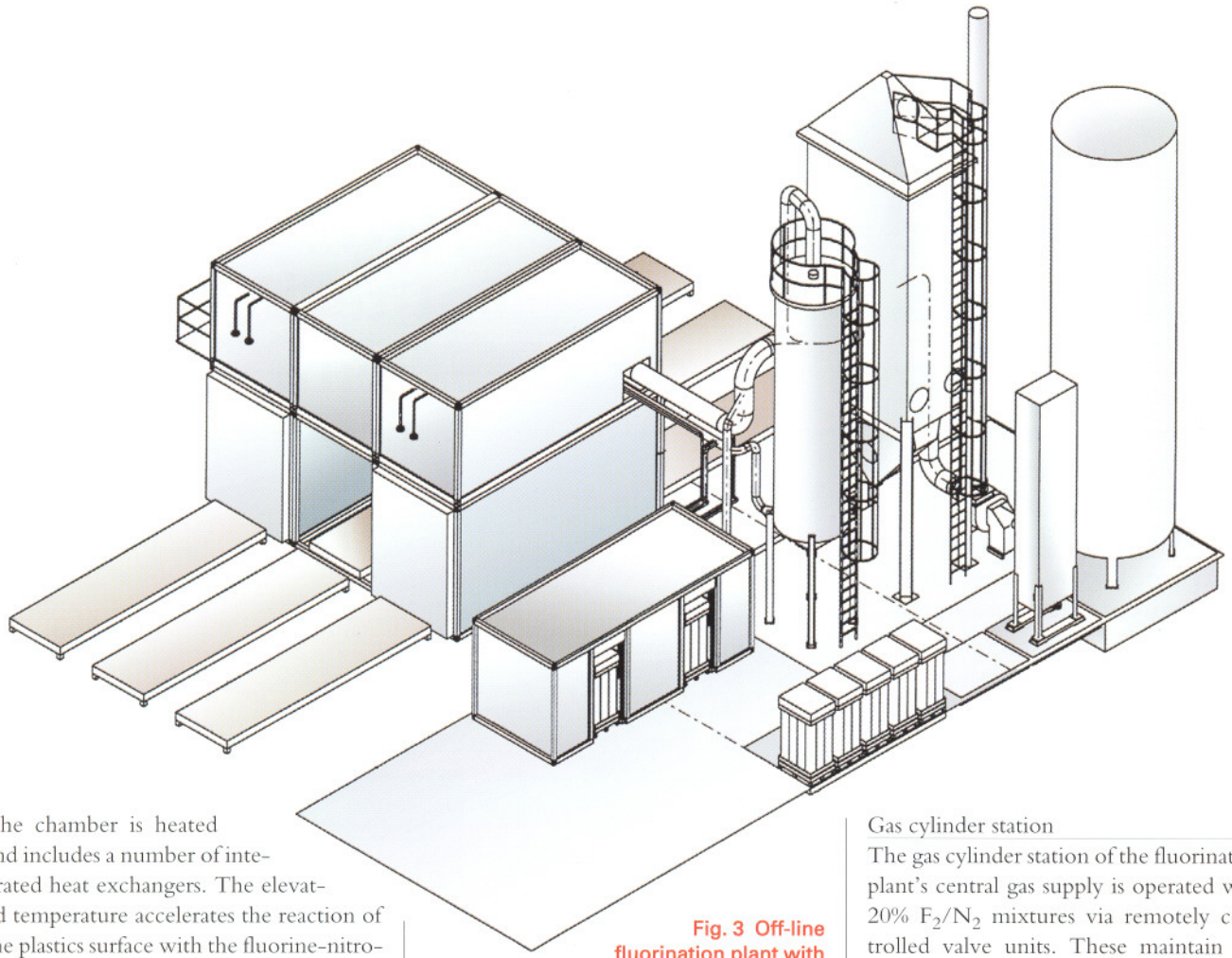

Fig. 3 Off-line fluorination plant with two 20 m³ vacuum chambers *(G.90.90.62.q)*

The chamber is heated and includes a number of integrated heat exchangers. The elevated temperature accelerates the reaction of the plastics surface with the fluorine-nitrogen gas mixture (F_2/N_2), which is then introduced. This gas mixture is supplied by Messer Griesheim in multiple compressed gas cylinders.

When the fluorination process is completed the pipelines and vacuum chamber are flushed with nitrogen. An absorber plant neutralizes the exhaust gases from the vacuum chamber, as well as the residual gases from the pipelines. For safety reasons, an ambient air-monitoring unit is installed at all key points.

The plants are notable for their modular construction, i.e. the main components are accommodated in standard containers (e.g. 20" or 10" containers). They are assembled by a technique akin to a building block system, so erection and dismantling can be undertaken at short notice (Fig. 3).

The new technique therefore also provides advantages in the relocation of manufacturing capacities. Transportable units can easily be moved from one site to another and recommissioned in a minimum of time by simply disconnecting and later reconnecting the service lines. Another advantage is that plants of this type can be erected in the production sector without special foundations. Such foundations are, however, required for the gas supply and gas disposal facilities in the outer zone of the production area.

Depending on the size of the plant, the main components consist of 3 or 4 containers with the following building groups:

- **Gas cylinder station with integrated multiple gas cylinder stand for F_2/N_2 mixtures**
- **Vacuum chamber**
- **Compact, low-maintenance vacuum pump stand with all facilities relevant to the process**
- **Heat generation equipment for the vacuum chamber**
- **Plant control facility**

Gas cylinder station

The gas cylinder station of the fluorination plant's central gas supply is operated with 20% F_2/N_2 mixtures via remotely controlled valve units. These maintain the supply of gas to the vacuum chamber and control the automatic nitrogen flushing operation. Measuring units and monitoring equipment operated via the plant control facility ensure that the station functions properly.

Vacuum pump stand

To make the system less susceptible to disruption, one major concern was to design the vacuum pump stand with the smallest possible number of rotating mechanical parts. As one of the main components, the pump stand forms the link between the vacuum chamber, absorber unit and gas cylinder station.

The pump system used is a two-stage type with integrated gas circulation for the vacuum chamber. The vacuum is generated by a dry-running chemical industry pump capable of producing an ultimate vacuum of less than 1-10-5 mbar. A pump with a very high throughput rate is used to circulate the gas. In the evacuation process it acts as a booster to the backing pump. This permits pumping times of less than five minutes in full plant scale operations.

When a closed hot water circuit is employed, an energy recovery facility operating via the pump stand is integrated in the water circulation.

Process heat generation

The process heat generation facility is a compact building block containing all of the units necessary for its operation. They include a circulating pump and heating units, as well as control and monitoring facilities. The heat transfer medium used is water. The water circulation is adjusted to the desired temperature with great accuracy via a cascade control system. Other forms of heating can, however, be provided on request.

If a large number of different products have to be fluorinated, the process temperature may need to be changed at frequent intervals. This can be done quite simply with the aid of a supplementary attachment.

Vacuum chamber

Messer Griesheim's standard vacuum chambers range in volume from less than 1 m^3 to more than 30 m^3 and feature various geometries (Fig. 4). The design variants are as follows:

- **single chambers with one sealing door**
- **single chambers with two sealing doors**
- **double chambers, each with one sealing door**
- **double chambers, each with two sealing doors**
- **combinations with preheating chamber, fluorination chamber, etc.**

Fig. 4 Single vacuum chamber with 20 m^3 volume and two sealing doors *(93.00.74.b)*

Each chamber has an integrated heat exchanger, uniform gas distribution systems, rapid temperature adjustment, even under vacuum, and symmetrical flow profiles. The chamber can be sealed manually, hydraulically or electropneumatically.

Loading and transport of components

Depending on the design of the plant, the loading and unloading facilities for the vacuum chamber are manual or automated. Rail-mounted floor conveyors transport the products into the vacuum chamber (Fig. 5). If the pick-up wagons are of a suitable design, the system can be installed straight on the end of existing production lines. Batchwise fluorination processes can then be automated.

Plant control

The plant has a computer-aided control system that allows fully automatic operation. The system is based on a Siemens S7 unit and allows a network linkage with Windows NT. A process computer in the control console acts as the link between the operator and the control system (Fig. 6).

Fig. 5 Rail-mounted floor conveyor wagon for loading the fluorination plant *(93.00.74.c)*

The off-line fluorination plants offer the option of batchwise operation. Batch recipes can be chosen from a large number of collected fluorination parameters by reference to a list of process parameters available in the well-known standard software applications Excel and Access under Windows NT. Microsoft Office can be used for more complex processing operations.

The operator can choose to have the batch logs produced as automatic printouts or recorded on a process computer. Data relating to the process can always be produced in parallel as a trend diagram on the monitor.

A wide variety of fluorination curve paths can be adapted to customers' particular requirements. It is also possible to use simplified automation systems, the design details of which will depend on the design of the plant itself.

The absorber plant

The absorber plant can consist of either single-stage fixed-bed absorbers with an integrated discharge system or else multi-stage absorbers. Other possibilities are combinations featuring single charging and continuous discharge of used absorbent.

Monitoring of ambient air

The ambient air is monitored by MAC monitoring sensors and the accompanying evaluation units. This is done to safeguard personnel and plant facilities. The measuring locations are chosen according to the erection conditions of the particular project.

Fields of application

Heating oil tank fluorination

An off-line fluorination plant is used for aftertreating PE heating oil tanks. In the vacuum chamber the tanks are given Teflon-like coatings, both inside and outside, which prevent absorption of aromatics by the tank walling. Any risk of heating oil permeating or diffusing right through the walling of the tank is thereby ruled out. Heating oil tanks generally, and double-walled polyethylene 2-in-1 safety tanks in particular, needed this form of barrier treatment because they are usually installed in the furnace room and consumers can generally discern any odor, however slight. From 1998 onwards this new system is also being used to fluorinate other tanks destined for the German market, namely those with capacities of up to 2,000 m³.

Fig. 6 Control console with process control computer *(93.00.74.d)*

Fluorination of tanks for agrochemicals

The off-line fluorination of tanks for agrochemicals creates a barrier layer that prevents permeation of the tank walls by components of the chemicals in the tanks. Such chemicals are not only toxic but also cause a severe odor nuisance. As the tanks are usually fabricated in polyethylene, they are very suitable for a barrier layer treatment with a fluorine-nitrogen mixture.

Fluorination in paint technology

Paint technology is about to witness the introduction of off-line fluorination on an industrial scale. Messer Griesheim has developed systems that allow some of the present operations in the painting of plastics to be replaced by a rapid fluorination process. By ensuring that the paint keys exceptionally well to the substrate, the fluorination treatment offers the major advantage of eliminating the need for primers.

Future prospects

The use of fluorination techniques for commercial sectors of all kinds is being evaluated in wide-ranging trials. Many of the results can be ascertained and appraised at Messer Griesheim itself. The most recent upshot of this evaluation program has been the introduction of hydrofluorination (see also "gas aktuell 50", page 42) as a conditioning stage prior to the actual fluorination process. This process technology developed by Messer Griesheim offers the scope for even more improvements in the future.

Dipl.-Ing. Siegfried Rödel

Advantages at a glance

- low investment costs
- modular structure for all main components
- mobility which facilitates relocation of production plant
- flexible process sequences
- high degree of automation
- suitability for plastics components of varying geometries
- plant technology geared to future needs

MESSER

Messer Griesheim GmbH · Industrial Gases Germany
Hardware / Special Gases · Fütingsweg 34 · 47805 Krefeld
Tel. (0 21 51) 3 79 - 3 75 · Fax (0 21 51) 3 79 - 5 54
http://www.messer.de
A member of the Hoechst Group