Corrosion Protection

How the Chemical Industry Achieves the Goal with Various Materials

Fluoropolymer system solutions are increasingly used in chemical plants for corrosion-protection tasks. They usually offer considerable advantages over alternatives such as stainless steel, enamel-coated steel or glass in dealing with corrosion. Practice has shown, however, that the plant operator's expectations could not always be completely fulfilled. Therefore, in this article, influencing factors such as the selection of the right materials, the application, the appropriate manufacturing methods or component design are analyzed in more detail in order to provide the designer and the operator of a chemical plant with additional information for a successful, durable plant design.

The chemically modified second-generation PTFE, 3M Dyneon TFM Modified PTFE, is a PTFE in which the molecular chains of the polymer have been chemically modified by perfluoropropylvinylether (PPVE), a similarly perfluorinated modifier. At the same time the molecular weight of this second-generation PTFE was lowered in order to significantly improve the particle fusion of this PTFE. It is being processed using press-sintering methods or paste extrusion.

If we consistently continue the polymer modification by lowering the molecular weight in combination with the incorporation of the co-monomer PPVE, then we obtain a perfluoroalkoxy polymer, better known under the name PFA. Thanks to the low molecular weight, the representatives of this product group can be processed using the common thermoplastic processing methods like extrusion or injection molding and thus significantly extend the product range of the perfluorinated polymers.

Whereas resistance lists are normally used with materials in connection with corrosive chemicals or solvents, this is not the case with PTFE, modified PTFE or PFA. These materials can be said to exhibit almost universal chemical resistance. Only a few critical exceptions have to be taken into consideration. Among these are fluorinated hydrocarbons; alkali metals; monomers such as styrene, butadiene or acrylonitrile; or, finally, high-energy radiation, which can destroy the polymer itself.

Constructive Measures Necessary Despite Special Property Profile

Against the background of their use in the corrosion protection, demands are made of fluoropolymers in particular with regard to their excellent chemical resistance, high temperature stability and very high barrier effect, i.e., low permeation rates in relation to the chemical mixtures that arise. Their good non-stick properties facilitate cleaning, even when CIP (cleaning in place) or SIP (sterilization in place) procedures are applied.

The aforementioned perfluorinated polymers fulfill all of these properties.

Despite the excellent barrier properties of modified PTFE and PFA, however, it must be considered that a not-inconsiderable permeation takes place, in particular at higher temperatures. The gaseous chemical components enter the polymer material on the side in contact with the product, cross through it, and exit the material again at the "rear side." Since permeation increases strongly with temperature, the values were determined at 100 °C for realism. Under these conditions TFM allows the lowest permeation, followed by PFA. The influence of the thickness of the barrier layer in the range between 1 and 3 mm also proves to be particularly significant. Therefore, linings should have a thickness of more than 2 mm if possible. Non-modified PTFE, which exhibits the highest permeation values, should therefore only be used conditionally as a barrier for corrosion protection in corrosive environments. However, standard PTFE also proves to be a good problem solver in full fluoropolymer constructions in which temperature and chemical resistance are demanded, but where the barrier properties can be classified as subordinate.

The barrier properties change at the different temperatures that occur in chemical plants. PFA exhibits the best barrier properties for hydrogen chloride gas up to temperatures of around 80 °C (355 K); at higher temperatures modified PTFE proves to be the material with even lower permeation.

Especially at elevated temperatures, permeation cannot be entirely avoided. This must be considered to achieve the goal of a durable construction. When lining chemical reactors, columns, tanks and pipes with a film of modified PTFE or PFA according to the "loose shirt method," i.e., fixing the liners by clamping between the flanges, care must be taken to ensure effective back ventilation. This ensures the removal of the gaseous corrosive substances diffusing in low amounts through the protective liner, and the dew point TD in the space between the liner and the wall of the duct is not reached: The system remains dry and therefore no corrosion can occur.

Systems Made Of Fluoropolymers

So which fully fluorinated products are used in chemical plants requiring corrosion protection? The table provides information on plant components for corrosion protection, the polymers that come into question and the polymer-specific production methods. The inclusion of the sintering material "standard or modified PTFE" on the one hand as well as the thermoplast-processible PFAs on the other hand enables the complete production of the required range of products.

The various options for polymer selection, the combination with the associated different processing methods, the presence of alternatives for most applications as well as the consideration of special design criteria for the layout of durable system solutions mean that a round-table discussion at the start of the project is an important component for success.

Closing the Cycle with End-of-life Products

Although corrosion protection systems based on fluoropolymers are usually durable system solutions, it may nevertheless be necessary because of the very aggressive conditions to partially or completely replace components and systems during inspections. Using the new Up-Cycling process developed by Dyneon, a subsidiary of the multitechnology company 3M, these waste products can now be split back into their raw components, the monomer tetrafluoroethylene (TFE). After purification, the TFE obtained is subsequently converted again into new fluoropolymers, which are no different from the original products in terms of their properties.

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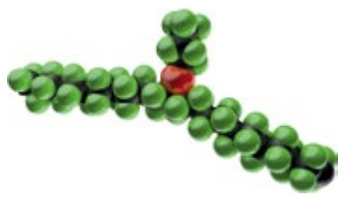
Plant components for corrosion protection, polymers that come into question and the polymer-specific production methods

Plant components for corrosion protection	Which polymer is suitable?	Production method
Films and sheets for the lining of distillation columns, reactors applied at high temperatures using the "loose shirt method"	Modified PTFE, TFM Modified PTFE (S-PTFE)	Skiving the film from large sintered blocks or hollow cylinders
Glass- or carbon-fabric-backed films and sheets for the lining of tanks applied at ambient or slightly elevated temperatures using the "bonded shirt method"	Modified PTFE, TFM Modified PTFE (S-PTFE) PFA	Skiving the film from large sintered blocks or hollow cylinders, followed by a laminating step. Extruded film (chill-roll method) or sheet, simultaneously laminated with glass or carbon-fabric backing
Tubes, straight or convoluted, general purpose or heat exchanger	PFA	Melt extrusion
	Modified PTFE, (E-PTFE)	Paste extrusion
Lining of complex components such as pumps, valves	PFA	Transfer molding
Molecular structures of PTFE, PFA, and TFM		
PTFE 	PFA 	TFM 

News from China

The Tianjin Explosions and Their Implications

On August 12, a fire at a dangerous goods warehouse operated by Ruihai Logistics at the Tianjin harbor quickly turned into a disaster as it triggered two substantial explosions, very likely due to chemicals stored in the warehouse. These included 700 tons of sodium cyanide, 800 tons of ammonium nitrate, 500 tons of potassium nitrate and unknown amounts of calcium carbide. More than 100 people died, many of them firefighters, and several hundred people were injured, many of them residents in apartment complexes near the warehouse.

Insufficient Implementation of Existing Regulation

In the aftermath of the explosions, local media uncovered several examples for regulation being ignored at the Tianjin site. For example, the amount of sodium cyanide stored at the warehouse exceeded the legal limit by a factor of 70. The warehouse is located only 600 meters away from residential buildings, not the mandated 1,000 meters. And state media revealed that the organization operating the warehouse had only received its authorization to handle dangerous chemicals less than two months earlier, meaning that it had been operating illegally between October 2014 and June 2015.

> *China is better at establishing decent regulations than at implementing them.*
> Dr. Kai Pflug, CEO, Management Consulting — Chemicals

Lack of Qualified Emergency Response

Other criticism has focused on the emergency response. According to a spokesperson of the fire department, it was known to the fire fighters that calcium carbide was stored at the warehouse, but the exact location was not known. Other sources such as the Beijing News state that the firefighters were not aware of the fire involving chemicals at all. In any case, the firefighters tried to stop the initial fire using water rather than sand or foam, which would have been the appropriate approach. This may have caused the formation of acetylene from the calcium carbide and the subsequent explosions. The apparent ignorance of firefighters regarding their approach may be partly explained by the two-tier structure of China´s firefighting force, in which a substantial share of the staff is low-paid and presumably has limited training as well.

> *So far the government has taken a fairly open approach in their response to the disaster.*

Initial Government Reactions

So far the government has taken a fairly open approach in their response to the disaster. For example, the State Council Work Safety Commission stated that the Tianjin blasts revealed a lack of safety awareness and lax implementation of safety regulations. The commission also mentioned other problems including inadequate safety management of dangerous materials at ports, irregular practices among workers, weak emergency responses to incidents and lax supervision by authorities. Other government measures include the arrest of the warehouse management and investigations regarding the current director of the State Administration of Work Safety, who also is a former deputy mayor of Tianjin. On a more proactive note, the government has announced that in the period until September 10, they will check all dangerous substances across the whole country.

> *Western companies need to be willing to choose their Chinese business partners based on their broader adherence to elevated standards.*

Long-term Implications

It remains to be seen whether this disaster will actually have substantial longer-term implications for the chemical industry — as always, China is better at establishing decent regulations than at implementing them. Currently such implementation certainly has some momentum. For Western chemical companies operating in China, a stricter implementation of existing regulation would certainly be a good thing — they generally adhere to this regulation already but sometimes suffer from local competition with laxer standards. On the other hand, some of the regulation is likely to lead to higher cost of doing business in China, for example when knowingly or unknowingly using the services of companies such as Ruihai in providing logistics services. Western companies therefore also need to be willing to choose their Chinese business partners not only based on price, but also on their broader adherence to elevated standards.

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