CORROSION PROTECTION WITH FLUOROPLASTICS

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INTRODUCTION

New fluoropolymer systems and coating processes have in the last 10 years been through a so rapid development that the most requirements put forward by the chemical and pharmaceutical industries, the flue gas industry and others can be fullfilled with respect to chemical resistanse, temperature level, “FDA-complying”, easy cleaning among other demands.

In the following is discussed properties for the different commercial polymers together with typical uses presented as case-stories.

TYPES AND PROPERTIES

PTFE-polytetrafluoroethylene is the most well known fluorplastic. PTFE cannot, however, be used as a corrosion protecting coating as it cannot melt and flow out evenly at very high temperatures above its melting point of about 326° C. It turns clear and becomes gel-like, but after cooling it becomes white again and returns to its crystaline state. It is possible, however, by modifying the PTFE-molecule to produce meltable fluor polymers suitable as corrosion protecting coatings.

In table 1 below is seen the chemisty and some physical properties of the commercial fluoropolymers for corrosion protection.

Next to the chemical configuration the table also contains the melting point, the maximum temperature of use and f.e. the critical surface tension of the fluoropolymers.

The properties of PE = Polyethylene are taken along for comparison as it can be seen that the only chemical difference between PE and PTFE is that all the hydrogen = H in PE has been replaced by fluor = F to obtain PTFE. That this change gives a remarkable improvement can easily be seen.

Generally it can be concluded that the more fluor in the molecule the better the properties and consequently the better the corrosion protecting ability. See the tables 1, 2

When there only is fluor = F together with carbon = C the polymer is called “fully fluorinated”. PTFE, PFA and FEP belong to this category.

Name	Chemical nage	Chemical structure	Temp. max.°C	γc	Melting point °C
PTFE	Polytetra-fluorothylen	F F -C-C- F F	260	18	327
PVDF	Polyvinyliden-fluoride	F H -C-C- F H	140	25	170
E-CTFE	Ethylen chloro-trifluorethylene	H H F F -C-C-C- C- H H CL F	150	31	245
FEP	Fluorinated ethylene propylene	F F-C-F F F F | (-C-C-)-(-C-C-) F F F F	205	16	270
PFA/TFA	Perfluoroalkoxy	(R = - C_3F_7) F F F O (-C-C-)- (-C-C-) F F F F	260	17	305
ETFE	Ethylentetra-fluorothylene	H H F F (-C-C-C-C-) H H F F	150	25	270
PE	Polyethylene	H H (-C - C-) H H	70	31	100

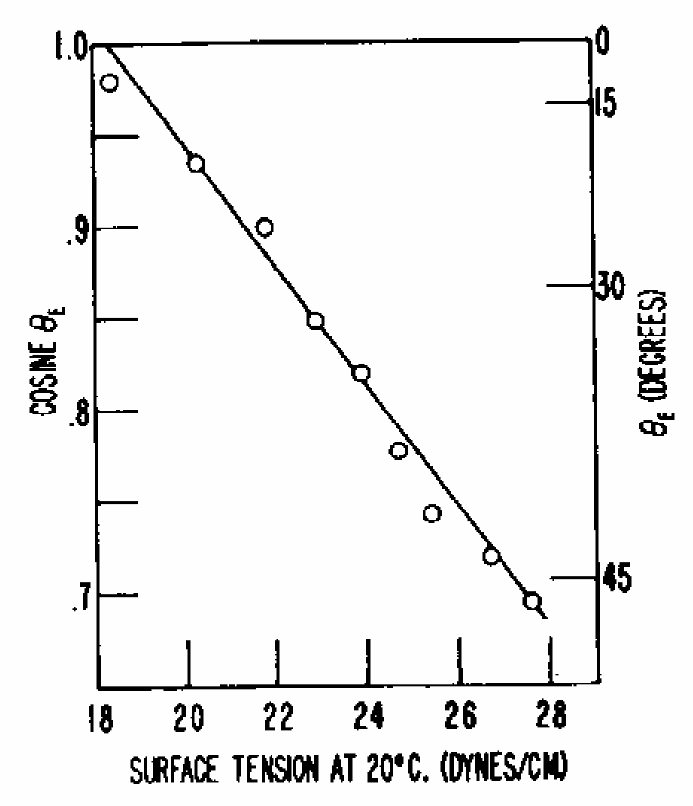
TABLE 1. PROPERTIES OF FLUOROPLASTICS

The reason for the excellent properties is the strong C-F bond, the highest bondstrength obtainable. At the samt time the bond-radius is the smallest. It is assumed that this fact gives the resistance to all common chemicals, the low surface tension (giving non-stick properties), low friction and the extreme low permeability of small molecules (see table 4), while in turn gives the excellent corrosion protection.

The critical surface tension γc is an important property of a plastic material. It is determined by placing organic solvents with known surface tension on the surface of the clean plastic surface. The surface tension of the liquid (existing or theoretical) that just spreads, that is, having a contact angle of zero is defined as the critical surface tension of the plastic. It is quite easy to measure or calculate γc for a surface. The contact angles for the different liquids are measured, cosine to the angle is calculated and plotted against the surface tensions of the liquids.

Cosine to the angle 0° is one. This means that where the (normally) straight like between the points cuts the line cosine = 1 is the critical surface tension of the plastic. See graph 1.
The lower the γc the better non-stick properties.

The critical surface tension of PTFE on graph 1 is 18.5 dynes/cm.



GRAPH 1. MEASURING THE CRITICAL SURFACE TENSION OF PTFE

The critical surface tension is found in the literature for the most plastic materials. See table 2.

PLASTMATICERIAL	CRITICAL SURFACE TENSION
FLUORINATED ETHYLENE PROPYLENE = FEP	16.2
PERFLUOROLKOXY = PFA	17
POLYTETRAFLUOROTHYLENE	18.5
POLYTRIFLUOROTHYLENE	22
ETHYLENTETRAFLUOROTHYLENE = ETFE	25
POLY(VINYLIDENFLUORIDE)	25
POLY(VINYLFLUORIDE)	28
POLYETHYLENE	31
POLYTRIFLUOROCHLOROTHYLENE = E-CTFE	31
POLYSTYRENE	33
POLY(METHYLMETHACRYLATE)	39
POLY(VINYLCHLORIDE) = PVC	39
POLY(ETHYLENETEREPHTHALATE) = PET	43

TABLE 2. THE CRITICAL SURFACE TENSION FOR DIFFERENT POLYMERS

It is seen that the fluoroplastics have the lowest surface tension of all polymers and that any replacement in the polymer by a non F-containing molecule increases the surface tension.

The low-energy surfaces are difficult to wet and cannot be bonded using ordinary adhesives. On the other hand they are easy to clean - it is a non-stick
surface that repels all common materials (form a large contact angle) and in
thick layers is characterized as a corrosion protecting coating.

The fact that the full-fluorinated polymers give the best chemical resistance and therefore also corrosion protection can be seen in table 3 below:

	TYPES OF MEDIAS		PTFE	PFA	FEP	ECTFE	PVDF	POM	PA6	PP	HDPE	PVC
1	ACIDS	INORGANIC	+	+	+	+	+	-	-	0	0	+
		ORGANIC	+	+	+	+	+	-	-	+	+	+
2	BASES	ORGANIC	+	+	+	+	-	+	+	+	+	+
3	SALTS		+	+	+	+	+	+	+	+	+	+
4	HALOGENS		+	+	+	0	0	-	-	-	-	0
5	SOLVENTS	ALIPHATIC HYDROCARBONS	+	+	+	+	+	+	+	+	+	0
		AROMATIC HYDROCARBONS	+	+	+	+	+	+	+	-	-	-
		CHLORINATED HYDROCARBONS	+	+	+	0	0	-	+	-	-	-
		KETONES	+	+	+	0	-	0	+	0	0	-
		AMINES	+	+	+	0	-	-	+	0	0	-
		ALCOHOLS	+	+	+	+	+	+	+	+	+	+
		FURANES	+	+	+	-	-	-	+	-	-	-
		ESTERS	+	+	+	0	0	-	+	0	0	-
		ALDEHYDS	+	+	+	0	+	0	0	+	+	+
6	PHENOLS		+	+	+	+	+	0	-	+	+	-

+ RECOMMENDED
0 MAY BE USED
- NOT RECOMMENDED

TABLE 3. CHEMICAL RESISTANCE OF FLUOROPOLYMERS

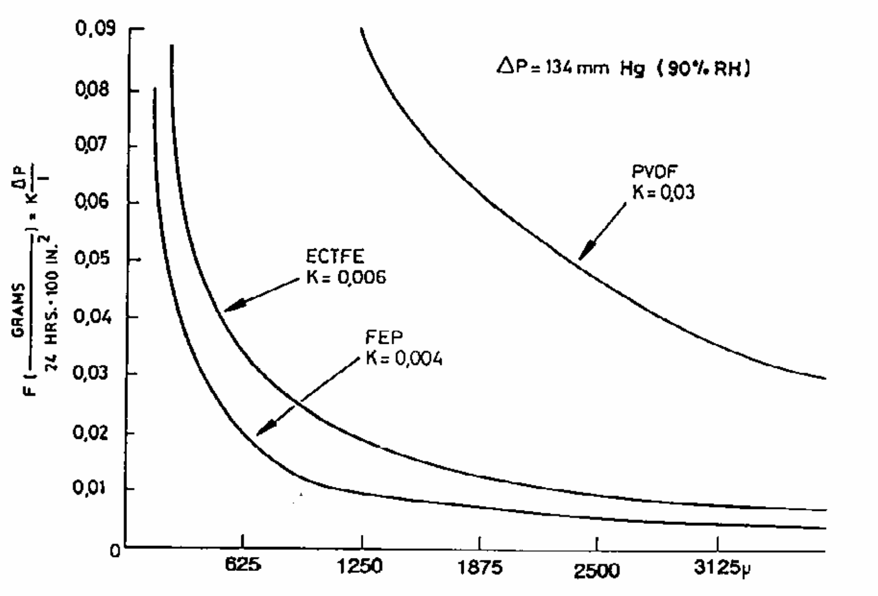
PTFE, PFA and FEP are completely resistant against all common used chemicals. The two first ones up to 260° C, while FEP resists up to about 200°C. FEP has, as can be seen in table 2, the lowest surface tension due to the highest concentration of F in the surface.

The only materials that may attack the full-fluorinated polymers are certain fluorobased solvents at high temperatures and metallic sodium. The latter fact is utilised to make PTFE and other fluoro plastics bondable by treating them in a (very noxious) mixture of metallic sodium dissolved in liquid ammonia. What happens is, that the surface is altered chemically to a surface with somewhat higher critical surface tension.

Chemical resistance is not the same as corrosion protection, allthough it is a prerequisite, see later.

COATING THICKNESS

The thickness of the coating has a large influence on the permeation and consequently on the corrosion protection. In Graph 2 is seen water permeation through polymers with different thicknesses at 100° C.



GRAF 2. PERMEATION VS FILM THICKNESS

The graph shows how permeation decreases with increased film thickness. When the thickness is above 500 - 600 µm (0,5-0,6mm) the value levels off.

On complicated parts like reaktors, tubes and the lige it is difficult to obtain a completly even film thickness. This means that if the minimum film thickness is specified at 600 µm than the mean film thickness is between 800 - 1000 µm for the fluoroplastic coating.

For less demanding jobs solving corrosion problems in the food industry, for ventilators in low aggressive areas and for bolts in the off-shore industry coatings with film thicknesses 25 - 200 µm may often be used. The ability for thin coating to protect against acid materials and salt can be seen in the daily use of pots and pans.

PERMEATION

Another unique property of fluoropolymers compared to other polymers is the low permeation of small aggressive molecules like water, solvents, chlorides bases and acids. In the table below is seen some values. Generally it can be concluded, that the larger the molecule the slower the diffusion. At lower temperatures the diffusion speed is also lower just as it is if the temperaturegradient is small.

The measurements are performed on 25 µm thick films of FEP after a modified ASTM E-96 method.

STEAM	TEMPERATURE °C	G/645CM^2(24 HRS)
ACETIC ACID	35	0.41
ACETONE	35	0.95
ACETOPHENONE	25	0.50
BENZENE	35	0.64
TETRACHLORKULSTOF	35	0.31
ETHYL ACETATE	35	0.76
HEXANE	35	0.56
HYDROCHLORIC ACID	25	LESS THAN 0.01
PIPERIDINE	25	0.04
CONC. NITRIC ACID	25	7.5-14.0
SODIUMHYDROXIDE	25	LESS THAN 0.01
SULPHURIC ACID	25	0.00001
WATER	39.5	0.40

TABLE 4. PERMEATION OF VAPOURS IN A FLUOROPOLYMER (FEP)

If there are salts, solvents, bases, acids or other polymers dissolved in the media permeation is lower.

Please note the large difference in permeation between water and sulphuric acid. This means that a coating that can be used for concentrated sulphuric acid at 200° C maybe only can be used in a water system up to 100° C due to the permeation speed of the tiny water molecule.

THE COATING PROCESS

The thick corrosion protecting coatings are normally applied on the clean sandblasted part using an electrostatic spraying process, where the fluoro polymer fine powder is charged to a high voltage in relation to the part, which is grounded. The powder seeks to the metal part from all sides saving the expensive powder and covering areas difficult to reach.

As the total process including pretreatment of the part takes place at temperatures between 300 - 400° C, the part has to resist being heated to 400° C several times.

CASE STORIES

Below is described typical applications for fluoroplastic coatings in the chemical, pharma centical and the galvanic industry, in the food processing industry and in the flue gas industry.

CASE 1	**PROCESS TANKS FOR MEDICAL PRODUCTS**
APPLICATION	Production of medicine in a water environment containing solvents, bases and acids.

FUNCTION	Separation of the media from the metal, corrosion protection, easy cleaning.
COATING	Accopon HBA, a fullfluorinated coating
FILM THICKNESS	600 - 1000°µm
TEMPERATURE	÷ 60 to 100°C
NOTES	The reactors are 7 years old and still in use

CASE 2 UNIT FOR PRODUCTION OF SODIUM HYDROXIDE PILLS

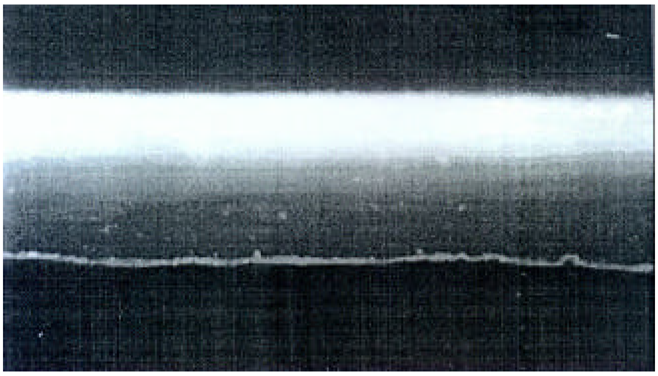
APPLICATION	"Dripmethod" for producing NaOH and KOH
FUNCTION	Corrosion protection, non-stick
COATING	Accopon HBA, a full fluorinated coating
FILM THICKNESS	600 - 1000 µm
TEMPERATURE	200°C

CASE 3 CONCENTRATION OF AQUA REGIA

APPLICATION	Production of noble metals
FUNCION	Corrosion protection
COATING	Accopon HBA a fully fluorinated coating
FILM THICKNESS	600 - 1000 µm
TEMPERATURE	App. 130°C

CASE 4. DESULPHERATION OF FLUE GAS

APPLICATION	Protection against concentrated sulphuric acid
FUNCTION	Protect against strong acids and high temperatures
COATING	Accoshield, a full fluorinated coating
FILM THICKNESS	600 - 1000 µm
TEMPERATURE	246°C
EXPOSURE	4 years
NOTES	On the picture 1 below of the exposed coating it can be seen that after 4 years of exposure at 246° C against concentrated sulphuric acid, less than half of the coating thickness has been decoloured, indicating that the sulphuric acid has permeated this far into the coating and oxidized the carbon that gives this the coating its black colour.



Picture 1 Accoshield, 246°C, 4 years, concentrated sulphuric.

CASE 5. VESSEL FOR GALVANIC LIQUIDS

APPLICATION	Vessel for acid mixtures of chromic acid and sulphuric acid
FUNCTION	Corrosion protection
COATING	Accotron, partly fluorinated coating
FILM THICKNESS	550 - 1000 µm
TEMPERATURE	35 - 40°C

Case 6. VENTILATOR FOR WATER CLEANING UNIT

APPLICATION	Ventilator for acid watery gasses
FUNKTION	Rust prevention from splashes, pitting etc.
COATING	Accoten S, a PTFE coating
FILM THICKNESS	25 - 40µm
TEMPERATURE	Room temperature
NOTE	The ventilator was pitted in many places. The coating stopped effectively the pitting and protected the ventilator against further corrosion

References:

1. W.A. Zisman, Contact angle, wettability and adhesion, Advances in Chemistry series nr. 43, 1964, p. 13.
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3. Symalit, Technical Handbook Fluoroplastic Products, 1989
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