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The fluorenon polyester ISO FPE of ISOVOLTA Company Austria

In the last two years the Isovolta Comp. has payed attention to a family of polymers which are thermally stable, of low flammability and which show in the case of combustion a low toxic gas emission. The aim was to cast a transparent film of a solution, in which no flame retardants are used to achieve the flammability requirements.

ISO FPE consists only of carbon, hydrogen and oxygen, that is to say that no nitrogen, fluorides, sulfur or antimony are incorporated in the polymer.

The selection of monomers was based on the aspects shown in previous papers, namely that the char yield and the amount of incombustible gases formed in thermal decomposition are the most significant characteristics of flame resistance, even in a quantitative way. For a large number of well known polymers the char yield under nitrogen atmosphere due to pyrolysis was determined. The char yield is related to the chemical structure of the polymer in a distinct way. Also, the amount of char yield can be predicted from the structure. Secondly, there is a significant relation between the char yield and the limiting oxygen index. The LOI is measured according to ASTM D 2863-76.

The linear correlation between the char yield Y_c^{800} under nitrogen atmosphere and the LOI is represented by the equation:

$$\underline{LOI = 17,5 + 0,4 \,.\, Y_c^{800}}$$

The char yield Y_c^{800} under nitrogen atmosphere is related to the chemical structure of the polymer by the equation :

$$\underline{Y_c^{800} = 1/M \,.\, 1200 \,.\, \sum_i (CFT)_i}$$

M means the molecular weight per structural unit

(CFT) the group contributation to the char forming tendency

The experimental results mach the theoretical values very well. Doing a thermogravimetric analysis a char yield of 58 % weight retention is found(Fig 1). This causes a theoretical LOI of 40,7 %, the value found by experiment is 40.

The group contribution to the char forming tendency is shown in the following table.

Group		Constribution to CFT (modified)
methyl	CH_3-	- 1,5
methylene	CH_2=	- 1
isopropylidene	$C(CH_3)_2$=	- 3
phenyl	C_6H_5-	+ 1
phenylene	C_6H_4= o	+ 2
	m	+ 3
	p	+ 4
fluorene-9-ylidene		+ 10

This table allows to predict the flammability behaviour of groups used to compose monomers.

In a comprehensive study of P.W.Morgan a large number ob bisphenols was studied. However, only two of these bisphenols showed sufficient quality of polymers resulting in a high value of LOI. This fact is due to the missing of groups with negative contribution to the char forming tendency. The monomer engaged for the preparation of ISO FPE is the 9,9-Bis(4-hydroxyphenyl)fluorenone, or fluorenone, which we call Diphenol F.

Diphenol F is prepared by a modification of the synthesis of Morgan in batches of 100 lb from fluorenone, phenol, hydrogen chloride and a co-catalyst. The synthesis is conducted by Isovolta Company in Austria. The yield of Diphenol F after one crystallisation process from 1,2 dichloroethane, is more than 90 percent.

Technical datas are shown in the table below:

Melting point	:	225°C		
Elemental analysis	:		% C	% H
		calculated	85,69	5,18
		experimental	85,54	5,03

The purity of Diphenol F is checked by high pressure liquid chromatography and yields a value of 99 percent.

Synthesis of ISO-FPE

One of the most common syntheses of polyesters is the reaction of chlorides of dicarboxylic acids with bisphenols. However, there are several ways described in the literature to conduct the synthesis of these polyesters:

The LOI of polyesters produced by solution condensation at high temperatures yields a low value compared to polyesters prepared with solution condensation at room temperature. The reason is, that even a low concentration of products which is obtained by decomposition due to these drastic temperature conditions causes the low value of LOI. On the other hand, the interfacial condensation is carried out at room temperature. Since Diphenol F shows a low solubility in aqueous sodium hydroxyde a solution condensation with stoichiometric amounts of hydrogen chloride acceptors - such as triethylamine or others - is preferred when working at room temperature. The advantage of this process is, that low boiling solvents such as dichloromethane or 1,2-dichloroethane are applicable at normal pressure. High molecular weight of the polyester is only obtained by the use of terephthalic and isophthalic acid chlorides of high purity.

With respect to mechanical properties we obtained the best results using a mixture of terephthalic and isophthalic acid chlorides within the range of a 1:1 to 3:1 mixture. Films cast from solutions of polyesters synthesized only with one of these two acid chlorides show brittleness.

The melting range of ISO-FPE is close to the heat distortion temperature at 480°C. Due to this fact and the high temperature resistance ISO-FPE is not suitable for injection molding and extrusion. ISO-FPE shows good mechanical and electrical properties over a wide range of temperature and frequency (see Fig 2). ISO-FPE is soluble in dichloromethane, chloroform, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, dimethylformamide, dimethylacetamide, cresol, tetrahydrofurane and methyl benzoate.
ISO-FPE is insoluble in water, acetone, methanol, ethanol, isopropanol, ethyl acetate and benzine.

Combustion of ISO-FPE coatings and films yields very low smoke and toxic gas generation. As shown in Fig 3 ISO-FPE produces some CO and CO_2, which are within the permitted ranges and no HF. The flame spread data according to ASTM E - 162 are given in Fig 4 and the smoke production in Fig 5. In both cases the film is compared with the data of a PVF film of same thickness.

Production of Powder and Films

After synthesizing ISO-FPE polyester in a laboratory scale we looked for a possibility to process the polyester in batches of some pounds. Therefore, a small pilot plant was developed to work with both the solution condensation method and the interfacial condensation method. This pilot plant is a sort of universal tool adaptable to the actual needs. The conditions of a small scale production could be studied with this machine. Now, batches of 40 pounds of polyester can easily be obtained in a second generation pilot plant. However, the preparation of pure, high molecular weight polyester demands a lot of tedious hand labour at the moment, restricting our output to one batch a week.

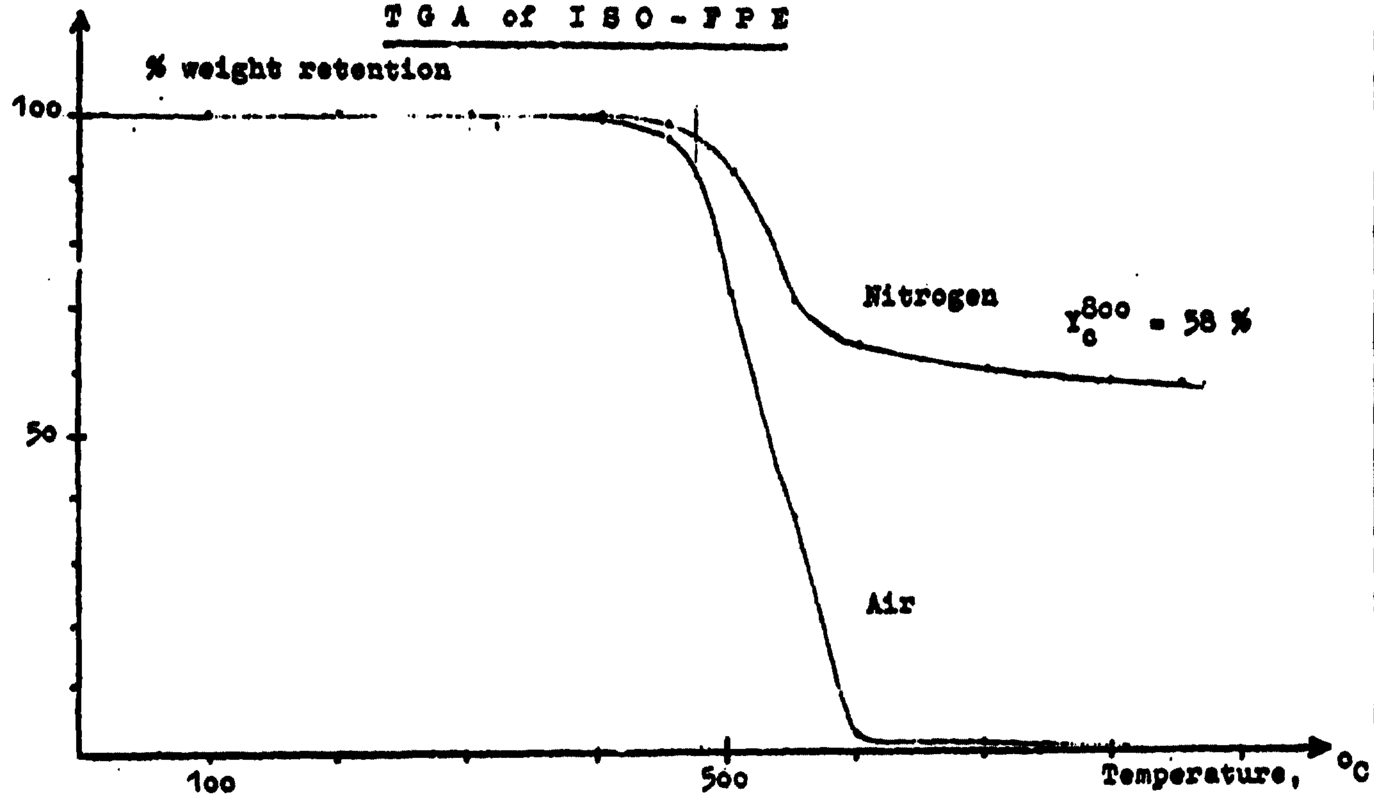
In spite of these and other difficulties we have been able to cast films in a continous process on a laboratory film casting machine using a 200μ Teflon foil as substrate. Plans are under consideration for a pilot plant equipment with a production of up to 20 tons of polyester per year.
Currently films are available in thicknesses from 1/4 of a mil up to 3 mil. In Addition preliminary studies have been conducted to evaluate the adhesive performance of various decorative inks on the film. The film may be embossed at temperatures between 100 and 180°C under a pressure of 290 psi using conventional pressing techniques.

The film can be pigmented with various inert inorganic pigments such as TiO_2 and various tinting agents and colorants. Furthermore, preliminary tests were conducted to evaluate the soil and smoke resistance according to Boeing standards which are shown in Fig 6.

As a conclusion we think that the ISO-FPE film has a potential use as a corative fire resistant film for aircraft interior application. However, additional work is required to evaluate this film in conjunction with current state of the art aircraft interrior panels and other advanced structures.

Thank you for your attention.

TGA of ISO-FPE



Thermogravimetric Analyses of ISO-FPE under nitrogen and air

Figure 3

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Technische Mitteilungen

Elektro-Isolierstoffe

Flexible Isolierstoffe

Properties of I S O - F P 3

Test		Unit	Average Value
Powder			
Glass transition temperature		°C	none
Melting range		°C	none
Heat distortion temperature		°C	48o
Inherent viscosity		$dl.g^{-1}$	o,6o
(phenol : tetrachloroethane = 6o : 4o o,5 g / 1oo ml)			
Film			
Thickness		mm	o,o5o
Density		$g.cm^{-3}$	1,22
Tensile strength		$Pa.1o^{5}$	662
Elastic modulus		$Pa.1o^{1o}$	o,21
Elongation		%	4,2
Dielectric strength		$kV.mm^{-1}$	286
Dielectric constant	1oo Hz		3,55
	1 kHz		3,52
	1 MHz		3,7o
Dissipation factor	2oo Hz		25,o . $1o^{-3}$
	1 kHz		8,o . $1o^{-3}$
	1 MHz		17,2 . $1o^{-3}$
Volume resistivity	5oo V	Ω.cm	1,o . $1o^{17}$
Surface resistance	1ooo V	Ω	6,o . $1o^{11}$
Weight loss after 24 hrs, 25o °C		%	1,48
Water absorption		%	< o,5
Solder float test (26o °C)		s	> 12o
Char yield Y_c^{8oo}, nitrogen		%	58
Limiting oxygen index film, 125 µ, room temp., vacuum		%	36
Rod			
(sintered at 22o °C under pressure)			
Limiting oxygen index		%	4o

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Toxic Gas Evolution of I S O - F P E - Film

N B S Chamber 4,o min

Film

o,oo1 inch Densil adhesive

3-ply laminate
(Ciba Geigy 971 G/1581)

	Tedlar o,oo2 inch	I S O - F P E o,oo2 inch
NO_x, ppm	7	2
C O	1oo	12o
CO_2	18oo	18oo
H F	1o2	o

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Flame Spread Data of I S O - F P E - Film

ASTM E - 162

Film

o,oo1 inch Densil adhesive

3-ply laminate
(Ciba Geigy 971 G/1581)

	I s	S.D.[x]
3-ply laminate + o,oo1 inch Densil adhesive	2,65	o,6o
o,oo2 inch Tedlar	1,82	o,43
o,oo2 inch I S O - F P E	2,oo	o,4o

S.D.[x] Standard Deviation

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Smoke Measurements of I S O - F P E - Film

N B S - Smoke Chamber 2,5 W/cm^2

	Specific Optical Density (Flaming Condition)		
	D s 1,5 min	D s 4,0 min	D m (max)
Tedlar o,oo2 inch	6,67	11,o7	15,13
I S O - F P E o,oo2 inch	1o,93	16,27	18,7o

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Soil Resistance and Smoke Stain Resistance of

I S O - F P E - Film

Tested by Boeing Material Specification 8 - 22o

Items : butter
mayonnaise
chocolate
soup
fruit stain (orange juice)

cigarette smoke (168 hours)

Washing agents : SU 126 SYRO (Unilever) 1o % solution
SU 9o4 JET (Unilever) 1o % solution

I S O - F P E - Film (o,oo2 inch) shows no discoloration when soiled and cleaned in accordance with Boeing Material Specification, Section 8.3. and 8.4.

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