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Preparation and Fire Test of Intumescent Powder Coatings

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Abstract

New regulations for hazardous air pollutants drove operations to compliant coatings. Powder coatings were the most popular choice. A screening of intumescent powder coatings was carried out comprising binders like thermoplastics as plasticised polyvinylchloride and polypropylene as well as non-cross linked thermosets as polyurethanes. Intumescence was achieved by addition of the intumescent ingredient bicyclopentaerythritol phosphate, by the intumescent combination polyethylene glycol as binder with ammonium polyphosphate and binders comprising intumescent phosphororganic polyesters. The intumescent ingredients and components were characterized by thermogravimetric analysis and described by chemical formulas together with their balances of weights and heats of formation. The electrically loaded powders were sprayed on grounded steel panels and subdued a fire test. The time, until the coated panels reached 500˚C, was observed. The panels coated with the plasticised polyvinylchloride plus bicyclopentaerythritol phosphate and those protected by the polyurethane comprising polyethylene glycol and ammonium polyphosphate delayed the period of time, until 500˚C were reached, significantly and were equal in efficiency with the reference, the commercial water borne intumescent varnish.

Keywords

Intumescence, Powder Coating, Fire Test

Subject Areas: **High Polymer Chemistry, Physical Chemistry, Thermochemistry**

1. Introduction

The National Emission Standards for Hazardous Air Pollutions address low level of volatile organic compounds, reduction or elimination of certain hazardous alkyl phenols [1]. They drive operations to compliant coatings as powder, electro, autophoretic, UV, high solid and water borne coatings. Recently powder coating has been the most popular choice [2] [3]. Water borne and solvent based intumescent varnishes are a growing market. Espe-

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cially steel constructions are protected by intumescent coatings in order to enlarge the time lag, until 500˚C are reached in the case of fire. At the temperature of 500˚C steel looses 50% of its strength and stiffness.

Until now there are no intumescent powder coatings available on the market. In literature only patents [4]-[8] treat the subject. Several companies provide the market with heat resistant powder coatings, which consist of silicone, such as Alesta HR from Du Pont, or polyester resins, such as Pyrotect FR from DGL international Camel and they are highly filled with mica, wollastonite or other minerals [9]. They are applied in film thicknesses between 35 and 100 µm. The film thicknesses of powder coatings are limited with 0.5 mm for cold items and with 2.5 mm for hot parts. By definition water borne intumescent paints use water as solvent in solutions or as dispersant in dispersions [10]. They are sensitive to dirt and oil, which tend to create blisters and lead to poor adhesion and accelerated corrosion, nevertheless high solid and water borne coatings are replacing solvent based paints at an increasing rate. Metals generally require a minimum of 5 - 6 stages and separate cleaning and conversion stages. Plastics generally use a minimum of 6 - 8 stages. The most typical types of applications are dip, flow coat and spray. Electro and autophoretic coatings are dip processes by design, although dipping can be used to apply waterborne and powder coatings but is not practicable for high solids. Spray is the most common method of paint application, including air spray, air assisted airless, airless, HVLP (high volume low pressure) and electrostatic spray. HVLP benefits the environment by reducing the amount of bounce back of paint resulting in an improved transfer efficiency and lower paint usage. A schematic diagram of the electrostatic powder spray system is represented in **Figure 1**.

The yield of powder coatings is determined by the film thickness and the density of the film after curing in Equation (1).

$$\text{Yield } (m^2/kg) = 1000/[\text{density } (g/cm^3) \times \text{thickness } (\mu m)] \quad (1)$$

The expected costs are given by the price of the powder coating €/kg divided by the yield in Equation (2).

$$\text{Costs } (€/m^2) = \text{price } (€/kg)/\text{yield } (m^2/kg) = \text{price} \times \text{density} \times \text{thickness}/1000 \quad (2)$$

The costs are driven by price, density and film thickness after curing.

Today ovens for the curing or melting of powder coatings are available even for parts as large as 7 m length and as heavy as 5 tons [11]. **Figure 2** demonstrates the large dimensions of a curing oven showing the small labourer in comparison with the huge oven.

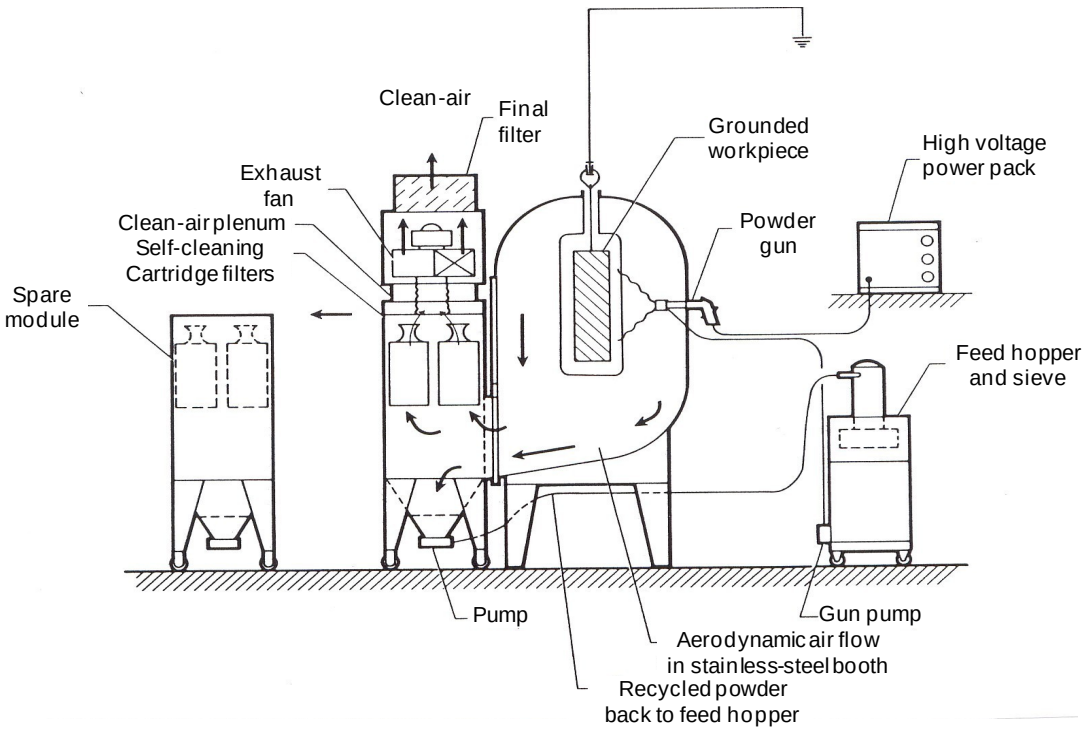


Figure 1. Schematic diagram of electrostatic powder spray system [2].

Figure 2. Dimensions of ovens available for curing and sintering of powder coatings [11].

In order to obtain a general view over the whole scope of intumescent powder coatings, seven recipies are developed: two formulations based on thermoplastic binders, namely plastisized polyvinylchloride PPVC and polypropylene PP comprising bicyclopentaerythritol phosphate as intumescent ingredient. PPVC is chosen for char formation and low combustion. PP is selected, because it can be degraded to well flowing low molecular products by the addition of peroxides. Five non-cross linked thermosets comprising uretdione and linear polyesters as well as polyethylene glycol react to polyurethanes. Bicyclopentaerythritol phosphate is added as intumescent ingredient in the cases, when the binders show no intumescence by themselves. Use is made of the intumescent phosphororganic polyesters as binding component as well as intumescent mixtures of polyethylene glycol and ammonium polyphosphate. Polyurethanes are very familiar in powder coatings, for instance, Vestagon from Evonik and Crelan from Bayer are well known commercial products.

In principle, powder coatings are manufactured by dry blending or by melt mixing processes, which is described as flow diagram in **Figure 3**.

The milled powders and the water borne commercial paint Nonfire S168 are applied to steel panels and subdued a fire test.

2. Experimental

2.1. Materials

In **Table 1** all chemicals and products used as well as their suppliers were listed.

2.2. Methods

The intumescent ingredients were characterized by thermal gravimetric analysis (TGA) on a Mettler Toledo TMA/SDTA with TGA/SDTA 851 Modul. The samples were placed in aluminium oxide crucibles of 900 µl

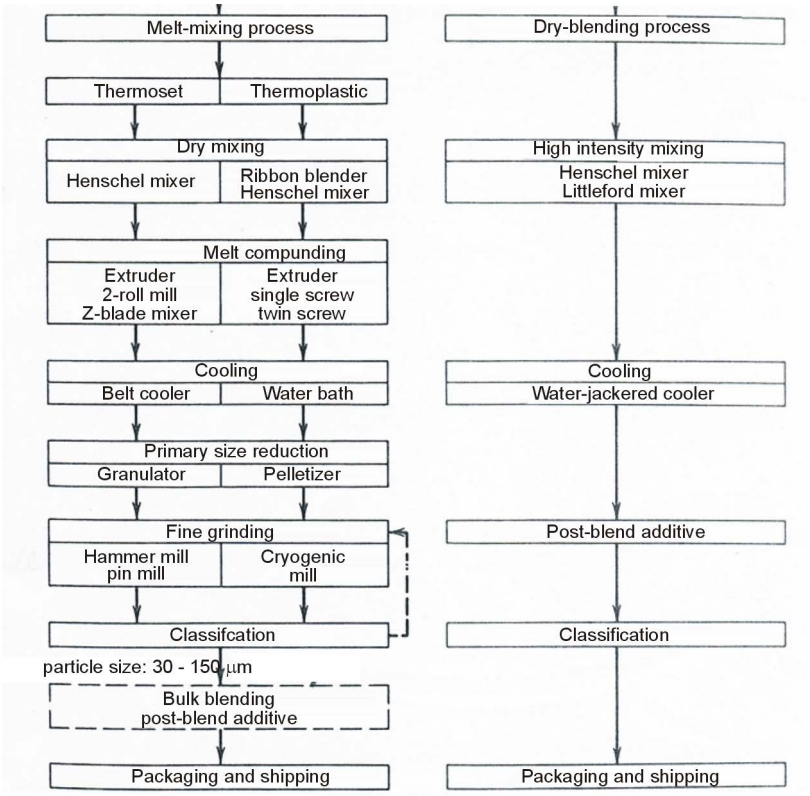


Figure 3. Flow diagram of powder coating manufacturing [2].

Table 1. Chemicals, brand names, abbreviations, formulas, suppliers.

Chemical	Brand name	Abbreviation	Formula	Supplier
Ammonium polyphosphate	Exolit 422	APP	NH_4PO_3	Clariant
Titanium oxide	Kronos 2300	TiO_2	TiO_2	Kronos
Bicyclopentaerythritol phosphate	NH-1197	BCPP	$C_5H_9PO_5$	Great Lakes
Plastisized Polyvinylchloride	Rottolin 02535	PPVC	CH_2CHCl	Rottolin
Polypropylene	US 10	PP	CH_2-$CHCH_3$	Borealis
2,5 Bis(ter.Butyldimethyldioxo)hexane	Interox DH BP451C	Peroxide	$C_{16}H_{34}O_4$	Interox
Polyethylene wax	Hostalub		CH_2-CH_2	Hoechst
Calcium stearate		Castearate	$Ca(C_{17}H_{35}CO_2)_2$	Dr.L.C.Marquart GmbH
Montan Wax		Montan	C_{26}-C_{32}	BASF
Isophorondiisocyanate uretdione	Crelan LS 2147	Uretdione	$C_{12}H_{19}N_2O_2$	Bayer
Polyethylene glycol	Pluriol E1500	PEG	CH_2-CH_2-O	BASF
Tin octoate		Snoctoate	$Sn(O_2C$-$(CH_2)_6CH_3)_2$	Bärlocher
Diazabicyclooctane	DABCO	Dabco	$C_6H_{12}N_2$	Bayer
Aluminium silicate	Zeolithe P	Zeolithe	$Na,Ca[Al_2Si_4O_{12}]xH_2O$	Bayer
Dibutyltindilaurate	DBTDL	DBTDL	$(C_4H_9)_2Sn(C_{11}H_{23}CO_2)_2$	Bärlocher
Succinic acid			$HOOCCH_2COOH$	DSM
1,4 Butanediol			$OH(CH_2)_4OH$	BASF
Diethylene glycol	DEG		$OH(CH_2)_2O(CH_2)_2OH$	Hoechst
Triethylamine			$(C_2H_5)_3N$	BASF
N,Ndihydroxyethylmethylaminediethyl-phosphonate	Levagard N4090		$C_9H_{22}NO_5P$	Clariant
Maleic anhydride		MSA	$C_4H_2O_3$	DSM
p-Toluene sulfonic acid		TS	$C_7H_7SO_3H$	Fluka
Silicone oil	DC 193	Silicone	$(CH_3)_2$-Si-O	Dow Corning
Water borne intumescent paint	Nonfire S168			Tikkurila Comp.

volume (ME 511119, 960) with 12 mm diameter covered by punctured lids. The TGA measurements took place under nitrogen with 80 ml/min at a heating rate of 5 K/min. The TMA measurements were performed in aluminium oxide crucibles with 7 mm diameter and 4.6 mm height covered by 6mm diameter lids in air at a heating rate of 50 K/min under nitrogen.

All formulations were made by the dry blending process.

The powdery ingredients of intumescent powder coatings were mixed in a high speed Henschel impeller mixer. The mixtures were cooled in water jacketed cooler. Under cooling the mixtures were ground on a Baumeister pin mill and classified by sieving. The particle sizes of the ground mixtures were determined with Master Sizer XSB.OD from Malvern Instruments.

The melt viscosities of the thermoplastic powders were measured on a Rheograph 2000 (Göttfert) at low shear forces 230 sec^{-1} according to DIN 54811. The curing of the thermosets was investigated on a Plasticorder (Göttfert). The measurement started at a product temperature of 100˚C and stopped at 200˚C after 20 minutes at a constant heating rate of 5 K/min.

A Wagner powder spraying device with a PEM-C3 spray gun, a steering device EPG 2007 and a powder injector PJ 2020 PRS was used for the process of spraying. The powders were blown through a voltage field of 50 kV. Small steel boards with the dimensions 25 × 25 × 0.5 cm^3 were the objects of spraying, which were equipped with two iron Constantan thermocouples.

The film thickness was measured by the inductive method with MiniTest 7.400 (Elektrophysik).

Curing and melting was performed in a small oven at temperatures between 160˚C - 250˚C and times of 10 - 15 minutes.

The fire tests were performed in a 1 × 1 × 1 m^3 furnace from company Riedhammer.

The panels were placed between two 20 mm silicate boards of Promatect H. The board looking to the furnace had 9 windows: one for the naked panel, one for the reference sample and the seven left for the panels coated with the powder coatings. The whole arrangement was placed at the front of the furnace, which was heated according to the ISO curve.

The decomposition of intumescent components was described with chemical formulas F, complete balances of weights MW (g/mole) and heats of formation H (kJ/mole). The formulas and the weight balance had to be in agreement with the weight residues R determined by thermogravimetric measurements. In the following the method was exemplified on the example ammonium polyphosphate NH_4PO_3:

325˚C; h = 0.6 kJ/g; R = 82.5%
F(I) $NH_4PO_3 = NH_3 + HPO_3$
MW 97 = 17 + 80
H − 1085 + 58 = −46 − 981
400˚C; h = 1.1 kJ/g; R = 73%
F(II) $HPO_3 = 0.5H_2O + 0.5P_2O_5$
MW 80 = 9 + 71
H − 981 + 110 = −121 − 750
F(III) = F(I) + F(II) $NH_4PO_3 = NH_3 + 0.5\ H_2O + 0.5P_2O_5$ h = 1.7 kJ/g; R = 73%
MW 97 = 17 + 9 + 71
H − 1085 + 168 = −46 − 121 − 750

3. Results

3.1. Synthesis of Linear Polyesters

3.1.1. Succinic Acid 1,4 Butanediol Polyester (1)

A 1000 ml three necked round bottom flask equipped with mechanical stirrer, reflux condenser, thermometer, addition funnel and dry nitrogen inert was loaded with 161.2 g (1.5 m) succinic acid and 135 g (1.5 m) 1.4 butanediol. Under nitrogen 3 g of p-toluene sulphonate were added. The temperature was raised to 200˚C and kept for 3 h. Then the nitrogen supply was stopped and vacuum was applied. Heating at 200˚C was continued for further 5 h. The solid polyester melted at 68˚C and showed an hydroxyl number of 56 and acid number of 4.8.

3.1.2. Pentaerythritol Diphosphite Diethylene Glycol Polyester (2) and of Pentaerythritol Diphosphate Diethylene glycol Polyester (3)

A 2000 ml three necked round bottom flask was equipped with a mechanical stirrer, reflux condenser, ther-

mometer, addition funnel and dry nitrogen inert.

In case (2) a solution of 0.5 mol (132.5 g) dichloropentaerythritoldiphosphite [12] in 500 g toluene and in case (3) a solution of 0.5 mol (148.5 g) dichloropentaerythritoldiphosphate [13] in 500 g toluene were added over a period of 1 h to a solution of 0.53 m (56.2 g) diethylene glycol (Hoechst) and 101 (1 mol) triethylamine (BASF) in 800 g toluene. Both solutions were heated at reflux for 5 h. The precipitated triethyl amine hydrochloride was filtered. The filtrates were concentrated by heating to a final temperature of 160˚C/5 mm vapour pressure. The solid final products were characterized:

Polyester (2) Melting point Tm = 90˚C, elementary analysis: 37.2% C, 5.8% H, 18.6% P

Acid number (DIN 53240): 2, hydroxyl number (DIN 53402): 112

Polyester (3) Melting point Tm = 80˚C, elementary analysis 34.5% C, 5.5% H, 16.2% P

Acid number: 150, hydroxyl number: 1050

The high hydroxyl number indicated hydrolysis of polyester (3) in the presence of watery bases during titration, when the hydroxyl number was determined.

3.1.3. N, N Dihydroxyethylmethylamine Diethylphosphonate Fumaric Acid Polyester (4)

The equipment was used as already mentioned. The 1000 ml flask was loaded with 1.1 mol (280 g) dihydroxyethylmethylamine diethylphosphonate, Levagard 4090 N (Clariant). Through a powder funnel 1mol (98.1 g) maleic anhydride (DSM fine Chemicals) was added. The temperature was raised to 60˚C. When the solution was clear, the temperature was raised until reflux occurred. The mixture was stirred at reflux for 6 h. 19 g water was removed under vacuum. After cooling the low molecular impurities were removed by solving in benzene and precipitating in petrol ether. The solid residue was characterized:

Melting temperature Tm = 95˚C, elementary analysis: 45.7% C, 7.0% H, 4.4% N, 9.8% P

Acid number: 18, hydroxyl number: 90.

In **Figure 4** the synthesized linear polyesters were described by chemical formulas.

3.2. Characterization of Intumescent Addives and Components

In **Figure 5** the residues by weight R of bicyclopentaerythritol phosphate BCPP and of the mixture polyethylene glycol PEG and ammonium polyphosphate APP 1:1 parts by weight were determined in dependence of temperature. BCPP exerted intumescence at 350˚C and the mixture polyethylene glycol and ammonium polyphosphate at 275˚C.

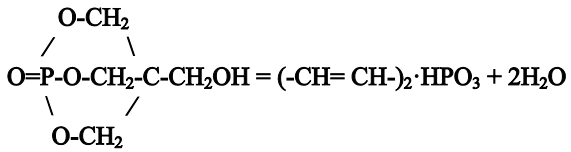
TMA measurements failed, because the produced foams were not stable enough. Intumescence was followed visually.

Formulas and their balances of molar weights and heats of formation were set up, which described the loss of weights measured by TGA.

BCPP Bicyclopentaerythritol phosphate $C_5H_9PO_5$:

340˚C h = −0.26 kJ/g; R = 80%

F1: $C_5H_9PO_5 = C_5H_4 \cdot HPO_3 + 2H_2O$



MW (g/mole) 180 = 144 + 36

H (kJ/mole) − 1380 − 47 = −943 − 2 × 242

Intumescence: 350˚C h= −0.02 kJ/g; R = 66%

F2: $C_5H_4 \cdot HPO_3 = CH_4 + 0.5H_2O + C_4PO_{2,5}$

MW 144 = 16 + 9 + 119

H − 943 −3 = − 121 − 75 − 750

F1 + F2: $C_5H_9PO_5 = 2.5H_2O + CH_4 + C_4PO_{2,5}$ h = −0.28 kJ/g

MW 180 = 45 + 16 +119

H − 1380 − 50 = 605 − 75 − 750

PEG Polyethylene glycol—APP Ammonium polyphosphate 1/1 by weight = 76% 1 m EG/1 m APP and 24% EG in excess:

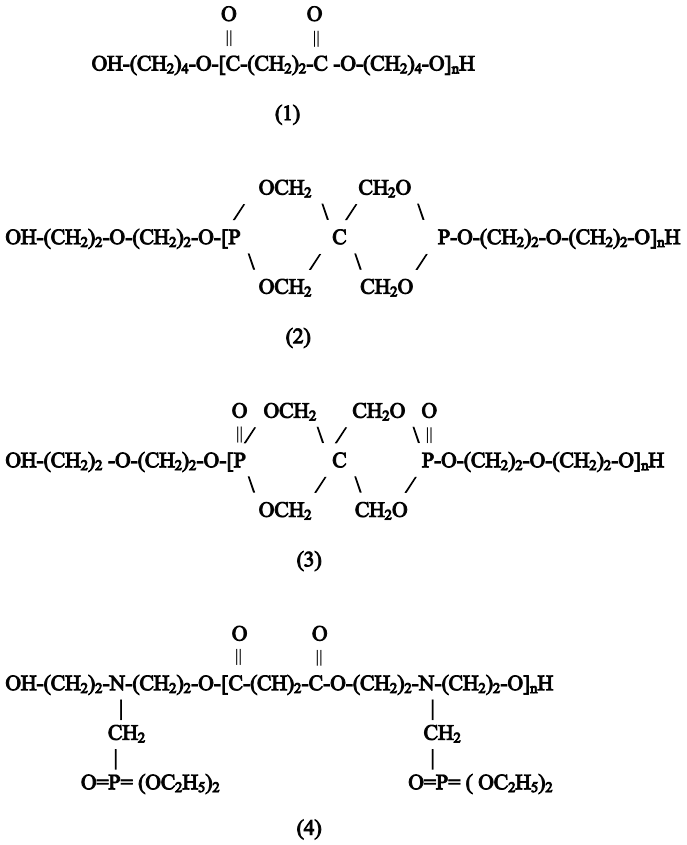


Figure 4. Linear Polyesters: Succinic acid 1,4 Butanediol (1), Pentaerythritoldiphosphite diethylene glycol (2), Pentaerythritoldiphosphate diethylene glycol (3), N,N Dihydroxyethylmethylamine diethylphosphate fumaric acid (4).

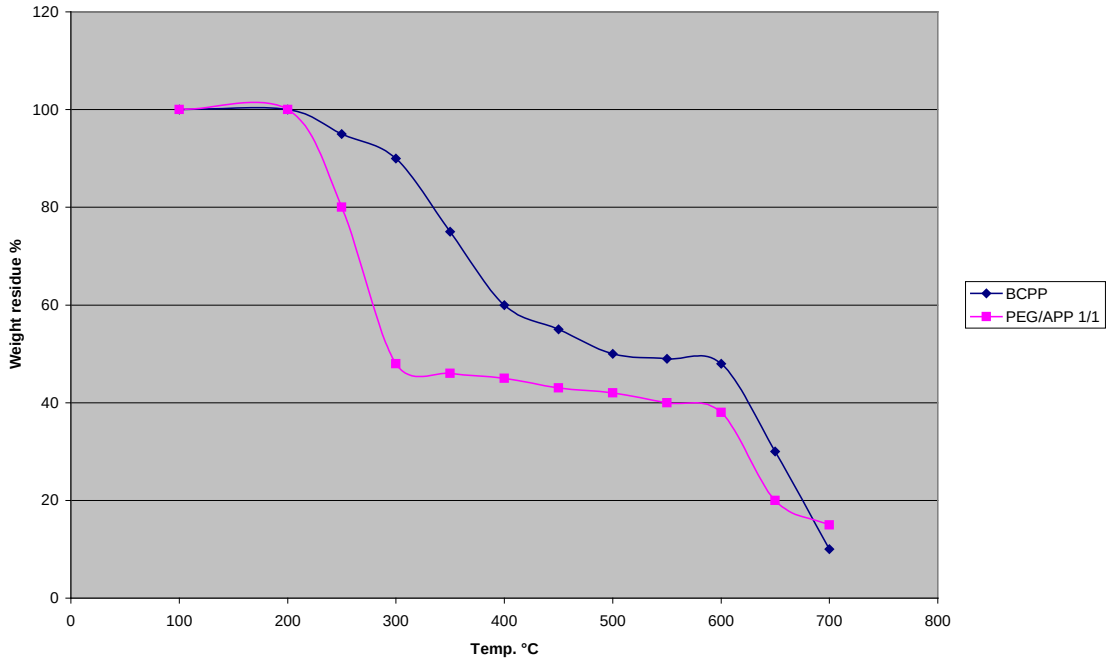
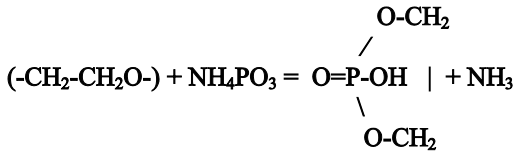


Figure 5. TGA of the intumescent additives BCPP and PEG/APP = 1/1 by weight, air, 5 K/min.

250˚C h = 0.76 × 0.69 = 0.52 kJ/g; R= 100 − 0.76 × (100 − 88) = 91%

F3: $(-CH_2-CH_2O-)n + nNH_4PO_3 = n(-CH_2-O-)_2POHO + nNH_3$ (cyclo Ethylene phosphate)



MW 44 + 97 = 124 + 17

H − 200 −1085 + 97.5 = −1141.5 − 46

250˚C h = 0.76* − 0.04= −0.03 kJ/g; R= 100 − 0.76 × (100 − 75)= 81%

F4: $(-CH_2-O-)_2POHO = C_2H_2 \cdot HPO_3 + H_2O$

MW 124 = 106 +18

H − 1141.5 − 6 = −905.5 − 242

Intumescence: 275˚C h = 0.76* − 0.02 = −0.015 kJ/g; R= 0.76 × 63%= 48%

F5a: $C_2H_2 \cdot HPO_3 = 0.5CH_4 + 0.5\ H_2O + C_{1,5} \cdot PO_{2,5}$

MW 106 = 8 + 89 + 9

H − 905.5 − 3 = − 37.5 – 121 − 750

300˚C: h = 0.24 × 3.39 = 0.81 kJ/g; R = 0%

F5b: $(-CH_2-CH_2O-) = -CH_2-CH_2O$-gas

MW 44 = 44

H − 200 + 149 = −51

F3+ F4 +F5a: $C_2H_4O + NH_4PO_3 = C_{1,5}PO_{2,5} + 1.5H_2O + NH_3 + 0.5CH_4$ h = 0.76 × 0.63 = 0.47 kJ/g; R = 0.76 × 63 = 48%

MW 44 + 97 = 89 + 27 + 17 + 8

H − 200 − 1085 +88.5 = −750 − 363 − 46 − 37.5

The PEG/APP mixture 1:1 degraded under heat uptake of 0.52 − 0.03 − 0.015 + 0.47 = 0.945 kJ/g. Intumescence was observed at 275˚C. BCCP expanded by intumescence under heat evolution of −0.28 kJ/g at 350˚C.

By the same method the linear polyesters were investigated.

In **Figure 6** the synthesized polyesters were subjected to thermogravimetric analysis (TGA).

All polyesters degraded in the range of 250˚C - 700˚C. The succinic-polyester (1) degraded at 300˚C without intumescence. The phosphite-polyester (2) decomposed under intumescence at 350˚C. The phosphate-polyester (3) showed the highest degree of intumescence at the same temperature. The phosphonite-polyester (4) exerted no intumescent behaviour. The expansion was estimated by visual examination, the exact measurement was tried by TMA investigation but failed, because the foams were not stable enough and collapsed. In the following degradation and intumescence were described by the balance of heats of formation and weights.

Succinic-polyester (1) with the repetition unite $C_8H_{12}O_4$ (MW = 172 g/mole); $R_{500˚C}$ = 0%; h = 0.3 kJ/g

350˚C: h = 0.3 kJ/g, R = 0%

F7: $C_8H_{12}O_4 = 2CO_2 + 3C_2H_4$

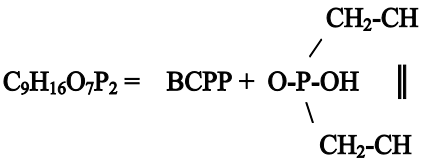
MW 172 = 88 + 84

H − 681 + 51= −786 + 3 × 52

Phosphite-polyester (2) with the repetition unite $C_9H_{16}O_7P_2$ (MW= 298 g/mole); $R_{500˚C}$ = 35%; h= −0.28 kJ/g

250˚C: h = −0.5 kJ/g; R = 100%

F8: $C_9H_{16}O_7P_2 = C_5H_9PO_5 + C_4H_7PO_2$



MW 298 = 180 + 118

H − 2113 + 149 = −1380 − 584

300˚C: h = −0.04 kJ/g; R = 71.8%

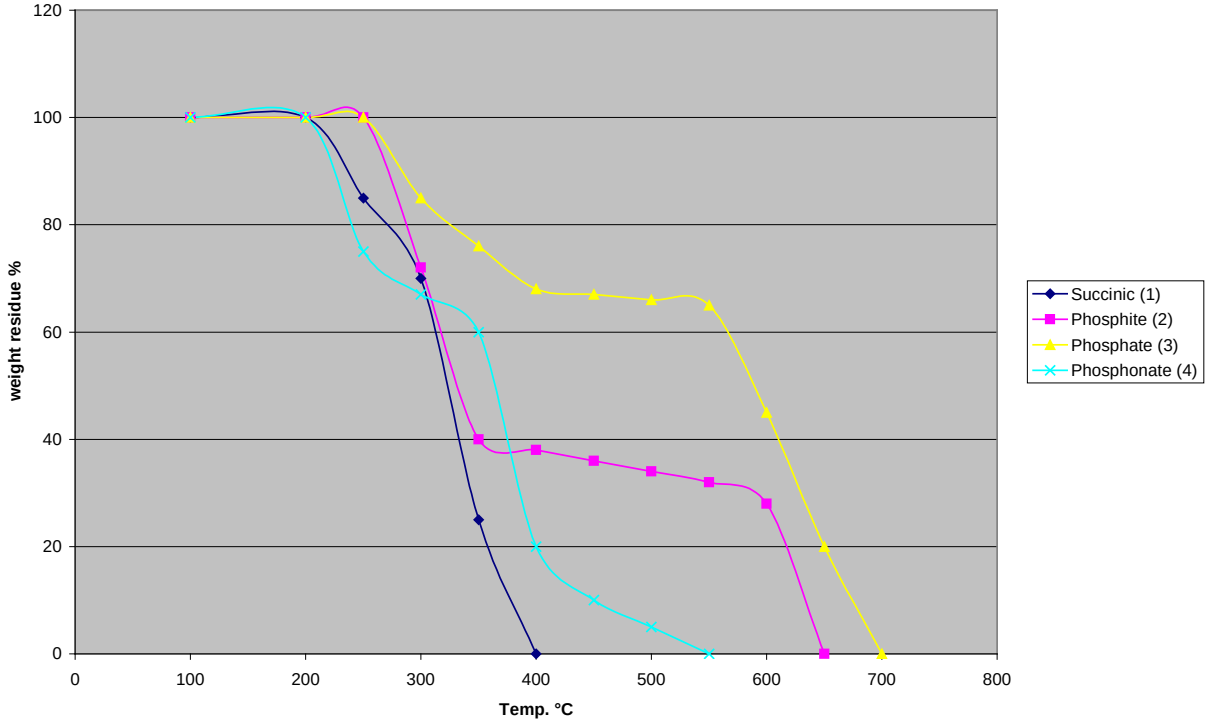
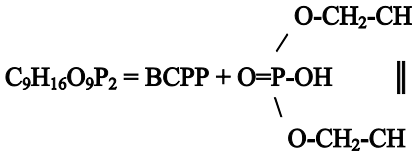


Figure 6. TGA of the linear Polyesters: Succinic acid (1), Polyphosphite (2), Polyphosphate (3) and Polyphosphonate (4), air, 5 K/min.

F9: $C_4H_7PO_2 = 0.5H_2O + C_2H_2 + C_2H_4 + PO_{1,5}$
MW 118 = 9 + 26 + 28 + 55
H − 584 − 30 = −121 + 227 + 52 − 712
340˚C: h = −0.16 kJ/g; R = 48%
F10 = F1: $C_5H_9PO_5 = C_5H_4HPO_3 + 2H_2O$
Intumescence 350˚C: h = −0.01 kJ/g; R = 40%
F11 = F2 $C_5H_4HPO_3 = CH_4 + 0.5H_2O + C_4PO_{2,5}$
F9 + F10 + F11: $C_9H_{16}O_7P_2 = 3H_2O + CH_4 + C_2H_2 + C_2H_4 + PO_{1,5} + C_4PO_{2,5}$ h = −0.28 kJ/g; R = 40%
MW 298 = 54 + 16 + 26 + 28 + 55 + 119
H − 2113 + 83 = −726 − 121 + 227 + 52 −712 − 750

Phosphate-polyester (3) with repetition unite $C_9H_{16}O_9P_2$ (MW= 330 g/mole); $R_{500^\circ C}$ = 68.5%; h = −0.21 kJ/g

250˚C: h = −0.5 kJ/g; R = 100%
F12: $C_9H_{16}O_9P_2 = C_5H_9PO_5 + C_4H_7PO_4$

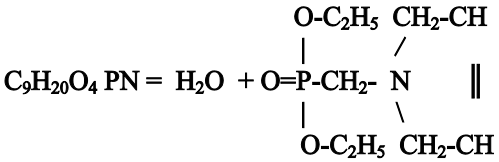


MW 330 = 180 + 150
H − 2548 + 165 = −1380 − 1003
350˚C: h = 0.12 kJ/g; R = 94.5%
F13: $C_4H_7PO_4 = C_4H_4 \cdot HPO_3 + H_2O$
MW 150 = 132 + 18
H − 1003 + 41 = −720 − 242
Intumescence 350˚C: h = −0.32 kJ/g; R = 87%
F14: $C_4H_4 \cdot HPO_3 = CH_4 + 0.5H_2O + C_3PO_{2,5}$

MW 132 = 16 + 9 + 107
H − 720 – 226 = − 75 − 121 − 750
340˚C h = −0.14 kJ/g, R = 76%
F15 = F1: $C_5H_9PO_5 = 2H_2O + C_5H_4{\cdot}HPO_3$
Intumescence 350˚C: h = −0.01 kJ/g; R = 68.5%
F16 = F2: $C_5H_4{\cdot}HPO_3 = CH_4 + 0.5H_2O + C_4PO_{2,5}$
F12 + F13 + F14 + F15 + F16: $C_9H_{16}O_9P_2 = 4H_2O + 2CH_4 + C_7P_2O_5$ h = −0.21 kJ/g; R = 68.5%
MW 330 = 72 + 32 + 226
H − 2548 −70 = −968 − 150 − 1500

Phosphonate-polyester (4) with the repetition unite $C_{13}H_{22}O_7PN$ (MW = 335 g/mole); $R_{500^\circ C}$ = 5%, h = 1.76 J/g

250˚C h = 1.4 kJ/g; R = 70.7%
F17: $C_{13}H_{22}O_7PN = C_4H_2O_3$ gas + $C_9H_{20}O_4PN$
$C_{13}H_{22}O_7PN$ = maleic anhydride + morpholino methane phosphonic acid diethyl ester
MW 335 = 98 + 237
H − 1947 + 461 = −415 − 1071
350˚C: h = −0.1 kJ/g; R = 65%
F18: $C_9H_{20}O_4$ PN = H_2O + $C_9H_{18}O_3PN$



MW 237 = 18 + 219
H − 1071 − 33 = −242 −862
355˚C: h = 0.28 kJ/g; R = 0%
F19: $C_9H_{18}O_3PN = CH_2O + 2C_4H_6 + NH_3 + 0.5H_2O + PO_{1,5}$
MW 219 = 30 + 2 × 54 + 17 + 9 + 55 H – 796 + 94 = −116 + 2 × 146.5 − 46 – 121 − 712
F17+ F18 + F19: $C_{13}H_{22}O_7PN = 1.5H_2O + PO_{1,5} + 2C_4H_6 + NH_3 + C_4H_2O_3 + CH_2O$ h = 1.76 kJ/g; R = 0%
MW 335 = 27 + 55 + 2 × 54 + 17 + 98 + 30
H − 1947 + 588= −363 – 712 + 2 × 146.5 − 46 − 415 − 116

The intumescent Phosphite-Polyester (2) and the Phosphate-Polyester (3) degraded to the same intumescent product BCPP. They developed exotherm heats of decomposition and the residues at 500˚C amounted to 40% and 68%. The nonintumescent Succinic-Polyester (1) and Phosphonic-Polyester (4) degraded under endotherm heat uptake and their residues at 500˚C amounted to 0%.

3.3. Powder Coating Manufacturing Process

In **Table 2** the formulations for intumescent powder coatings were summarized: In order to be comparable, all recipes comprised the same amount of titanium dioxide, which reacted with phosphorous pentoxide to titanium pyrophosphate. Recipe No.1 comprised thermoplastic plastisized polyvinylchloride PPVC, titanium dioxide TiO_2, ammonium polyphosphate APP and the intumescent additive bicyclopentaerythritol phosphate BCPP.

In recipe No. 2 polypropylene PP plus peroxide degraded to a well flowing binder. TiO_2, APP and BCCP were added. Recipe No. 3 comprised the linear polyester (1), uretdione and BCPP as intumescent additive as well as titanium dioxide and ammonium polyphosphate.

In Recipe No. 4 the intumescent polyesters (2) reacted with uretdione to polyurethane in the presence of TiO_2. Recipe No. 5 comprised the intumescent polyester (3) uretdione and TiO_2. As the polyester (4) was not intumescent, in recipe No. 6 in addition to uretdione, TiO_2, APP the intumescent compound BCPP was added. In recipe No. 7 use was made of the intumescent mixture polyethylene glycol with ammonium polyphosphate.

All formulations were manufactured by the dry blending process. The obtained fine powders were classified by sieving. The particle size distributions were measured on a Master Sizer XSB.OD (Malvern Instrument). The white powders with particles between 30 and 150 µm showed the characteristic data of **Table 3**.

Table 2. Formulations of intumescent powder coatings.

No	1	2	3	4	5	6	7
Binder 1	70 PPVC	69.7 PP	48.7 Polyester1	50.8 Polyester2	47.8 Polyester3	41.8 Polyester4	36 PEG
Binder 2			21.6 Uretdione	45 Uretdione	48 Uretdione	29 Uretdione	17 Uretdione
TiO_2	4	4	4	4	4	4	4
APP	11.5	11.5	11.5			11,5	41
BCPP	13.5	13.5	13.5			13,5	
Auxiliary 1	1 Castearate	1 Castearate	0.1 Dabco	0.1 Dabco	0.1 Dabco	0.1 Dabco	1.7 Zeolithe
Auxiliary 2		0.3 Peroxide	0.1 Snoct.	0.1 Snoct.	0.1 Snoct.	0.1 Snoct	0.2 Silicone
Auxiliary 3			0.5 Montan wax				0.1 DBTDL

Table 3. Characteristic data of the powders.

No	1	2	3	4	5	6	7
Tglass (˚C)	70	150	65	90	80	95	55
bulk density (g/cm^3)	0.65	0.7	0.65	0.6	0.7	0.65	0.8
viscosity 175˚C (Pas)	650	250	160	10	15	30	100
Tfusion (˚C)	140	165	180	190	200	170	140
cure time (min/˚C)	15/250	15/240	10/200	10/210	10/210	10/200	10/160
film density (g/cm^3)	1.5	1.4	1.45	1.05	1.05	1.45	1.55
apply (g) (d = 0.5 mm)	21	22.5	21.5	30	30	21.5	20

In **Figure 7** the melt viscosities at low shear forces 230 sec^{-1} were measured in dependence of the temperature in a Rheograph 2000 for the thermoplastic formulations PPVC No. 1 and PP No. 2 according DIN 54811.

The curing of thermosets No. 3-7 was investigated on a plasticorder. The results for the formulations No. 3 with polyester (1), No. 4 with the phosphite polyester (2), No. 5 with the phosphate polyester (3), No. 6 with the phosphonate polyester (4) and No. 7 with the 1/1 mixture polyethylene glycol PEG and ammonium polyphosphate APP were plotted in **Figure 8**. At time 0 the product temperature was 100˚C and the heating rate was 5K/min. After 20 minutes 200˚C was reached and further heating was stopped.

In comparison with the viscosities of thermoplastic formulations the viscosity minima of thermosets were lower, which was also manifested by a smoother surface of the obtained films.

Due the lower particle volume concentrations the films of the intrinsic intumescent powder coatings No.4 and No.5 showed more gloss.

3.4. Spraying

The electrically loaded powders were sprayed on preheated and grounded steel panels. The film thicknesses varied between 0.88 and 1.2 mm according the applies given in **Table 3**.

3.5. Curing and Melting

The curing temperatures with 250˚C at most were below the required temperature of intumescence of 275˚C and 350˚C. The coatings on the panels showed film thicknesses of about 500 µm in average.

3.6. Fire Test

The coated panels with a horizontal perimeter to area factor Hp/A= 400 m^{-1} were equipped with two thermocouples, each for continuous measurements of temperature. The measured data were averaged out.

In **Figure 9** a picture showing the front side of the furnace was taken, when the burning test had been finished.

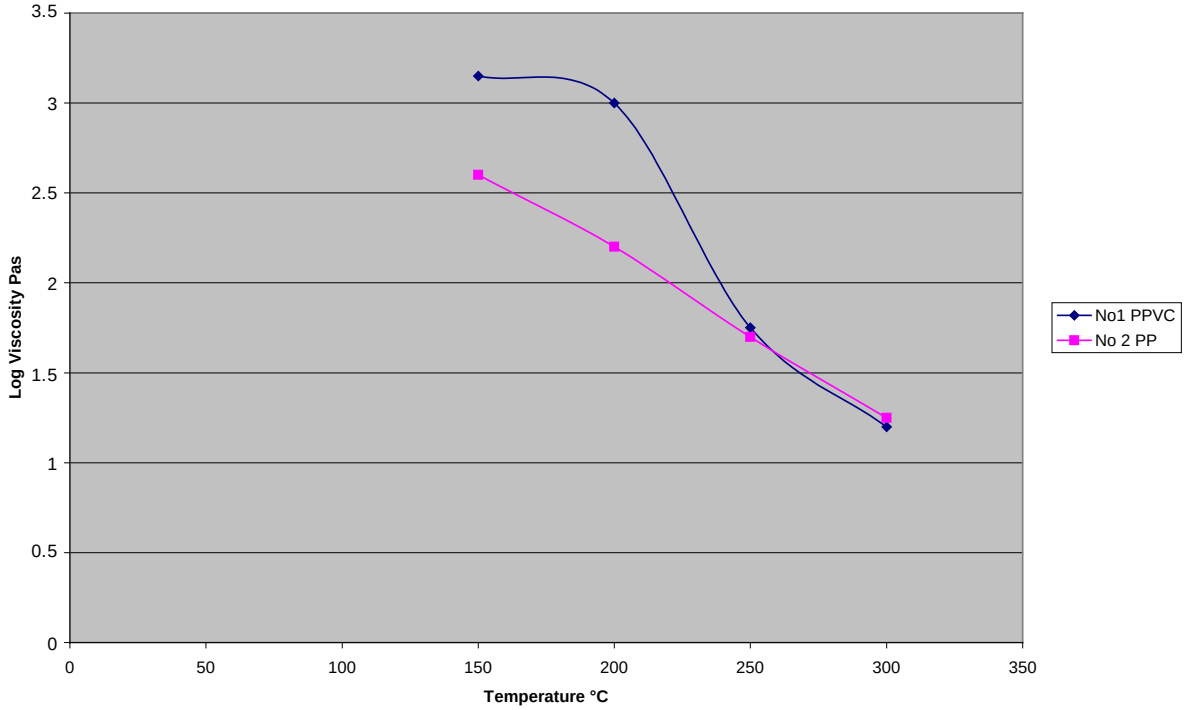


Figure 7. Viscosity as a function of temperature for the thermoplastics No. 1 PPVC and No. 2 PP.

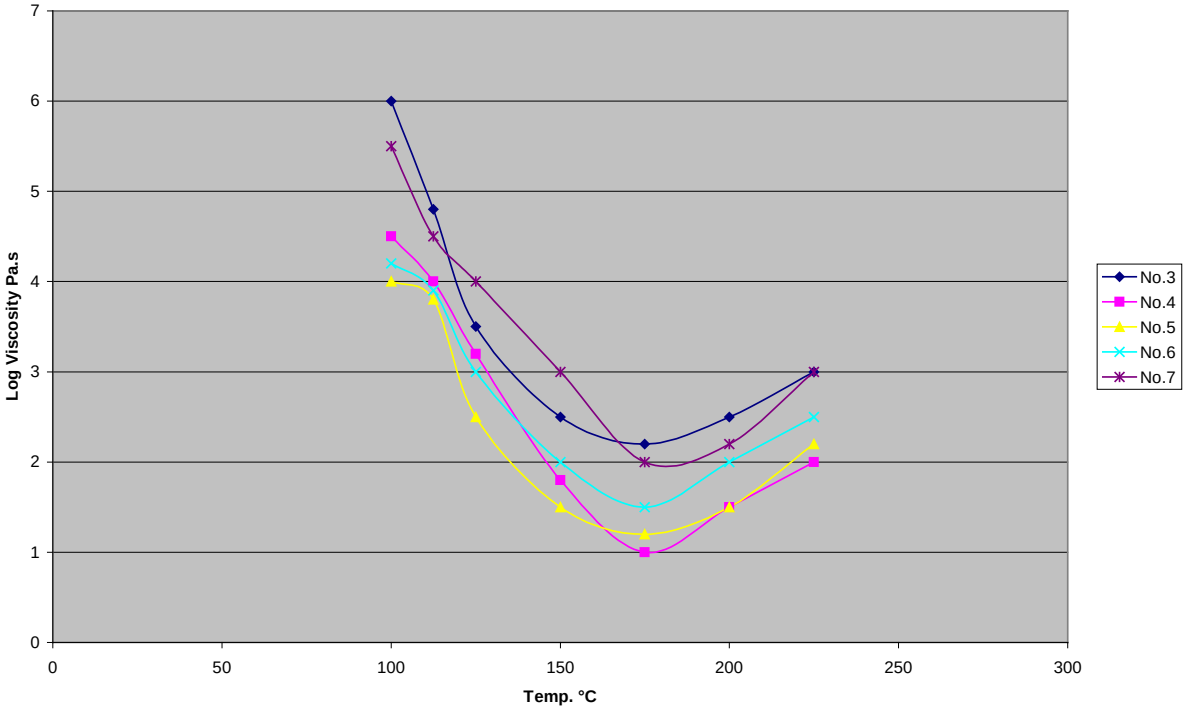


Figure 8. Viscosity as a function of temperature, heating rate 5 K/min starting from 100˚C for the thermosets No. 3, No. 4, No. 5, No. 6 and No. 7.

In **Figure 10** the temperatures of the uncoated panel as well as those of the panels protected by the different powder coatings and by the commercial water borne varnish Nonfire S168 were recorded in dependence of time. The efficiency was measured by the time lag until 500˚C were reached. Under this aspect following ranking was

Figure 9. The front side after the burning test showing the 7 samples No. 1, No. 2, No. 3, No. 4, No. 5, No. 6, No. 7, the uncoated panel and the reference panel Nonfire S168.

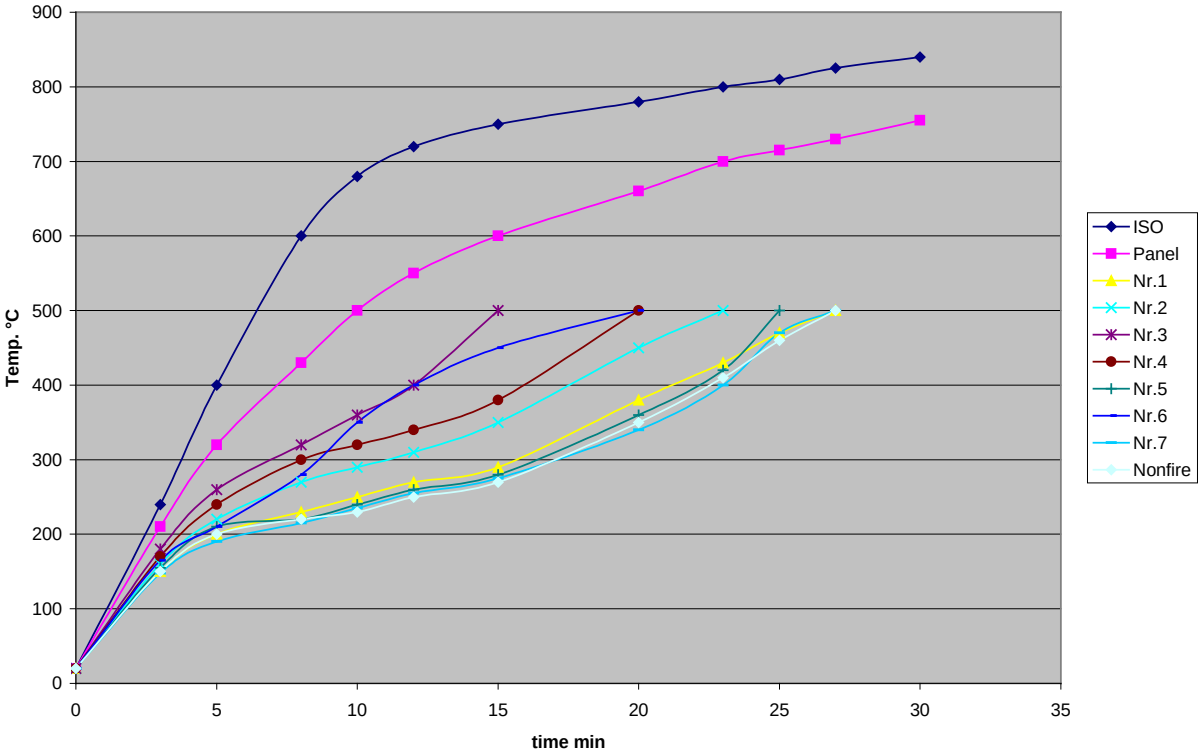


Figure 10. Fire test: temperatures versus time for the furnace, for the uncoated panel with a perimeter to area Hp/A = 400 m^{-1}, for the seven powder coated panels and for the reference panel coated with the water borne varnish Nonfire S168 all at 0.5 mm film thickness.

achieved in **Table 3**: the PPVC plus BCPP (No. 1) and PUR with PEG/APP (No. 7) were the favourites and were more or less equal in efficiency with the reference coating Nonfire S168.

In **Table 4** the time lags until 500˚C were reached, the film thickness after expansion df and the expansion factor EF as well as the amount of inorganic compounds were recorded.

Nonfire S168 had the highest film density and the highest expansion followed by PPVC (No. 1) and PEG/Uretdione (No. 7).

4. Discussion

The temperature differences dT_1 between the temperature curve of the furnace and that of the naked 5 mm panel served for the calculation of the heat flux per area Q/F according to Equation (4).

$$Q/F = dT_1/(1/a + Do/lambda) = 150/(0.3333 + 0.1666) = 150/0.5 = 300\ W/m^2 \quad (4)$$

In Equation (4) the temperature difference dT_1 =150˚C, the heat transmission number for free air convection a= 3W/(m^2*K), the thickness of the panel Do= 0.005 m and the heat conductivity of air lambda= 0.03 W/(m*K) were introduced. A heat flux per area of 300 W/m^2 was calculated, which was used in order to estimate the temperature difference between the naked and the coated panel dT_2 [14].

The difference in temperature between the naked panel and the coated panel dT_2 was calculated in Equation (5).

$$dT_2 = Q/F \times (1/a + d \times (EF)^2/(3 \times lambda_f) = 300 \times [1/3 + 0.0005 \times 27^2/(3 \times 1)] = 135^\circ C \quad (5)$$

In Equation (5) the film thickness of the coating d was 0.0005 m and the expansion factor EF = 27. The heat conductivity of the unexpanded film $lambda_f$ amounted to 1 W/(m^2*K).

In **Figure 10** a temperature difference between uncoated and coated panel of about 150˚C was observed. In principle Equations (4) and (5) described correctly the results and predicted the task for further improvements by increasing the expansion factor and reducing the heat conductivity.

The fire tests showed that the efficiency of the powder coating was increased by a highly expanded but stable char with low thermal conductivity. A low temperature of intumescence was of advantage. Formulation No. 7 based on PEG/APP reacted under intumescence at 275˚C and cured at 160˚C, but the low temperature of fusion caused difficulties in the manufacturing process. The other extreme was formulation No. 1 based on PPVC with 350˚C temperature of intumescence and 250˚C temperature of curing. High degree of fillers caused unsmooth surfaces in every case. Therefore the formulations based on intumescent polyesters with No. 4 and No. 5 had a higher potential of further improvement, because they offered the possibility of additional dosage of fillers or ingredients.

5. Conclusions

The screening of seven very different formulations indicates the possibility of manufacturing and applying intumescent powder coatings based on thermoplastic as well as thermoset non-cross linked binders. Intumescence is realized by the addition of the intumescent ingredient BCPP, by intumescent polyesters comprising phosphate or phosphite groups and by the mixture of PEG/APP. In every case intumescence follows the common reaction in Equation (6).

$$C_nH_mHPO_3 = (m/4) \times CH_4 + (n\text{-}m/4) \times C0.5P_2O_5 + 0.5H_2O \quad (6)$$

Table 4. Performance in fire test: time, until 500˚C were reached, expansion factor EF, expanded film thickness df, film density and amount of inorganic compounds.

No	1	2	3	4	5	6	7	Nonfire S168
time (min)	27	24	15	20	25	20	27	27
Expansion factor EF= (df/d-1)	19	17	11	14	15	19	29	35
Expanded film thickness df (mm)	10	9	6	7.5	8	10	15	18
film density (g/cm^3)	1.5	1.4	1.45	1.05	1.05	1.45	1.55	1.6
Inorganic compounds (%)	15.5	15.5	15.5	4	4	15.5	46.7	35

In a comparative fire test, the powder coating based on the thermoplastic binder PPVC No. 1 as well as that based on the polyurethane thermoset binder No. 7 are comparative in efficiency with commercial water borne coating No. 8 Nonfire S168 at the same film thickness of 0.5 mm.

Nevertheless the restriction remains that the film thickness of powder coatings can not be increased to any high value wished. A higher potential of further improvements is granted to formulations based on intumescent polyesters No. 4 and No. 5, because their low amount of fillers allows the further addition of performance improving ingredients.

Among intumescence, intumescent powder coatings have to fulfil several demands as strong adhesion to the substrate, flexibility and hardness in the right balance. They have to resist humidity and sun shine, tested by the Salt Spray test and the Florida test. The present results and the advantages of powder coatings as well as the circumstance that powder coating are not restricted to steel protection alone will encourage further work. In a future vision building parts, such as columns and pipes, coated by intumescent powder coatings could be continuously manufactured in such a way that the still hot cast or moulded specimens are sprayed in a one step process.

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