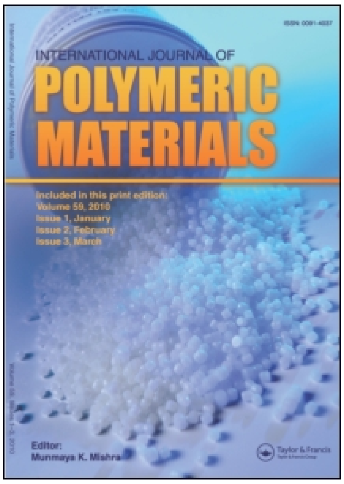

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Melamine Cyanurate, Halogen and Phosphorus Free Flame Retardant

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Melamine cyanurate chemistry, manufacturing, and application as a flame retardant are reviewed.

KEY WORDS Flame retardant polymers, nylon 6, melamine cyanurate

1. INTRODUCTION

In human history mankind has always used new materials. The first human tools were produced from stones, then mankind learned to gain metals and alloys like bronze and iron. The entrance into the plastic century has increased hazards of fire because nearly all polymers are not selfextinguishing without additives. Therefore, plastics are the largest field of application for flame retardation.

In the European Common Market, the producers of flame retardants (FR) are optimistic about the future because they expect an increasing demand for FR by rules and legislation. Figures show that in 1991 214,000 tons of flame retardant chemicals were sold; by 1995 an increase to 275,000 tons is expected.

The realization of the common European market abolishes borders and restrictions of commerce. The new European Community's rules give profit to these companies that produce FR that are in agreement with legislation.

2. SYNTHESIS

Melamine cyanurate (MC) is synthesized by the reaction of melamine with cyanuric acid or isocyanuric acid.[1-11] In general the ketostructure (Isocyanurate) is more stable than the hydroxy structure (Cyanurate). Therefore, the name melamine isocyanurate would be rather more correct. Another route to MC starts from urea in the presence of melamine.[8] Urea reacts to cyanuric acid and further to MC. Cyanuric acid is a weak tribasic acid with the constants 10^{-7}, 10^{-11} and 10^{-14}, melamine is a weak triacidic base with the constants 10^{-9}, 10^{-14} and 10^{-17}. As the solubility of the reaction product of one mole melamine with one mole cyanuric

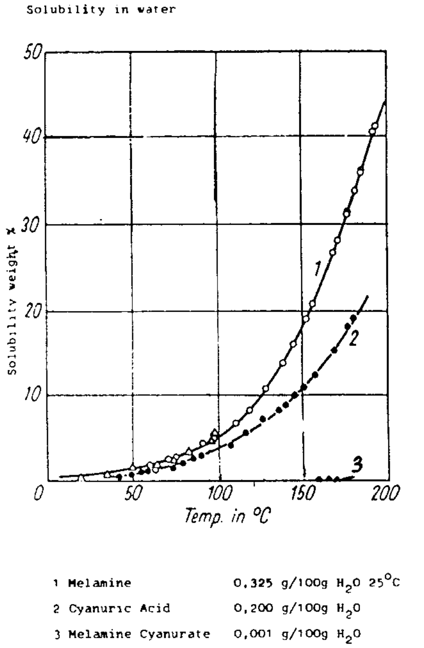

FIGURE 1 Solubility of melamine, cyanuric acid and melamine cyanurate in water. Effect of temperature.

acid is very low (Figure 1), the salt precipitates and no other stoichiometric compounds are known.[12]

This neutralization reaction can be performed homogeneous in high dissolution or with less water in dispersion, as a batch process or in a continuous production line.

The reaction product is a real salt proved by the IR spectrum. The γ (R) vibration band is shifted to 774 cm^{-1}, a new band appears at 1718 cm^{-1} and new NH valence vibration bands are detected at 2900 and 2880 cm^{-1}.

In the CL process the primary particles have a size of about 0.5 μm, but they agglomerate to particles with a much larger size so that the product has to be ground (Figure 2).

As a consequence of solid state, the performance is better with very small particles but handling is naturally easier with coarse particles. To overcome these difficulties many attempts have been made in producing definite particle size distributions, in agglomerizing, in pelletizing, and in the formation of master batches. Also the technique of coating or microencapsulation are applied to powders. A vast field of activities are the successful application of flow- and dispersing aids, compatiblizers and coupling agents.

In the family of plastic additives FR have a unique position; nearly every polymer needs FR. By improving their glass-transition temperature and their burning behavior plastics become more and more ready to substitute metals.

The FR applied to polymers are divided into different chemical groups:

inorganic, water releasing compounds as metallic hydroxides;

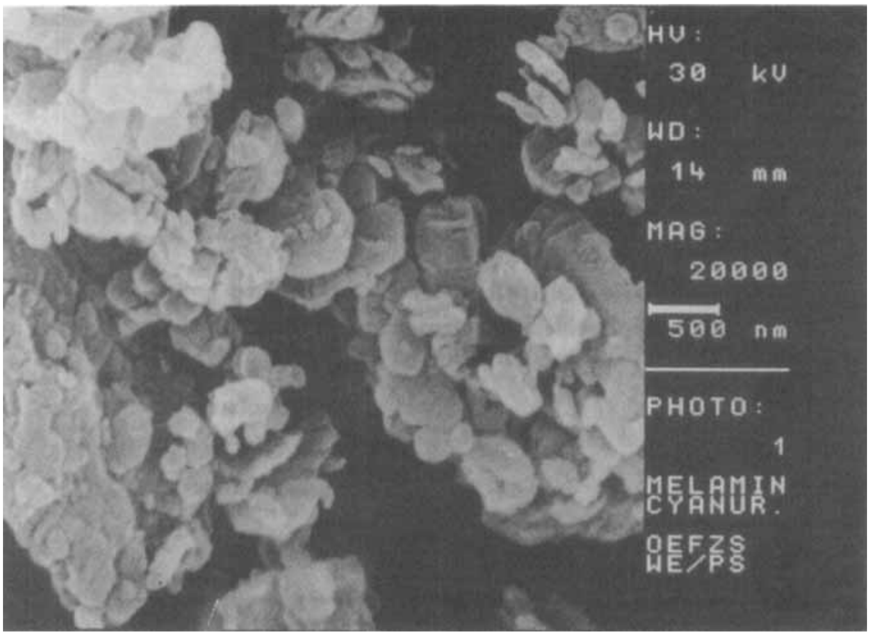

FIGURE 2 Electro-microscopy of MC particles.

organic halogen compounds;
organic phosphorous compounds;
organic nitrogen compounds;
inorganic compounds that contain nitrogen, phosphorous boron, tin and zinc.

The share of N-FR in the total FR market is 13% and that of MC is 3%.

Melamine cyanurate is a white crystalline powder with a molecular weight of 255.21 g/mole and a nitrogen content of 49.4 weight percent. It crystallizes in a hexagonal lattice.

Methods of grafting and surface reactions are frequently described and often used. As the specific area A_f changes strongly with particle size a, it has a large influence on burning behavior, physical properties, color and gloss (Figure 3).

For spheres the specific surface A_f is reverse proportional to the particle size a and the density $\rho_f = 1.7$ g/cm^3 of MC.

$$A_f = \frac{6}{a.\rho_f} \tag{1}$$

For a particle size of 1 μm, the specific surface is calculated to be 3.5 m^2/g.

MC is characterized by the particle size, the specific surface, the flowability, the bulk density, the compression set, and the dispersibility. The particle size and the specific surface are measured by different methods, the flowability is tested after Jenike, the bulk density in accordance with DIN 53466, the compressibility in a force-distance diagram, and the dispersibility during the extrusion process by the pressure filter value (Figure 4).

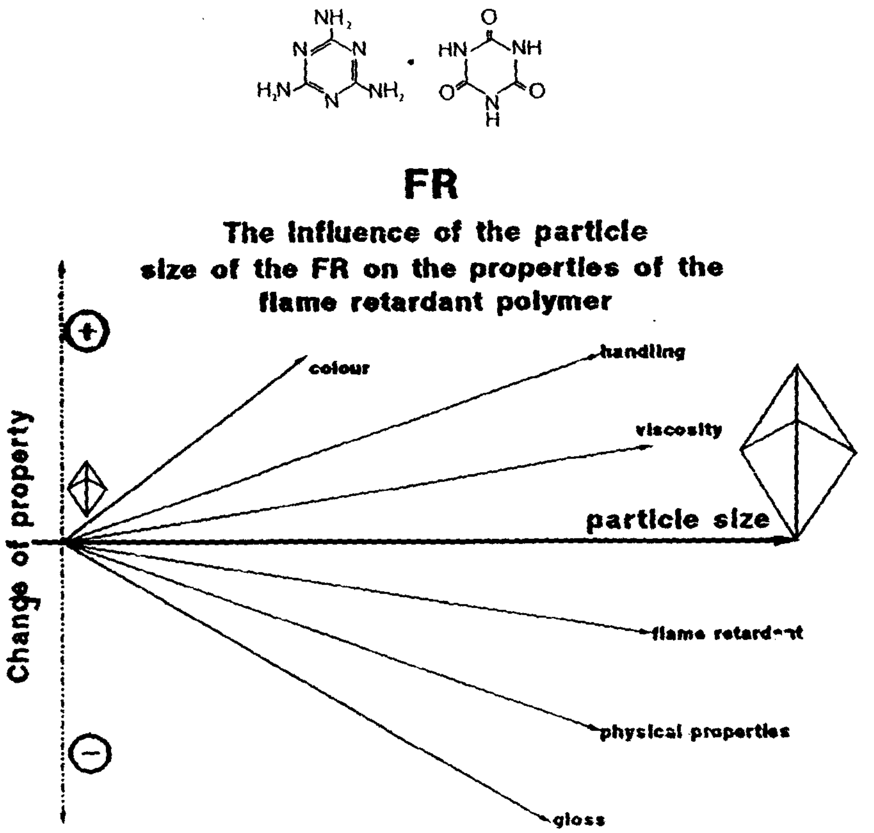

FIGURE 3 The influence of FR particle size on the properties of the flame retardant polymer.

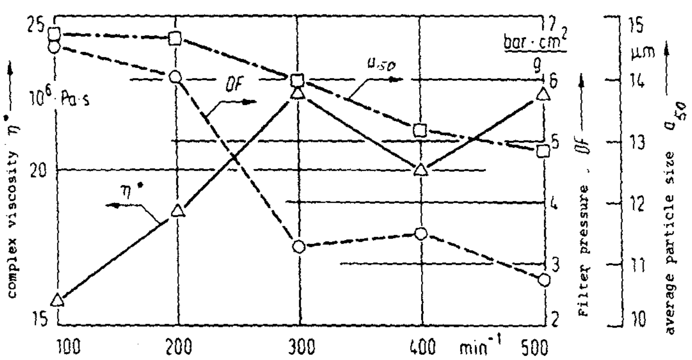

FIGURE 4 The influence of revolution rate n during extrusion on the complex viscosity η^*, average particle size a_{50} and filter pressure DF at an output of 4 kg/h for polyamide 6 + 10 weight % MC.

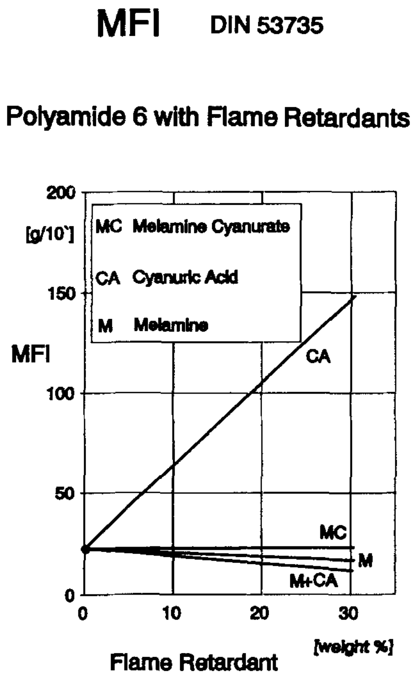

FIGURE 5 Melt flow index (MFI) of polyamide 6 with flame retardants.

In general the mechanical properties increase with decreasing particle size of the additive. The slope B of the correlation of mechanical properties versus volume fraction of filler is proportional to the specific surface A_f of the filler:

$$B = (1 + l \cdot A_f \cdot \vartheta_f) \cdot \ln \delta^{y_i} / \ln \delta_{y_j} \qquad (2)$$

where l is the thickness of the sample, ϑ_f is the density of the filler, δ_{y_i} is the property of the interface, and δ_{y_j} is the property of the matrix.[13]

Therefore, the particle size of MC should be as small as possible. But handling, dosage, and dust oppose particles below 1 μm. If melamine and cyanuric acid are not reacted in a stoichiometric ratio, one component is present in excess. Cyanuric acid increases the melt flow index (MFI). In respect to MFI, a mixture of melamine and cyanuric acid are equivalent, but the burning behavior of a nylon sample containing 10% of a mixture will be worse than that containing 10 percent MC (Figure 5). In addition, the decomposition temperatures are different: melamine decomposes at 350°C, cyanuric acid at 380°C, and melamine cyanurate at 410°C.

3. MECHANISM

Nitrogen compounds are applied as FR, as blowing agents (CBA), and as explosives (E). Their chemical compositions are similar and they exert the same mechanism in performance: they decompose to gases under high gas yields. Ideally, the liberated

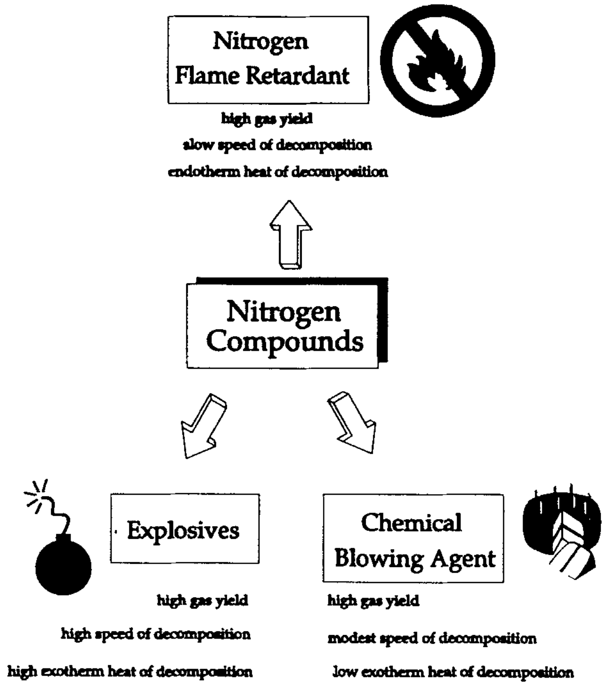

FIGURE 6 Schematics of decomposition rates and heat of decompositions for flame retardants, chemical blowing agents and explosives.

gases are non-burning and non-toxic as nitrogen, carbon dioxide and water. The velocity of decomposition increases from FR over CBA to E. For a successful application, FR and CBA need accommodated decomposition temperatures (Figure 6).

A homologous series with an increasing amount of nitrogen is melamine as a FR, trihydrazinotriazine as a CBA, and triazidotriazine as an E.

The decomposition temperature of pure MC lies at 410°C (maximum of decomposition) and the heat loss per 1 gram of MC has an amount of 0.25 kJ/g. One mole of MC produces 32 l of gases. In comparison to water one mole produces 22.4 l vapor and the heat loss per 1 g is 0.13 kJ/g.

MC acts similar to water by heat sink and diluting the burnable gases by non-burning gases. Ideally, the decomposition temperature of the polymer should coincide with that of MC (Figure 7).

The rate of heat release is measured in the CONE calorimeter and is slowed down by the addition of MC. The heat sink derives from the endotherm heats of sublimation and decomposition as can be shown by a rough calculation using the Kirchhoff law:

$$T = H/Cp \tag{3}$$

Nylon with 10 weight percent MC loses 0.15 kJ/g heat. The specific heat of nylon is 0.30 kJ/(mole.grade) and the molecular weight 113 g/mole.

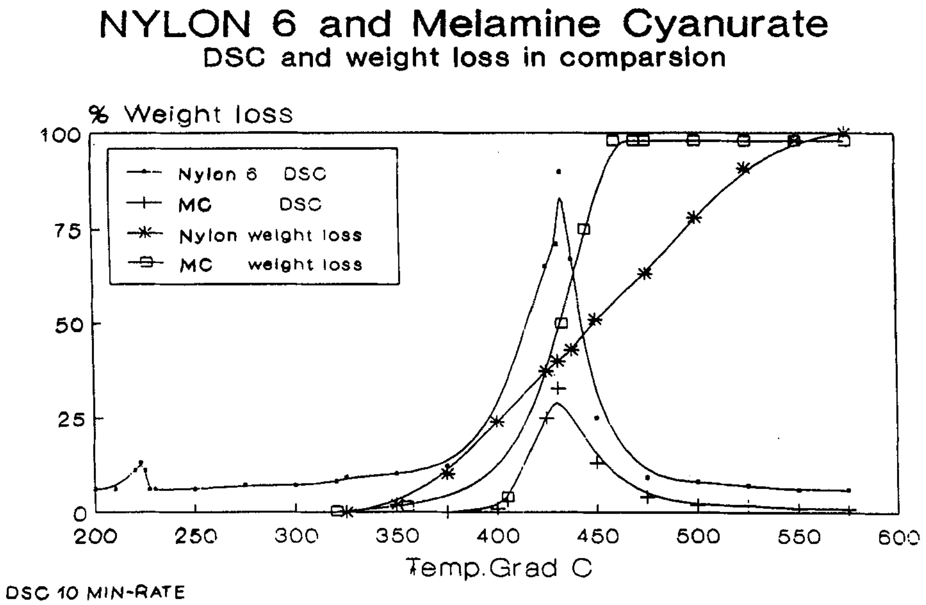

FIGURE 7 DSC and weight loss comparison of nylon 6 and melamine cyanurate.

$$T = 0.15/0.3/113 = 56.5°C \quad (4)$$

The calculated heat sink is about 50°C.

4. COFLAME RETARDANTS

From the literature, a nitrogen–phosphorus synergism is well known, though in a deeper insight the actual examples are very rare.[14,15] Zinc borate, magnesium hydroxide, hexamethoxymethylmelamine, intumescent graphite, melamine, dicyandiamide, thiourea and cyanuric acid are applied in combination with MC.

In many cases dripping is a problem with MC especially if in the UL 94 test a V-O classification should be reached. Burning drops ignite the cotton and the sample has failed. Therefore, antidripping agents as trisglycidylisocyanurate or Teflon powder are added in small amounts.

5. APPLICATION

Looking at the patents,[17] MC is applied to many plastics. But the application of economic importance is in its use as a FR for nylons. MC is fed in concentrations of 10 weight percent to nylon 6, 66 and 66/6 to reach V-O in the UL test 94. Nylon 11 and 12 are more similar to polyethylene and need a higher dosage of 15 weight percent to meet the UL 94 test. With the increase in the amount of MC in polyamide, the LOI-value increases (Figure 8) and the mechanical properties de-

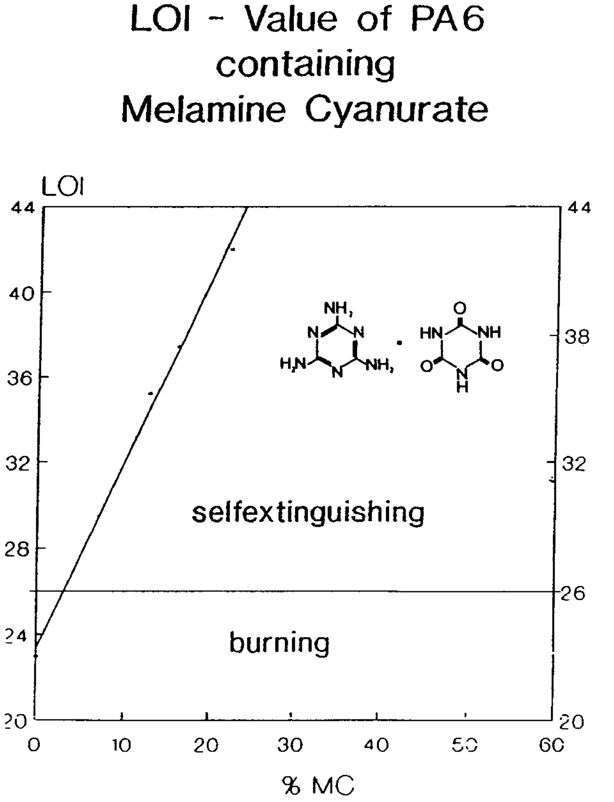

FIGURE 8 LOI values of polyamide 6 containing melamine cyanurate.

TABLE I

Melamine cyanurate as flame retardant in polyamide properties

Material:	Unit				
Polyamide 6	Parts	100	90	85	80
Melamine cyanurate	Parts	-	10	15	20
Test:					
Tensile strength	N/mm²	78	73,9	72,7	61,2
Elongation	%	29,7	5,2	4,7	3,0
Flexural strength	N/mm²	82,8	89,9	87,4	90,3
E-Modulus	N/mm²	2535	2966	2997	3138
Shrinkage	%	1,14	0,82	0,84	0,90
Impact strength	kJ/m²	w.b.	w.b.	73,3	44,5
Impact strength notched	kJ/m²	8,3	7,5	7,3	5,0
Water content	%	0,14	0,15	0,16	0,14
LOI	%	23	35	37	42

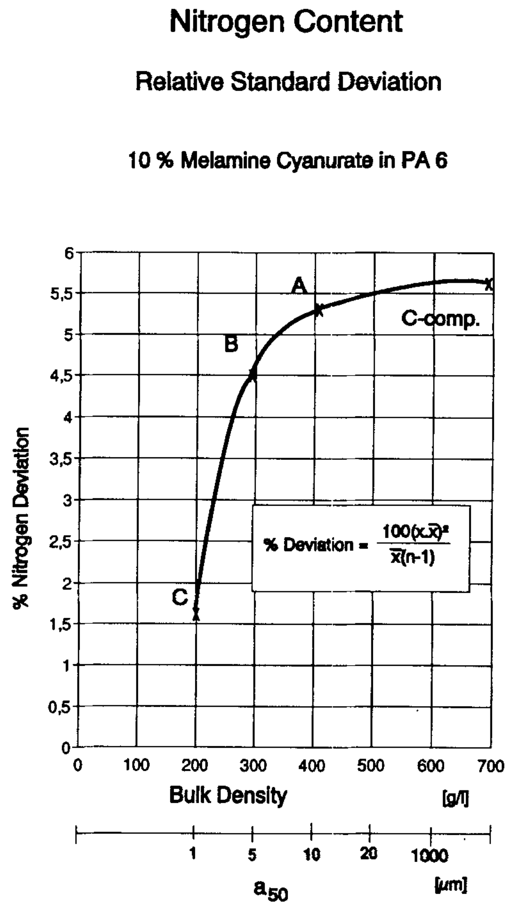

FIGURE 9 Effect of the particle size and bulk density of MC on the relative standard deviation of nitrogen content.

crease as described in Table I. Therefore, the skilled manufacturer goes to the limiting concentration just meeting the burning test. The limiting concentration depends on the particle size and the smoothness of distribution. The deviation of the MC content was measured as the deviation of the nitrogen content in nylon 6 containing 10 weight percent MC in dependence of the particle size or the bulk density of the MC. The relative standard deviation corresponds to 100 times the standard deviation divided by the average value. With decreasing particle size and bulk density the deviation decreases (Figure 9) and the distribution becomes very even.

The decomposition temperature of pure MC lies at 410°C and goes down with increasing amounts of polyamide to 200°C. The heat loss per one gram of MC was measured 0.25 kJ/g and falls down to 0.13 kJ/g at 50 weight percent polyamide (Figure 10).

Much care has to be taken of the equipment: the feeder and the extruder. Fine powders such as MC should always be dosed by feeders with mechanical trans-

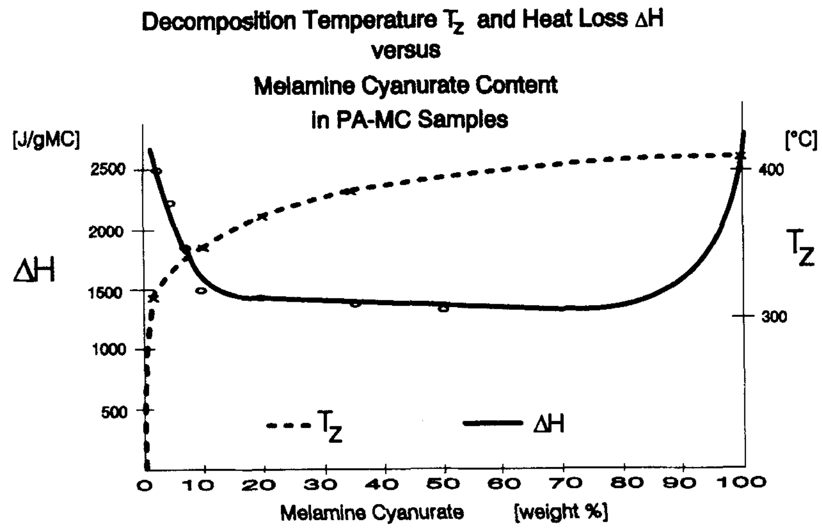

FIGURE 10 Decomposition temperature T_z and heat loss ΔH versus melamine cyanurate content in polyamide 6 - MC samples.

portation and not by gravity. In respect to an even distribution, only twin screw extruders achieve good results. Also, the design of the screw is of importance especially in highly filled systems as in glass reinforced nylons. In nylons that contain glass fibers, MC alone cannot grant a V-O specification. It is necessary that 6 weight percent of Dechlorane Plus or 3 weight percent of red phosphorus be added, as in Table II.

MC is also applied to other plastics as an effective flame retardant. In regard to the coincidence rule, all polymers with a decomposition point of about 400°C should be appropriate. These are listed in Table III. MC is used as a FR for polyesters as PET and PBT as in Table IV; as a FR in thermoplastic polyurethane, shown in Table V; and as a FR in rubber as polyisoprene. The addition of 17 weight percent of MC, 5 weight percent of chloroparaffine, and 1 weight percent antimonium trioxide to rubber increases the LOI from 19 to 28.

Very sophisticated is the application of MC in nylon alloys because it often has a bad influence on the distribution of the dispers polymer phases in micro droplets.

The MC concentration in plastics can be estimated by the specific volume or density of the sample or by RAMAN-IR spectra of such specimen. Air bubbles and crystallinity can lead to wrong values if the density is measured. The determination of the nitrogen content by elementary analysis gives very accurate contents of MC.

The bulk density is a function of the particle size a. With decreasing diameter of the crystals, the porosity e_V of the bulk increases:

$$e_V = 1 - \text{bulk density/crystal density} = 1 - 0.3/1.7 = 0.82 \tag{5}$$

For MC exists an empirical relationship between particle size and bulk density:

$$\text{Bulk density} = (\lg a_{50} - \lg a_{50^\circ})/\text{const} \tag{6}$$

TABLE II

Flame retardant polyamide

Material:	Supplier:	A	B	C
Polyamide 66	Basf	100	90	50
Glass fiber	Vetrotex	-	-	16
Melamine Cyanurate	Chemie Linz	-	10	25
Zinc Borate 2335	Borax	-	-	3
Dechlorane plus	Occidental Ch.	-	-	6
Test:	Unit:			
MFI	g/10'	57,7	73,0	20,2
E-Module	N/mm^2	1180	1530	5080
Tensile Strength	N/mm^2	53,7	50,3	66,1
Bending Strength	N/mm^2	41,7	50,0	106,0
Impact Strength	kJ/m^2	w.b.	w.b.	4,52
UL 94 (2mm)	-	V-2	V-0	V-0

Effect of flame retardant additives in polyamide

Material:						
Polyamide 6	39	41	36	-	-	-
Polyamide 66	-	-	-	38	47	47
Glass fiber	27	27	27	27	25	25
Melamine Cyanurate	12,5	10	15	15	-	-
Melamine	-	-	-	-	18	20
Zinc Borate 2335	7	10	10	8	4	3
Dechlorane plus	12,5	10	10	12	6	5
Sb_2O_3	2	2	2	-	-	-
Test:						
UL 94	V-0	V-0	V-0	V-0	V-0	V-0
Tensile Strength	93	95	88	92	133	128

The term a_{50° is the hypothetical particle size at the bulk density 0. As the powder has a particle size distribution, the particle size at 50% a_{50} was chosen for all correlations.

$$\text{Bulk density BD[g/l]} = \frac{\lg a_{50}[\mu m] + 3.278}{0.0157} \tag{7}$$

A bulk of MC with a corn size of 1 μm has a bulk density of 209 g/l as such, one with 10 μm particles has a bulk density of 270 g/l.

The flowability measured as volume per time flowing through a funnel by gravity is theoretically independent of the bulk density and the particle size. Nevertheless, in practice, fine powders with low bulk densities tend to bridging and blocking, and the dosage is sometimes difficult.

6. SUMMARY

In the development and application of FR in plastics much work, endeavor, and investigation has been invested.[18-37]

TABLE III

Thermoplastics

	T_g [°C]	T_m [°C]	HDT FidW [°C]	Water uptake (Wasseraufn.) 24 Std. [%]	Water uptake staturation (Sattigung) [%]	Ignition temp. (Entzündungstemp.) [°C]	Decompose temp. (Zersetzungstemp.) [°C]
Polyimide PI	310–365	—	277–360	0.26	1.2		
Polyamide imid PAI	275	—	274		0.28		
Polyphenylsulfone PAS	220	—	204		1.1–1.3		
Polyathersulfone PES	230	—	203	0.43			
Polyatherimide PEI	215	—	200	0.25	1.25		
Polysulfone PSU	190	—	174	0.3	0.7		
Polyacrylester	190	—	174	0.27	0.71		
Polyatheratherketon PEEK	143	340	160				
Polyphenylensulfide PPS	88	290	135	<0.02			
Polycarbonate PC	150	—	132	0.15			
Polyacetal POM	−60	168	110	0.22	0.8		222
Polyamide 66 PA 6.6	50	265	80	1.3–1.9	8.5–10.0	485–575	
Polyamide 6 PA 6	40	216	70	1.0–1.3	8.5	421	310–380
Polyathylenterephthalate PETP	80	255	80	0.1–0.2			
Polybutylenterephthalate PBTP	40	223	65	0.08–0.09			
Polypropylene PP	−30	165				570	328–410
Polyvinylchloride PVC	100	—				—	260
Polyethylene PE	−120	110				341	335–450
Polyurethane PUR	50					310	330–380
Polystyrene PS	100	—				345–360	300–400
HIPS ABS	100	—					327–430

TABLE IV

Effect of Melapur® PET in polyethyleneterephthalate

Material:	I	II		Supplier:
Arnite D 02 300	100	75		Akzo
melapur® PET	-	25		Chemie Linz
Test			Unit:	Method:
MFI	145	130	g/10 min.	DIN 53735
E-Modulus	3100	3700	N/mm²	DIN 53457
Flexural strength	80	72	N/mm²	DIN 53452
Impact strength	70	6 5	kJ/m²	DIN 53453
Burning classification	V-2	V-2	-	UL 94 (1,6mm)
Burning time	-	2,5	sek.	UL 94 (1,6mm)

masterbatch: Arnitel UM 550 -- melapur® PET 50:50 : V-0

TABLE V

Thermoplastic polyurethanes (TPU)

Polymer: Elastollan C 85-A								
FLame Retardant (%)								
melamine						5	10	
melamine cyanurate		25	10	5	5		10	
ATH					20			
melapur	C*							15
Properties								
Hardness	87	91	89	86	92	87	80	80
Elongation [%]	500	473	590	680	520	690	450	450
Tensile Strength [MPa]	40	16	34	38	-	15	30	30
Tear Strength [N/mm]	70	63	125	114	-	95	80	80
MFI [g/10']	9	114	23	26	-	-	490	15
UL 94	V-2	V-1	V-1	V-1	V-0	V-1	V-0	V-0

*Melapur C coated or microencapsulated melamine.

The following advantages convince many manufacturers and compounders to use MC as a FR: MC is not toxic, it has a high LD_{50} value of more than 10 g/kg and a high MAK-value of 6 mg/m^3 (dust). MC is a white powder and does not heavily interfere with color pigments. MC is not blooming as melamine.

MC does not reduce the glass transition temperature of the polymers it is applied to. During extrusion, molding or pressing MC does not evolve any toxic gases—only NH_3 and CO_2 are detectable. In the case of burning, MC does not split off corrosive gases. In nitrogen containing polymers, MC does not contribute any other element as already present in the polymer. Hydrogen cyanide is produced in rare cases at high temperatures above 800°C and in the lack of oxygen.

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