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Common Features and the Unique Role of Phosphorus in the Bioproducts ATP as Well as DNA and in Intumescent Flame Retardants

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Abstract

The natural product Adenosintriphosphate ATP and steel coatings comprise carbohydrate, amine and phosphoric acid. Both exert intumescence, but ATP produces more expanded volume than steel coating. The expansion is determined by Thermomechanical Analysis TMA, the amount of residue by Thermogravimetric Analysis TGA and the evolved or consumed heats by Differential Scanning Calorimetry DSC. Formulas of degradation allow the calculation of decomposition, char formation and expansion. A requirement for intumescence is the product $CnHmHPO_3$ of degradation. Boric and Silicic acids, which also occur as meta acids, showed no capability of intumescence. Only phosphoric esters or amides exert intumescence. Amines are not essential for intumescence. Another common feature of the natural products ATP and DNA Desoxyribonucleic acid and of the amine salts Melamine Polyphosphate, Cyanurate and Barbiturate as well as Guanidinium Polyphosphate, Cyanurate and Sulfamate is self organization. DNA, which self organizes in a helix structure, is comparable with amine salts self organized in lattices. The energies of lattice are dependent on the strength of interaction, they are higher for ion-ion and lower for dipol-dipol arrangement.

Subject Areas

Green Chemistry, High Polymer Chemistry, Physical Chemistry, Thermochemistry

Keywords

Intumescent Flame Retardance, Thermogravimetry, Differential Scanning Calorimetry, Thermomechanic Analysis, Self organization, Lattice Energy

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1. Introduction

The common trend initiated by climate change and green movements accelerates the substitution of halogen flame retardants FRs by FRs based on nitrogen, phosphorus, silicic and boron. Especially intumescent FRs are in the focus of interest. Intumescent is defined as the swelling of a substrate when exposed to heat typically forming a multilayer carbonaceous or ceramic layer, which acts as a heat barrier. Ingredients of intumescence are mainly composed of inorganic acid or material yielding acidic species upon heating and of a char former. Intumescent steel coatings comprise Ammonium polyphosphate, Melamine, Pentaerythritol or Dipentaerythritol and Titanium dioxide. Plastics derived from growing natural raw materials require environmental friendly FRs, which are based on natural products and not on petrochemical products. [1] Adenosine triphosphate ATP CAS 200-283-2 has been tested for its flame retardant properties and has been characterized as an all in One Green FR with extreme formation of intumescent char. [2]-[5] Nevertheless ATP's high water solubility, degradation at low temperature and high costs prohibit its application as FR. ATP serves as carrier of energy in many biochemical reactions and has a high price of 899 €/kg. But remarkable is the fact that ATP and steel coating comprise the same components, namely a nitrogen base: Adenosin-Melamine, carbohydrate: Ribose-Pentaerythritol plus a phosphorus acid donator as Polyphosphate-Ammonium polyphosphate. The Hexaphosphate of Phytin, another example of a potential green FR, is separated from maize [6]. Boric and Silicic acids and their salts are applied in flame retardance, for instance as Zink borate $2ZnO^{*} 3B_2O_3^{*}3.5H_2O$ and Sodiumsilicate $Na_2 Si_3O_7$. Silicic acid is present in Horsetail and Diatoms. Boromycin CAS 34524-20-4 is one of the few natural organic boron compounds. Boromycin has been gained from a Streptomyces family and is commercially available at a price of 466€/mg. The only halogen-free FR acting as halogen FR in flame retardance by radical scavenging is DOPO and its descendants. The PO_2 radical shows a similar efficiency as the Br radical. 9,10 Dihydro 9 oxa 10 phosphophenanthrene 10 oxide DOPO CAS 35948-25-5 is intended to substitute PBDE 99 Pentabromodiphenylether CAS 32534-81-9, which acts as a radical scavenger in the radical chain reaction of combustion. Because of PBDE's toxicity and persistence, its industrial production is to be eliminated under the Stockholm Convention. Promising candidates for substitution are DOPO and its descendants. Commercial and semicommercial products are DOPO CAS 35948-25-5, EDA-DOPO CAS 1421927-53-8, PIP-DOPO CAS 141927-52-7 and ETA-DOPO CAS…., EG-DOPO CAS…. A multiparameter toxicity assessment claims that DOPO exhibits distinct neuroselective cytoflame retardenticity at conc > 10 µM, ETA-DOPO and EG-DOPO displaces adverse effects at conc > 10 µM. DOPO and EDA-DOPO are neither neurotoxic nor do they exhibit an influence on neutral crest cell migration, or in the integrity of human skin equivalents. Furthermore, they do not display inflammatory activation potential nor do they effect algea growth or daphnia viability at conc > 400 µM. At conc > 100 µM

DOPO and EDA-DOPO do not display skin irritation but ETA-DOPO and EG-DOPO are harmful to skin. [7]-[9]

Compounds comprising nitrogen bases, carbohydrates and acids are synthesized and characterized by thermogravimetric analysis TGA and differential scanning calorimetry DSC and differential mechanic analysis DMA. In accordance with these measurements equations of reactions are established. Their capability to intumescence, their amount of residue, their water solubility and their price are a measure of possible application. [10]-[12] Another common property of ATP, Desoxyribonucleic and Ribonucleic acids and amine salts, which are applied as FRs, is their self organization in lattices, for example such as Melamine Polyphosphate, Cyanurate, Barbiturate, Polyborate and Guanidine Sulfamate, Polyphosphate and Polyborate. Their lattice energies are originated by hydrogen bridging and are calculated in the Born Haber cycle. More over their possibilities of interaction with the substrate by hydrogen bridging and influence of self organization on flame retardance are considered.

2. Materials

Commercial FR are bought, others are synthesized. Synthesis is very simple, in most cases mixing in presence of water is sufficient. The precipitate is separated and dried.

In Table 1 the Nitrogen bases used with different base strengths are collected.

Table 1. Amines with different basic strengths.

Name	Formula	K1	K2	K3	Company	CAS
Ammonia	NH_3	$1.75.10^{-5}$			Agro Melamine	7664-41-7
2Aminoethanol	C_2H_5NO	8.10^{-3}	$1.9.10^{-8}$		Carl Roth	141-43-5
Guanidine	C_5HN_3	very strong			Agro Melamine	113-00-8
Urea	CH_4N_2O	$1.5.10^{-14}$			Agro Melamine	57-13-6
Ethylenediamine	$C_2H_8N_2$	$3.7.10^{-7}$	$5.1.10^{-10}$		BASF	107-15-3
Melamine	$C_3H_6N_6$	$1.3.10^{-9}$	$1.6.10^{-14}$	$1.0.10^{-17}$	Agro Melamine	108-78-1
135Triaminotriazine	$C_3H_9N_9$	2.10^{-2}			Agro Melamine	1015-42-7
Morpholine	C_4H_9NO	1.10^{-6}	$2.3.10^{-6}$		Merck Millipor	110-41-8
Piperazine	$C_4H_{10}N_2$	7.10^{-5}	$3.5.10^{-9}$		Merck Millipore	110-85-0
2Aminoethylether	$C_4H_{12}N_2O$				Carl Roth	141-43-54.5

In Table 2 the applied Acids with different acid strengths are summarized.

Table 2. Acids with different acid strengths.

Name	Formula	K1	K2	K3	Company	CAS
Phosphoric acid	H_3PO_4	$1.1.10^{-2}$	$1.2.10^{-7}$	$1.8.10^{-12}$	Fluka	1571-33-1
Boric acid	H_3BO_3	6.10^{-10}	2.10^{-13}	2.10^{-14}	Carl Roth	10043-35-3

Continued

Cyanuric acid	$C_3H_3N_3O_3$	$1.3.10^{-7}$	4.10^{-12}	$3,5.10^{-14}$	Wego Chemical	108-80-5
Barbituric acid	$C_3H_4N_2O_3$	1.10^{-4}			PharmaWiki	67-52-7
Hydrochloride	HCl	strong			Che Mondis	7647-01-0
Sulfamid acid	NH_3SO_3	1.10^{-1}			DuPont	5329-14-6
Silicic acid	H_4SiO_4	$1.6.10^{-10}$	$7.4.10^{-13}$		Merck	3067-63

Table 3 shows the carbohydrates applied.

Table 3. Carbohydrates.

Name	Formula	Company	CAS	g/l in Water 25˚C
D-Mannit	$C_6H_2(H_2O)_6$	AppliChem	69-65-8	850
Pentaerythritol	$C_5H_4(H_2O)_4$	Perstorp	115-77-5	72
Neopentylglycol	$C_5H_8(H_2O)_2$	System Chemie	204-781-0	830
Starch	$C_6(H_2O)_6$	Agrana	9005-25-8	0
Dipentaerythritol	$C_{10}H_8(H_2O)_7$	Perstorp	126-58-9	2.5

3. Methods

For the measurements of heat and weight Mettler TMA/STD A840 with TGA Modul STDA 851 is used. The sample size is 9 - 11 mg in 900 ml Al_2O_3 crucibles with punched lids and heating rates from 5 to 40 K/min. TMA measurements determine intumescence with sample sizes 2 - 3 mg and a load of 0.02 - 0.2 N at a heating rate of 20 - 50 K/min. They give the expansion factor EF = V/Vo − 1. (V the volume of the sample at temperature T, Vo is the specific volume of the unexpanded sample at room temperature). The maximum expansion factor of the sample EFmax correlates with Vg/Vo. Vg is the volume of gas in 1 g sample:

The balance of weights gives the moles of gas evolved n, which allow the calculation of the maximum expansion EFmax by multiplying the ideal gas volume 22400 cm^3/mole with n the moles of gas evolved from one-mole of sample and with rho the bulk density of the unexpanded sample divided by the molecular weight MW of the sample.

$$\text{EFmax} = \left(22400 * \text{n}/\text{MW}\right) * \text{rho} \tag{1}$$

The Born Haber cycle is used for the calculation of the energies of ion-ion and dipol-dipol lattices.

For comparison the maximum expansion Emax of the natural products ATP, Hexaphosphoric Inosite and Boromycin and the important commercial FRs Pentabromodiphenylether and DOPO was determined by TMA measurements: ATP is intumescent with EFmax = 69 and 50% residue. The high solubility in water, the low temperature of degradation and the high price inhibit a realistic application. Hexa phosphoric Inosite [13] [14] is not intumescent but provides with 75% residue a high char yield. The high solubility in water and the high acid number are disadvantages. Boromycin with 4% residue is not intumesent and does not indicate any flame retardance. Pentabromodiphenylether with 13% residue evolves five Br radicals/mole and DOPO with 17% residue gives off one PO_2 radical/mole. Both show no intumescence but are active as radical scavengers. Phosphoric acid is a medium-strong acid. With Ammonia phosphoric acid reacts to prim, sec, and tert Phosphates. Ammonium polyphosphate is an ingredient in many intumescent formulations. In the following its degradation is described by formulas, molar weight balances MW(g/mole) and heat of formation balances H (kJ/mole). hex/cal (kJ/g) means experimental/calculated heats, Rex/cal (%) experimental and calculated percentage of residues, EA (kJ/g) experimental heats of activation.

4. Results

Degradation of Ammonium polyphosphate APP CAS 10124-31-9
T = 350˚C, hex/cal = 0.56/0.56, Rex/cal = 82/82%, EA = 2.2 kJ/g
$NH_4PO_3 = NH_3 + HPO_3$
MW 97 = 17 + 80
H − 996 + 54 = −46 − 896
T = 400˚C, hex/cal = 0.25/0.25 kJ/g, Rex/cal = 75/73%, EA = 1.1 kJ/g
$HPO_3 = 0.5H_2O + PO_{2.5}$ solid
MW 80 = 9 + 71
H − 896 + 25 = −121 − 750
T = 700˚C, hex/cal = 0.26/0.26 kJ/g, Rex/cal = 13/0%, EA = 1.05 kJ/g
$PO_{2.5} = PO_{2.5}$ gas
H − 750 + 25 = −725

$NH_4PO_3 = NH_3 + 0.5H_2O + PO_{2.5}$ gas hex/cal = 1.10/1.07 kJ/g, Rex/cal = 12/0%
MW 97 = 17 + 9 + 71
H − 996 + 104 = −46 − 121 − 725

4.1. Ammonium Polyphosphate and Carbohydrate Mixtures, Which Degrade to CnHmHPO$_3$

APP alone is not intumescent. The blowing reaction at 400˚C suffers from the lack of carbonaceous char. In the presence of a carbohydrate, for instance Pentaerythritol as a source of carbon, the mixture becomes intumescent.

Degradation of a mixture of 1m Ammonium polyphosphate NH_4PO_3 and Pentaerythritol $C_5H_{12}O_4$

T = 250˚C, hex/cal = 0.60/0.63 kJ/g, Rex/cal = 73/73%, EA = 0.43 kJ/g
$NH_4PO_3 + C_5H_{12}O_4 = C_5H_8PO_{4.5} + NH_3 + 2.5H_2O$
MW 97 + 136 = 171 + 17 + 45
H − 931 − 1030 + 82 = − 1228 − 46 − 605
T = 300˚C, hex/cal = 0.20/0.20 kJ/g, Rex/cal = 60/62%, EA = 0.86 kJ/g
$C_5H_8PO_{4.5} = C_5H_3PO_3 + 1.5H_2O$
MW 171 = 144 + 27

H − 1228 + 47 = −818 − 363

T = 350˚C, hex/cal = −0.50/−0.55 kJ/g, Rex/cal = 54/54%, EA = 0.56 kJ/g

$C_5H_2HPO3 = 0.5CH_4 + 0.5H_2O + 0.5\ P_2O_5 + 4.5C$ Intumescence

MW 144 = 8 + 9 + 71 + 54

H − 818 − 90.5 =−37.5 − 121 − 750

$C_5H_{16}NPO_7 = 4.5H_2O + NH_3 + CH_4 + 0.5P_2O_5 + 4C$ hcal = 0.28 kJ/g

MW 233 = 81 + 17 + 16 + 71 + 48

H − 2026 + 66 = −1089 −46 − 75 − 750

In **Figure 1** the coefficient of expansion EF is measured for mixtures of APP and PER as well as for Bicyclopentaerythritolphosphate BCPP.

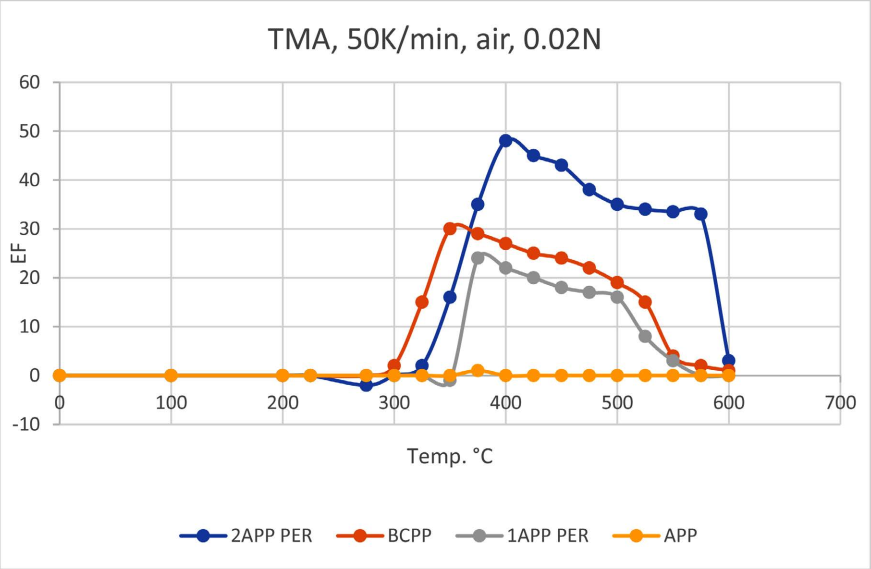


Figure 1. Expansion factor EF of mixtures of Ammoniumpolyphosphate APP and Pentaerythritol PER as well as Bicyclopentaerythritolphosphate BCPP.

When the moles of evolved gas are known, then EFmax of **Figure 1** can be calculated by the ideal gas law:

$$\text{EFmax} = \left(\text{n} * 22400/\text{MW}\right) * \text{rho} \qquad (1)$$

rho is the density of the unexpanded sample.

For APP and PER mixtures the empirical Equation (2) [10] is valid:

$$\text{EFmax} = 0.25 * \left(\text{nAPP/PER}\right) * \text{MWAPP} \qquad (2)$$

nAPP/PER are the moles of Ammoniumpolyphosphate divided by the moles of Pentaerythritol and MWAPP is the molecular weight of Ammoniumpolyphosphate.

Both equations lead to the same result, when rho is introduced:

The mixture of 2mAPP and 1mPER shows a maximum expansion EFmax = 48.5

$$\text{EFmax} = 2 * 0.5 * 22400 \big/ \left(2 * 97 + 136\right) * 0.71 = 0.25 * 2 * 97 = 48.5 \qquad (1)$$

For APP and Dipentaerythritol DPER mixtures the empirical Equation (4) [10] is given:

$$\text{EFmax} = 0.20 * (\text{nAPP}/\text{nDPER}) * \text{MWAPP} \quad (3)$$

The mixture of 2mAPP and 1mDPER exerts a maximum expansion of 38.8

$$\text{EFmax} = 2 * 0.5 * 22400/(2 * 97 + 254) * 0.78 = 0.20 * 2 * 97 = 38.8 \quad (3)$$

According to **Figure 1** the mixtures of APP and PER as well as the ester BCPP degrade to $C_3H_9N_6PO_4$, which reacts further to Phosphorus pentoxide, graphite, methane and water [11]

$$C_nH_mHPO_3 = m/4CH_4 + (n - m/4)C + 0.5H_2O + 0.5P_2O_5 \quad (4)$$

4. 2. Ammonium Salts, Which Degrade to CnHmHPO₃

The phosphorus salts of amines, like Ethylenediamine, 2-Aminoethylether, Ethanolamine, Piperazine, Morpholine, degrade by heating to amides and further to the decomposition product $C_nH_mHPO_3$, which reacts under intumescence to Methane, Graphite, Water and Phosphorus Pentoxide:

Degradation of Di-Ethylenediamine phosphate DEDAP CAS NA
T = 300˚C, hex/cal = 0.10/0.08 kJ/g, Rex/cal = 91/88%
$C_4N_4H_{19}PO_4 = C_4H_{16}N_3PO_4 + NH_3$
MW 218 = 201 + 17
H − 1561 + 17 = −1498 − 46
T = 350˚C, hex/cal = 0.40/0.43 kJ/g, Rex/cal = −/61%
$C_4H_{16}N_3HPO_3 = C_4H_5PO_3 + 3NH_3 + H_2O$
MW 201 = 132 + 51 + 18
H − 1302 +93 = −1025 − 184
T = 400˚C, hex/cal = 0.35/0.36 kJ/g, Rex/cal = 49/49%
$C_4H_4HPO_3 = 0.5H_2O + 0.5P_2O_5 + CH_4 + 3C$ Intumescence
MW 132 = 9 + 71 + 16 + 36

$$\text{EFmax} = (22400 * 0.5/218) * \text{rho} = 51 \quad (1)$$

H − 1025 + 79 = −121 − 750 − 75

$C_4H_{19}N_4PO_4 = 4NH_3 + 1.5H_2O + 0.5P_2O_5 + 3C + CH_4$ hcal = 0.86 kJ/g
MW 218 = 68 + 27 + 71 + 36 + 16
H − 1561 + 189 = −184 − 363 − 750 − 75

In **Figure 2** the expansion EF of amine salts, which degrade to intumescent $CnHmHPO_3$ is depicted.

Melamine phosphate does not degrade to the intumescent degradation product $CnHmHPO_3$ but to the thermal stable $C_3N_4PO_{2.5}$

$$C3H_9N_6PO_4 = C_3N_4PO_{2.5} + 1.5H_2O + 2NH_3$$

Melamine phosphate consumes phosphorus without intumescence.

The Phosphoric acid ester of PER is intumescent but has the disadvantage of high solubility in water and high acid number.

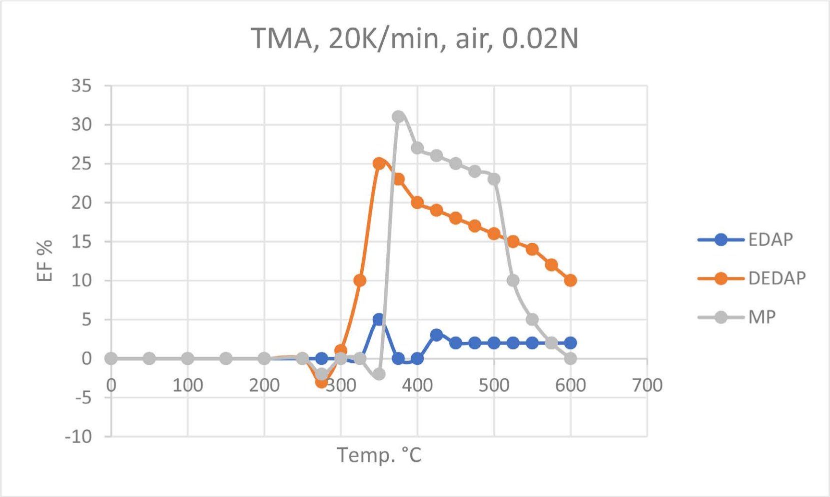
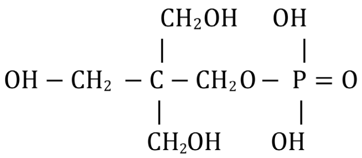


Figure 2. Intumescence of Ethylenediamine phosphate EDAP, Diethylenediamine phosphate DEDAP, Morpholine phosphate MP.

Pentaerythritol phosphoric acid



$$\begin{matrix} & & CH_2OH & & OH \\ & & | & & | \\ OH-CH_2 & - & C & -CH_2O- & P=O \\ & & | & & | \\ & & CH_2OH & & OH \end{matrix}$$

$C_5H_{13}PO_7$ MW = 216, EW = 108

Water soluble and a Acid Number = 56100/EW = 56100/108 = 519

EW = equivalent weight = molecular weight MW divided by functionality f = MW/f

EFmax = 26*rho

The high solubility of Pentaerythritolphosphate in water and the high acid number are serious disadvantages. Bicyclopentaerythritolphosphate, which is available commercially and is the reaction product of Phosphoroxytrichlorid and Pentaerythritol [15]-[17], eliminates the mentioned disadvantages.

Degradation of Bicyclopentaerythritolphosphate Tf = 225˚C CAS 5301-78-0

T = 300˚C, hex/cal = −0.20/−0.11 kJ/g; Rex/cal = 80/80%

$C_5H_9PO_5 = C_5H_5PO_3 + 2H_2O$

MW 180 = 144 + 36

H − 1394 – 20 = −930 − 484

T = 350˚C, hex/cal = −0.15/−0.09 kJ/g; R = 55//66%

$C_5H_5PO_3 = CH_4 + 0.5H_2O + 4C + PO_{2.5}$ Intumescence

MW144 = 16 + 9 + 48+ 71

H − 930 − 16 = −75 – 121 − 750

T = 700˚C hex/cal = /0.56 kJ/g; Rex/cal = 25/26.7%

$4C + PO_{2.5} = 4C + PO_{2.5}$ gas

MW 48 + 71 = 48 + 71

H − 750 + 100 = −650

$C_5H_9PO_5 = 2.5H_2O + CH_4 + 0.5P_2O_5$ gas + 4C   hcal = 0.36 kJ/g

MW 180 = 45 + 16 + 71 + 48

H − 1394 + 64 = −605 − 75 − 650

$$\text{EFmax} = (22400 * 0.5/180) * (\text{rho} = 0.72\ \text{g/cm}^3) = 45 \quad (1)$$

$$\text{EFmax} = 0.25 * (\text{nP}/\text{nBCPP}) * \text{MWBCPP} = 0.25 * (1/1) * 180 = 45 \quad (5)$$

Equation (2) valid for Pentaerythritol APP mixtures can be modified and applied on phosphorus Pentaerythritol esters, then nP are the numbers of phosphorous atoms in the ester compound.

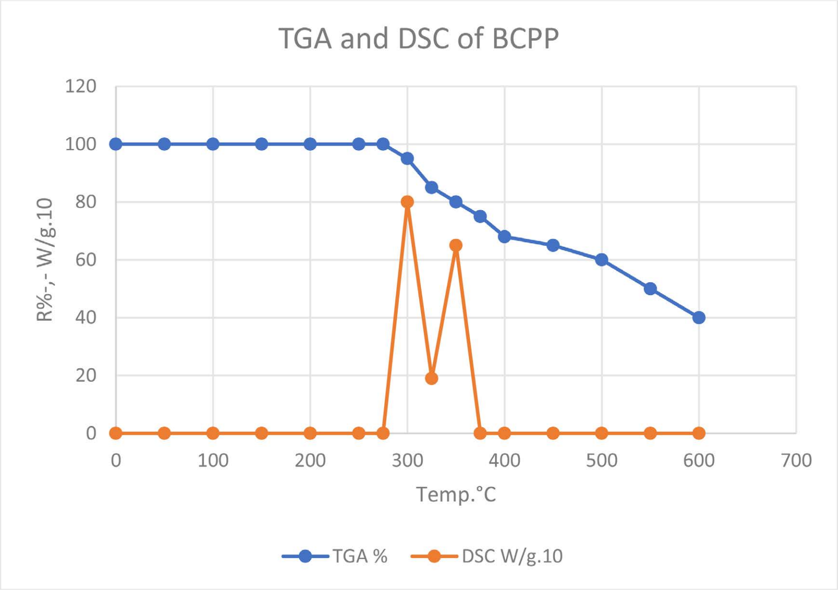


Figure 3. Degradation of Bicyclopentaerythritolphosphate with two exotherm peaks.

In **Figure 3** the two exotherm peaks −0.21 kJ/g and −0.18 kJ/g are remarkable. They correlate with the reactions:

300˚C $C_5H_9PO_5 = C_5H_5PO_3 + 2H_2O$ and 350˚C $C_5H_5PO_3 = CH_4 + 0.5H_2O + 4C + PO_{2.5}$

Neopentylglycol is an alternative carbohydrate source besides Pentaerythritol.

Neopentylglycol Phosphoric acid ester. CAS ND

1 m Neopentylglycol and 1m Phosphoric acid in 0.5l water refluxed for 2 h. Then cooled, the precipitate was decanted, washed and dried. Elementary analysis C 37.9 (32.8), H6.8 (6.8), P17 (16.9), O43.5 (43.7).

Degradation of Neopentylglycol Phosphoric acid ester

T = 250˚C, hex/cal = 0.29/0.3 kJ/g, Rex/cal = 90/89%

$C_5H_{12}PO_5 = H_2O + C_5H_{10}PO_4$

MW 183 = 18 + 165

H−1497.5 + 55 = −242 − 1200.5

T = 300˚C, hex/cal = 0.28/0.3 kJ/g, Rex/cal = 80/81%

$C_5H_{10}PO_4 = C_2H_4 + C_3H_6PO_4$

$MW165 = 28 + 137$

$H - 1200.5 + 55 = +52 - 1093.5$

$T = 350^\circ C$, hex/cal = 0.3/0.4 kJ/g, Rex/cal = 50/54%

$C_3H_6PO_4 = 1.5H_2O + PO_{2.5} + 3/4CH_4 + 9/4C$ Intumescence, char formation

$MW\ 137 = 27 + 71 + 12 + 27$

$H - 1093.5 + 75.75 = -363 - 750 - 56.25$

$C_5H_{12}PO_5 = 2.5H_2O + C_2H_4 + PO_{2.5} + 3/4CH_4 + 9/4C$ hcal = 0.76 kJ/g

$MW183 = 45 + 28 + 71 + 12 + 27$

$H-1497.5 + 138.25 = -605 + 52 - 750 - 56.25$

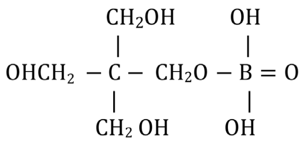
$$\text{EFmax} = \left[(22400 * 0.5)/183\right] * \text{rho} = 61 * \text{rho} \quad (1)$$

As the ester $CnHmHPO_3$ is responsible for intumescence, the esters of $CnHmHBO_3$ and $CnHmHSiO_4$ are investigated in the following.

4.3. Phosphoric, Boric and Silicic Esters with Pentaerythritol and Neopentylglycol

Pentaerythritol boric acid

Preparation: 600 ml Ethanol 1 m PER and 1 m Boric acid are refluxed for 2 h, then cooled. The precipitate is filtered, washed and dried. Elementary analysis: C34.5% (theory 33.4%), H 7.8 (7.2), O 53.4 (53.4%), B 4.3 (6.0) suggests the formula $C_5H_{13}BO_6$.



$$\begin{array}{ccccc} & CH_2OH & & OH & \\ & | & & | & \\ OHCH_2 - & C - & CH_2O - & B = & O \\ & | & & | & \\ & CH_2\,OH & & OH & \end{array}$$

$C_5H_{13}BO_6$ MW = 180

The results of TGA, DSC and TMA measurements on Pentaerythritol Boric acid are provided in **Figure 4**.

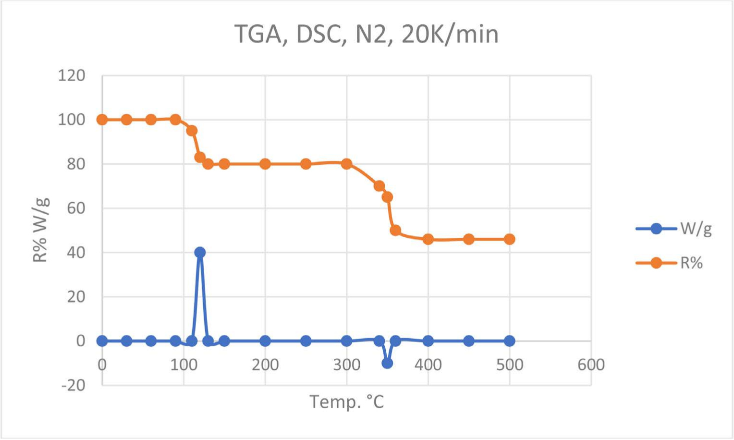
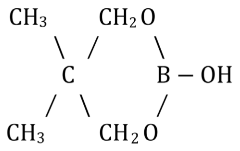


Figure 4. Degradation of Pentaerythritol borate. TGA determined the weight loss and DSC showed an endotherm and a small exotherm peak.

Neopentylglycol boric acid ester CAS ND



1 m Neopentylglycol and 1m boric acid are refluxed in 1 l water for 2 h, then cooled. The precipitate is filtered, washed and dried. Nearly 100% yield. The elementary analysis is in agreement with the formula of the Neopentylglycol boric ester.

During degradation no intumescence was observed.

Synthesis of Pentaerythritol Silicilic acid CAS N.A.

Silicic esters are described in Kirk Othmer, Encyclopedia of Chem Technol. Vol 22 p 68-81.

The most conspicuous material is Tetraethylorthosilicate $Si(OC_2H_5)_4$.

Water glass was the silicic source for the Pentaerythritolsilic ester.

Natron water glass CAS 1344-09 (Fa. Roth) SiO_2 25.8 % - 28.5%, Na_2O 7.8% - 8.5% with a solid content of 35% comprises 8.75 g Na_2O and 26.25 g SiO_2. The solid product consists of 25% Na_2O and 75% SiO_2, which corresponds with $Na_2Si_3O_7$ MW = 242 g/mole.

1000 g water glass contains 87.5 g = 1.41 moles Na_2O and 262.5 g SiO_2. For neutralization 2.82 moles HCl = 28.2 ml 1nHCl are added under stirring. Then to 262.5 g SiO_2 1.3 moles Melamine are added. After washing with cold water and drying

$C_3H_6N_6{*}H_2Si_3O_7$ was obtained with nearly 100% yield.

Neutralization

$Na_2Si_3O_7 + 2HCl = H_2Si_3O_7 + 2NaCl$

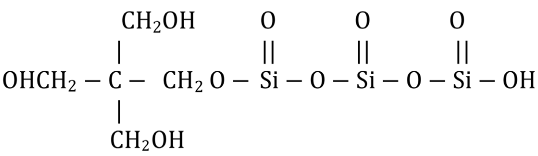
MW 242 + 2*36.5 = 198 + 2* 58.5

$Na_2Si_3O_7$ MW = 62 + 180 = 242 comprises 25% Na_2O and 75% SiO_2

A 35% aqueous solution contains 8.75% Na_2O and 26.25% SiO_2

1000 g water glass contains 87.5 g = 1.41 moles Na_2O and 262.5 g SiO_2. For neutralization 2.82 moles HCl = 28.2 ml 1nHCl are added under stirring. Then to 262.5 g SiO2 1.3moles Pentaerythritol are added. After washing with cold water and drying

$C_3H_{12}Si_3O_{10}$ is obtained with nearly 100% yield. Elementary analysis: C: 18.9% (19.0%), H 4.0% (3.8%), Si 25.4% (26.6%), O 51.7% (50.9%)



$$OHCH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CH_2O-\overset{O}{\overset{\|}{Si}}-O-\overset{O}{\overset{\|}{Si}}-O-\overset{O}{\overset{\|}{Si}}-OH$$

$C_5H_{12}Si_3O_{10}$ MW = 316

Though all three esters degrade in a similar way at 350˚C, only the phosphoric ester exerts intumescence:

$C_5H_{13}PO_7 = 4H_2O + C_5H_5PO_3$

$C_5H_4HPO_3 = CH_4 + 0.5H_2O + 0.5P_2O_5 + 4C$

M 144 = 16 + 9 + 71 + 48

$R = 55\%$, Intumescence $EFmax = 0.5 * 22400 * rho/216 = 52 * rho$ (2)

$C_5H_{13}BO_6 = 4H_2O + C_5H_5BO_2$

$C_5H_4HBO_2 = CH_4 + 0.5H_2O + 0.5B_2O_3 + 4C$

R = 46%, No intumescence

$C_5H_{12}Si_3O_{10} = 3H_2O + C_5H_6Si_3O_7$

$C_5H_4Si_2O_4H_2SiO_3 = CH_4 + H_2O + 3SiO_2 + 4C$

R = 49%, No intumescence

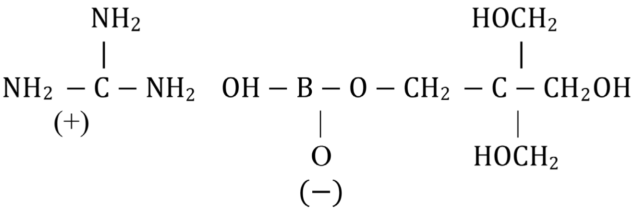
The esters are acidic, they react with Guanidine and Melamine further to salts.

4.4. Ammoniumsalts of Esters

Guanidinium pentaerythritol boric acid CAS ND

1 m Pentaerythritol and 1m boric acid were dispersed in 600 ml water distilled and refluxed for 2 h. Then 0.5 m Guanidine carbonate was slowly added and refluxed for further 2 h. The product was filtrated, washed with cold water and dried at 100˚C.

The elementary analysis indicated the salt of guanidinium and the ester of pentaerythritol and boric acid: C 30.8% (theory 30.4), H 7.1 (6.8), N 18.1 (17.7), O 38.0 (40.5), B 6.0(4.6).



$$\begin{array}{cccccccccc}
 & NH_2 & & & & & & HOCH_2 & \\
 & | & & & & & & | & \\
NH_2 - & C & - NH_2 & OH - & B & - O - CH_2 - & & C & - CH_2OH \\
 & (+) & & & | & & & | & \\
 & & & & O & & & HOCH_2 & \\
 & & & & (-) & & & &
\end{array}$$

$C_6H_{18}N_3BO_6$ MW = 239

Degradation of Pentaerythritol borate CA N.A.

T = 200˚C hex/cal = 0.73/0.57 kJ/g; Rex/cal = 60/68%

$C_6H_{18}N_3BO_6 = C_6H_{10}N_3BO_2 + 4H_2O$

MW 239 = 167 + 72

$H - 1978 + 136 = -874 - 968$

T = 350˚C, hex/cal = 0.70/0.53 kJ/g, Rex/cal = 35/37%

$C_6H_{10}N_3BO_2 = BO_{1.5} + 0.5H_2O + 3/4CH_4 + 41/4C + CN + 2NH_3$ No intumescence

MW 167 = 35 + 9 + 12 + 51 + 26 + 34

$H - 874 + 127 = -632 - 121 - 56 + 154 - 92$

$C_6H_{18}N_3BO_6 = 4.5H_2O + 2NH_3 + 0.5C_2N_2 + BO_{1.5} + 3/4CH_4 + 41/4C$

h = 1.1 kJ/g

MW 239 = 81 + 34 + 26 + 35 + 12 + 51

H −1978 + 263 = −1089 − 92 + 154 − 632 − 56

Guanidinium Bis-Neopentylglycol boric acid ester CAS N.A.

In 1 l ethanol 1 m Neopentylglycol and 0.5 m boric acid are dispersed and refluxed for 2 h. After cooling to RT 0.25 mole GC are slowly added. Then reflux is continued for further 2 h. After cooling the contence is filtered and washed with water. The solid residue as dried. Yield about 80%, elementary analysis: C 47.7 (48.0), H 9.5 (9.5), N 15.6 (15.3), B 3.9 (4.0), O 23.3 (23.2).

Degradation of Guanidine Bis-Neopentylglycol borate

Tf = 250˚C, hf = 0.07 kJ/g,

T = 300˚C, hex/cal = 0.55/0.37 kJ/g, R = 0/0%

$C_{11}H_{26}N_3BO_4 = 2C_2H_6 + 2C_2H_4 + 2CO_2 + CH_2N_2(1/3M) + H_4NB$

M = Melamine

MW 275 = 60 + 56 + 88 + 42 + 29

H − 1610 + 102 = 104 − 168 – 787 – 24 – 633

Guanidinium Dineopentylglycol boric acid is remarkable, because in TGA measurements no residue is observed. The boric acid evaporates completely and the evolution of H_4NB gas or HNB gas has to be assumed.

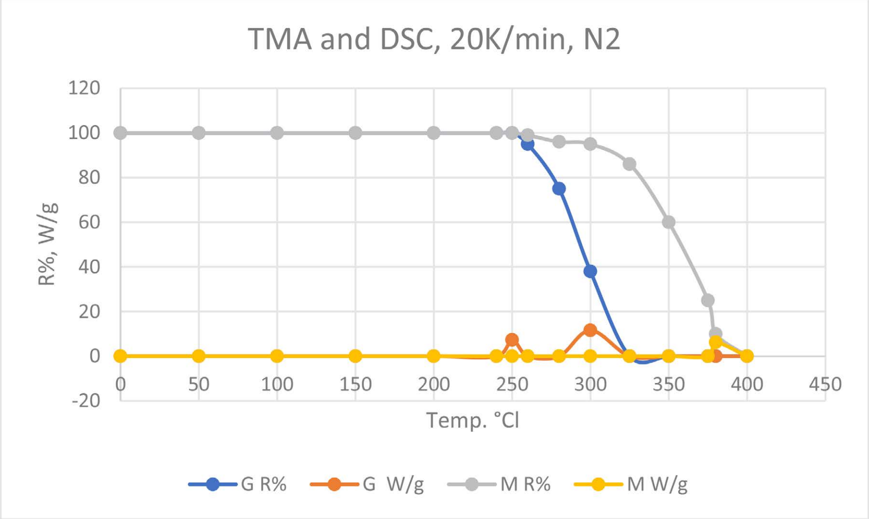


Figure 5. TMA and DSC of Melamine Bis Neopentylglycol boric ester M and Guanidine Bis Neopentylglycol boric ester G.

Degradation of Melamine Bis Neopentylglycol boric ester

T = 370˚C, hex/cal = 0.50/1.54 kJ/g, Rex/cal = 0/0%

$C_{13}H_{27}N_6BO_4 = BNH_4 + C_2N_2 + NH_3 + N_2 + 2CO_2 + 4C_2H_4 + CH_4$

MW 342 = 29 + 52 + 17 + 28 + 88 + 112 + 16

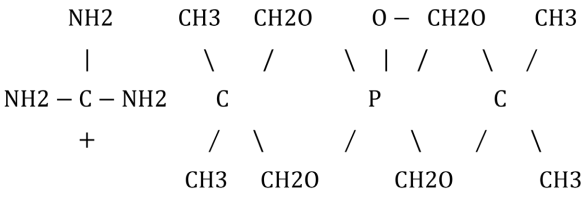
H − 1561 + 528 = −633 + 308 − 46 − 787 + 200 − 75

Melamine and Guanidine Bis Neopentyl boric ester degrade in the same way. The results of TGA and DSC measurements are documented in Figure 5. By way of comparison Guanidine Bis Neopentylglycol phosphoric acid, Guanidine Neopentylglycol phosphoric acid and Melamine Bis Neopentylglycol phosphoric acid ester are synthesized and analysed.

Guanidine Bis-Neopentylglycol phosphate CAS N.A.

1 l Ethanol, 1 m Neopentylglycol and 0.5 m phosphoric acid were heated under stirring to reflux. After cooling 0.25 m GC were added. 2 h reflux, then cooling. The precipitate was washed and dried. Elementary analysis: C 31.9% (32.0), H 7.0% (7.1), N 18.5% (18.7), 13.5% (13.8) P, O 28.8% (28.4).

Guanidine Bis-Neopentylglycol phosphoric acid



Degradation of Guanidine Bis Neopentylglycol phosphate

T = 280˚C, hex/cal = 0.25 /0.30 kJ/g, Rex/cal = 80/81%

$C_{11}H_{26}N_3PO_5 = 2NH_3 + CN + C_{10}H_{20}PO_5$

MW 311 = 34 + 26 + 251

H1727 + 93 = −92 + 154 − 1696

T = 400˚C, hex/cal = 0.20/0.19 kJ/g, Rex/cal = 25/24%

$C_{10}H_{20}PO_5 = PO_{2.5} + 2.5H_2O + 15/4CH_4 + 25/4C$ Intumescence

MW 251 = 71 + 45 + 60 + 75

H − 1696 + 60 = −750 − 605 − 281

$C_{11}H_{26}N_3PO_5 = PO_{2.5} + 2.5H_2O + 2NH_3 + CN + 15/4CH_4 + 25/4C$

MW 311 = 71 + 45 + 34 + 26 + 60 + 75 hcal = 0.49 kJ/g

H − 1727 + 153 = −750 − 605 − 92 + 154 − 281

$$EF = 0.5 * 22400 * rho/311 = 36 * rho \tag{1}$$

Degradation of Guanidine Neopentylglycol phosphate

T = 270˚C, hex/cal = 0.4/0.4 kJ/g, Rex/cal = 85/84%

$C_6H_{16}N_3PO_4 = NH_3 + H_2O + C_6H_{11}N_2PO_3$

MW 225 = 17 + 18 + 190

H − 1375 + 90 = −46 − 242 − 997

T = 280˚C, hex/cal = 0.45/0.35 kJ/g; Rex/cal = 60/65%

$C_6H_{11}N_2PO_3 = NH_3 + 0.5C_2N_2 + C_5H_7.HPO_3$

MW 190 = 17 + 26 + 147

H−997 + 80.25 = −46 + 154 − 1025

T = 400˚C hex/cal = −/0.1, Rex/cal = 48/49%

$C_5H_7.HPO_3 = 7/4CH_4 + (5 - 7/4)C + 0.5P_2O_5 + 0.5H_2O$ Intumescence and char formation

MW 147 = 28 + 39 + 71 + 9

H−1025 + 22.75 = −1.75*75 − 750 − 121

$C_6H_{16}N_3PO_4 = 2NH_3 + 1.5H_2O + 0.5C_2N_2 + 1.75CH_4 + 3.25C + 0.5P_2O_5$

hcal = 0.9 kJ/g

MW 225 = 34 + 27 + 26 + 28 + 39 + 71

H−1375 + 193 = −92 − 363 + 154 − 131 − 750

$$\text{EFmax} = \left(22400 * 0.5/225\right) * \text{rho} = 50 * \text{rho} \tag{1}$$

Degradation of Melamine Bis Neopentylglycol phosphate

T = 350˚C, hex/cal = 0.50/0.46 kJ/g, Rex/cal = 48/47%

$C_{13}H_{27}N_6PO_5 = PO_{2.5} + C_3N_4 + 2NH_3 + 2.5H_2O + 4CH_4 + 6C$

MW 378 = 71 + 92 + 34 + 45 + 64 + 72

H − 1679 + 174 = −750 + 242 − 92 − 605 − 300

No intumescence is observed.

4.5. Selforganized Lattices of Melamine and Guanidine Salts

DNA self organizes in helix structure, Melamine and Guanidine salts applied as FR self organize in lattices. A lattice based self organization predicts more robustness to perturbations and destruction. The Melamine salts are examples for dipol-dipole salts and the Guanidinium salts are representatives for ion-ion salts.

Melamine Polyphosphate is an effective FR for glass fibre reinforced Polyamides and Polyesters. It is organized in a crystal structure consisting of layers of cationic melamine chains alternating with anionic polyphosphate chains. The hydrogen-bonding distance between donor and acceptor amounts to 3A. [18] For the calculation of the lattice energy Uo, the Born Haber Cycle is applied:

Uo = Q heat of reaction + S heat of sublimation + I heat of ionization − E heat of electron affinity.

Melamine polyphosphate MPP $C_3H_6N_6HPO_3$ CA 56386-64-2

Degradation of Melamine polyphosphate

Tdec = 350˚C, hex/cal = 0.9/0.9 kJ/g, Rex/cal = 80/79%

$C_3H_6N_6HPO_3 = C_3N_4 + 0.5P_2O_5 + 0.5H_2O + 2NH_3$

MW 206 = 92 + 71 9 + 34

H − 974 + 184 = 172 − 750 − 121 − 92

Heat of reaction Q = −6 kJ/mole

M + PP = MPP

H − 72 − 896 − 6 = −974

As only Melamine is able to sublime, the heat of sublimation is the heat of sublimation of melamine with 121kJ/mole: S = 121*126/206 = 74

Electron affinity E = 354 kJ/mole

$NaPO_3 = Na^+ + PO_3^-$

H−782 = −240 − 542

$HPO_3 = H^+ + PO_3^-$

H−869 + 354 = −542

Heat of Ionization I = 322.5 for one proton transfer and I = 244.5 kJ/mole for three protons.

$MH_3PO_4 = MH^+ + H_2PO_3^-$ $\qquad$ $MH_3PO_4 = MH_3^{3+} + PO_4^{3-}$

$H - 1112.5 = 250.5 + 1363 \qquad -1112.5 = 172.5 - 1285$

$M + H = MH^+ \qquad M + 3H^+ = MH_3^{3+}$

$H - 72 + 322.5 = 250.5 \qquad -72 + 0 + 244.5 = 172.5$

$$Uo = Q(-6)+S(74)-E(354)+I(322.5)=36.5\ \text{kJ/mole}$$

Guanidine polyphosphate is organized in cationic Guadinium chains and anionic polyphosphate chains. [19]

Decomposition of Guanidine polyphosphate CA N. A.

Tf = 135˚C, hf = 0.15 kJ/mole

Tdec = 305˚C, hex/cal = 0.60/0.88 kJ/g Rex/cal = 50/51%

$CH_6N_3PO_3 = NH_3 + CH_2N_2$ (1/3 Melamine) $+ 0.5H_2O + 0.5P_2O_5$

MW 139 = 17 + 42 + 9 + 71

H − 1023 + 123 = −46 + 17 − 121 − 750

Heat of reaction Q = 3 kJ/mole

G + PP = GPP

H−130 − 896 + 3 = 1023

E = 354 kJ/mole

Heat of ionization I = 470 kJ/mole $CH_5N_3H_3PO_4 = CH_6N_3^+ + H_2PO_4^-$

H − 1023 = 340 − 1363

$CH_5N_3 + H^+ = CH_6N_3^+$

H − 130 + 470 = 340

$$Uo = Q(3)+S(40)-E(354)+I(470)=159\ \text{kJ/g}$$

Melamine borate is applied as FR in coatings [20] and degrades to Melon and Boron trioxide.

Melamine borate CAS 53587-44-3

Degradation of Melamine borate

T = 150˚C, hex/cal = 0.51/0.51 kJ/g; Rex/cal = 83/86%

$C_3H_9N_6BO_3 = 1.5H_2O + C_3H_6N_6BO_{1.5}$

MW 188 = 27 + 161

H − 1142 + 96 = −363 − 682

T = 300˚C, hex/cal = 0.25/0.31 kJ/g; Rex/cal = 49/54%

$C_3H_6N_6BO_{1.5} = BO_{1.5} + C_2HN_3 + NH_3 + N_2 + 0.5C_2H_4$ (Melon)

MW 161 = 35 + 67 + 17 + 28 + 14

H − 682 + 59 = −632 + 49 − 17 + 26

T = 600˚C; hex/cal =−/1.12 kJ/g; Rex/cal = 16/19%

$C_2HN_3 + BO_{1.5} = N_2 + 0.5C_2N_2 + 0.5C_2H_2 + BO_{1.5}$

MW 102 = 28 + 26 + 13 + 35

H − 585 + 210 = 154 + 103.5 − 632

$C_3H_9N_6BO_3 = 1.5H_2O + 0.5C_2N_2 + BO_{1.5} + NH_3 + 2N_2 + 0.5C_2H_4 + 0.5C_2H_2$

hcal = 2.05 kJ/g

MW 188 = 27 + 26 + 35 + 17 + 56 + 14 + 13

H − 1142 + 384.5 = −363 + 154 − 632 − 46 + 0.5*52 + 0.5*207

In the steps of degradation Boron trioxide B_2O_3 occurs but no Perborate BO_2 is observed. The Born Haber Cycle calculates a lattice energy Uo = 387.5

kJ/mole.

Electron affinity E = 35 kJ/mole

$B(OH)_3 = BO_3H_2^- + H^+$

H − 1089 + 35 = −1054

I = 322.5 kJ/mole

Heat of reaction Q = 19 kJ/mole

$M + B(OH)_3 =$ Melamine borate

H − 72 − 1089 + 19 = −1142

Heat of sublimation S = 121*126/188 = 81 kJ/g

$$Uo = Q(19) + S(81) - E(35) + I(322.5) = 387.5 \text{ kJ/g}$$

In comparison to Melamine borate Guanidinium borate [21] [22] is investigated.

Guanidinium borate CA 5423-22-3

Degradation of Guanidinium borate

T = 200˚C, hex/cal = 0.5/0.5 kJ/g, Rex/cal = 8078%

$CH_8N_3BO_3 = 1.5H_2O + CH_5N_3BO_{1.5}$

MW 121 = 27 + 767.5

H − 1190.5 + 60 = −363 − 767.5

T = 400˚C, hex/cal = 0.90/0.93 kJ/g, R = 30/29%

$CH_5N_3BO_{1.5} = N_2 + CH_2 + NH_3 + BO_{1.5}$

MW 94 = 28 + 14 + 17 + 35

H − 767.5 + 112.5 = 26 − 46 − 632

$CH_8N_3BO_3 = 1.5H_2O + NH_3 + 0.5C_2H_4 + N_2 + BO_{1.5}$ hcal = 1.45 kJ/g

MW 121 = 27 + 17 + 14 + 28 + 35

H − 1190.5 + 175.5 = −363 − 46 + 26 − 632

Heat of reaction Q = 22 kJ/mole

$CH_5N_3 + B(OH)_3 = CH_8N_3BO_3$

H − 131 − 1089 + 22 = −1190

E = 35 kJ/g

I = 470 kJ/g

$$Uo = Q(22) + S(46) - E(35) + I(470) = 503 \text{ kJ/mole}$$

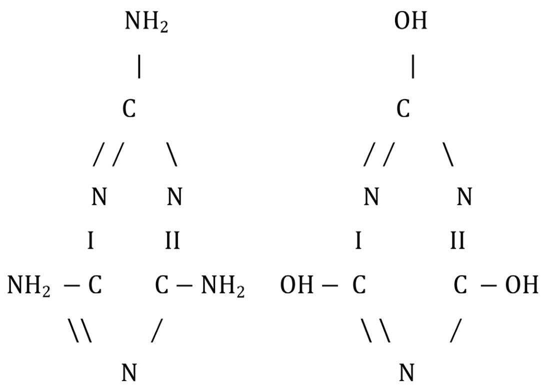
The lattice energy of Guanidinium borate is much higher than that of Melamine borate.

A prominent example of a dipol-dipol salt is Melamine Cyanurate, which self organizes in a hexagonal lattice.

Melamine Cyanurate CAS 37640-57-6

Melamine M is tribasic and Cyanuric acid C triacid, therefore mono-di- and tribasic- as well As mono-, di- and triacid- salts are possible. In the case of a mono basic and mono acidic salt, the weak base Melamine with Kb = $1.3*10^{-7}$ reacts with the weak Cyanuric acid with Ks $1.0*10^{-7}$.

Synthesis of prim. Melamine Cyanurate MC:



Aqueous dispersions of equimolecular amounts of Melamine M and Cyanuric acid C are heated to reflux under stirring or heated at 350˚C in a furnace. After 1h the samples are dried. The degree of conversion can be estimated by DSC measurements. When a peak of Melamine hM or such one of Cyanuric acid hC is detectable in the DSC measurement, then

$$\%\ \text{Conversion} = \left[1 - \text{hM}/(0.97 * 0.49)\right] * 100 = \left[1 - \text{hC}/(1.24 * 0.51)\right] * 100 \quad (6)$$

Melamine CA 108-78-1

T = 350˚C, hex/cal = 0.96/0.97kJ/g, Rex/cal = 0/0% hex/cal = 3.5 kJ/g

Melamin = Melamine gas $C_3H_6N_6 = 2NH_3 + 3/2C_2N_2 + 1/2N_2$

MW 126 = 126 MW 126 = 34 + 1.5*52 + 14

H – 72 + 122 = 50 H – 72 + 442 = −92 + 1.5*308

Cyanuric acid CA 108-80-5

T = 400˚C, hex/cal = 1.2.5/1.24 kJ/g

$C_3H_3N_3O_3 = C_3H_3N_3O_3$gas

MW129 = 129

H – 691 + 160 = −531

When neither a Melamine nor a Cyanuric acid peak but only a Melamine Cyanurate peak hmc is detectable, then the conversion is given by

$$\%\text{Conversion} = 100 * \frac{\text{hmc} - \text{hMCadditive}}{\text{hMC} - \text{hMCadditive}} = 100 * (\text{hmc} - 1.1)/1.7 \quad (7)$$

An equimolar mixture of Melamine and Cyanuric acid evolves a decomposition heat of hMC additive = 1.1 kJ/g.

$$\text{hMCadditive} = (126/255) * 0.97 + (129/255) * 1.24 = 1.1\ \text{kJ/g} \quad (8)$$

100% pure MC salt such a heat of decomposition hMC of 2.8 kJ/g.

hMC-hMCadd = 1.7 kJ/g or 434 kJ/mole, which comprises the lattice energy Uo and the heat of reaction Hreac. Independent of this calculation the heat of reaction Hreac = −721 kJ/mole and the lattice energy Uo = 145 kJ/mole are determined, which amounts 721 – 145 = 576 kJ/mole in sum. The agreement is not perfect but not out of any comparison.

Degradation of Melamine Cyanurate CAS 37640-57-6

T = 400˚C, hex/cal = 2.8/2.79 kJ/g, Rex/cal = 0/0%

$C_6H_9N_9O_3 = 3CO + 3NH_3 + 1.5C_2N_2 + 1.5N_2$

MW 255 = 84 + 51 + 78 + 42

H = −721 + 712 = −333 − 138 + 462

When the components are united to salt, then vaporization and sublimation of the components are oppressed.

Table 4. Synthesis of MC in dependence of water content.

MC in Water	Temp.	Viscosity	pH	Convers.	hMC
%	˚C	mPas		%	kJ/g
0.01	1 h/100˚C	1	4.9	100	2.8
10	"	16	3.6	88	2.6
25	"	1000	3.0	70	2.3
100	1 h/350˚C	solid	4 µm particle	58	2.1

Table 4 shows that the conversion of Melamine and Cyanuric acid to salt is strongly dependent on the water content. The pH value decreases with decreasing water content.

In order to achieve the point of equivalence a millimolar solution of Cyanuric acid C was titrated by a millimolar solution of Melamine M at 90˚C. **Figure 6** describes the titration. The point of equivalence correlates with pH 5.

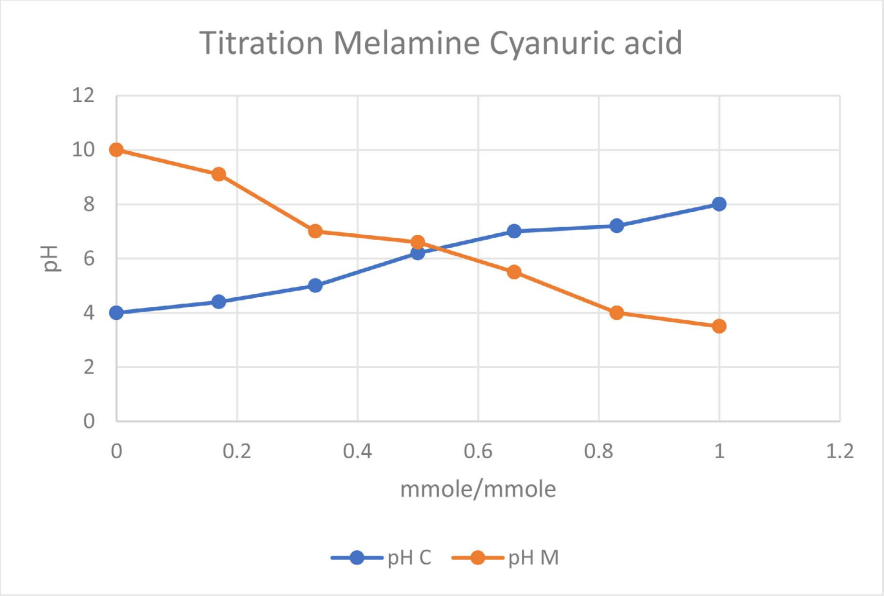


Figure 6. Titration at 90˚C of MC in millimolar concentrations.

The Cyanuric Acid-Melamine lattice is held together by a network of 18 hydrogen bonds and is one of the most stable nonbiological supramolecular aggregates synthesized to date. See **Figure 7**. The exchange reaction appears to occur by dissociation with a heat of 100 kJ/mole. [23] [24]

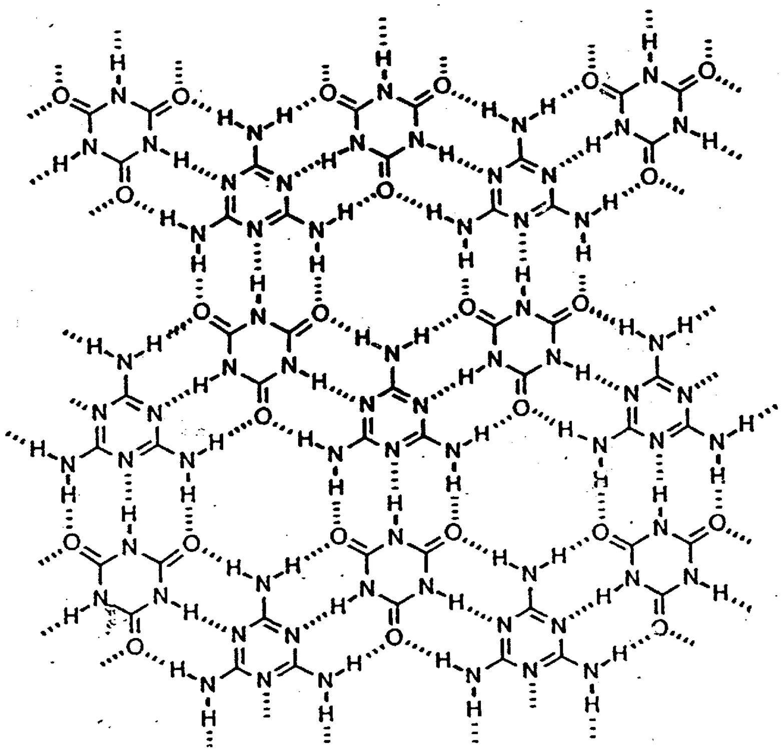


Figure 7. Hexagonal lattice of Melamine Cyanurate.

160 kJ/mole the heat of sublimation was measured by weight loss under vacuum with increasing temperature.

Electron affinity of Cyanuric acid E = 301.5 kJ/mole

$C_3N_3O_3Na_3 = 3Na^+ + C_3N_3O_3^{3-}$

$H - 624 = 234.5 - 389.5$

$C_3H_3NO_3 = C_3N_3O_3^{3-} + 3H^+$

$H - 691 + 301.5 = 389.5 + 0$

Ionization of Melamine I = 244.5 kJ/mole

$C_3H_6N_6{*}H_3PO_4 = C_3H_9N_6^{3+} + PO_4^{3-}$

$H - 1112.5 = 172.5 - 1285$

$C_3H_6N_6 + 3H^+ = C_3H_9N_6^{3+}$

$H - 72 + 244.5 = 172.5$

$E - I = 301.5 - 244.5 = 57$

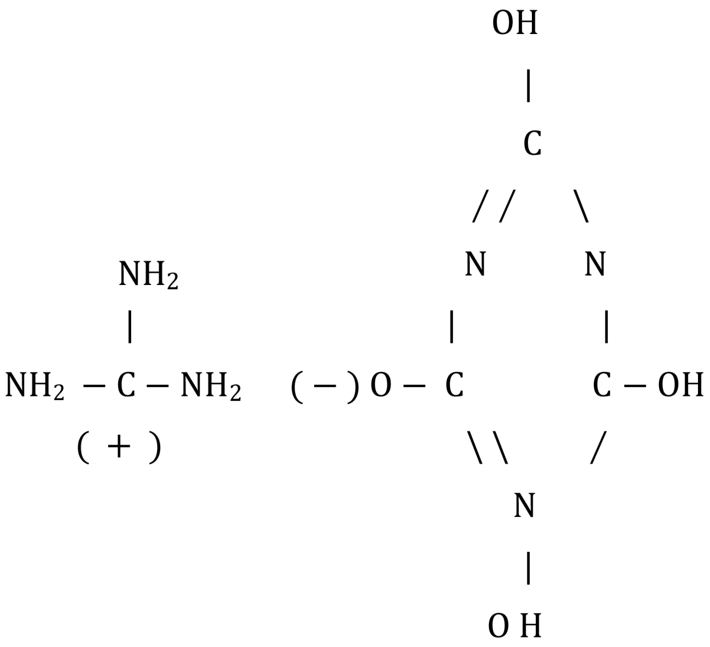
Born Haber Cylce of Melamine Cyanurate MC

Uo=145
MCsolid > M+g C-g
-721 - 655
/ \
Q=42 E-I =57
\ /
Ms Cs < Mg Cg
-72 – 691=-763 - 603
S=160

$$\mathrm{Uo}(145)=\mathrm{Q}(42)+\mathrm{S}(160)-(\mathrm{E}-\mathrm{I})(57)=145\ \mathrm{kJ/mole}$$

Melamine Barbiturate is a dipol dipol lattice. The 17 hydrogen bonds [25]-[28] enable selforganization to a stable dipol dipol lattice.

A ion ion salt is Guanidinium cyanurate.



Preparation

1 m Cyanuric acid was dispersed in distilled water, then 0.5 m GC was slowly added under stirring. CO_2 was developed. The 25% dispersion was heated for 1 h at 80˚C. Under vacuum water was evaporated. The residue was dried at 120˚C. Elementary analysis: C, H, N, O proved the conversion to GC.

Degradation of Guanidinium Cyanurate CAS N.A.

T = 360˚C, hex/cal = 0.63/0.63 kJ/g, Rex/cal = 39/31%

$C_4H_8N_6O_3 = CH_5N_3\text{gas} + C_3H_3N_3O_3$

MW 188 = 59 + 129

H − 760.5 + 118 = +48.5 − 691

T = 450˚C, hex/cal = −/1.81 kJ/g, Rex/cal = 0/0%

$C_3H_3N_3O_3 = 3HNCO$

MW 129 = 3*43

H 691 + 340 = 3*117

$C_4H_8N_6O_3 = 3HNCO + CH_5N_3\text{gas}$ hcal = 2.44 kJ/g

MW 188 = 129 + 59

H − 760.5 + 458 = −351 + 48.5

In **Figure 8** the lattice of Guanidinium Cyanurate is depicted. Cyanuric acid loses one Proton to Guanidine. The negative charge of the anionic Cyanuric acid is not fixed.

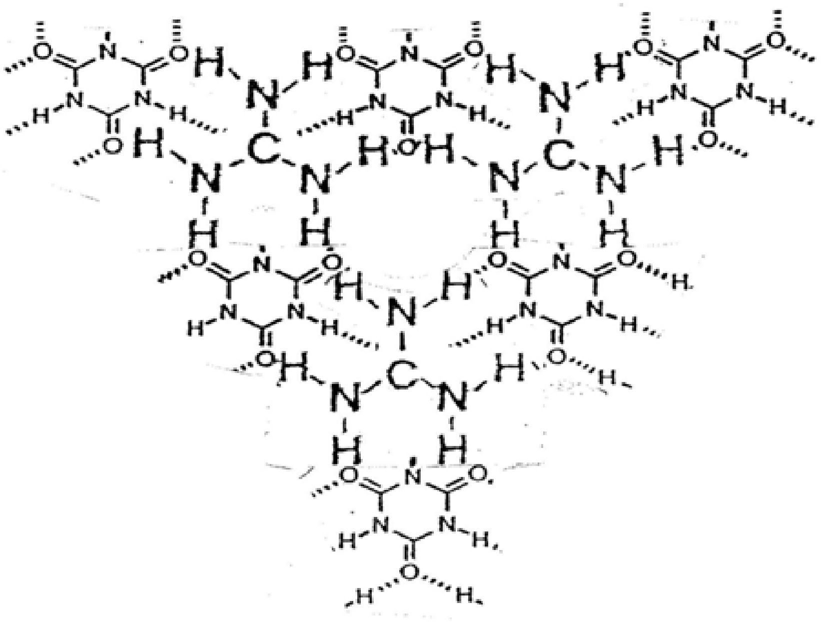


Figure 8. Crystal lattice of Guanidinium Cyanurate.

When the Born Haber cycle is applied a Lattice energy of 94.5 kJ/mole is calculated:

Heat of ionization I = 410 kJ/mole

$CH_5N_3{*}H_3PO_4 = CH_6N_3^+ + H_2PO_4^-$

$H - 1309 = 280 - 1303$

$CH_5N_3 + H^+ = CH_6N_3^+$

$H - 130 + 0 + 410 = 280$

Heat of electron affinity E = 462.5 kJ/mole

$C_3H_2N_3O_3Na = Na^+ + C_3H_2N_3O_3^-$

$H - 485 = -240 - 228.5$

$C_3H_3N_3O_3 = C_3H_2N_3O_3^- + H^+$

$H - 691 + 462.5 = -228.5 + 0$

$(E - I) = -4.5$ kJ/mole

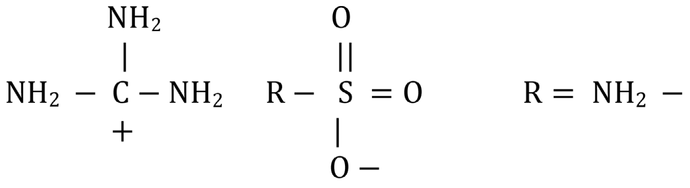
The heat of sublimation S amounts 94*59/188 = 29.5 kJ/mole.

The heat of reaction Q = 60.5 kJ/mole

$$\text{Uo} = \text{Q}(60.5) + \text{S}(29.5) - (\text{E} - \text{I})(-4.5) = 94.5\ \text{kJ/mole}$$

Guanidinium sulfamates, which carry linear alkanes as residue R, are described in the literature [29]-[34]. They self organize in rings.

Guanidinium sulfamate CAS 51528-20-2



$$NH_2 - \overset{\overset{NH_2}{|}}{\underset{+}{C}} - NH_2 \qquad R - \overset{\overset{O}{\|}}{\underset{\underset{O\,-}{|}}{S}} = O \qquad R = NH_2 -$$

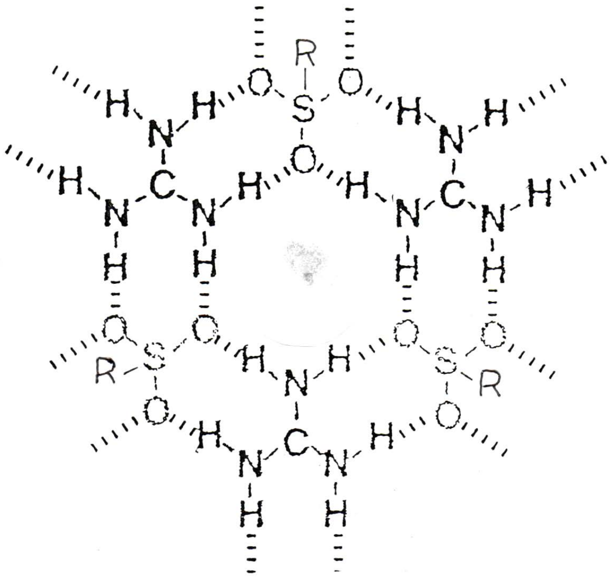


Figure 9. Self organization of Guanidinium sulfamate R = n-Alkane.

In Figure 9, Degradation of Guanidinium sulfamates

Tf = 127˚C, hf = 0.19 kJ/g T = 250˚C, hex/cal = 0.15/0.15 kJ/g, Rex/cal = 89%

$CH_8N_4SO_3 = CH_5N_3SO_3 + NH_3$

MW 156 = 139 + 17

H − 747 + 24 = −677 − 46

T = 330˚C, hex/cal = 0.25/025 kJ/g, Rex/cal = 62%

$CH_5N_3SO_3 = NH_4HSO_3 + NH_3 + CN$

MW 139 = 96 + 17 + 26

H − 677 + 40 = −712 − 46 − 242

T = 400˚C, hex/cal = 0.6/0.81, Rex/cal = 0%

$NH_4HSO_3 = H_2O + NH_3 + SO_2$

MW 96 = 18 + 17 + 64

H − 712 + 127 = −242 − 46 − 297

$CH_8N_4SO_3 = SO_2 + 2NH_3 + H_2O + 0.5C_2N_2 + 0.5N_2$ hcal = 1.7 kJ/g

MW 156 = 64 + 34 + 18 + 26 + 14

H − 747 + 270 = −297 − 92 − 242 + 154

5. Discussion

Amino phosphates, which degrade to phosphoric amides and phosphoric esters exert intumescence. They are collected in Table 5.

Melamine is an exception, it inhibits intumescence, but provides residue by the reactions:

$C_3H_6N_6 + NH_4PO_3 = 0.5H_2O + 3NH_3 + C_3N_4 + PO_{2.5}$ (78.5% Carbonitride + Phosphorus Pentoxide)

$C_3H_6N_6 + C_5H_9PO_5 = 2.5H_2O + 2C_2HN_3 + PO_{2.5} + 2C_2H_4$ (45% Melone + Phosphorus pentoxide)

Boric and Silicic esters degrade in the same way as phosphoric esters, but in contrast to phosphoric esters without intumescence. The reason for this is to be seen in the high affinity of P_2O_5 to water and the low affinity of B_2O_3 and SiO_2 to water.

Table 5. Phosphoric Esters and Amides, which exert intumescence.

Compound	EFmax	R %	Water solubility
PER Phosphate	26	55	low
DPER Diphosphate	37	58	low
BCPP	45	25	low
2-Aminoethylphosphate	55	53	high
2-Aminoethylether phos.	80	62	medium
Morpholine phosphate	61	61	medium
Piperazin phosphate	0	50	low
DEDAP	51	49	medium
Inosite 6 phosphate	0	75	high
ATP	69	50	high

ATP comprises 3 components, namely Phosphoric acid, Adenosine and Ribose and is comparable with compounds consisting of 3 similar components: Phosphoric, Boric and Silicic acid, Melamine or Guanidine and Carbohydrates. According to **Table 6** only the Guanidinium carbohydrate phosphoric compounds show intumescence.

Remarkable is the degradation of Guanidinium- and Melamine Bis Neopentylglycol boric ester, which degrade without residue so indicating the gases BNH_4 or BNH as degradation product.

Table 6. Melamine and Guanidinium carbohydrate phosphoric, boric and silicic esters.

Melamineium and Guanidinium esters	EFmax	R%
Guanidinium PER boric ester	0	43
Guanidinium PER phosphoric ester	41	45
Melamine PER boric ester	0	43
Melamine PER phosphoric ester	0	46
Guanidinium NPG boric ester	0	0
Guandinium NPG phosphoric ester	46	44
Melamine NPG boric ester	0	0
Melamine NPG phosphoric ester	0	47
Guanidinium bis NPG boric ester	0	0
Guanidium bis NPG phosphoric ester	36	49
Melamine bis NPG boric ester	0	0
Melamine bis NPG phosphoric ester	0	54

The reaction of intumescence is described by the formula:

$$C_nH_mHPO_3 = m/4CH_4 + (n - m/4)C + 0.5P_2O_5 + 0.5H_2O \tag{4}$$

The maximum amount of expansion is given by the dimensionless parameter EFmax.

$$\text{EFmax} = (22400 * n/\text{MW}) * \text{rho} \tag{1}$$

For mixtures and compounds, which comprise Melamine M, Ammonium polyphosphate APP, Pentaerythritol PER or Dipentaerythritol DPER, the maximum expansion is calculated according to

$$\text{EFmax} = 0.25 * \left[(\text{nAPP} - \text{nM})/\text{nPER}\right] * \text{MWAPP} \tag{2}$$

$$\text{EFmax} = 0.20 * \left[(\text{nAPP} - \text{nM})/\text{nDPER}\right] * \text{MWAPP} \tag{3}$$

For BCPP Equation (5) is valid

$$\text{EFmax} = 0.25 * (\text{nP}/\text{nBCPP}) * \text{MWBCPP} \tag{5}$$

As heat resistant residues graphite C, Carbonitride C_3N_4, Melone C_2HN_3, Silicic dioxide SiO_2, Boric oxide $BO_{1.5}$ and phosphorus pentoxide P_2O_5 are observed. Carbonitride and melone are also degradation products of melamine under pressure. At atmospheric pressure Melamine sublimes but its bondage in salts prevents melamine from sublimation.

The role of Phosphoric acid is unique in intumescence. Neither boric nor Silicic acid has the capability of intumescence. Self organization depends on hydrogen bridges between Nitrogen and Oxygen and occurs in ion-ion salts as well as in dipole-dipol salts.

In the synthesis of dipole-dipol salts CA consisting of cationic C and an anionic A parts attention has to be paid to the degree of conversion. The elementary analysis does distinguish between compound and mixture. The heats of decomposition for the mixture hCAadd, for the pure salt hCA and for the sample hca provide the information for the conversion of the sample in Equation (7):

$$\text{Conversion\%} = 100 * (\text{hca} - \text{ hCA add})/(\text{hCA} - \text{hCA add}) \tag{7}$$

In the case that heats of decomposition of the salt components are detectable, conversion is calculated in Equation (6):

$$\text{Converson\%} = 100 * \left[1 - \text{hc}/(\text{xc} * \text{hC})\right] = 100 * \left[1 - \text{ha}/(\text{xa} * \text{hA})\right] \tag{6}$$

hc and ha are the measured heats of decomposition of the components, hC and hA those of the pure components. xc and xa are the mole ratios of the components in the salt.

In Table 7 Melamine and Guanidine salts, which show self organization, are summarized. The ion-ion salt NH_4Cl has a 7 time higher lattice energy than the investigated salts.

Self organization is not only dependent on the possibility of hydrogen bridging but also on the transfer of protons. In comparison the Guanidine ion-ion salts have higher lattice energies than the Melamine dipole-dipol salts with the exception of Melamine Cyanurate due to the transfer of 3 protons.

Table 7. Self organization of ion-ion and dipole-dipol salts and their lattice energies Uo.

Compound	Transfer of protons	Salt	Uo kJ/mole
Melamine Polyphosphate	1	dipole-dipol	36.5
Melamine Borate	1	dipol-dipol	387.5
Melamine Cyanurate	3	dipol-dipol	145
Guanidine Polyphosphate	1	ion-ion	159
Guanidinium Borate	1	ion-ion	503
Guanidinium Cyanurate	1	ion-ion	94.5

7. Conclusion

Phosphor is a life element and Phosphoric acid plays a unique role in life science and in intumescence. The chief requirement for intumescence is the degradation to $CnHmHPO_3$. Boric and Silicic acids are present as meta acids and react with carbohydrates to esters and with amines to amides or salts, but in contrast to Phosphoric acid they exert no intumescence. The reason for this is to be seen in the high affinity of phosphoric oxide to water and the low affinity of silicic and boric oxide to water. In comparison with radical scavengers intumescence has the advantage of heat protection by char formation. Intumescent samples produce carbonaceous char under expansion. The insulating effect is supported by other heat resistant residues such the oxides P_2O_5, B_2O_3, SiO_2, Carbonitride C_3N_4 and Melone C_2HN_3. Expandable coatings [35], which comprise a blowing agent and a binder, are strictly speaking no intumescent system, because they suffer under the lack of simultaneous char building and expanding. 1,3,5 Triaminotriazine is a blowing agent but no intumescent FR. Beneath intumescence other properties are important as for instance the water solubility in respect to outdoor applications and acidity in respect to corrosion. Self organization is observed in DNA and in Melamine Polyphosphate, Cyanurate, Barbiturate as well as Guanidine Sulfamate. At the first glance self organization does not influence the FR efficiency, but in more detail as for instance in the cases of the complex formation of Melamine Cyanurate with Polyamide [36] and of Melamine Polyphosphate in glass reinforced polyamide it is the key for understanding. Beside intumescence the characteristic functions of phosphorus in its compounds are self organization and interaction with the substrate by hydrogen binding and its capability to evolve PO_2 radicals, which interfere with the radical chain of combustion.

Conflicts of Interest

The author declares no conflicts of interest.

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