



Gaskets with Expandable Graphite Treated with Nitric, Sulphuric, Phosphoric Acids and Ferric Chloride

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Abstract

The task was to find out the most appropriate expandable graphite intercalation compound GIC for intumescent seals. The application in fire seals required GICs, which exerted high expansion at low burning rates. Therefore graphite was treated with nitric, sulphuric, phosphoric acids and ferric chloride. Phosphoric acid with its flame retardant properties was the favourite, but graphite treated with it, did not exfoliate, therefore expandable graphite was post treated with phosphoric acid. Elemental analysis and thermogravimetric measurements led to chemical formulas of GICs. Their heats of exfoliation were determined by differential scanning calorimetry, by the work done given by the product of increased specific volume and atmospheric pressure, by the Arrhenius plot of exfoliated specific volume dependent on temperature and were calculated in a complete balance of weights and heats of formation. It turned out that the sum of heats of intercalation and exfoliation corresponded with the heats of decomposition and gasification of the intercalated compounds. When the heat of intercalation was added to the lattice energy of graphite, the lattice energy of GIC was obtained. Electron microscopy indicated that expansion did not happen in monolayers but in nanoplatelets consisting of about 40 atomic layers. The expandable GICs were incorporated into polyvinyl acetate strips and applied as fire gaskets in gaps. In a fire test, the gap protected by the strip comprising the GIC treated with sulphuric and phosphoric acid showed the best performance, which corresponded with the highest observed expansion and with the second highest temperature of maximum speed of combustion.

Keywords

Nanomaterials, Thermal Properties, Industrial Application, Exfoliated Graphite

Subject Areas: High Polymer Chemistry, Nanometer Materials, Physical Chemistry, Thermochemistry

1. Introduction

Intercalated graphite compounds GICs were intensively discussed in literature [1]-[3]. Less information was available concerning expandable intercalated graphite compounds [4] [5]. In order to receive detailed data about maximum expanded specific volumes, temperatures of maximum rate of combustion, heats of formation, heats of intercalation and exfoliation as well as lattice energies between the layers of graphite, expandable GICs were prepared by incorporating nitric, sulphuric, phosphoric acids as well as ferric chloride [6].

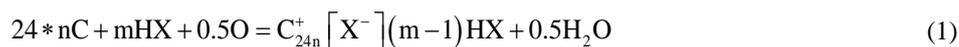
In 1840, Schafhäütl [7] discovered expandable graphite intercalation compounds.

Until now only one type of expandable GIC was available commercially, such one treated by sulphuric acid (H₂SO₄).

In literature also other types of expandable GICs were described such as graphite treated with nitric acid (HNO₃), bromine (Br₂), ferric chloride (FeCl₃), chromo oxide (CrO₃) potassium tetrahydrofuran (K(THF)₂) and potassium permanganate (KMnO₄) [8]-[12].

Also the influence of synergistic additives was investigated: alcohols, aldehydes, sugars, hydrogen peroxide (H₂O₂) [13] and phosphoric acid (H₃PO₄) [10].

These efforts can be understood under the background of growing applications as foils, seals, electrically conductive or shielding material and flame retardant. Graphenes and related materials received much attention, when their thicknesses approached atomic levels. Microelectronics was focused on monolayer graphenes. Fuel cells, batteries, solar cells, sensors and polymer composition extended their interest to nanoplatelets consisting of up to 10 atomic layers which deviate from bulk graphite. Pure single layer graphene was manufactured by self assembling approach [14] and from GIC by microexplosion method [15]. According to the nomenclature and terminology [16]-[20] graphite intercalation compounds were described as donor acceptor complexes or as graphite salts:



In Equation (1), C stands for graphite, HX for acid, n for the stage index and m for the stoichiometric factor.

The thickness of the constitutional repeating unit I_c, which was the distance between two successive intercalated layers, were calculated according to Equation (2).

I_c was given by the thickness of the intercalated layer d_s plus the product of the stage index n minus 1 multiplied by the original distance between two adjacent graphenes c_o = 3.35 Angstrom.

$$I_c (\text{Angstrom}) = d_s + (n-1) * c_o \quad (2)$$

Stage index 2	Stage index 3	
000000000000	000000000000	graphene
_____	_____	intercalated compound
_____	_____	
000000000000	000000000000	

Chung [5] described intercalation and exfoliation of bromine GIC C₈Br CAS [12079-58-2] and wondered, that the heat of exfoliation amounted to 71 kJ/mole, which did not correspond with 31 kJ/mole the heat of vaporization of liquid bromine. This discrepancy was eliminated, when the heat of vaporization 31 kJ/mole was not put in relation with 71 kJ/mole, the heat of exfoliation, but with the added heats of intercalation and exfoliation: -40 + 71 = 31. Anderson [21] cited several heats of intercalation for bromine and graphite -41.9 kJ/mole second stage heat of intercalation, -45.2 kJ/mole third stage and -46.1 kJ/mole fourth stage. In the following the mass balances of the molecular weights MW (g/mole) and the heat balances of the heats of formation H (kJ/mole) were set up for each formula F, which led to heats of intercalation H_{inter} of -40 kJ/mole or h_{inter} of 0.21 kJ/gC:

Intercalation: h_{inter} = -40/192 = -0.21 kJ/gC; -40/352 = -0.11 kJ/gGIC

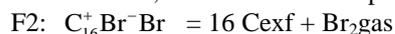
F1: 2*8 C + Br₂ = C₁₆⁺Br⁻Br

MW (g/mole): 192 + 160 = 352

H (kJ/mole): 0 - 40 = -40

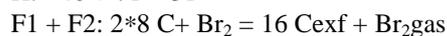
Exfoliation: h_{exf} = 71/192 = 0.37 kJ/gC; 71/352 = 0.20 kJ/gGIC, maximum expansion (l-lo)/lo = 32.5 lo

initial thickness, l thickness after expansion [5]



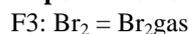
$$MW: 352 = 192 + 160$$

$$H: -40 + 71 = 31$$



$$H: 0 + -40 + -40 + 71 = -40 + 31$$

Vaporization of bromine at 59°C:



$$H: 0 + 31 = 31$$

From the above formula it became obvious that the heat of intercalation H_{inter} plus the heat of exfoliation H_{exf} was equal to the heat of vaporization H_{vap} :

$$H_{inter} + H_{exf} = H_{vap} \quad (3)$$

$$-40 + 71 = 31 \text{ kJ/mole}$$

For a second stage intercalation of bromine graphite the identity distance l_c was 10.4 Angstrom.

$$l_c = 7.05 + (2 - 1) \cdot 3.35 = 10.4 \text{ Angstrom} \quad (4)$$

The lattice energy was defined as the energy accompanying the process of bringing layers, when separated from each other by an infinite distance, to the distance they occupy in a stable lattice. By definition the lattice energy of GIC LGIC should be equal to the sum of the lattice energy of graphite LC plus the heat of intercalation h_{inter} related to 1gC:

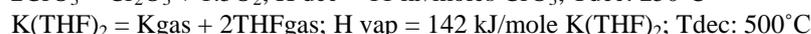
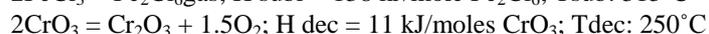
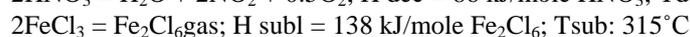
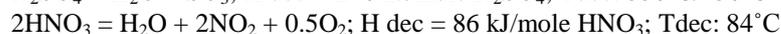
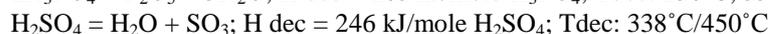
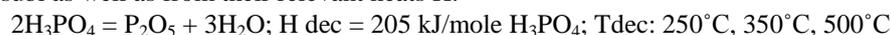
$$LGIC(\text{kJ/gC}) = LC + h_{inter} \quad (5)$$

Dappe [23] published a graphite lattice energy LC of -65 meV , which correlated with -520 J/g or -0.52 kJ/g at a layer distance of $l_c = 3.1 - 3.2 \text{ Angstrom}$. ($1 \text{ meV} = 1.6 \times 10^{-22} \text{ J}$) \times ($N_A = 6.023 \times 10^{23} \text{ mole}^{-1}$) = 96.4 J/mole divided by 12 g/mole the molecular weight of graphite gave the conversion factor 7.88. Novoselov [24] measured -0.07 eV complying with -0.56 kJ/g at an equilibrium distance of 3.35 Angstrom . In Gmelins Handbook [25] -334 erg/cm^2 were stated, which were converted to -0.445 kJ/g by extending the volume of $1 \text{ cm}^2 \times 3.35 \text{ Angstrom}$ to 1 cm^3 by the factor 3×10^7 divided by the density of graphite 2.25 g/cm^3 .

Henning [22] determined -1.3 eV lattice energy for the bromine graphite with the molecular weight of 352 g/mole GIC and 192 g/mole C . ($1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$) \times ($N_A = 6.023 \times 10^{23} \text{ mole}^{-1}$) = 96.4 kJ/mole , therefore the bromine GIC had a lattice energy of $-1.3 \times 96.4/352 = -0.356 \text{ kJ/g GIC}$ or -0.653 kJ/gC at a layer distance of 10.4 Angstrom . When the heat of intercalation $h_{inter} = -0.21 \text{ kJ/gC}$ was subtracted from the lattice energy of the GIC $C_{16}Br_2 -0.653 \text{ kJ/gC}$ according to Equation (5), then a graphite lattice energy of -0.443 kJ/gC was obtained in Equation (6). Comparing the data in literature Gmelins Handbook [25] with -0.445 kJ/g made the best fit, nevertheless the recent published lattice energy of -0.56 kJ/g [24] was taken for further calculations.

$$LC = -0.633 + 0.21 = 0.443 \text{ kJ/gC} \quad (6)$$

$C_{16}Br_2$ was not considered for the application of fire gaskets, because of the low MAK value of 0.7 mg/m^3 of bromine. The wanted GICs should have low temperatures of expansion, a high volume increase by expansion and a low burning rate. Indications for the suitability of GICs were expected from the properties of the intercalated compounds, such as their temperatures of decomposition T_{dec} , of vaporization T_{vap} and of sublimation T_{subl} as well as from their relevant heats H :



Cancer causing chromo oxide (CrO_3) was considered as harmful and was rejected. Nitrogen dioxide NO_2 with a MAK value of 9 mg/m^3 and sulphur trioxide (SO_3) with such one of 1 mg/cm^3 were pardoned. In comparison tetrahydrofuran (THF) showed a high MAK value of 50 ppm , but was highly burnable and therefore unfit.

The research purpose was to find out the most appropriate expandable GIC for the application in intumescent

fire seals. Starting from this state of knowledge GICs were prepared from nitric, sulphuric, phosphoric acids and ferric chloride. They were characterized, applied in intumescent strips and screened in a simplified fire door test. The fire performance was correlated with the properties of GICs such as maximum expansion and temperature of maximum burning rate.

2. Experimental

For the preparation of the expandable GICs as well as for intumescent strips the chemicals of **Table 1** were used.

2.1. Preparation of GICs

2.1.1. No. 1 Nitric Acid GIC

100 g nitric acid was added to 100 g of graphite in 15 minutes at such a velocity that the temperature did not surpass 45°C. Intercalation took place under heat development. In a calorimeter -0.11 kJ/gC (kJ related to 1g graphite) heat development was measured. A pressure of 2 bar nitrogen was put upon the mixture which was stirred for further 30 minutes. The graphite was separated and dried in a nitrogen stream. Elemental analysis confirmed a nitrogen content of 2.1%.

Then 70 ml of water were added under stirring so that the temperature did not exceed 45°C.

The water was sucked off. This operation was repeated, until the water was weakly acidic. The graphite was dried by flowing nitrogen for 5 minutes.

60 ml of 4% ammonia water were added for further neutralization. The mixture was stirred for 5 minutes, afterwards the ammonia water was sucked off and the graphite was dried under streaming nitrogen for 45 minutes at RT and for 4 h at 60°C.

The graphite so prepared showed a nitrogen content of 2.0% and a weight loss during exfoliation of 10%. These data led to the formula $C_{48}^+NO_3^- \cdot H_2O$.

2.1.2. No. 2 Phosphoric and Nitric Acids GIC

Searching in literature for phosphoric acid intercalated compounds graphite phosphate with the common formula $C_xH_3PO_4$ CAS [79081-31-6] was detected. A stage 2 GIC with the identity distance 2×11.38 Angstrom and the formula $C_{48}^{++}H_2P_2O_7^{--}$ was described, when graphite was treated by 100% phosphoric acid in the presence of chromo oxide at 80°C - 100°C [10]. When graphite was stored in 100% phosphoric acid at RT as well as at 90°C for 5 hours the treated graphite exerted no expansion. Chromo oxide was not added, because of its danger of cancer. Therefore the expandable product $C_{48}^+NO_3^- \cdot H_2O$ was applied for further treatment.

100 g of $C_{48}^+NO_3^- \cdot H_2O$ were dispersed in 100 g 80 w% phosphoric acid.

After 5 h at 65°C H_3PO_4 was sucked off and the residue was blown dry by a stream of nitrogen. Then twice 100 ml water was added under stirring and filtered off. After filtration the graphite was dried under flowing nitrogen for 45 minutes at RT and dried for 4 h at 80°C.

The graphite treated by phosphoric acid comprised 1.9% N and 4.2% P, which corresponded with the formula $C_{48}^+NO_3^- \cdot H_3PO_4$.

Table 1. Chemicals used.

Madagascar graphite particle size smaller 3 mm, 80% > 315 µm, density 2.25 g/ml, bulk density 0.60 g/ml Ludolph Struve & Co GmbH.
nitric acid [7967-37-2] density 1.53 g/cm ³ , 98% Chemapol
ammonia water [1336-21-6] 4%
phosphoric acid [7664-38-2] 80%, Fluka
sulphuric acid [7664-93-9]density 1.84 g/cm ³ , 96%, Fluka
nitro methane [75-52-5], Fluka
Iron (III)chloride [7705-08-0], Fluka
Evatane 24 03 (Arkema) 24% Vac, MFI = 3 g/10min, Melting point = 79°C, density = 0.95 g/cm ³

2.1.3. No. 3 Sulphuric Acid GIC

To 100 g graphite 10 ml 30 w% H₂O₂ and afterwards 150 ml 96 w% sulphuric acid with a density of 1.84 g/cm³ were added under stirring. When the dosage was complete, the mixture was stirred further for 15 minutes at RT. The procedure of washing and drying was repeated twice until the pH-value of the waste water amounted to more than 4. Then the product was dried for 45 minutes at RT and for 4 hours at 60°C.

The so prepared graphite had a sulphur content of 2.9% and a weight loss of 18% during exfoliation. These data were in agreement with a formula of C₇₂H₂SO₄⁺ · 5H₂O.

2.1.4. No. 4 Phosphoric and Sulphuric Acids GIC

100 g C₇₂H₂SO₄⁺ · 5H₂O were dispersed in 100 g 80% phosphoric acid and stirred 5 h at 65°C.

After filtration the residue was dried under streaming nitrogen. After washing and drying for two times, as already described, the product accomplished an elementary analysis of 2.8% P and 2.9% S, which corresponded with the formula C₇₂H₂SO₄⁺ · 2H₂O · H₃PO₄.

2.1.5. No. 5 Ferric Chloride GIC

100 g graphite was mixed with 300 ml nitro methane and 250 g FeCl₃.

The mixture was stirred at RT for 18 hours, then washed two times with 150 ml nitro methane and blown dry under nitrogen. The ultimate drying was performed at 60°C for 4 hours.

The graphite obtained was specified by an iron content of 13.5% and a weight loss of 39% after exfoliation. The expected formula was C₂₁FeCl₃.

2.2. Characterization by TMA, TGA, DSC and Muffle Furnace Test

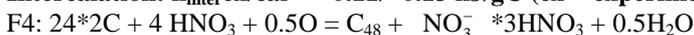
A Mettler Toledo TMA/SDTA 840 was used for thermogravimetric analysis TGA, for thermomechanic analysis TMA and for differential scanning calorimetry DSC. In the case of TGA and DSC the samples were placed in aluminium oxide crucibles of 900 µl (ME 51119, 960) with 12 mm diameter covered by punctured lids. TGA were performed in air at 20 K/min heating rate and DSC in nitrogen at 20 K/min. The TMA investigations were exerted in aluminium crucibles with 7 mm diameter and 4.6 mm height covered by 6 mm lids in air at a heating rate of 20 K/min and a load of 1 N which is equal to a pressure of 0.36 bar.

In the muffle furnace test a 1 g sample was placed in a calibrated quartz tube and put into a muffle furnace of defined temperature for 5 minutes. The specific volume (ml/g) was determined immediately after the withdrawal from the furnace.

2.2.1. No. 1 C₄₈⁺NO₃⁻ · H₂O

In order to achieve agreement with elemental analysis and heat development during intercalation the formula F4 had to be assumed, followed by the reaction of washing in formula F5.

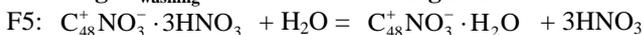
Intercalation: h_{inter} ex/cal = -0.11/-0.13 kJ/gC (ex = experimental/cal = calculated)



$$MW(g/mole) 576 + 4 \cdot 63 + 8 = 827 + 9$$

$$H(kJ/mole) 4 \cdot 174 - 74 = -648.5 - 121.5$$

Washing: h_{washing} ex/cal = -/+0.23 kJ/gGIC



$$MW: 827 + 18 = 656 + 3 \cdot 63$$

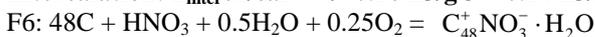
$$H: -648.5 - 287 + 189.5 = -224 - 3 \cdot 174$$

The reaction with nitric acid led to a stage 2 GIC with stoichiometric factor 4 under heat development of -0.11 kJ/gC with a calculated constitutional repeating unit I_c of 11.4 Angstrom.

$$I_c = 7.79 + 1 \cdot 3.35 = 11.14 \text{ Angstrom} \quad (7)$$

The theoretical intercalation was described by F6.

Intercalation: h_{inter} ex/cal = -/+0.16 kJ/gC = 0.14 kJ/gGIC



$$MW: 576 + 63 + 9 + 8 = 656$$

$$H: -174 + -143 + 93 = -224$$

Exfoliation: h_{exf} ex/cal = 0.02/0.02 kJ/gGIC; 0.026 kJ/gC; Rex/cal = 90%/88%

F7: $C_{48}^+ NO_3^- \cdot H_2O = 48C_{ex} + NO_2 + H_2O_{gas} + 0.5O_2$
 MW: $656 = 576 + 46 + 18 + 16$
 H: $-224 + 15 = 0 + 34 - 243$
 F6 + F7: $48C + HNO_3 + 0.5H_2O + 0.5O = 48C_{ex} + NO_2 + H_2O_{gas} + 0.5 O_2$
 MW: $576 + 63 + 9 + 8 = 576 + 46 + 18 + 16$
 H: $-174 + -143 + 93 + 15 = 34 - 243$

Decomposition and vaporization at 84°C:

F8: $HNO_3 = NO_2 + 0.5H_2O + 0.5O$
 MW: $63 = 46 + 9 + 8$
 H $173.5 + 86 = 34 + -121.5$
 F9: $0.5 \cdot (H_2O = H_2O_{gas})$
 H: $0.5 \cdot (-286 + 43 = -243)$
 F8 + F9 $HNO_3 + 0.5H_2O = NO_2 + H_2O + 0.5O$
 MW: $63 + 9 = 46 + 18 + 8$
 H: $-173.5 - 143 + 107.5 = 34 - 243$

The sum of the heats of intercalation and of exfoliation corresponded to the sum of the heats of decomposition and vaporization:

$$H_{inter} + H_{exf} = H_{dec}(HNO_3) + H_{vap}(H_2O) \quad (8)$$

$$93 + 15 \cdot 86 + 21.5$$

$$H_{inter} + H_{exf} = 93 + 15 = 108 \text{ kJ/mole}$$

$$H_{dec}(HNO_3) + H_{vap}(H_2O) = 86 + 21.5 = 107.5 \text{ kJ/mole}$$

In **Figure 2** a sample of the GIC was subjected to thermal mechanical analysis.

Expansion started at 150°C and reached a maximum of 2250% at 250°C. Above 600°C combustion was observed and reached its maximum rate at 900°C (**Figure 1**).

A 1 g sample was placed in a calibrated quartz tube and heated for 5 minutes at defined temperatures in a muffle furnace.

In **Figure 2** the specific volume V (ml/g) increased proportionally with the temperature T (°C) according to Equation (9).

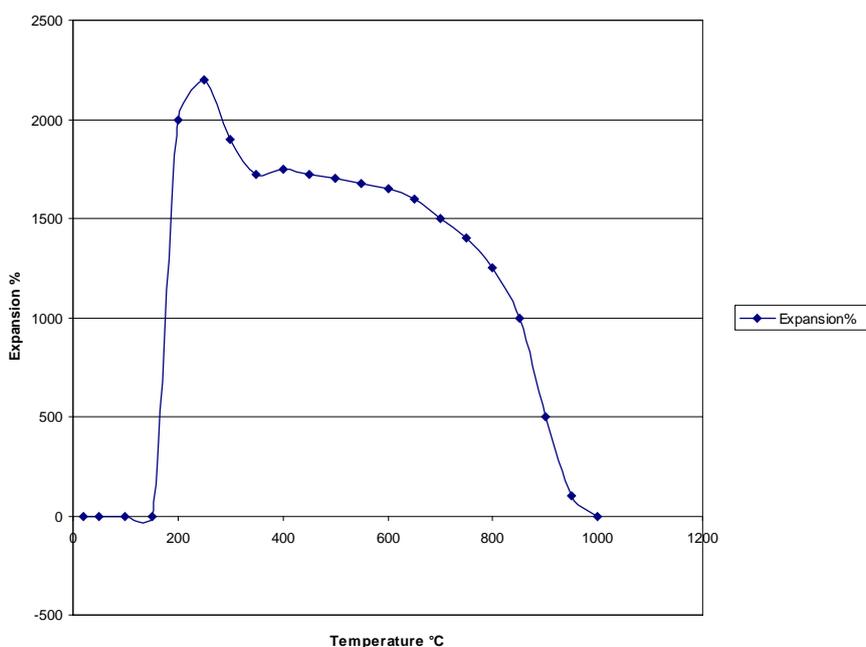


Figure 1. TMA: expansion% versus temperature of No. 1 $C_{48}^+ NO_3^- \cdot H_2O$, 20 K/min, air.

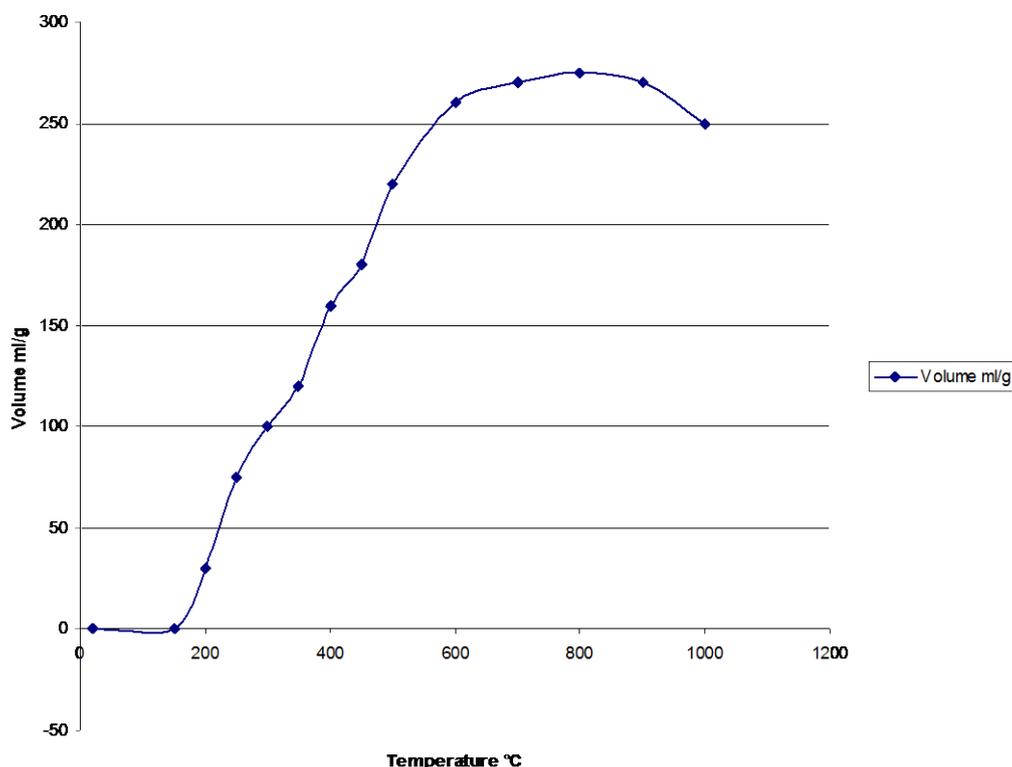


Figure 2. Furnace test: Specific volume V (ml/g) versus temperature T of No. 1 $C_{48}NO_3 \cdot H_2O$ in air.

$$V = -80 + 0.60T \quad (9)$$

In Figure 2 the sample extended to a specific volume of 40 ml/g at 200°C and such one of 275 ml/g at 800°C. At low temperatures up to 300°C the thermal history of the samples subdued to TMA with a heating rate of 20 K/min and furnace test with a heating time of 5 min were similar and the results were somehow comparable, for instance in TMA an extension of 2000% measured at 200°C. As the initial specific volume was 1.66 cm³/g at 200°C, a volume of $1.66 \cdot 2000\% / 100 = 33.2$ ml/g resulted.

The specific volume at 800°C was put into the ideal gas equation and the moles of gases evolved during exfoliation were calculated.

$$n = V * MW / [22,400 * (1 + T/273)] = 275 * 656 / [22,400 * (1 + 800/273)] = 1.86 \text{ moles} \quad (10)$$

According to Equation (10) 1.86 moles of gases were evolved.

When the GIC expanded fully, the only counter force was the atmospheric pressure of 1 bar. The work done to expand the bulk volume from 1.66 to 275 cm³/g was w_{exf} , which was given by the product of the maximum specific volume in Figure 2 and the pressure of 1 bar.

$$w_{\text{exf}} = 1 \text{ bar} * (275 - 1.66) \text{ cm}^3/\text{g} = 0.027 \text{ kJ/gGIC} \quad (11)$$

When the data of Figure 2 were treated according Clausius Clapeyron or Arrhenius in Table 2, 13.8 kJ/mole heat of exfoliation H_{exf} or h_{eff} 0.021 kJ/gGIC was determined.

In a plot $\lg V$ versus $10^3/T$ the inclination $d \lg V / d(10^3/T)$ was -0.72 and H_{exf} was calculated by Equation (12):

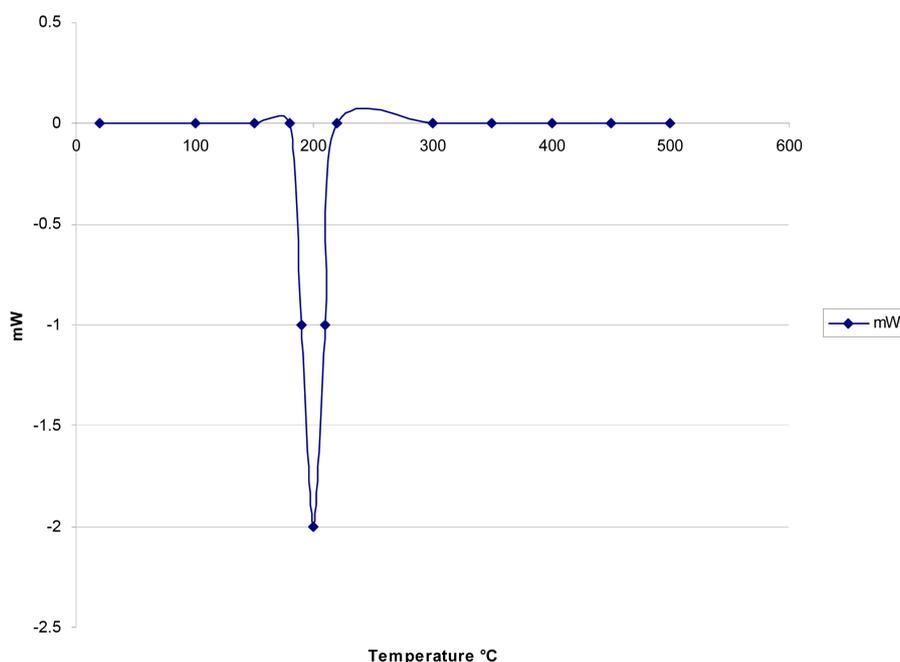
$$H_{\text{exf}} = -19.14 * \text{inclination} = 13.8 \text{ kJ/mole or } 0.021 \text{ kJ/gGIC} \quad (12)$$

In differential scanning calorimetry DSC exfoliation occurred under heat uptake of 0.020 kJ/g GIC or 13.1 kJ/mole at 200°C in Figure 3. During exfoliation a weight loss of 10% was measured by TGA investigation in Figure 4.

Equation (13) allowed the calculation of the lattice energy LGIC.

Table 2. Clausius Clapeyron or Arrhenius: heat of exfoliation.

T(°)	1000/T (K ⁻¹)	V (ml/g)	lgV (ml/g)	dlgV	D (1000/T)	Hexf (kJ/mole)
250	1.91	75	1.875	0	0	
300	1.745	100	2	0.125	-0.165	14.5
350	1.61	123	2.09	0.219	-0.3	14
400	1.485	160	2.2	0.325	-0.425	14.6
450	1.38	180	2.255	0.38	-0.53	13.7
500	1.295	220	2.34	0.465	-0.615	14.5
600	1.145	260	2.415	0.54	-0.795	13
700	1.03	270	2.43	0.55	-0.88	12.1

**Figure 3.** DSC: Heat mW versus temperature of No. 1 $C_{48}H_{12}N_{12}O_{12} \cdot H_2O$, 20 K/min, N_2 , $h_{\text{exf}} = 0.02$ kJ/gGIC.

$$LGIC = LC + h_{\text{inter}} = -0.56 - 0.11(F4) = -0.67 \text{ kJ/g} \quad (13)$$

During exfoliation 2.5 moles of gases, namely NO_2 , H_2O and $0.5O_2$, were evolved according F6 under 15 kJ/mole heat consumption. When the maximum expanded specific volume was introduced into the ideal gas law only 1.86 moles of gases were determined. DSC measurements delivered 13.1 kJ/mole or 0.020 kJ/g heat of exfoliation and the Clausius Clapeyron plot of **Figure 2** led to 13.8 kJ/mole or 0.019 kJ/gGIC heat of exfoliation.

The work of maximum exfoliation w_{exf} with 0.027 kJ/gGIC was higher than those derived from DSC with 0.020 kJ/gGIC and from the specific volume in dependence of temperature with 0.019 kJ/gGIC.

2.2.2. No. 2 $C_{48}H_{12}N_{12}O_{12} \cdot H_3PO_4$

The expandable nitric acid GIC was post treated with phosphoric acid and characterized by elemental analysis. In **Figure 5** the maximum expansion was reduced to 1150% and the temperature of maximum heat of combustion was shifted from 900°C to 1100°C.

Phosphoric acid did not contribute to expansion but acted as a flame retardant.

13.3% phosphoric acid shifted the temperature of maximum combustion $T_{\text{max comb}}$ to higher temperatures, namely from 900°C to 1030°C. With increasing content of phosphoric acid the temperature of combustion was

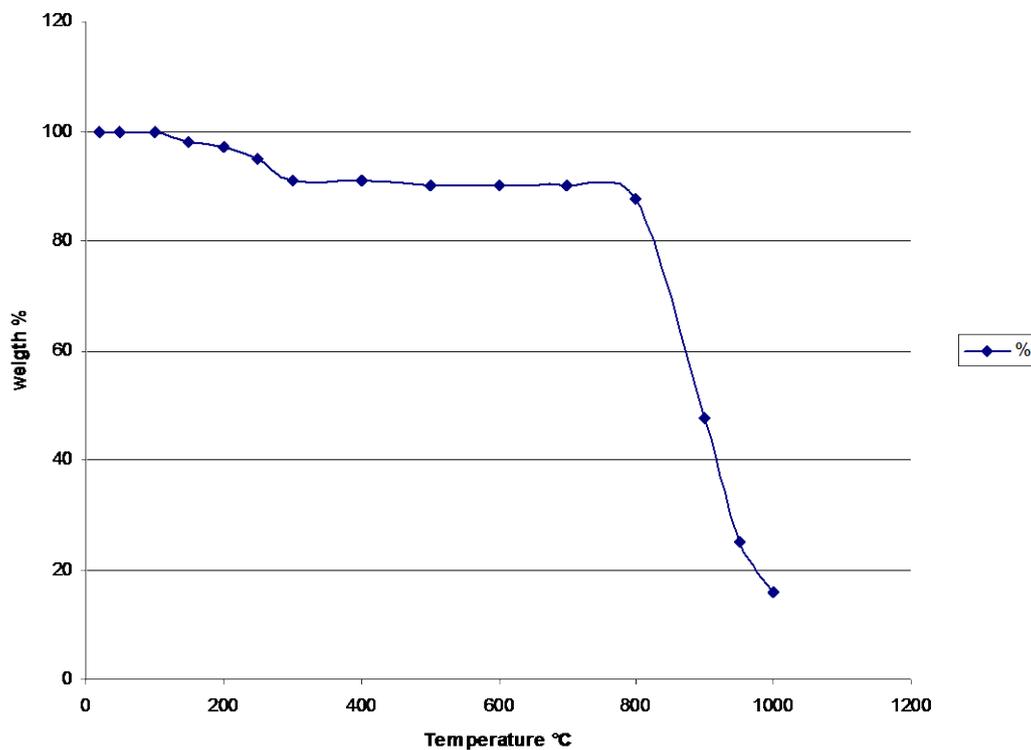


Figure 4. TGA: weight residue % versus temperature of No. 1 $C_{48}^{+}NO_3^{-} \cdot H_2O$, 20 K/min, air.

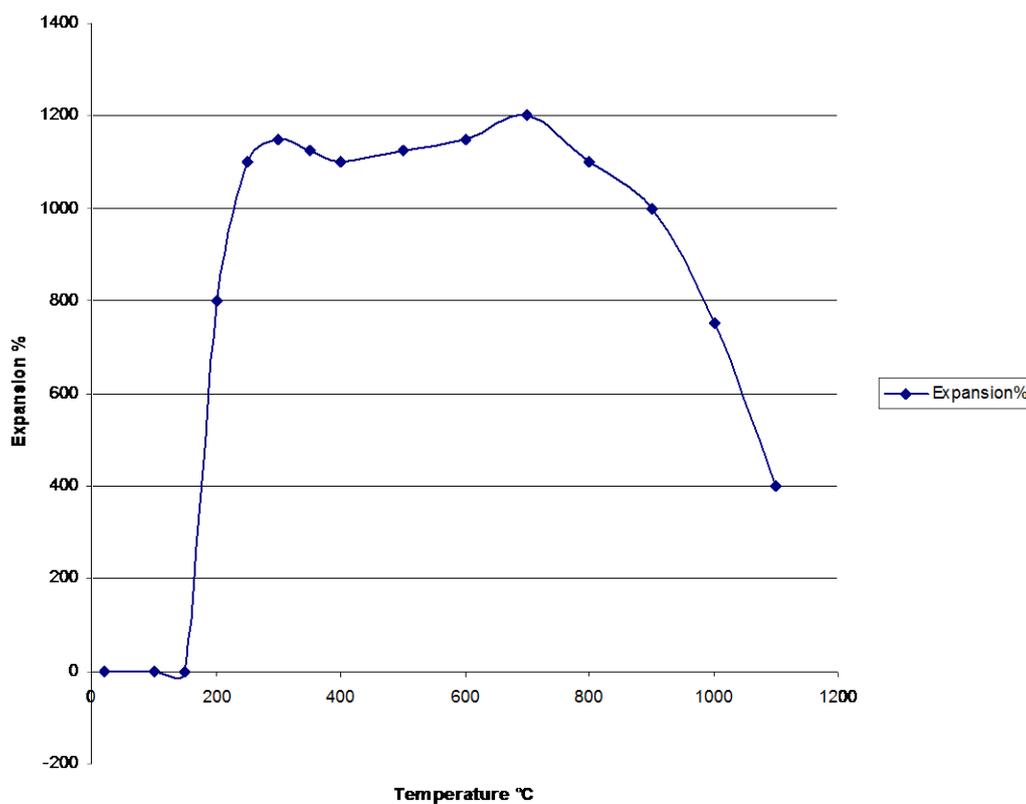


Figure 5. TMA: expansion% EF versus temperature T of No. 2 $C_{48}^{+}NO_3^{-} \cdot H_3PO_4$, 20 K/min, air.

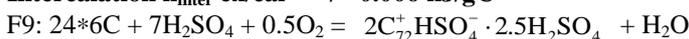
shifted to higher values, which was documented in **Figure 6**. content for $C_{48}^+NO_3^- \cdot H_3PO_4$
 $T_{max\ comb}$ was proportional with the phosphoric acid content.

$$T_{max\ comb} = 900 + 9.6 * \%H_3PO_4 \quad (14)$$

2.2.3. No. 3 $C_{72}^+HSO_4^- \cdot 5H_2O$

According to literature [26] the intercalation process proceeded in first stage intercalation reaction under formation of $C_{72}^+HSO_4^- \cdot 2.5H_2SO_4$ with a very low heat of intercalation of -11 kJ/mole .

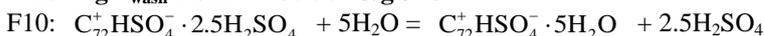
Intercalation $h_{inter\ ex/cal} = -/-\ 0.006\text{ kJ/gC}$



$$MW\ 1728 + 686 + 16 = 2*1206 + 18$$

$$H\ 7* - 889 - 11 = 2* - 3117$$

Washing $h_{wash\ ex/cal} = -/0.36\text{ kJ/gGIC}$.



$$MW\ 1206 + 5*18 = 1051 + 2.5*98$$

$$H: -3117 + 5* - 287 + 435.5 = -1894 + 2.5* - 889$$

14.71 Angstrom as repeating unit was calculated for a third stage intercalation.

$$Ic(\text{Angstrom}) = 8.01 + 2 * 3.35 = 14.71 \quad (15)$$

In **Figure 7** the specific volume of the GIC was a linear correlation with the temperature in the muffle furnace and followed Equation (16):

$$V = -80 + 0.4 * T \quad (16)$$

The sample was also investigated by TMA in **Figure 8**. Expansion started at 200°C and reached a maximum expansion of 2250% at 300°C .

A sample taken out from the muffle furnace at 800°C was investigated by secondary electron microscopy in **Figure 9**. From the picture an expanded layer distance of about 1 - 2 mm was estimated.

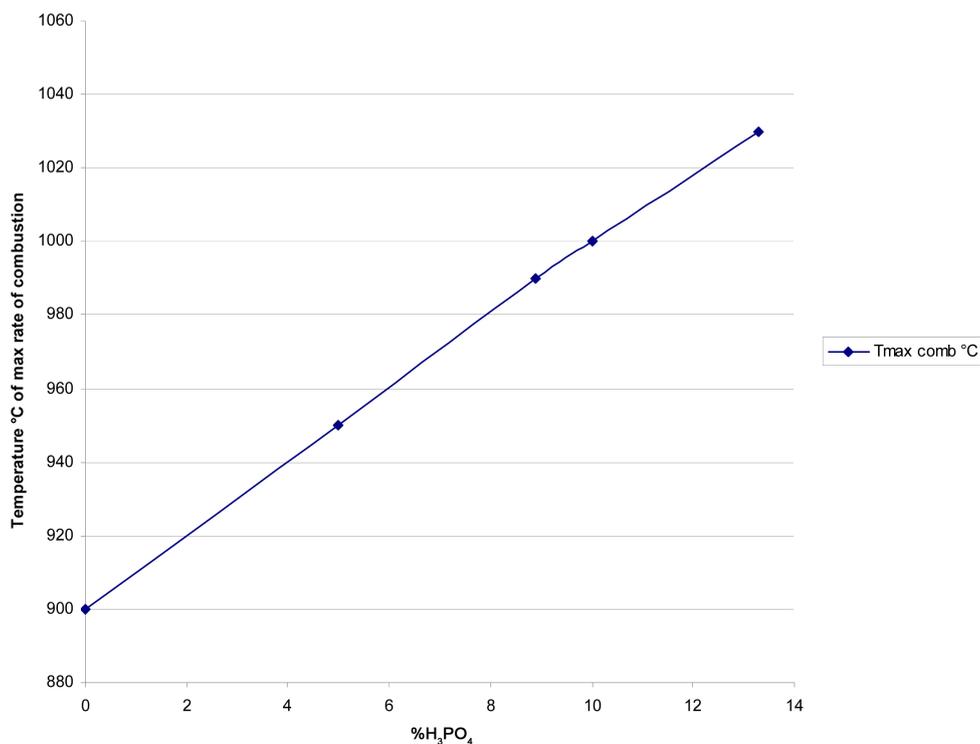


Figure 6. Temperature of maximum rate of combustion $T_{max\ comb}$ in relation with the H_3PO_4 content for $C_{48}^+NO_3^- \cdot H_3PO_4$.

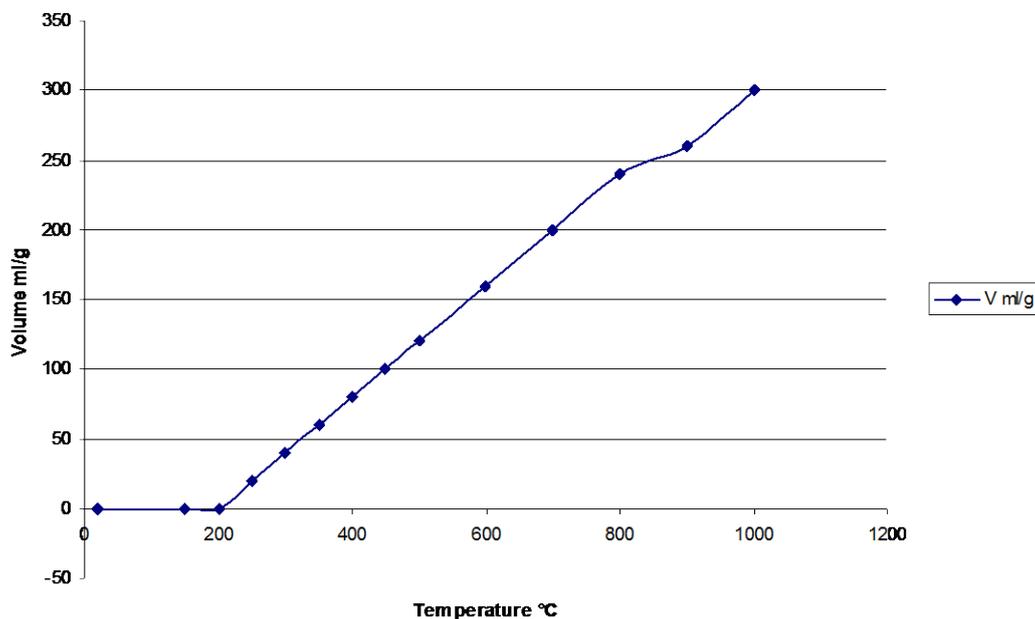


Figure 7. Furnace test: Specific volume ml/g versus temperature of No. 3 $C_{72}HSO_4^- \cdot 5H_2O$.

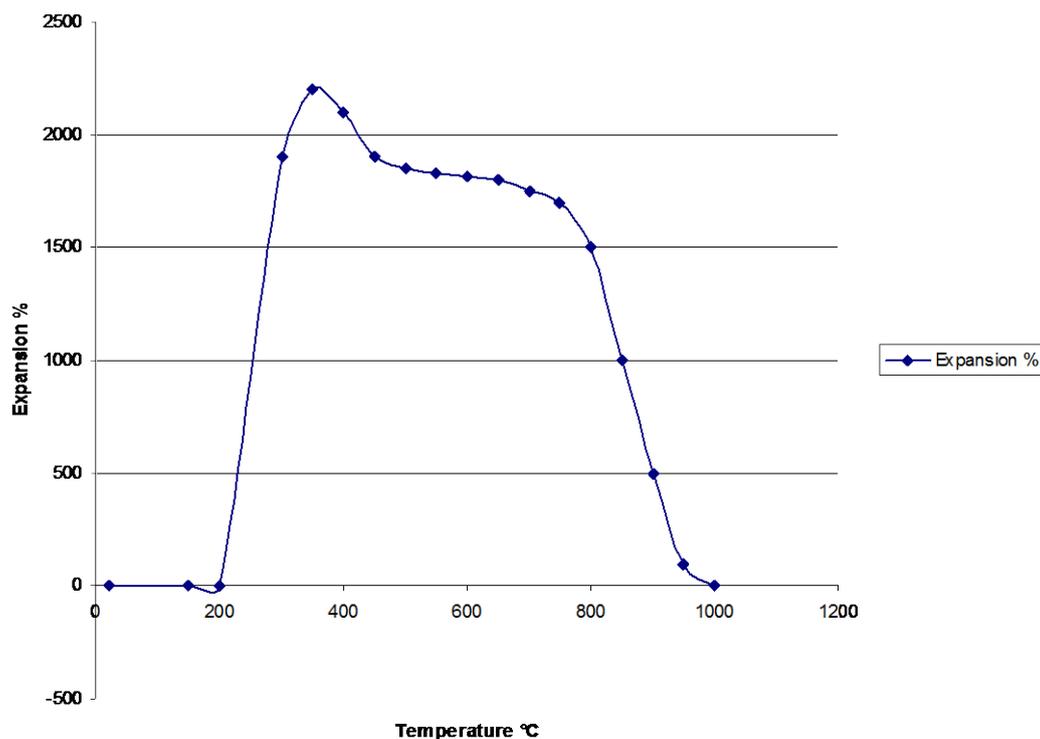


Figure 8. TMA: expansion% versus temperature of No. 3 $C_{72}HSO_4^- \cdot 5H_2O$, 20 K/min, air.

From the observed averaged distance of about 1.5 mm resulted a 10 μ m expanded interlayer distance I_c exp, when the enlargement of 150 was taken in account.

A rough calculation was established under the assumption, that one platelet had the area A and the thickness $x_1 \cdot I_c$, when I_c was the interlayer distance and x_1 the numbers of interlayer distances in one platelet.

The specific volume at room temperature V (RT) in the unexpanded state resulted from N_1 such platelets in 1

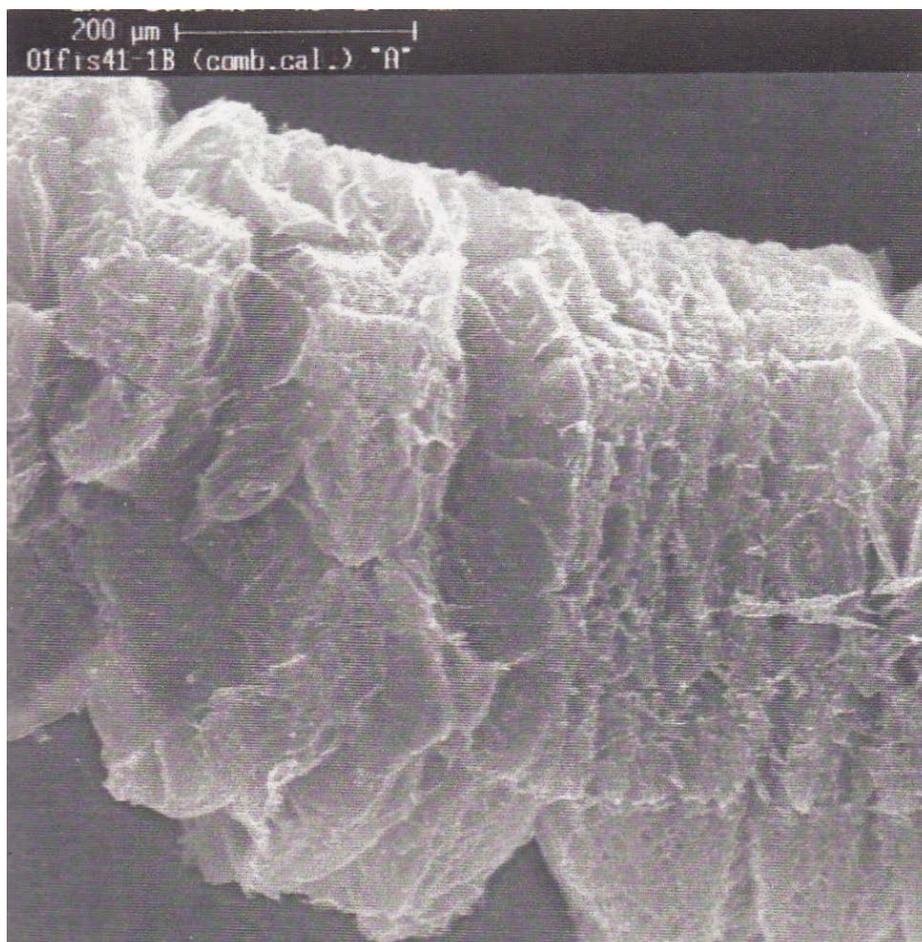


Figure 9. SEM of No. 3 $C_{72}^+HSO_4^- \cdot 5H_2O$ exfoliated at $800^\circ C/5$ minutes. Enlargement 1:150.

g. After expansion at $800^\circ C$ the specific volume increased from V (RT) to $V(800^\circ C)$, because the platelets expanded due to the growing thickness of $x_2 \cdot Ic_{exp}$ by exfoliation. Therefore Equation (17) was valid.

$$N_1 \cdot A \cdot x_2 Ic_{exp} / (N_1 \cdot A \cdot x_1 \cdot Ic) = V(800^\circ C) / V(RT) \quad (17)$$

Under the assumption that neither the number of platelets N_1 nor their area A had changed during expansion Equation (17) simplified to Equation (18).

$$x_2 Ic_{exp} / (x_1 \cdot 14.71) = 280 / 1.66 \quad \text{or} \quad (x_2/x_1) \cdot Ic = 2.481 \text{ Angstrom} = 0.248 \mu m \quad (18)$$

When $10 \mu m$, the observed Ic_{exp} , was introduced into Equation (18), then resulted 40 for (x_2/x_1) , which meant, that platelets of about 40 layers had developed, or in the case of monolayers an expanded interlayer distance of $0.25 \mu m \cdot 150 = 37 \mu m = 0.037 \text{ mm}$ was expected, which was not observed in **Figure 9**.

In **Figure 10** the thermogravimetric analysis showed that exfoliation happened under a weight loss of 18%.

In a graph of $\lg V$ versus $10^3/T$ a heat of exfoliation $H_{exf} = 15 \text{ kJ/mole}$ or 0.014 kJ/gGIC was obtained which was half the heat of exfoliation of 0.029 kJ/gGIC at $300^\circ C$ measured by DSC investigation in **Figure 11**.

When the ideal gas law was applied and 240 ml/g at $800^\circ C$ from **Figure 8** were introduced, 3 moles of gases were obtained according to Equation (19).

$$n = 240 \cdot 1051 / [22,400(1 + 800/273)] = 3 \text{ moles} \quad (19)$$

As atmospheric pressure was the only counter force against expansion, the work done by exfoliation w_{exf} was calculated to be 0.03 kJ/g in Equation (20), when 300 ml/g the maximum specific volume of **Figure 7** was taken.

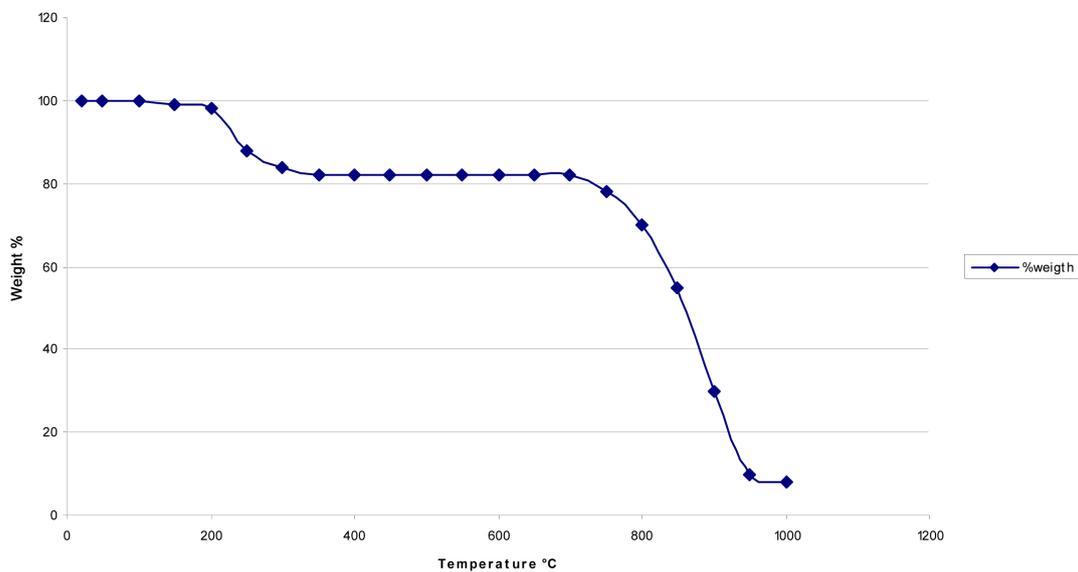


Figure 10. TGA: weight residue temperature of No. 3 $C_{72}^+HSO_4^- \cdot 5H_2O$, 20 K/min, air.

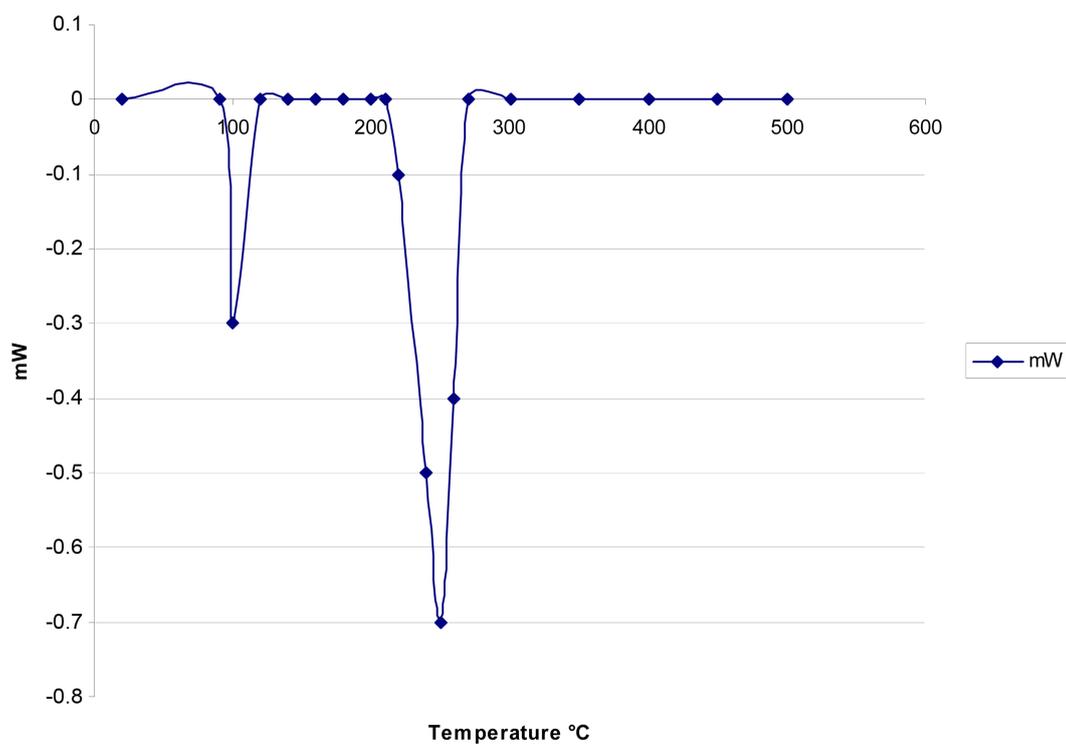


Figure 11. DSC: Heat mW versus temperature of No. 3 $C_{72}^+HSO_4^- \cdot 5H_2O$, 20 K/min, N_2 , $h_1 = 0.01$ kJ/g(H_2O), $h_2 = 0.029$ kJ/g (exfoliation).

$$w_{\text{exf}} = 1 \text{ bar} * (300 - 1.66) \text{ cm}^3/\text{g} = 0.03 \text{ kJ/g} \quad (20)$$

The chemical equations were set up for the theoretical intercalation and for exfoliation:

Intercalation: $h_{\text{interex/cal}} = -0.51 \text{ kJ/gC} = -0.39 \text{ kJ/gGIC}$

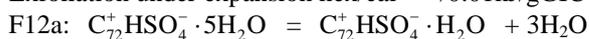
F11: $72C + H_2SO_4 + 4.5H_2O + 0.5O = C_{72}^+HSO_4^- \cdot 5H_2O$

MW: $864 + 98 + 81 + 8 = 1.051$

$$H: -886 - 1.291.5 + 414 = -1.763.5$$

Exfoliation: $h_{\text{exf}} \text{ ex/cal} = 0.029/0.029 \text{ kJ/gGIC}$; $R_{\text{ex/cal}} = 82/82\%$

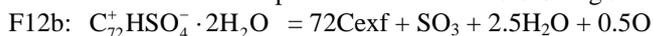
Exfoliation under expansion $h_{\text{ex/cal}} = -/0.01\text{kJ/gGIC}$



$$\text{MW: } 1.051 = 997 + 54$$

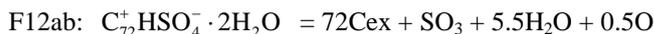
$$H: -1.763.5 + 10 = -1.024.5 - 729$$

Exfoliation under decomposition $h_{\text{ex/cal}} = -/0.019\text{kJ/gGIC}$



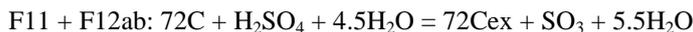
$$\text{MW: } 997 = 864 + 80 + 45 + 8$$

$$H: -1.024.5 + 20 = -397 - 607.5$$



$$\text{MW: } 1.051 = 864 + 80 + 99 + 8$$

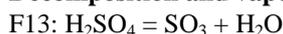
$$H: -1.763.5 + 30 = -397 - 1.336.5$$



$$\text{MW: } 864 + 98 + 81 = 864 + 80 + 99$$

$$H: -886 - 1.291.5 + 444 = -397 - 1.336.5$$

Decomposition and vaporization at 338°C:

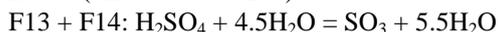


$$\text{MW: } 98 = 80 + 18$$

$$H \ 86 + 246 = -397 - 243$$



$$H \ 4.5 * (-286 + 43 = -243)$$



$$\text{MW: } 98 + 81 = 80 + 99$$

$$H: -886 - 1287 + 439.5 = -397 - 1336.5$$

Then the heats of intercalation and exfoliation were added and put in relation to the heats of decomposition and vaporization:

$$H_{\text{inter}} + H_{\text{exf}} = H_{\text{dec}} (\text{H}_2\text{SO}_4) + H_{\text{vap}} (\text{H}_2\text{O}) \quad (21)$$

$$H_{\text{inter}} + H_{\text{exf}} = 414 + 10 + 30 = 444 \text{ kJ/mole} \quad \text{F11, F12}$$

$$H_{\text{dec}} (\text{H}_2\text{SO}_4) + H_{\text{vap}} (\text{H}_2\text{O}) = 246 + 193.5 = 439.5 \quad \text{F13, F14}$$

The formula F12 postulated 6.75 moles of evolved gases under heat evolution of 0.029 kJ/gGIC, which correlated with a weight loss of 18% measured by TGA accompanied with a heat evolution by exfoliation of about 0.029 kJ/gGIC measured by DSC and a work of expansion of 0.03 kJ/gGIC. Whereas 3 moles of gases were determined, when the ideal gas equation was applied to the expanded specific volume accompanied with 0.014 kJ/gGIC heat of exfoliation measured by the expanded specific volume in dependence of temperature. These results led to the conclusion, that exfoliation happened in two steps: one accompanied with expansion F12a and one without F12b.

In Equation (22) the lattice energy LGIC of -0.566 kJ/gC was calculated.

$$\text{LGIC} = \text{LC} + h_{\text{inter}} = -0.56 - 0.006(\text{F9}) = -0.566 \text{ kJ/gC} \quad (22)$$

2.2.4. No. 4 $\text{C}_{72}^+ \text{HSO}_4^- \cdot \text{H}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$

In the TMA measurement given in [Figure 12](#) two maxima of expansion were observed at 350°C and 800°C. 8.9% incorporated phosphoric acid shifted the maximum rate of combustion from 900°C to 990°C in [Figure 6](#).

2.2.5. No. 5 $\text{C}_{21}\text{FeCl}_3$

$\text{C}_{21}\text{FeCl}_3$ was interpreted as a mixture of 50% $\text{C}_{24}\text{FeCl}_3$ (stage 3) and 50% $\text{C}_{18}\text{FeCl}_3$ (stage 4).

16.1 Angstrom for stage 3 and 19.45 Angstrom for stage 4 were calculated for the constitutional repeating units Ic:

$$\text{Ic} = 9.4 + 2 * 3.35 = 16.1 \text{ Angstrom} \quad (23)$$

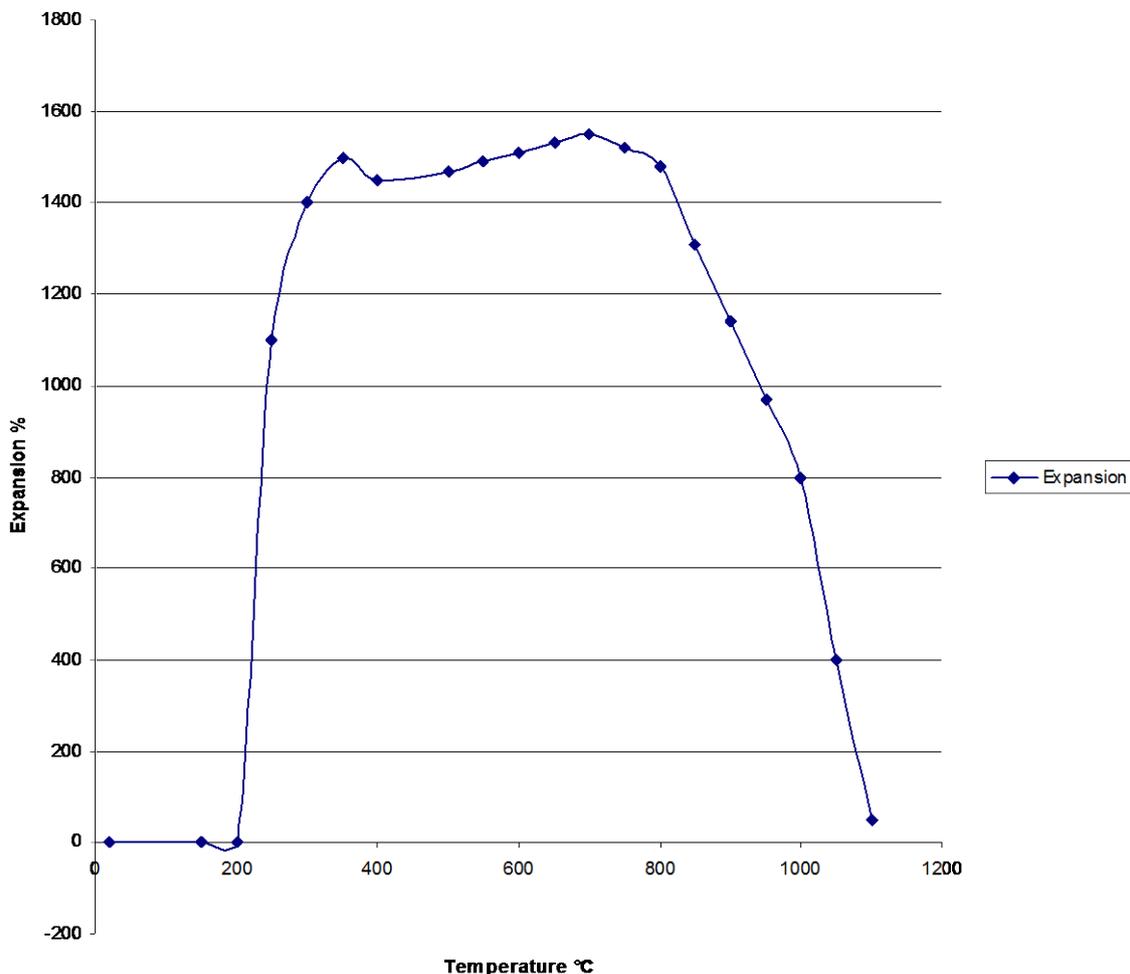


Figure 12. TMA: expansion versus temperature of No. 4 $C_{72}HSO_4^- \cdot H_3PO_4 \cdot 2H_2O$, 20 K/min, air.

$$I_c = 9.4 + 3 \cdot 3.35 = 19.45 \text{ Angstrom}$$

The intercalation process proceeded in the absence of water and no change was observed by washing with nitro methane. For the first stage intercalation-121 kJ/mol $FeCl_3$ building heat was cited in literature [19].

Intercalation and exfoliation were described:

Intercalation: $h_{inter} \text{ ex/cal} = -/0.515 \text{ kJ/gC} = -/0.31 \text{ kJ/gGIC}$

$h_{inter} \text{ ex/cal} = -/0.58 \text{ kJ/gC}; -0.33 \text{ kJ/gGIC}$

F15a: $3 \cdot 6C + FeCl_3 = C_{18}FeCl_3$

MW: $216 + 162.5 = 378.5$

H: $-402 - 125 = -527$

$h_{inter} \text{ ex/cal} = -/0.45 \text{ kJ/gC}; -0.29 \text{ kJ/gGIC}$

F15b: $4 \cdot 6C + FeCl_3 = C_{24}FeCl_3$

MW: $288 + 162.5 = 450.5$

H: $-402 - 130 = -532$

Exfoliation: $h_{exf} \text{ ex/cal} = -/0.03 \text{ kJ/gGIC expansion}; 0.45 \text{ kJ/gGIC decomposition}; R_{ex/cal} = 61/61\%$

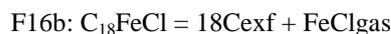
Exfoliation and expansion at 300°C $hex/cal = 0.03 \text{ kJ/gGIC}$

F16a: $C_{18}FeCl_3 = C_{18}FeCl + Cl_2$

MW: $378.5 = 307.5 + 71$

H: $-527 + 14 = -513$

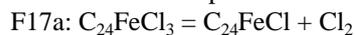
Exfoliation under decomposition $hex/cal = -/0.48$



$$\text{MW: } 307.5 = 216 + 91.5$$

$$\text{H: } -513 + 183 = -330$$

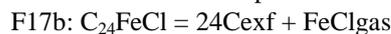
Exfoliation and expansion at 400°C hex/cal = -/0.03 kJ/gGIC



$$\text{MW: } 450.5 = 379.5 + 71$$

$$\text{H: } -532 + 14 = -518$$

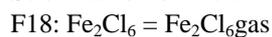
Exfoliation and decomposition hex/cal = -/0.42 kJ/gGIC



$$\text{MW: } 379.5 = 288 + 91.5$$

$$\text{H: } -518 + 188 = -330$$

Sublimation of the dimer of ferric chloride at 315°C:



$$\text{H: } -804 + 138 = -666$$

The molar heats of intercalation in F15 $H_{\text{inter}} = 0.5*(-125 - 130)$ and exfoliation in F16 and F17 $H_{\text{exf}} = 0.5*(14 + 183 + 14 + 188)$ were more or less equivalent with the heat of sublimation H_{subl} in F18.

$$H_{\text{inter}} + H_{\text{exf}} \approx H_{\text{subl}} \quad (24)$$

$$H_{\text{inter}} + H_{\text{exf}} = 0.5*(-125 - 130) + 0.5*(28 + 371) = 72 \text{ kJ/mole}$$

$$H_{\text{subl}} = 0.5*138 = 69 \text{ kJ/mole}$$

The TMA investigation in **Figure 13** indicated that the GIC expanded in two steps at 210°C (3.stage) and 400°C (4.stage). Above 450°C the last 5% of FeCl_3 were evaporated and a maximum expansion of 2400% was reached at 500°C. The GIC exerted its maximum speed of combustion at 900°C.

The sample in the muffle furnace obeyed Equation (25)

$$V = -47 + 0.31T \quad (25)$$

When the data of Equation (25) were plotted according to Arrhenius 0.033 kJ/gGIC was determined as the heat of exfoliation.

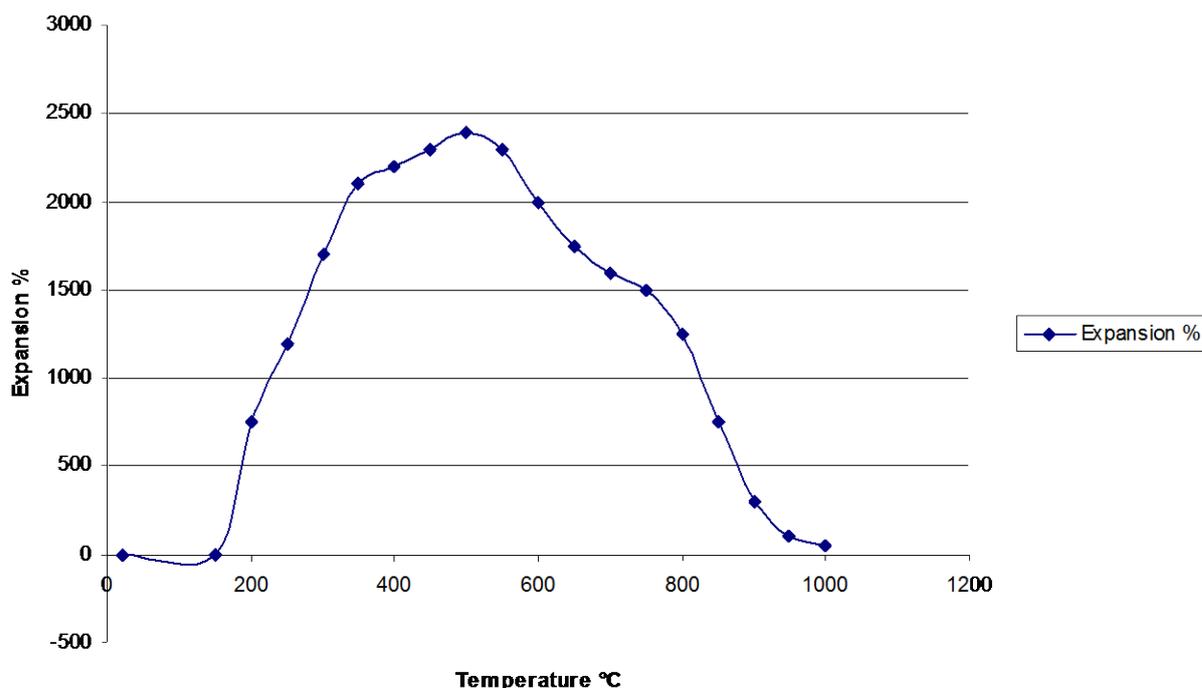


Figure 13. TMA: expansion% versus temperature of No. 5 $\text{C}_{21}\text{FeCl}_3$, 20 K/min, air.

The specific volume at 800°C was applied to the ideal gas law and 0.94 mole of gas was the result of the calculation in Equation (26).

$$n = 200 * 414.5 / [22,400 * (1 + 800/273)] = 0.94 \text{ mole} \quad (26)$$

0.0275 kJ/gGIC was the calculated work of exfoliation w_{exf} in Equation (27).

$$w_{\text{exf}} = 1 \text{ bar} * 275 \text{ cm}^3/\text{g} = 0.0275 \text{ kJ/gGIC} \quad (27)$$

The lattice energies calculated in Equation (28) were unexpected high due to the high heats of intercalation.

$$\text{C}_{18}\text{FeCl}_3 \text{ L GIC} = \text{LC} + h_{\text{inter}} = -0.56 - 0.579 = -1.139 \text{ kJ/gC} \quad (28)$$

$$\text{C}_{24}\text{FeCl}_3 \text{ L GIC} = \text{LC} + h_{\text{inter}} = -0.56 - 0.450 = -1.010 \text{ kJ/g}$$

2.3. Manufacture and Application of Intumescent Strips as Fire Gaskets

Mixtures of 55 parts of polyethylene vinylacetate, Evatane 24-03, and 45 parts of the before investigated GICs were fed to a single screw extruder Alpha 45 from Cincinnati Company. The temperature of extrusion was 130°C and the output 5 kg/h. The extrudates passed a rectangular die, so that strips of the perimeter $10 \times 2 \text{ mm}^2$ were obtained.

The strips were used as gaskets for gaps in a fire test simulating fire doors. All tests were performed in a furnace heated according the standard ISO temperature curve. The front side of the furnace was closed by a heat resistant 40 mm thick Calcium silicate board of Promatect. The board showed six $1000 \times 8.5 \times 40 \text{ mm}^3$ gaps. Five gaps were equipped with 1000 mm long strips glued to the 40 mm wide wall in such a way that they were placed in the middle. Iron Constantan thermocouples were situated above the empty and above the five protected joints. Then a 40 mm thick Rockwool was placed above the whole front side for thermal insulation. In the fire test the gaps closed after 2 minutes at 300°C. After closure the temperature dropped to 50°C. When the gaps opened, a jump in temperature was detected. In **Figure 14** a difference in temperature between furnace and open gap of about 500°C and between closed and open gap of about 300°C was observed.

3. Results and Discussion

In **Table 3** all data of the five GICs were collected. Some discrepancies of the data could be explained by the

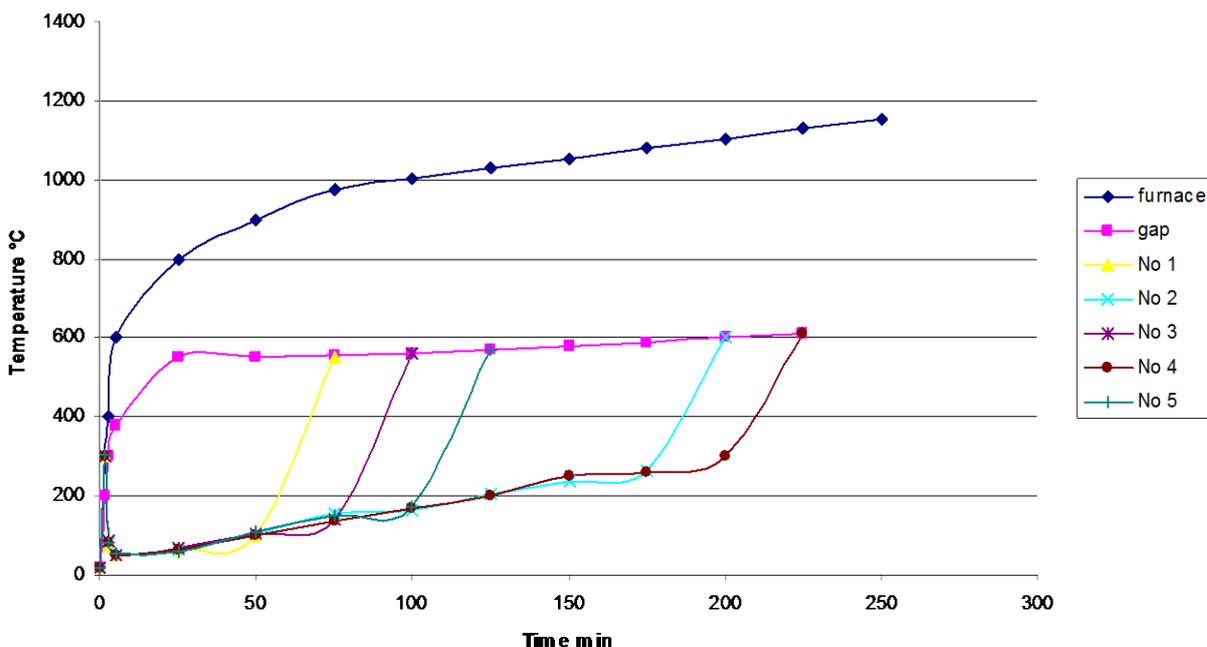


Figure 14. Fire test in gaps of 8.5 mm width, 40 mm depth and 1000 mm length: temperature of furnace, of open gap and of gaps protected by $10 \times 2 \text{ mm}^2$ intumescent strips No. 1-5.

Table 3. Characteristic data of GICs.

Properties	No. 1	No. 2	No. 3	No. 4	No. 5
Intercalated compound	Nitric acid	Nitric phosphoric	Sulphuric acid	Sulphuric phosphoric	Ferric chloride
CAS	79642-57-2	Acid	60496-50-6	Acid	81591-79-9
CAS formula	C ₅₆ HNO ₃		C ₇₂ H ₂ SO ₄		C ₁₇ FeCl ₃
Experimental formula	C ₄₈ ⁺ NO ₃ ⁻ ·H ₂ O	C ₄₈ ⁺ NO ₃ ⁻ ·H ₃ PO ₄	C ₇₂ ⁺ HSO ₄ ⁻ ·5H ₂ O	C ₇₂ ⁺ HSO ₄ ⁻ ·3H ₂ O·H ₃ PO ₄	C ₂₁ FeCl ₃
H ₃ PO ₄ %	0	13.3	0	8.9	0
GIC MW (g/mole)	656	736	1051	1095	414.5
GICexf MW (g/mole)	576	640	864	920	252
Elemental Analysis %	2.0 N	1.9 N; 4.2 P	2.9 S	2.9 S; 2.8 P	13.5 Fe
Calculated	2.1 N	1.9 N; 4.2 P	3.0 S	2.9 S; 2.8 P	13.5 Fe
TMA onset temp. (°C)	150 Figure 1	150 Figure 5	200 Figure 8	200 Figure 12	150 Figure 13
TMA max. expansion (%)	2250	1150; 1200	2250	1200; 1250	2400
TMA temp. of max. exp. (°C)	250	300	350	400	500
TMA expansion rate (%/K)	22.5	13	16	10	7
TMA temp. of max. comb. (°C)	900	1030	900	990	900
Furnace Vol. 800°C (ml/g)	270 Figure 2	170	245 Figure 7	190	200
Furnace equation V (ml/g)=	0.60*T-80 Figure 2		0.42*T-80 Figure 7		0.31*T-47
Furnace h _{exf} (kJ/gGIC)	0.021		0.014		0.033
DSC h _{exf} (kJ/gGIC)	0.02		0.029		
h _{exf} calculated (kJ/gGIC)	0.02		0.01; 0.019		0.03; 0.45
w _{exf} (kJ/gGIC)	0.027		0.03		0.0275
TGA degree of intercal. (%)	10	12	18	15	39
Degree of intercal. cal. (%)	12	13	18	16	39
I _c before washing (Angstrom)	11.29		14.71		16.10 C ₁₈ ; 19.45 C ₂₄
H _{inter} before washing (kJ/gC)	-0.11		-0.006		-0.58; -0.45
L GIC (kJ/gC) before washing	-0.67		-0.57		-1.14; -1-01

circumstance that not all evolved gases contributed to expansion. In respect to the suitability as fire gaskets the GICs with the numbers 2 and 4, which exerted high expansion and high temperature of maximum combustion, were expected to be the most suitable. In the course of this investigation it turned out that also heavy metals were considered to be environmental harmful. Therefore No. 5 was not treated with phosphoric acid nevertheless the untreated sample was incorporated in a strip and tested as fire gasket with good results.

In **Table 4** the data of the gaskets were summarized. The task was to find out the correlation between the properties of GICs and their performance as gaskets.

At a first view the gaskets based on GICs with phosphoric acid No. 2 and No. 4 showed better results, than those without. The time of closure t_c increased with increasing amount of phosphoric acid.

$$\text{GIC intercalated with nitric acid: } t_c = 50 + 9.5 * \% \text{H}_3\text{PO}_4 \text{ GIC} \quad (29)$$

$$\text{GIC intercalated with sulphuric acid: } t_c = 75 + 14 * \% \text{H}_3\text{PO}_4 \text{ GIC} \quad (30)$$

The same type of dependence had been already derived for the maximum temperature of combustion, namely GIC intercalated with nitric acid: $T_{\text{max comb}}(^{\circ}\text{C}) = 900 + 9.6 * \% \text{H}_3\text{PO}_4 \text{ GIC}$ Equation (14).

When the gaskets based on GICs without phosphoric acid were further investigated, then a correlation

Table 4. Fire Gaskets: t_c time until the joints remained closed and dT difference in temperature between open and protected gap.

No.	GIC	t_c (min)	dT ($^{\circ}\text{C}$)
1	$\text{C}_{48}^+\text{NO}_3^- \cdot \text{H}_2\text{O}$	50	450
2	$\text{C}_{48}^+\text{NO}_3^- \cdot \text{H}_3\text{PO}_4$	175	350
3	$\text{C}_{72}^+\text{HSO}_4^- \cdot 5\text{H}_2\text{O}$	75	450
4	$\text{C}_{72}^+\text{HSO}_4^- \cdot 2\text{H}_2\text{O} \cdot \text{H}_3\text{PO}_4$	200	300
5	$\text{C}_{21}\text{FeCl}_3$	100	400

between t_c and EF_{\max} was detected: t_c increased with increasing maximum expansion EF_{\max} independent of the chemical composition.

For GICs intercalated with nitric, sulphuric acids and ferric chloride Equation (31) was valid:

$$t_c = -380 + 0.2 * EF_{\max} \quad (31)$$

The furnace was characterized by the heat flux per area Q/F . The heat flux per area Q/F could be estimated from the difference in temperature dT between furnace and open gap using a heat transmission number a of $3 \text{ W/m}^2\cdot\text{K}$ for free convection and $0.04 \text{ W/m}\cdot\text{K}$ for the heat conductivity λ of air [27].

$$Q/F = dT / (1/a + \text{depth}/\lambda) = 500 / (1/3 + 0.04/0.04) = 375 \text{ W/m}^2 \quad (32)$$

For the protected joints the difference in temperature dT between open and protected gap was calculated according to Equation (33) for the case of 10 mm wide protective strip with a heat conductivity λ of $1 \text{ W}/(\text{K}\cdot\text{m})$ and a maximum expansion of strip = 12. As the strip comprised 45% GIC, the maximum expansion of the strip correlated with 2700 EF_{\max} of GIC: $(2700/100) \times (45\%/100) = 12$.

$$dT = Q/F \left[1/a + d * (12)^2 / (\lambda * 3) \right] = 375 * \left[1/3 + 0.01 * 12^2 / (1 * 3) \right] = 304^{\circ}\text{C} \quad (33)$$

304°C was in good agreement with the experimental values of dT in **Table 4**.

4. Conclusions

Intumescent strips manufactured from GICs and polyethylene vinylacetate were applied as gaskets in gaps and subdued fire tests. The strips containing GICs treated with phosphoric acid showed better fire performance than those without phosphoric acid. The strip comprising the GIC treated with phosphoric and sulphuric acids closed the gap for the longest time, which corresponded with the second highest temperature of maximum speed of combustion but the highest specific volume at 800°C . The GIC treated with FeCl_3 showed also good fire performance, but was not further considered in respect to environmental incrimination by heavy metal. Phosphoric acid was not intercalated and did not contribute to expansion, but shifted the temperature of maximum speed of combustion from 900°C to about 1000°C , which was important for the application as expandable GICs in intumescent gaskets. Gaskets based on GICs without phosphoric acid performed better with GICs with high expansions irrespective of chemical composition. The influence on the time of closure was significant larger for phosphoric acid than for the maximum expansion illustrated by the factors of correlation 9.5 for phosphoric acid and 0.2 for expansion factor.

Intercalation and exfoliation were measured and described by formula as well as by balances of weights and heats. The original heats of intercalation were exotherm determined in a calorimeter. After washing stable compounds with calculated heats of intercalation were obtained. Data could be given for the heat of intercalation and exfoliation, which were derived from DSC measurements, from specific volumes determined in muffle furnace and treated according to Clausius Clapeyron and from the work of exfoliation given by the product of atmospheric pressure and the volume of maximum expansion. Not all intercalated compounds contributed to expansion. High expansion was observed, when high weight loss of the intercalated compound contributing to expansion occurred. Exfoliation happened in nanoplatelets consisting of about 40 atomic layers. The heats of exfoliation were endotherm in every case. The theoretical heats of intercalation together with the heats of exfoliation

corresponded with the heat of evaporation, sublimation and or decomposition of the intercalated compound. The lattice energy of the GIC was the sum of the graphite lattice energy plus the work or heat of intercalation.

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