

**METAL CATALYSED INTUMESCENCE OF
POLYHYDROXYL COMPOUNDS**

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POLYHYDROXYL COMPOUNDS**

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METAL CATALYSED INTUMESCENCE OF POLYHYDROXYL COMPOUNDS

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SYNOPSIS

Fire presents a great risk to humans and their possessions. Polymeric compounds are highly flammable and compounds are added to increase their fire resistance. These additives are referred to as flame retardants. Intumescent flame retardants are systems that form a carbon rich foam on the surface of the polymer during thermal degradation. A new field of metal catalysed intumescence is discussed in this document. The influence of both the metal ion and organic backbone of polyhydroxylcarboxylic acid metal salts was studied. The intumescence and foaming properties of selected salts were studied in more detail.

Gluconic acid proved to be the best intumescent and showed the best combination of carbon char yield, foam structure and volume, stability and open flame characteristics. As a general rule of thumb, the char volume and structure improved with an increased number of hydroxyl groups in the compound. Carbon char yield increased with an increase in the number of hydroxyl groups for a constant number of carbons in the complex. The number of acid groups in the compound played a lesser role in intumescence. Most metal complexes catalyse intumescent decomposition of polyhydric compounds such as polyhydroxylcarboxylic acids and pentaerythritol. The reduction in the volatilisation losses implies that the metal cations catalyse carbonisation reactions in the polyhydroxyl compound. Unfortunately, the resultant carbon-foams are unstable: the metal residues also catalyse the further oxidative degradation of the char. The low thermal stability of the compositions tested, as well as the afterglow effect makes them unsuitable for use as flame retardant additives in plastics. From the studies of the different metal complexes with acetylacetone and gluconic acid, it was concluded that the calcium ion exhibited the most promise.

When pyrolysed in air with an open gas flame or in a furnace, calcium gluconate monohydrate produces voluminous foam. The foam is of a closed cell structure, densely packed and has no mechanical strength. The cell walls are very thin (5 to 50 nm) and the cells are between 50 μm and 200 μm in size. If the sample is compressed before heating, the resultant foam produced during pyrolysis is less voluminous than that of the loose powder. The BET surface area of the calcium gluconate monohydrate foamed at 300°C for 5 min. is 16.0 m^2/g . The foam produced after 5 min heating at 300°C has a thermal conductivity similar to standard polystyrene foam.

Adding leached silica to the calcium gluconate monohydrate increases mechanical strength of the foam, but influences the foam volume negatively. The optimum silica level was calculated to be 1:1 gluconate to silica on a mole ratio (11.8% SiO_2 by mass). The mechanical strength of the foam can also be increased with the addition of expandable graphite. The graphite has a lesser influence on the foam volume than the silica, but also reduces the foam volume. However, the addition of the expandable graphite gives the sample more “opening” force, as the foam volume of a compressed sample pyrolysed, is similar to that of the heated loose powder.

Calcium gluconate monohydrate starts to degrade at 120°C, losing its crystal water and shows a mass loss of 4% at 180°C. The exothermic peak (shown in the DSC/TGA data) associated with the metal catalysed carbon oxidation (afterglow) is observed at 570°C in air. For the calcium gluconate monohydrate the transition from CaCO_3 to CaO occurs above 650°C in air.

It has been shown that the foaming of polyhydroxylcarboxylic acids is due to the formation of water vapour during degradation. For calcium gluconate monohydrate, foaming starts due to the loss of crystal water and is continued by the loss of hydroxyl groups as water. The bulk of the foaming is due to the second reaction. It has been shown that compounds with crystal waters produce a more voluminous and lower density foam. The foam is an amorphous carbon rich residue. The molecular mass of the carbon residue increases up to a heating temperature of 300°C. This implies that the carbon residue crosslinks during formation, forming a stretchable cell wall for the foam. Compounds with a “free” hydroxyl group at the end of the carbon chain produce a foam of larger volume and lower density. This supports the crosslinking theory. The foam produced when calcium

gluconate monohydrate is heated for 5 min at 300°C in air is of very low density – 2.5 kg/m³ based on residual mass.

The density of the calcium gluconate monohydrate pyrolysed at 1000°C for 5 min in air yields a CaO with a density of 20 kg/m³. This implies that the high temperature pyrolysis of calcium gluconate can produce an inorganic oxide of low bulk density and possible high specific surface area. The BET surface area of CaCO₃ from the gluconate pyrolysed at 600°C is ~ 12 m²/g.

An intumescent coating containing calcium gluconate monohydrate, leached silica and expandable graphite as a system was prepared and compared to commercial formulations. This gluconate based system was at least as efficient as the commercial formulations when painted on balsa wood planks or aluminium plates. On cardboard sheets it did not perform as well as the commercial systems.

More work should be done to overcome the afterglow effect observed with metal-based intumescent systems. The crystal structure of calcium gluconate monohydrate should be determined as to understand the decomposition better. It is unclear whether the decomposition is catalysed inter- or intramolecularly.

KEY WORDS: carbon foam, char, latent base catalysed intumescence, metal catalysed intumescence, carbonisation, intumescent flame retardants

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A PhD dissertation is never complete. There is always something else still to be done, something more to be added, to make it ... even more complete.

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NOMENCLATURE

Symbol	Property	Unit	
A	cross section area	square meter	[m ²]
I	electric current	Ampere	[A]
<i>l</i>	electric path length	meter	[m]
R	electrical resistance	Ohm	[Ω]
V	electric potential	volt	[V]
Σ	electric conductivity	-	[Ω ⁻¹ .m ⁻¹]

ABBREVIATIONS

ABS	acrylonitrile-butadiene-styrene
ASTM	American Society for Testing of Materials
APP	ammonium polyphosphate
ATH	aluminium trihydroxide or alumina trihydrate
BET	Brunauer, Emmett and Teller

ca.	<i>circa</i> (approximately)
CaDex	calcium complexes produced from dextrose monohydrate
DMSO	dimethyl sulfoxide
DSC	differential scanning calorimetry
DTA	differential thermal analysis
e.g.	<i>exempli gratia</i> (for example)
EDS	energy dispersive spectroscopy
EDX	energy dispersive analysis of X-rays
<i>et al.</i>	<i>et alibi</i> (and elsewhere)
etc.	<i>et cetera</i> (and so forth)
FeDex	iron complexes produced from dextrose monohydrate
FEP	perfluoro(ethylene/propylene)
IR	infrared
LCP	liquid crystal polymers
LOI	limiting oxidation index
LPG	liquefied petroleum gas
LV	low vacuum
MALDI-TOF-MS	matrix assisted laser desorption ionisation – time of flight – mass spectrometry
MetDex	metal complexes produced from dextrose monohydrate
P	property
PA	polyamide
PAI	poly(amide imide)
PAN	polyacrylonitrile
PBT	poly(butylene terephthalate)
PC	polycarbonate
PE	polyethylene
PEEK	poly(ether ether ketone)
PEI	poly(ester imide)
PEO	poly(ethylene oxide)
PER	pentaerythritol
PES	polyethersulphone
PET	poly(ethylene terephthalate)
PMMA	poly(methyl methacrylate)

POM	polyoxymethylene
PP	polypropylene
PPO	poly(phenylene oxides)
PPS	poly(phenylene sulphide)
PS	polystyrene
PSU	polysulphone
PTFE	poly(tetrafluoroethylene)
PUR	polyurethane
PVA	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
rpm	revolutions per minute
SABS	South African Bureau of Standards
SAN	styrene-acrylonitrile
SDTA	simultaneous differential thermal analysis
SEM	scanning electron microscope
TEM	transmission electron microscope
TGA	thermo gravimetric analysis
vs.	<i>versus</i> (against)
XRD	X-ray diffraction