

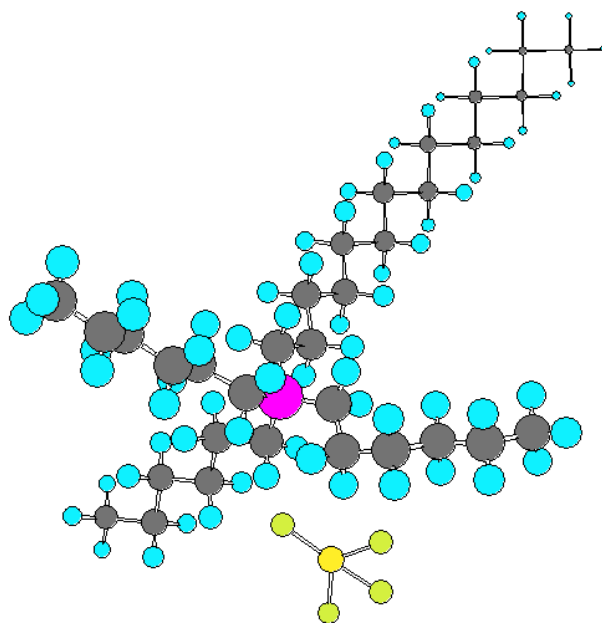
CYTEC

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CYPHOS® IL 111

Phosponium Ionic Liquid



Introduction:

Why consider a “phosphonium” ionic liquid?

Soon after the discovery that certain nitrogen based room temperature liquid salts were found to be useful as battery electrolytes (1a,1b,), interest in these and similar salts as novel fluids and solvents developed. There were a scant number of papers during the 1980s and early 1990s but mainly due to the efforts of the group at The Queen’s University – Belfast, headed up by Professor Ken Seddon, there has been an exponential rise in interest and number of publications in the last 7 to 8 years. (2) Indeed, almost an entire issue of Green Chemistry (3) has been devoted to ionic liquids.

Perhaps one of the most influential publications to direct industrial attention to ionic liquids was a feature article entitled “Designer Solvents” in C&E News – March 30,1998 in which Ken Seddon, Robin Rogers, Tom Welton, Helene Olivier and others elaborated on the potential of ionic liquids. While the article dealt almost entirely with nitrogen based ionic liquids, there was a brief reference by Ken Seddon which alluded to the fact that phosphonium salts are also a potential source of numerous ionic liquids. This brief reference to phosphonium ionic liquids is very much representative of the current fraction of publications relating to phosphonium based ionic liquids. With the exception of several papers and patents by George Parshall in the mid 1970s using stannate and germanate salts and John Knifton et al in the early 1990s which centre on the use of molten tetrabutylphosphonium bromide as an ionic solvent, almost the entire volume of ionic liquid literature deals with nitrogen based systems and in particular, those based on 2-methylimidazolium salts.

There was a good reason for the lack of phosphonium based ionic liquid publications – availability of the starting material! While Cytec has been commercially producing phosphine derivatives since 1971, it was not until 1990 that tributylphosphine was produced on a large commercial scale. Since that time, not only has tetrabutylphosphonium chloride and bromide become available in multi ton scales, many other trialkylphosphines and the corresponding quaternary phosphonium salts are or can be manufactured on a large scale.

The phosphonium cation contains four substituents and the various combinations along with the multitude of various available anions represents an enormous number of possible salts. Even when one restricts the cation to the generic formula – $[\text{PR}_3\text{R}']^+$, the number is still very large. Of course, not all such phosphonium salts are liquid at room temperature, but by a judicious selection of R and R’ as well as the appropriate anion, there are many phosphonium salts which are in fact liquid at room temperature and many more which fall within the broad general definition of ionic liquids as salts which are low melting – that is less than 100 °C.

There are several reasons why one might consider a phosphonium ionic liquid. The most important one for those contemplating an industrial process is availability and cost. Phosphonium salts can meet both of these demands – already Cytec is manufacturing phosphonium salts on a multi ton scale and because of the high volumes, costs will be relatively low. For commercial products, chemical inventory registration is also part of the availability equation. While, most of the possible phosphonium ionic

liquids are still not registered, several are already listed on EINECS, TSCA, EEC, AICS, PICCS and DSL.

Ionic liquids, in general, are not going to be outrageously expensive, but they will not be in the same league as toluene, 2-hydroxypropane (IPA) or tetrahydrofuran (THF). This means that to be economically viable, they must be chemically as well as thermally very stable for multiple recycle use. Even 0.5 to 1% decomposition can lead to major losses after 10 to 20 cycles. Not only will there be solvent losses but there will also be contamination of the ionic liquid solvent and/or products with decomposition byproducts.

In this regard, phosphonium salts are much more thermally stable than the corresponding ammonium salts and even have an edge on imidazolium salts. This is very important for processes which operate at temperatures greater than 100 °C. In addition to being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert. They are somewhat acidic which can result in carbene formation. Phosphonium salts, on the other hand have no such acidic protons.

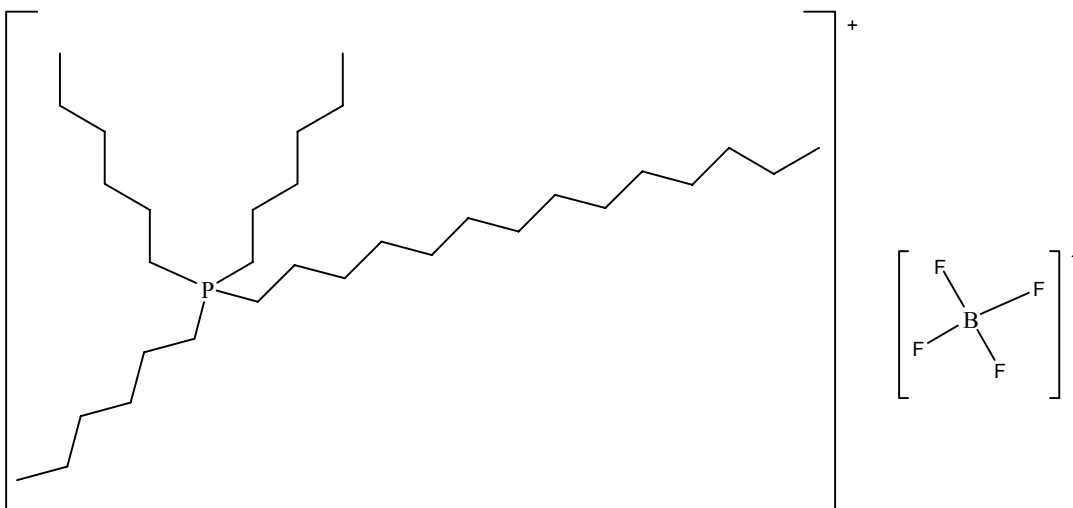
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

Trade Name: **CYPHOS IL 111**

Chemical Name: tetradecyl(trihexyl)phosphonium tetrafluoroborate

C.A.S. Number: [374683-55-3]

Registration: None



CYPHOS IL 111 is a low melting solid (Mp 37 °C). It is prepared via a metathesis route from the corresponding chloride salt and consequently will be contaminated with up to 0.1% chloride ion. (5,6)

Miscibility:

CYPHOS IL 111 is immiscible with water and consequently will form a biphasic mixture. When fully saturated, **CYPHOS IL 111** will contain up to 1.8% water. It is miscible with most common organic solvents such as those listed in Table 1.

Table 1

CYPHOS IL 111 Miscibility

Diluent	Miscible
water	No
hexane	Yes
toluene	Yes
2-hydroxypropane (IPA)	Yes
diethylether	Yes
tetrahydrofuran	Yes
dichloromethane	Yes

Density:

The density of the melt is slightly less than 1. (Figure 1)

Viscosity:

The viscosity is moderate (Figure 2), however, like all ionic liquids, the viscosity is dramatically lowered by the addition of reagents, organic diluents or reaction products. (7) This is readily demonstrated in Figure 3. Additionally, the viscosity decreases exponentially with temperature. Consequently at typical reaction temperatures of 80 to 100 °C, the system is quite water-like with regards to viscosity.

Thermal Stability:

Typically standard TGA plots are used to determine the relative thermal stability of ionic liquids. Heating rates of 5 to 10 °C per minute either under an inert atmosphere or under oxidative conditions such as air are usually reported. Under these conditions, the onset for weight loss for **CYPHOS IL 101** is approximately 380 and 260 °C under dinitrogen and air respectively. (Figure 4). However, in reality, the true temperature at which an ionic liquid is thermally stable is much lower. Figures 5 and 6 are isothermal TGA plots under dinitrogen and air respectively. The respective safe operating temperatures would appear to be 150 and 140 °C.

Hydrolytic Stability:

The tetrafluoroborate anion, like hexafluorophosphate, is prone to hydrolysis and the liberation of low levels of HF. The latter is a health hazard and will be a corrosion issue with glass equipment.

However, if hydrolysis is not an issue, then **CYPHOS IL 111**, can be used in many organic reactions such as Heck coupling, Suzuki cross coupling, carbonylation and hydroformylation. (4)

Analysis:

An assay procedure for **CYPHOS IL 111** is under development, however, based on ^{31}P NMR data, it typically will assay >97%. The only contaminant will be traces of chloride ion.

The chloride content can be readily determined by titration with standardized AgNO_3 in a 75% 2-hydroxypropane (IPA) water medium. Karl-Fischer titration is adequate to determine residual water.

^{31}P NMR is generally not suitable for precise analysis. However, the distinctive signal at +33 ppm can be useful for qualitative analysis.

While electrospray mass spectral analysis (ESMS) is generally not available in every laboratory, this also a very useful tool for both quantitative and qualitative analysis.

References:

- 1a) Fannin, A. A, Jr; King, L. A.; Levisky, J. A.; Wilkes, J. S.; J. Phys. Chem., 1984, **88**, 2610-2614
- 1b) Fannin, A. A. Jr; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; and Williams, J. L., J. Phys. Chem. 1984, **88**, 2614-2621
- 2) "Forward", Professor Ken Seddon, Green Chemistry April, 2002.
- 3) Green Chemistry April, 2002
- 4) Private communications from Alwar Ramani (The Queen's University – Belfast)
- 5) "Industrial Preparation of Phosphonium Ionic Liquids"; Christine Bradaric, Andrew Downard, Christine Kennedy, Allan Robertson, Yuehui Zhou; Green Chemistry, 2003, **5**, 143-152
- 6) "Phosphonium Salts"; A Robertson; WO 01/87900 A1
- 7) K.R. Seddon, A. Stark, M.J. Torres; Pure Appl. Chem. , 2000, **72**, 2275

Figure 1

CYPHOS IL 111 – Density vs. Temperature

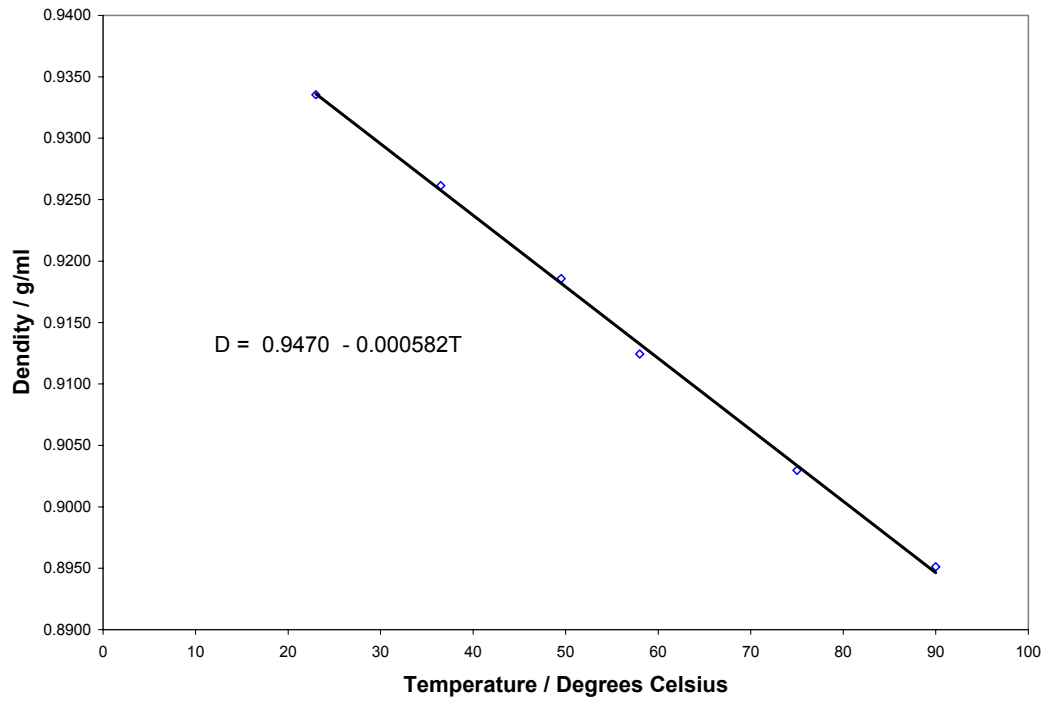


Figure 2

CYPHOS IL 111 – Viscosity vs. Temperature

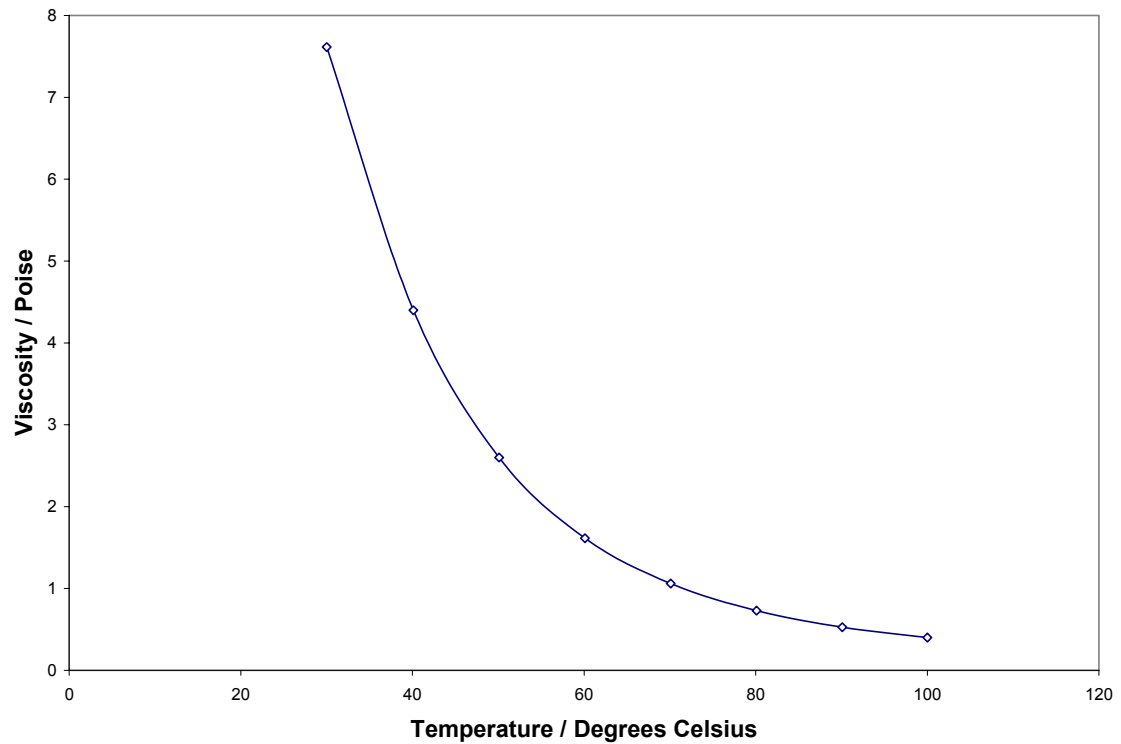


Figure 3

CYPHOS IL 111 – Effect of Solute on Viscosity

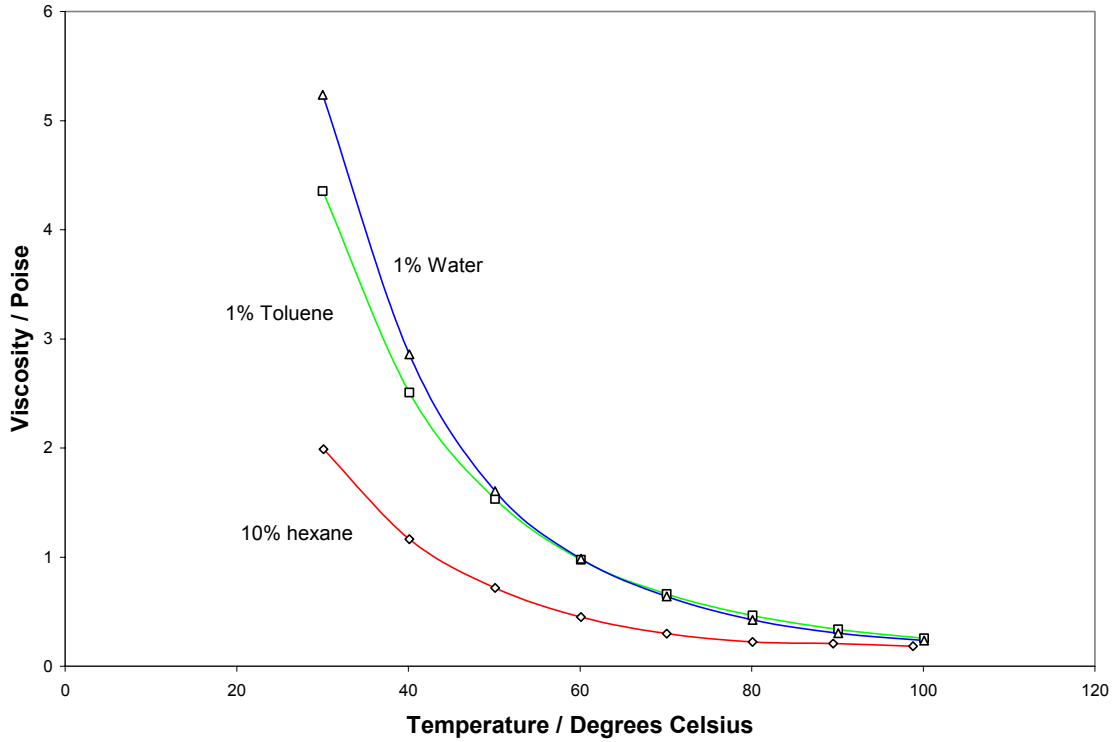


Figure 4

CYPHOS IL 111 – Standard TGA Plots Under Air and N₂

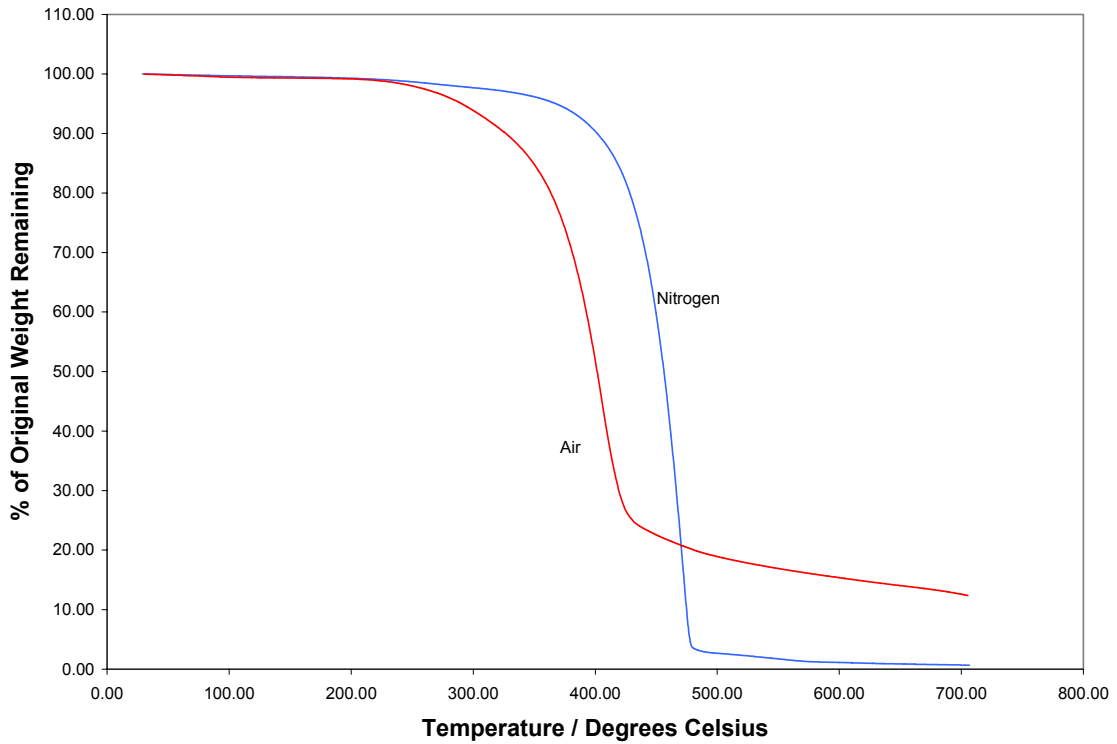


Figure 5

CYPHOS IL 111 – Isothermal TGA Plots Under Air

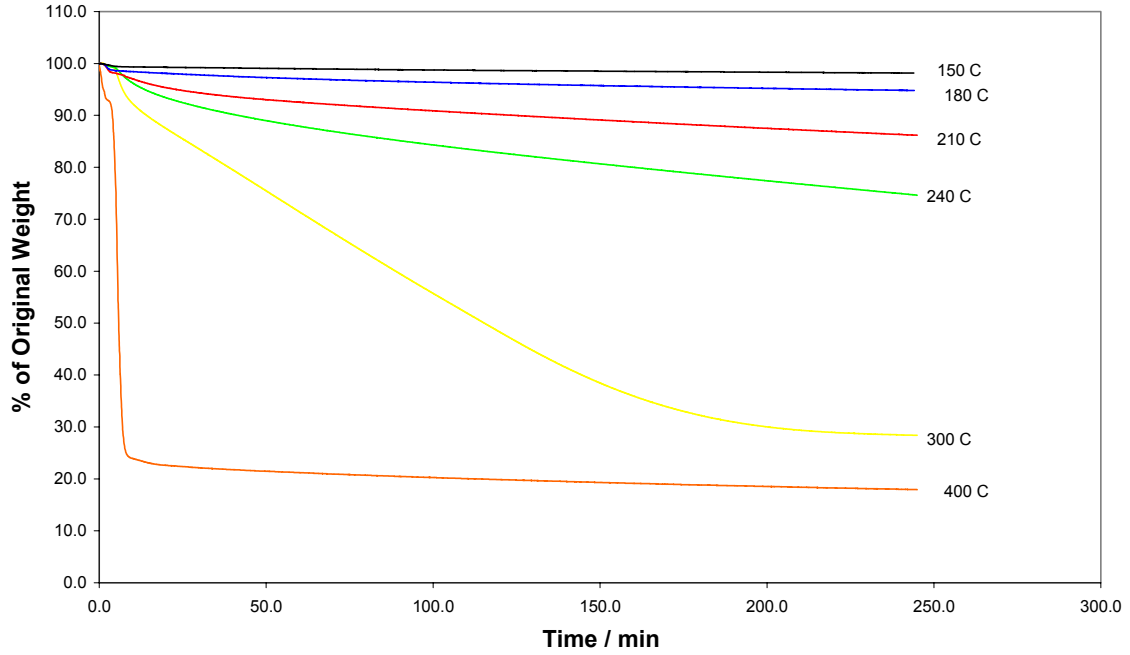
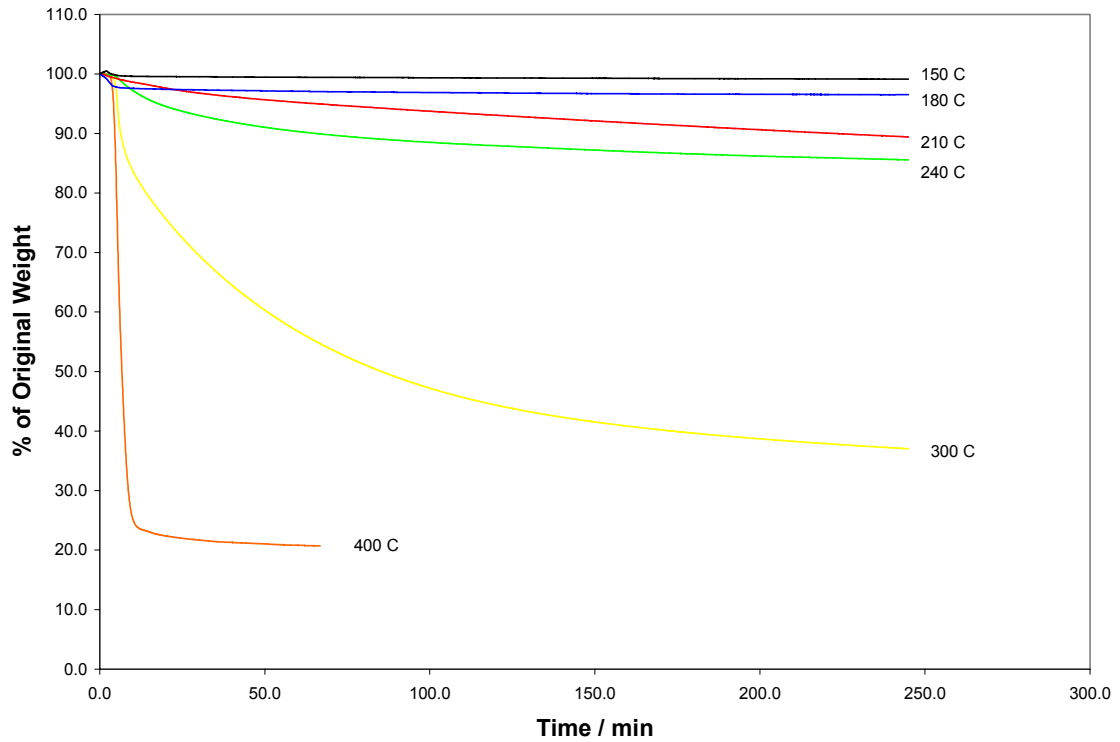


Figure 6

CYPHOS IL 111 – Isothermal TGA Plots Under N₂



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Last up-dated : April 27, 2004