

**CYTEC**

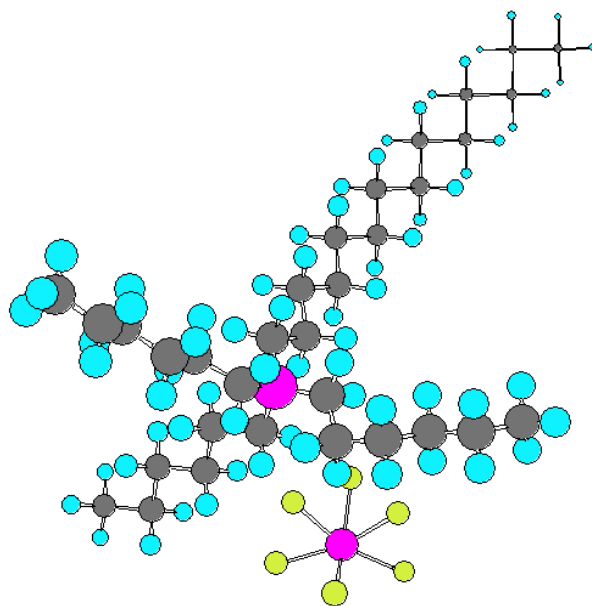
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## CYPHOS® IL 110

### Phosphonium 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.

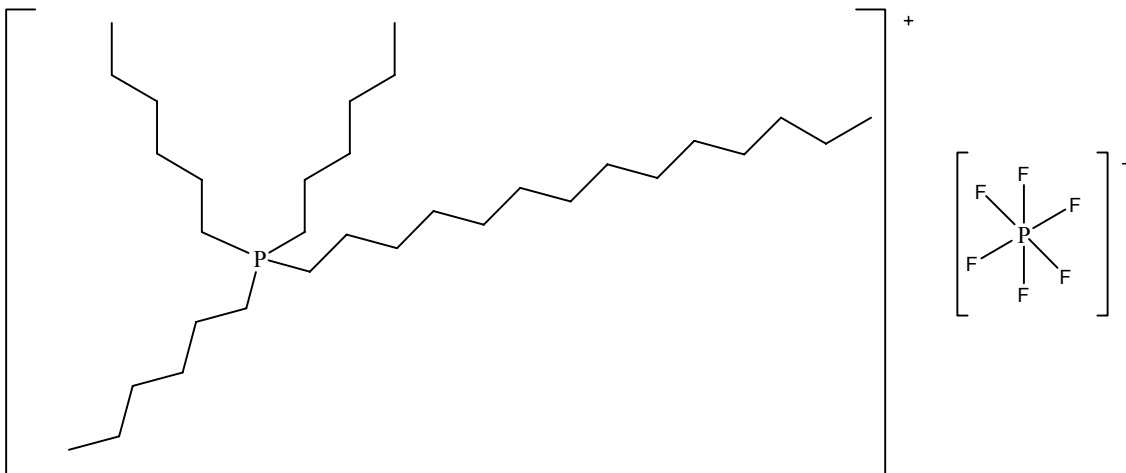
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

**Trade Name:** ..... **CYPHOS IL 110**

**Chemical Name:** ..... tetradecyl(trihexyl)phosphonium hexafluorophosphate

**C.A.S. Number:** ..... [374683-44-0]

**Registration:** ..... None



**CYPHOS IL 110** is a low melting solid ( Mp 50 C ). It is the most hydrophobic of the current list of phosphonium ionic liquids. While it is essentially halogen free, but because it is prepared by a metathesis route from the corresponding chloride salt, it will contain up to 0.1% chloride. ( 5, 6 )

### **Miscibility:**

**CYPHOS IL 110** is relatively hydrophobic and will form biphasic mixtures with water. When fully saturated, **CYPHOS IL 110** will contain up to 2.2% water. It is miscible with most common organic solvents such as those listed in Table 1.

**Table 1**

**CYPHOS IL 110 Miscibility**

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

**Density:**

The density of the liquid state can be either  $>$  or  $<$  1 depending on the temperature ( Figure 1 ). This property may be advantageous in certain applications.

**Viscosity:**

It has a modestly high viscosity ( Figure 2 ), but like all ionic liquids, addition of solutes – be they reagents, diluents or reaction products – will have a dramatic effect on reducing the viscosity. ( 7 ) Additionally, the viscosity will decrease exponentially with temperature and consequently at typically reaction temperatures of 80 to 100 °C, the system is quite water-like with regard to viscosity. ( Figure 3 )

**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 110** is approximately 340 and 280 °C under nitrogen 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 180 and 120 °C. Unlike all other phosphonium ionic liquids, thermal decomposition of **CYPHOS IL 110** is accompanied by an exotherm which can perpetuate the decomposition and can be a process hazard.

**Hydrolytic Stability:**

While the hexafluorophosphate anion provides an ionic liquid which is non-coordinating and which is very hydrophobic, like the tetrafluoroborate anion, it can slowly hydrolyze to yield low levels of HF. The latter is a health hazard and will cause

corrosion issues with glass lined equipment. In general, ionic liquids with the hexafluorophosphate anion should be avoided.

### **Applications:**

If hydrolysis can be avoided, then **CYPHOS IL 110** is quite suitable for many organic reactions such as Heck coupling, Suzuki cross coupling, carbonylation and hydroformylation. ( 1 )

### **Analysis:**

An assay procedure for **CYPHOS IL 110** is under development, however, based on  $^{31}\text{P}$  NMR data, it typically will assay >98%. The only contaminant will be traces of chloride ion.

The chloride content can be readily determined by titration with standardized  $\text{AgNO}_3$  in a 75% 2-hydroxypropane ( IPA ) water medium. Karl-Fischer titration is adequate to determine residual water.

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

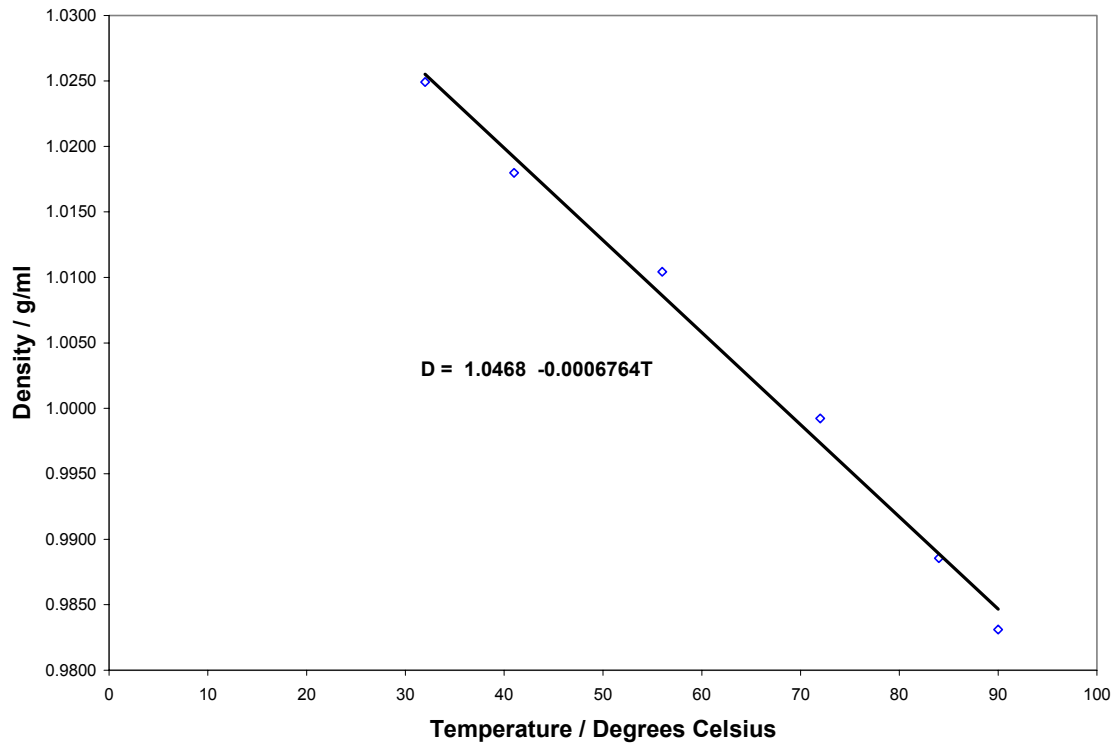
While electrospray mass spectral analysis ( ESMS ) is generally not available in every laboratory, this also a very useful tool for both quantitative and qualitative analysis.

### **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 communication 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 110 – Density vs. Temperature**



**Figure 2**

**CYPHOS IL 110 – Viscosity vs. Temperature**

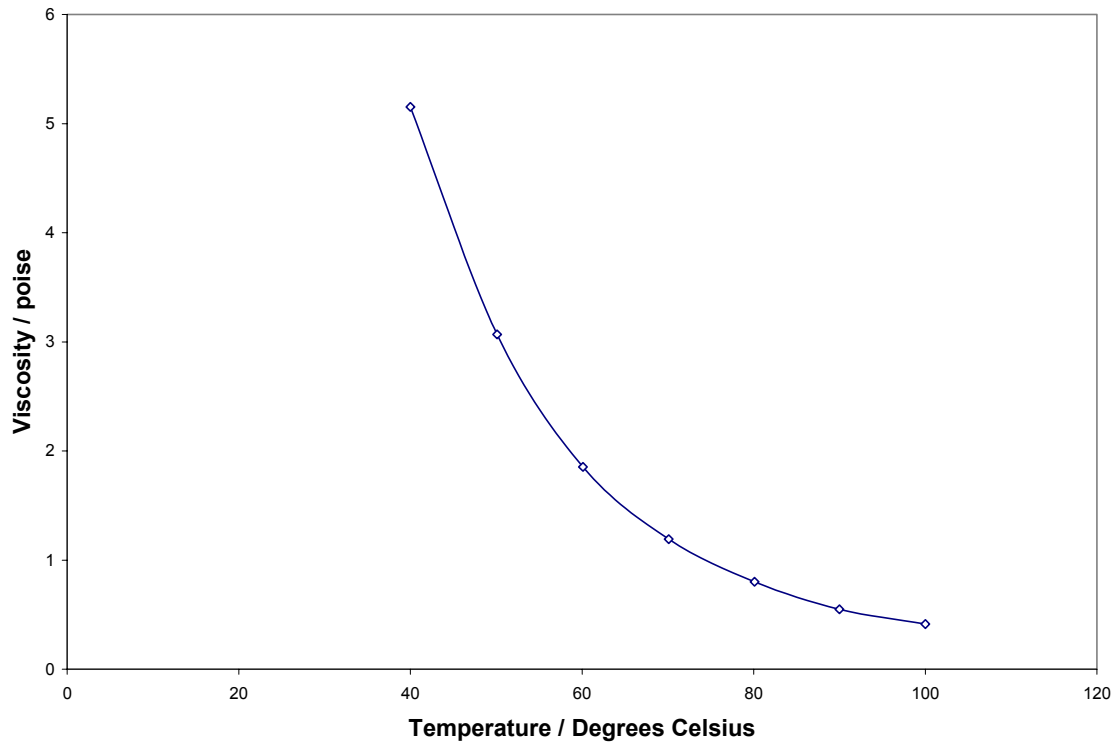


Figure 3

CYPHOS IL 110 – Effect of Solute on Viscosity

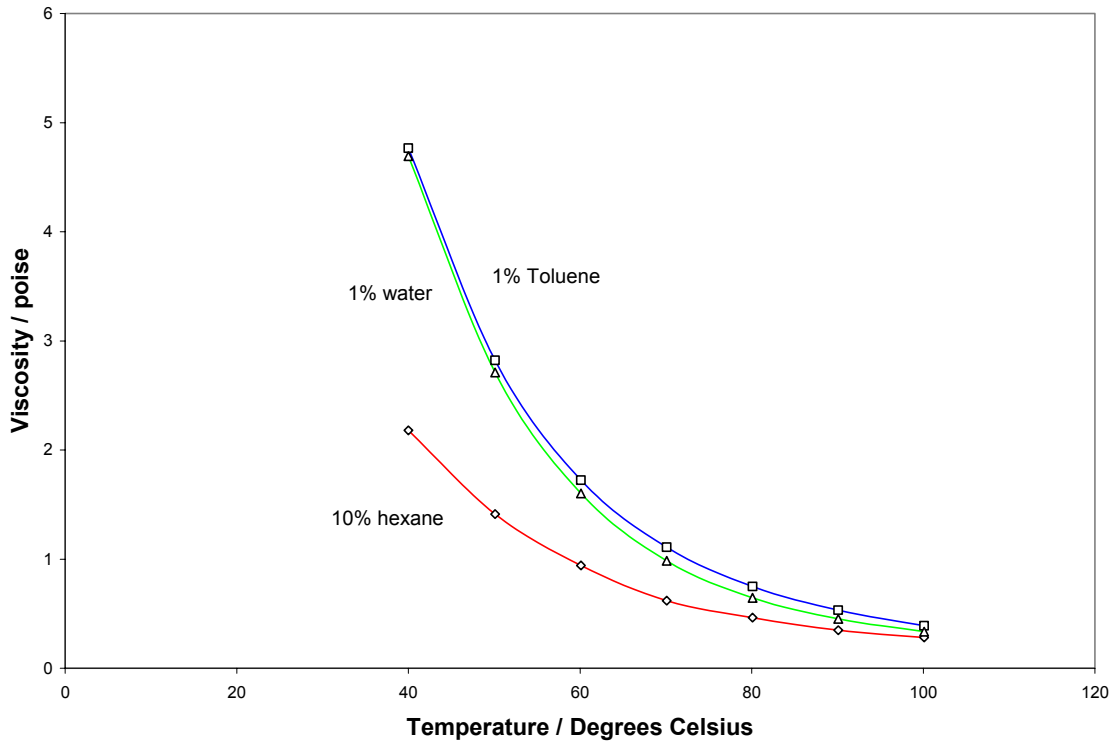


Figure 4

CYPHOS IL 110 – Standard TGA Plots Under Air and N<sub>2</sub>

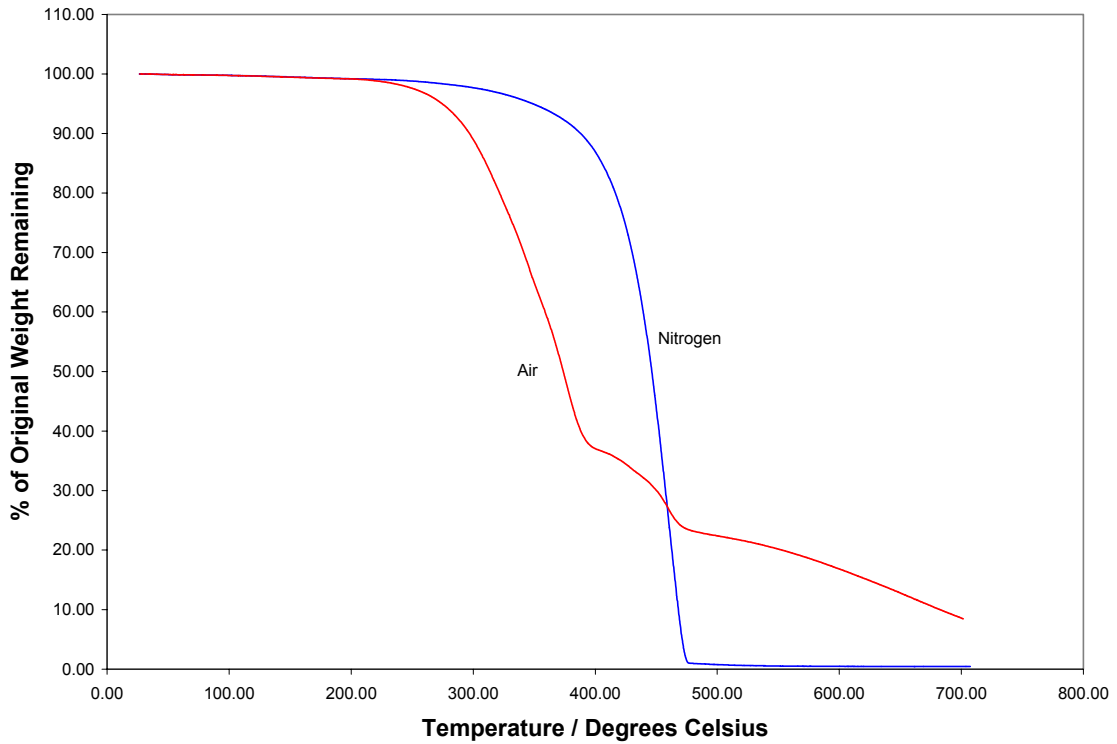


Figure 5

**CYPHOS IL 110 – Isothermal TGA Plots under Air**

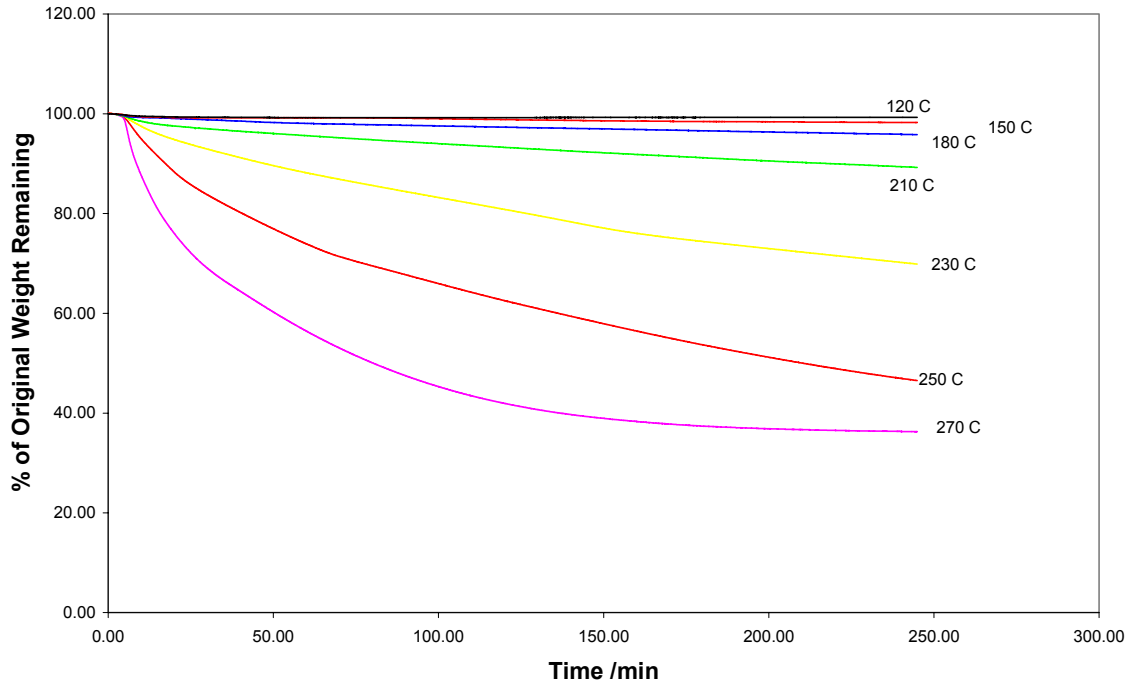
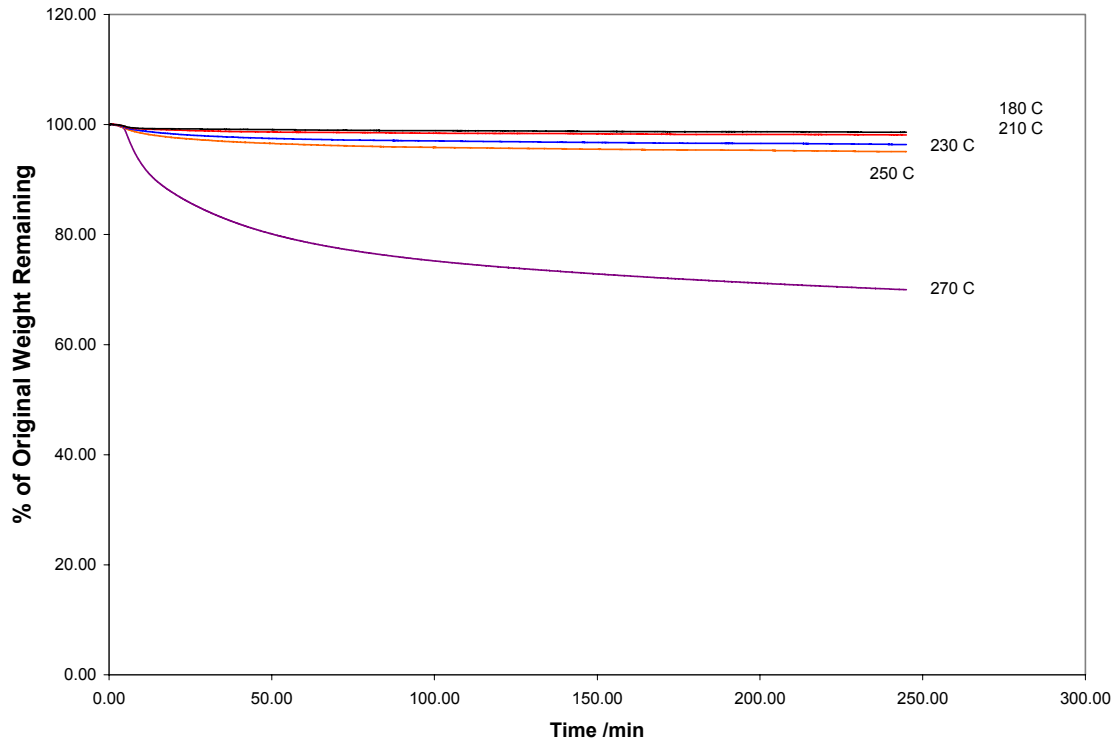


Figure 6

**CYPHOS IL 110 – Isothermal TGA Plots under N<sub>2</sub>**



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