

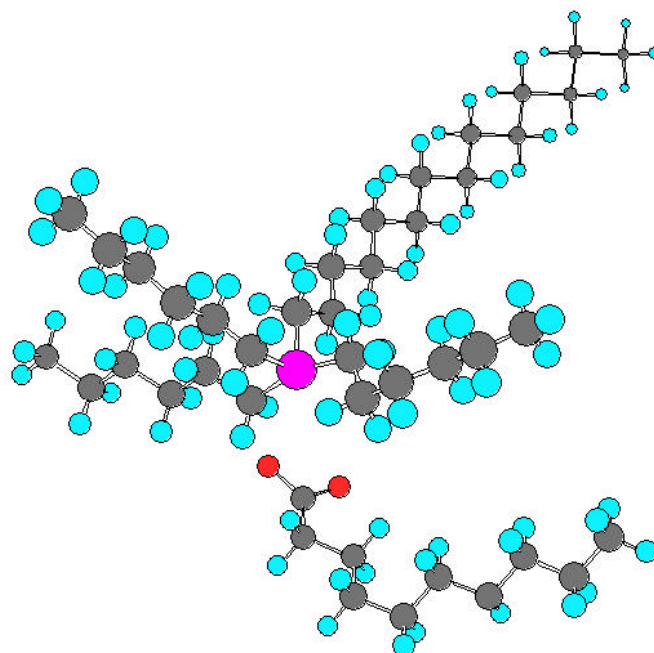
**CYTEC**

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# CYPHOS® IL 103

## 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 –  $[PR_3R']^+$ , 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.

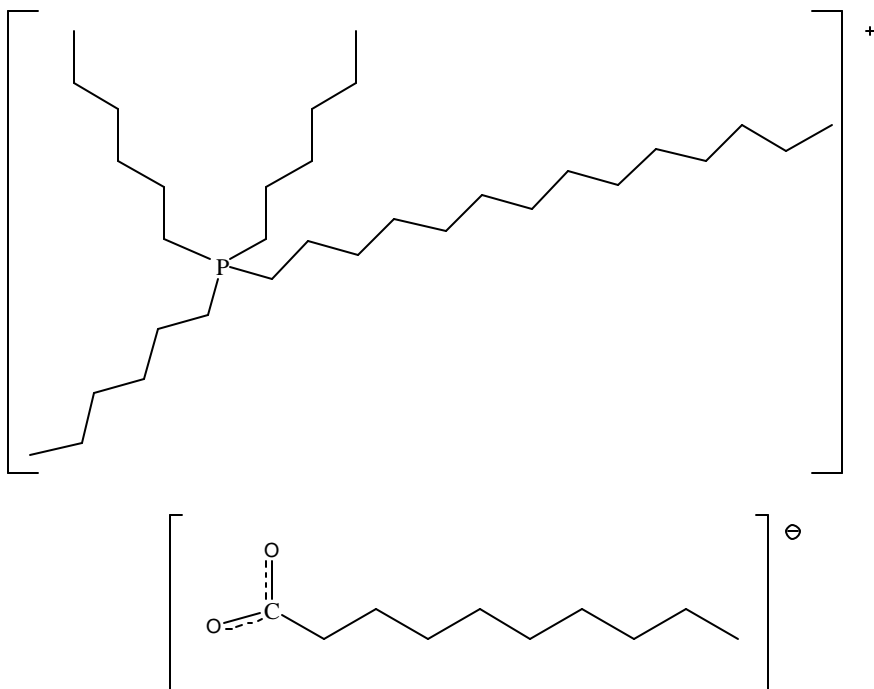
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

**Trade Name:** **CYPHOS IL 103 phosphonium ionic liquid**

**Chemical Name:** tetradecyl(trihexyl)phosphonium decanoate

**C.A.S. Number:** [465527-65-5]

**Registration:** None



**CYPHOS IL 103 phosphonium ionic liquid** is prepared via the metathesis of the corresponding phosphonium chloride with sodium decanoate. It is essentially halogen free but will typically contain 0.1% chloride ion. (4, 5)

### **Density and Miscibility:**

Like the majority of alkylphosphonium ionic liquids, the density is  $< 1$  ( see Figure 1 ). and is immiscible with water although it is sparingly soluble in water and can dissolve up to 21.1% water when fully saturated. When dry, it is totally miscible with a wide range of organic solvents such as indicated in Table 1.

**Table 1**

**CYPHOS IL 103 Miscibility**

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

**Thermal Stability:**

Literature reports of ionic liquid thermal stabilities using standard TGA conditions – that is heating a sample at 5 to 10 °C per minute under an inert atmosphere such as nitrogen or under oxidizing conditions such as under an air atmosphere will indicate unduly high thermal stabilities – even in excess of 300 °C. ( Figure 2 ) However, the true thermal stability of such salts is best determined under isothermal conditions – that is heating a sample rapidly to the test temperature and then observing the weight loss over time. Figures 2 and 3 contain weight loss changes with time over several temperatures under air and nitrogen atmospheres. It would appear that safe operating temperatures for **CYPHOS IL 103** under air and nitrogen will be approximately 110 °C and 150 °C. ( Figures 3 and 4 )

**Applications:**

**CYPHOS IL 103** has been successfully been applied to palladium catalyzed homo coupling of arylbromides and bromopyridines as well as Heck coupling reactions ( 6,7). Alwar Ramani ( 6 ) has also clearly demonstrated that, in the case of the Heck coupling reaction, the **CYPHOS IL 103** / catalyst system can be recycled many times with fresh substrate without loss of catalyst activity. The latter study also demonstrates that the anion plays a role and that within this series, the carboxylate anion as represented by decanoate appears to perform the best. ( Figure 5 )

Another interesting successful application of **CYPHOS IL 103** is as a solvent for the Henry nitroaldo reaction. NcNulty et al have successfully demonstrated high yields of nitromethane to a variety of substituted benzaldehydes (8).

Bio-transformations are often limited to the concentration of either the substrate or products due to toxicity effects on either the enzymes or organisms. For example, 1500 mg/l of phenol is toxic to *Pseudomonas putida*. However, the bio-degradation can be carried out in a two phase system such as **CYPHOS IL 103** /(aqueous phenol), in which the phenol will partition into the IL phase at a concentration which is non-toxic to P.

putita. This organism is totally compatible with **CYPHOS IL 103** and is thus able to consume the phenol from the aqueous phase as it gradually partitions into the IL phase (9).

### **Analysis:**

Assay procedures for **CYPHOS IL 103** are currently under development. However, based on limited production data, it will typically assay > 95% with the main impurity being approximately 4% trihexylphosphine oxide. The product will also contain approximately 0.1% each of chloride ion and water.

The chloride content can be readily determined by titration with standardized AgNO<sub>3</sub> in a 75% 2-hydroxypropane (IPA) water medium. Karl-Fischer titration is adequate to determine residual water.

<sup>31</sup>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.

LC/MS is the most universal tool to identify and quantify cations and anions (10).

### **References:**

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- 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) "Industrial Preparation of Phosphonium Ionic Liquids"; Christine Bradaric, Andrew Downard, Christine Kennedy, Allan Robertson, Yuehui Zhou; Green Chemistry, 2003, **5**, 143-152
- 5) WO 01/87900 A1 "Phosphonium Salts"; A Robertson
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- 7) "Heck reactins of aryl halides in phosphonium salt ionic liquids: library screening and applications"; D. A. Gerritsma, A. Robertson, J. McNulty and A. Capretta; Tetrahedron Letters, 2004, 45(41), 7629-7631

- 8) "Phosphonium Salt Catalyzed Henry Nitroaldol Reactions"; J. McNulty, J. Dyck, V. Larichev, A. Capretta and A. J. Robertson; Letters in Organic Chemistry; 2004, 1, 137-139.
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- 10) "Development of an LC/MS Analytical Procedure for Ionic Liquids with Emphasis on Phosphonium Ionic Liquids"; 1<sup>st</sup> International Congress on Ionic Liquids, June 19-22, 2005, Salzburg, Austria; T.T. Chang and M.J. Piquette  
( also posted on [www.cytotec.com/business/phosphine](http://www.cytotec.com/business/phosphine) )

Figure 1

CYPHOS IL 103 – Density vs. Temperature

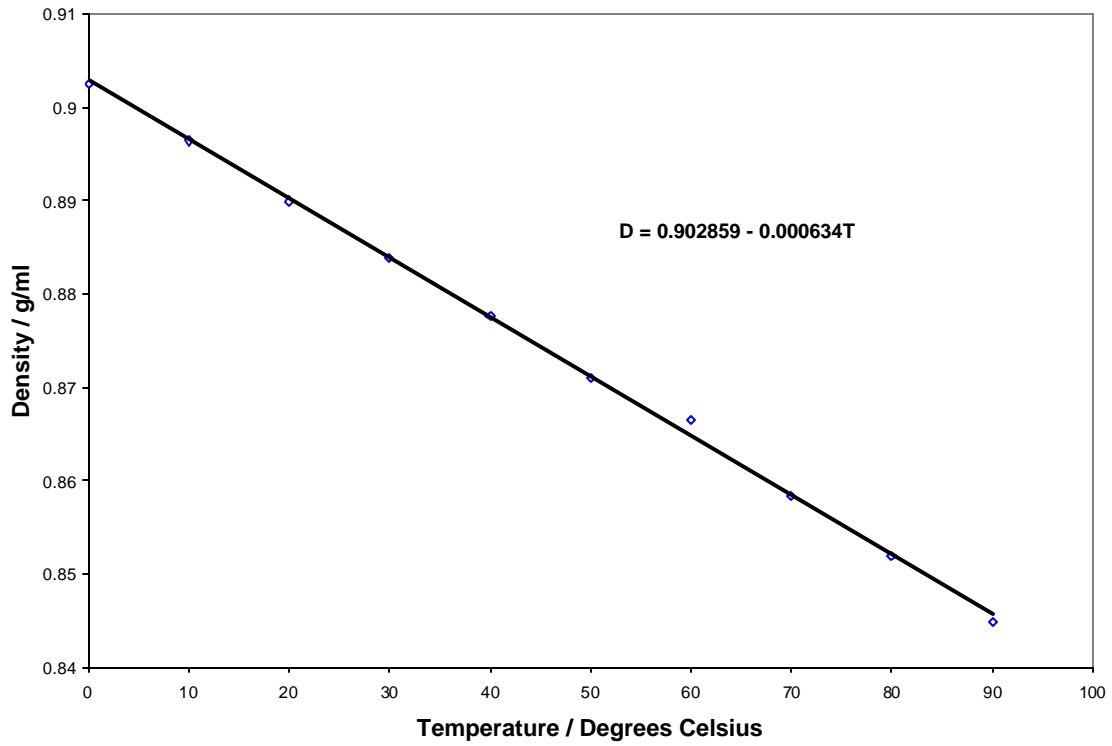


Figure 2

CYPHOS IL 103 – Standard TGA Plots under Air and Nitrogen

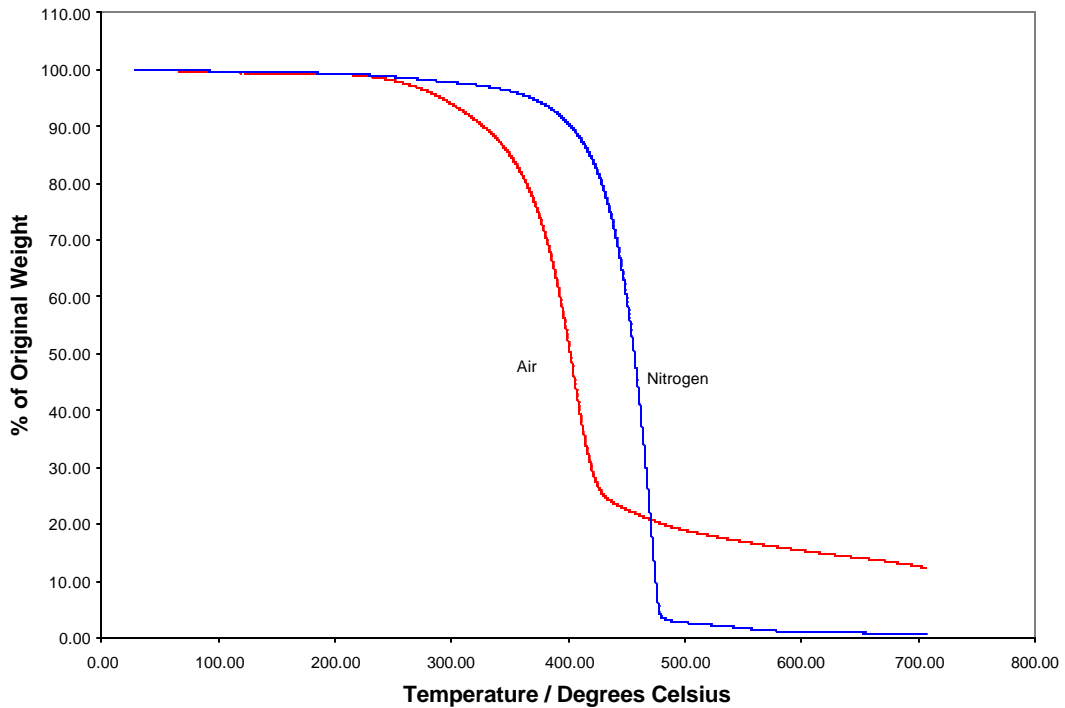


Figure 3

**CYPHOS IL 103 – Isothermal TGA Plots under Air**

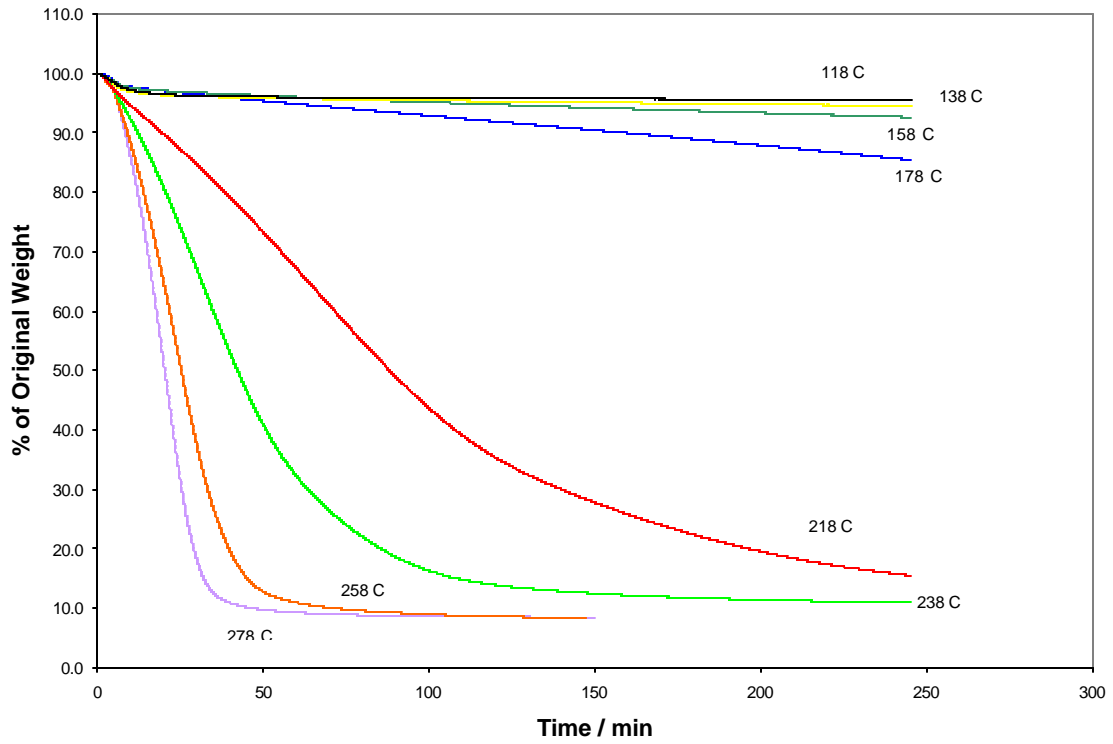


Figure 4

**CYPHOSIL 103 – Isothermal TGA Plots under Nitrogen**

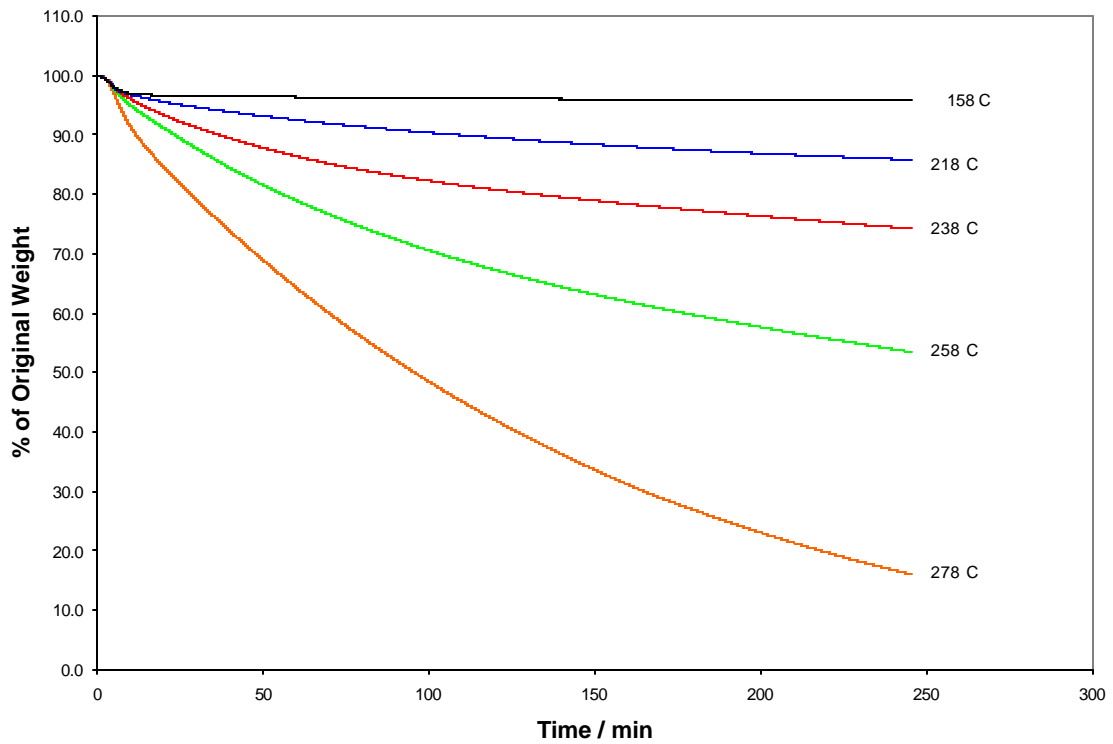
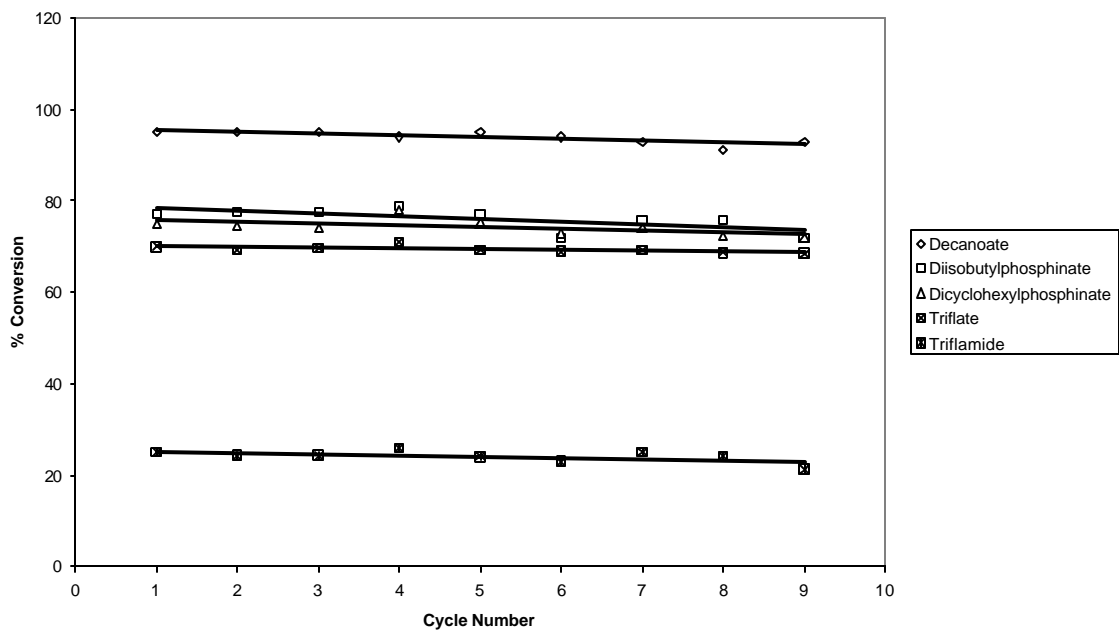


Figure 5

### Recycle of CYPHOS IL 103 / Catalyst

Solvent Recycle: % Conversion vs. Cycle Number  
Heck Coupling: Iodobenzene and Ethylacrylate  
Pd(OAc)<sub>2</sub>, 100 C, 8 hr



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