



Progress beyond

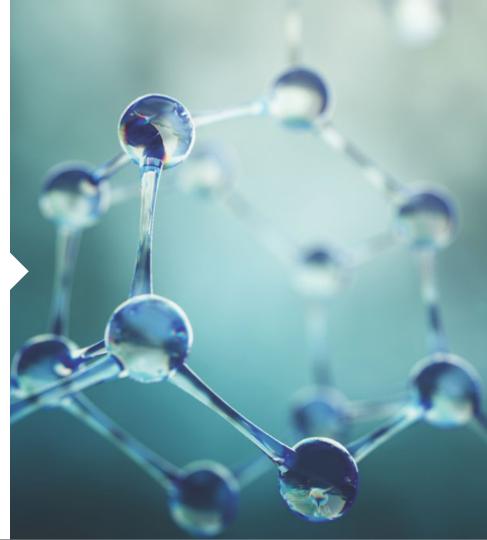
# The Secrets to Tailoring Phosphorus Molecules

## **Ascensus Specialties**

Ashley Bianco, Marketing Supervisor

## Solvay

Eamonn Conrad, Ph.D., Global BD Manager Jade Markham, Ph.D. Research Scientist William Stibbs, Ph.D., Senior BD Manager



## Overview



- Solvay Phosphorus Specialties Ascensus Specialties Partnership
- Phosphorus A Short History
- Tailoring Phosphorus to Meet Many Needs
- Questions

\*Solvay partners with Ascensus for sample distribution





## **Company Overview**

Strem was acquired by Ascensus in 2021

## Solvay partners with Strem for multi-kilo sample distribution!

### **About Ascensus**

Our specialty chemistries improve the way clients create their products by making what they do easier, more efficient, safer, and more selective. We have a global reach that ensures our customers can consistently manufacture their products to the highest standards so they can make the best possible products to change people's lives for the better. And, we are able to make the world a better place with **chemistry made for what matters.** 







**Providing R&D Expertise** for Custom Synthesis & cGMP Manufacturing Services







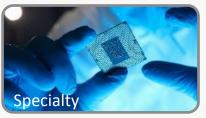




## **Market Overview**

Diverse and Stable









Pharmaceutical
Agrochemical
Nutraceuticals
Veterinary
Fine Chemicals
cGMP API

Electronics
Surfactants
Tissue
Petrochemicals
Coatings & Adhesives

Academic Research
Microelectronics
Pharmaceuticals
Chemical/Petrochemicals
Specialty Chemicals

Newsprint & Magazine
Packaging
Pulp & Paper





## **Our Products**

## Specialty Reagents that Matter

### **Borohydrides**

Typical applications are in Life Sciences, Specialty Markets, and Pulp & Paper

### **Strem Catalog**

Offering more than 6,000 specialty chemicals with an emphasis on metals, inorganics, organometallics, and nanomaterials for R&D and commercial applications

### **APIs**

Offering Cisplatin, Dexmedetomidine hydrochloride, and many more. Our Active Drug Master Files (DMFs) are maintained in over 20 countries.

### **Boranes**

Typical applications are in Life Sciences and Specialty Markets

### **Specialty Alcoholates**

Typical applications are in Life Sciences and Specialty Markets

### **Thin Film Deposition**

Our portfolio includes 500+ MOCVD, CVD, and ALD precursors and bubblers/cylinders for microelectronics applications.

### **Catalysis**

Portfolio includes thousands of catalysts and ligands such as Buchwald ligands and precatalysts, photocatalysts, metathesis catalysts, and biocatalysts

### **ASCENSUS** PORTFOLIO

We offer a broad portfolio to ensure we capture all our customer's needs. From catalog sales to commercial scale, we're the partner that delivers specialty reagents that matter.

## **Other Specialty Chemicals**

Portfolio includes TMB, NaK & K Metal. Typical applications are in Specialty Markets



# Solvay Today



We are a science company whose technologies bring benefits to many aspects of daily life.

Our innovative solutions contribute to safer, cleaner, and more sustainable products found in homes, food and consumer goods, planes, cars, batteries, smart devices, health care applications, water and air purification systems.

Our Group seeks to create sustainable shared value for all, notably through its Solvay One Planet plan crafted around three pillars: protecting the climate, preserving resources and fostering better life.





\*2020 figures

# 2030 Solvay One Planet Goals

10 ambitious objectives



### CLIMATE

Fight against climate crisis



Align **greenhouse gas emissions** with Paris Agreement

Reduce by 26% (-2%/y)



Phase out coal



Achieve 100%





30% reduction

**RESOURCES** 

Embed circular business



Increase Sustainable Solutions revenues

Achieve 65% vs 50%



Achieve 15% vs 7%

Reduce non-recoverable industrial waste



000

% 30% reduction

BETTER LIFE

Improve quality of life



Safety is a priority



Aim for zero accident

Accelerate Inclusion & Diversity



Parity in 2035 vs

24% for mid & senior management

Extend maternity leave time and open it to co-parents



16 weeks regardless of the gender in 2021

WE PARTNER WITH CUSTOMERS AND COLLABORATE ACROSS THE VALUE CHAIN TO REDUCE GLOBAL IMPACT

# Solvay:

# A Global Leader in Phosphorus Chemistry





# Differentiated products and technologies

We offer a wide range of phosphorusbased chemistry to meet precise application requirements



### **Innovation**

160 years of know-how and innovation in phosphorus chemistry



## Scale-up capabilities

From R&D to large scale; largest capacity in the industry



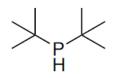
## Partnership

We work closely with customers to translate their needs into concrete solutions



# Secure and consistent supply source

Stringent quality control standards and timely order fulfillment due to global footprint and supply chain



**CYTOP**® 242 (Strem: 97-1000)

**CYTOP**<sup>®</sup> 208 (Strem: 97-1002)

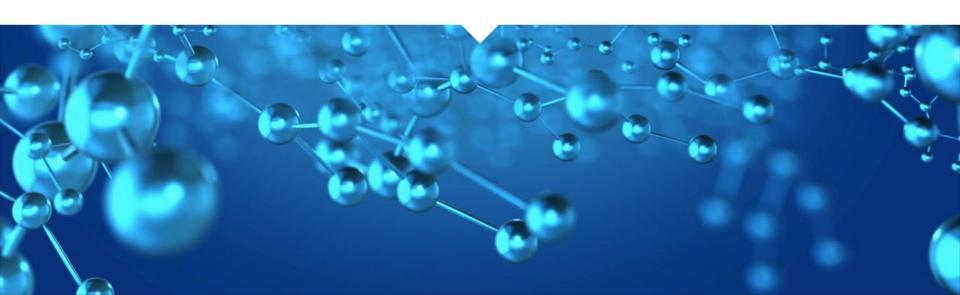
# Phosphorus - A Short History



Progress beyond



Multi-kilo samples available

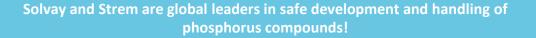


# The Basics of Phosphorus

- Phosphorus is ubiquitous in our world essential to sustaining life
- First isolated in 1669 as white phosphorus (Brandt)









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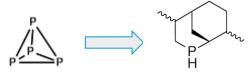




## **Facts about Phosphorus**

- Concentration in Earth's crust at 1g/kg (compare copper 0.06g/kg)
- Widely distributed in phosphate rocks (up to 8.7 wt%)
- Pentacalcium triorthophosphate fluoride is the chief commercial source
- Organic sources such as urine, bone ash and guano have historical importance but limited commercial use
- Red, yellow and black are the most common allotropes





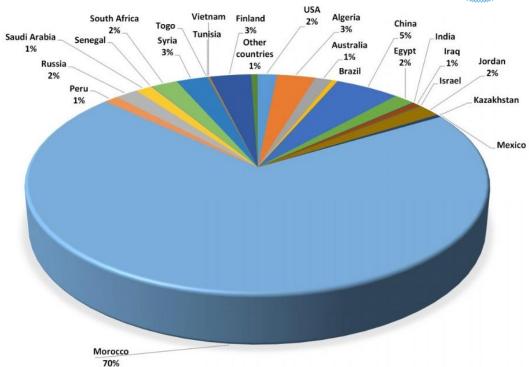
**CYTOP**<sup>®</sup> 170 (Strem: 15-7605)



# Phosphorus - Supply and Demand



- 2021 USGS estimated 71 billion tons in world reserves (do not reflect production)
- Mining production (2020) was 223 million tons
  - China leading producer
  - Others: USA, Vietnam, Khazakhstan
- Annual demand is growing twice as fast as growth of human population
  - Primary demand is fertilizer for food
- Phosphorus recovery methods are not yet economically viable but need to continue to be developed



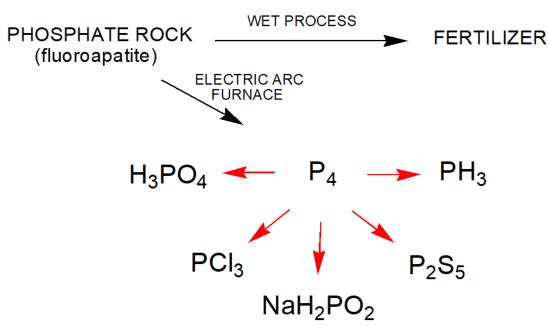


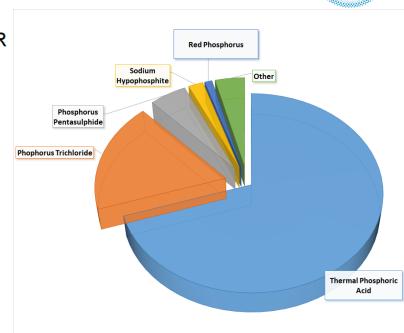
<sup>1.</sup> USGS, January 2021, Retrieved August 20, 2021

<sup>2.</sup> Arno Rosemarin (2016) <u>Phosphorus a Limited Resource – Closing the Loop</u>, Global Status of Phosphorus Conference, Malmö, Sweden (based on USGS Phosphate Rock Statistics and Information)

# Bringing Phosphorus to the Masses







Phosphate rock processing can involve beneficiation, drying, calcination, crushing, acid treatment Submerged Arc Furnace is relevant for phosphorus production (Wöhler process)



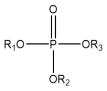
## The Markets we Serve

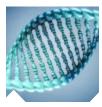




**Flame Retardant** 

- ✓ P-chemistry imparting flame-resistance to textiles & garments
- ✓ THPC for leather treatment applications

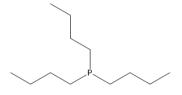




**Life Sciences** 

CYTOP® | RhodaPhos®

- ✓ Specialty phosphorus compounds for applications requiring stringent purity profiles
- Catalysis; oligonucleotide synthesis; reagents; intermediates



**CYTOP**® 340 (Strem: 97-5801)



**Electronics**CYPURE® | CYTOP® | CYPHOS® IL

- ✓ High-purity phosphine gases & derivatives used throughout the electronics supply chain
- ✓ Dopants for LED & semi-conductors; capping ligands; solvents; quantum dot materials



**CYTOP**® 242 (Strem: 97-1000)



## The Markets we Serve

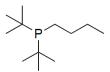




**Chemical Processing** 

CYPHOS° | CYTOP° | RhodaPhos°

- ◆ Phosphine derivatives used in the manufacture of chemical compounds
- ✓ Organic extraction, catalysis, ligands and additives



**CYTOP**® 202 (Strem: 97-1128)



**Plastics, Epoxy & Coating** 

CYPHOS® | AMGARD® | Albritect®

- Phosphorus additives optimizing the performance of plastics, epoxy, and coating systems
- Epoxy resin curing; flame retardant polymers; surface coating treatment; catalysts

$$\begin{bmatrix} C_4H_9 \\ \\ C_4H_9 \\ \\ C_4H_9 \end{bmatrix} \begin{bmatrix} C_2H_5 \\ \\ C_2H_5 \\ \\ C_2H_5 \end{bmatrix} \bigcirc \bigcirc \bigcirc$$

**CYPHOS**<sup>®</sup> **IL** 169 (Strem: 97-1330)



Other
Phos Acid | CYTOP\* | CYPHOS\* IL

- Phosphorus-based chemistries for commodity and niche applications
- ✓ Metal extraction & recycling; liquid extractions; ionic liquids; fertilizer; other applications

**CYTOP**® 502 (Strem: 97-6660)



# Tailoring Phosphorus to Meet Many Needs



Progress beyond





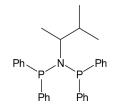
# Phosphorus - Versatile and User Friendly



• Unique properties - Predictability of resulting chemistry and structure/property relationships - *relevant* chemistry at commercial scale

- 1. 5 valence electrons
- 2. s,p,d orbitals
- 3. Multiple oxidation states (I, III, V, 0)
- 4. Lewis basic or acidic depending on structure
- 5. NMR active isotopes easy to get direct analysis!
- 6. Ability to form strong bonds with multiple atoms (O, C, S, H, N, etc.)

**CYTOP® 222** (Strem: 97-1460)



RhodaPhos® PNP 12M (Strem: 15-0745)

**CYPHOS**® **442** (Strem: 97-1579)

RhodaPhos® CP100R (Strem: 97-0165)

RhodaPhos® Phos Reagent (Strem: 97-0695)

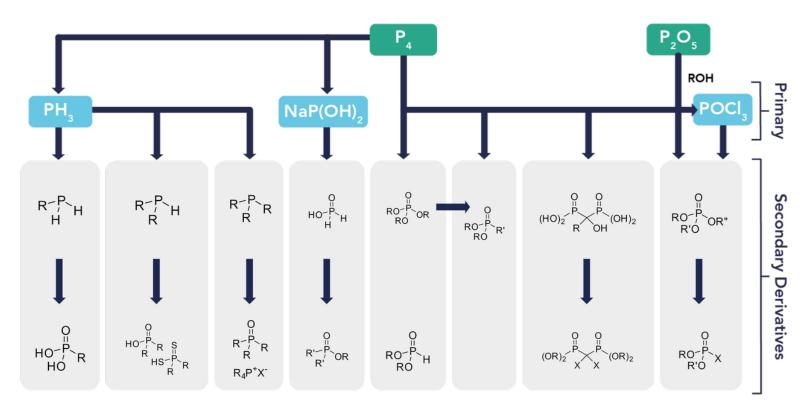


Phosphorus can be chemically converted into countless structures, and the predictability of structure property relationships is what makes it so versatile!



## Phosphorus Specialties Product Platform

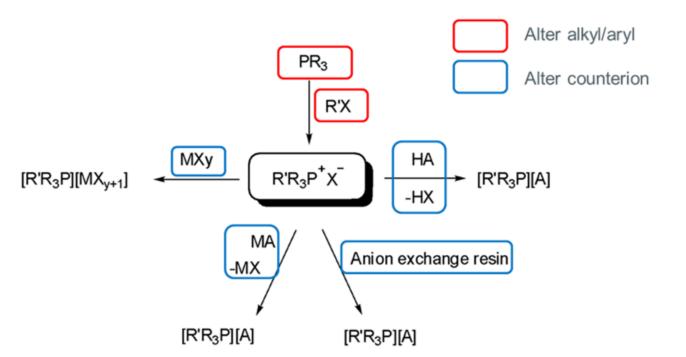






# Synthesis of Phosphorus Compounds





## Alterations can change:

- Solubility
- Viscosity
- Acidity
- Conductivity (T, E)
- Liquid range
- Miscibility
- Ionic Nature
- Melting point
- Many more!



# Viscosity



- Viscosity effects transit properties, including conductivity, diffusion and charge/mass transfer rates
- Phosphine longer chain, higher MW increased viscosity
- Lowest viscosity ILs have small anions with diffuse negative charge (unlikely to hydrogen bond), low ion pairing

## **Applications Impacted**

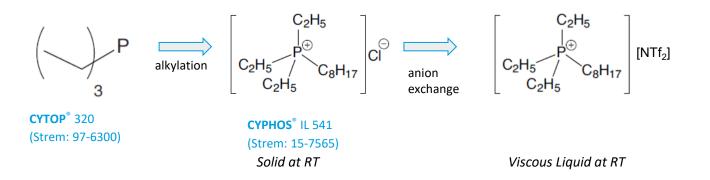
- **Electrochemical Applications**
- Battery
- Supercaps
- PTC
- Process Solvents
- Magnetic fluids



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Ionic Conductivity is related to viscosity - low viscosity leads to higher ionic conductivity



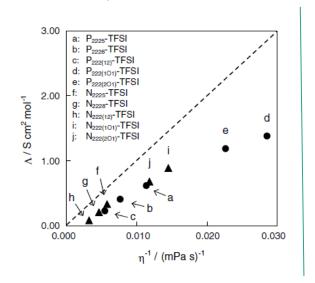
<sup>1.</sup> MacFarlane, D. et al. Aust. J. Chem. 2004, 57, 113

<sup>2.</sup> Tsunashima, K. et al. Electrochem. Commun. 2007, 9, 2353

# **Tailoring Viscosity**

Alkyl chain length and EDG/EWG effect viscosity

IL	Viscosity (mPa s)		
[P2225][NTf <sub>2</sub> ]	88		
[P2228][NTf <sub>2</sub> ]	129		
[P22212][NTf <sub>2</sub> ]	180		
[P222(1O1)][NTf <sub>2</sub> ]	35		
[P222(2O1)][NTf <sub>2</sub> ]	44		



Electrostatic interaction between cation/ anion is weakened (methoxy),
 which results in reducing both the viscosity and the melting point of the ILs



<sup>2.</sup> Tsunashima, K. et al. Electrochem. Commun. 2007, 9, 2353



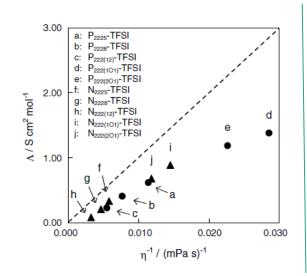


<sup>3.</sup> MacFarlane, D. et al. Science, 2021, 372, 1187-1191

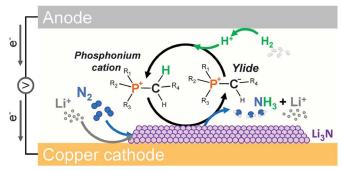
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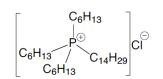






Conversion of N<sub>2</sub> to NH<sub>3</sub> Mass transport critical!

Electrostatic interaction between cation/ anion is weakened (methoxy),
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**CYPHOS**® IL 101 (Strem: 15-6382)



<sup>1.</sup> MacFarlane, D. et al. Aust. J. Chem. 2004, 57, 113

<sup>2.</sup> Tsunashima, K. et al. Electrochem. Commun. 2007, 9, 2353

<sup>3.</sup> MacFarlane, D. et al. Science, 2021, 372, 1187-1191

## Thermal Conductivity

- Thermal conductivity ( $\kappa$ ) is a material's basic property that is used to characterize its heat conducting capability.
  - High-κ materials (heat dissipating), low-κ (thermal insulation)
  - Increase efficiency of a product, save energy and money
- Phosphonium ionic liquids are thermally conductive materials and can add this property to liquids as an additive



## **Applications Impacted**

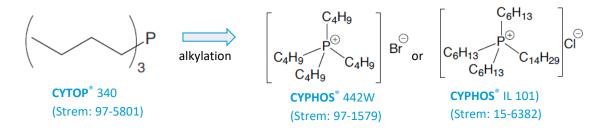
- Lubricants
- Greases
- Heat transfer fluids
- Batteries (EV)

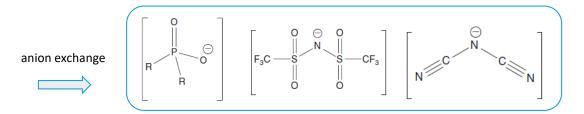




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## **Applications Impacted**

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<sup>1.</sup> Chen, Q.-L.; Wu, K.-J.; He, C.-H. *Ind. Eng. Chem. Res.* **2014**, *53*, 7224-7232

<sup>2.</sup> Ayatollahi, S. et al. Fluid Phase Equilibria, 2013, 354, 199-206

## Thermal Conductivity - ILs add Conductivity to Liquids

- Increasing the alkyl chain length of the cation causes a decrease in thermal conductivity
  - Anion more complex: factor of size, electrostatic interaction



0.238 W/(m · K)



• Conductivity decreases with temperature increase; Lower viscosity = higher conductivity

1. Chen, Q.-L.; Wu, K.-J.; He, C.-H. *Ind. Eng. Chem. Res.* **2014**, *53*, 7224-7232

**CYPHOS**® IL 101

(Strem: 15-6382)

C<sub>6</sub>H<sub>13</sub>

2. Tomida, D. Impact of Thermal Conductivity on Energy Technologies, 2018



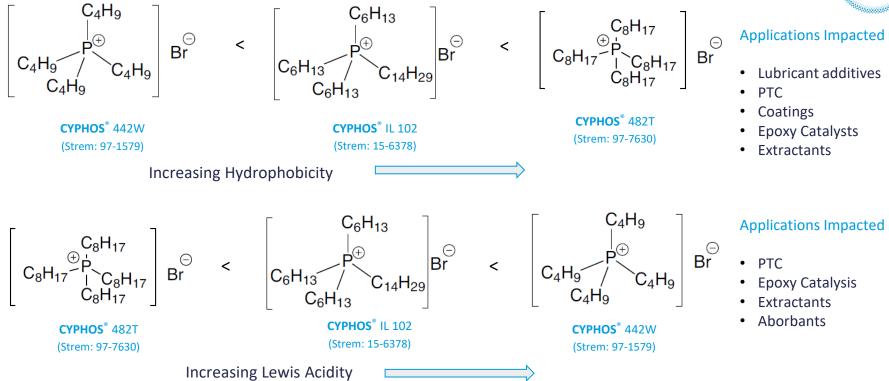
Anion exchange of basic

Systems leads to significant

alterations of thermal

# Hydrophobicity and Lewis Acidity



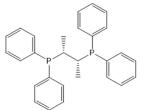


# Phosphorus in Catalysis

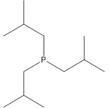


- The reactivity of a catalyst is dependent on the ligand environment of the metal.
- Phosphorus ligands offer structural and stereochemical diversity and allow for the tunability of the catalyst via modification of the ligand.

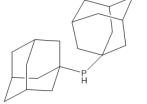
(R,R)-Me-DUPHOS (Strem: 97-0096)



RhodaPhos® CP100R (Strem: 97-0165)



**CYTOP® 341** (Strem: 97-5750)



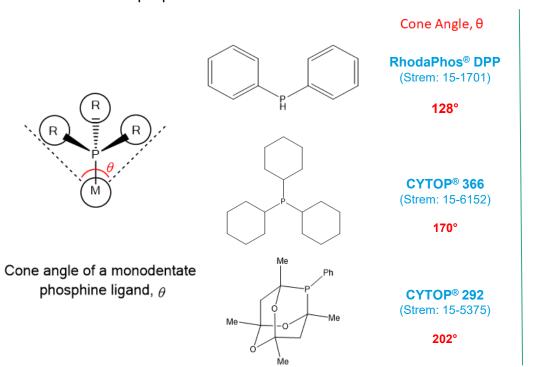
**CYTOP® 216** (Strem: 97-1310)

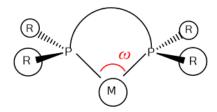


# Versatility of Phosphine Ligands



The cone or bite angle depending on if your ligand is monodentate or bidentate has a profound effect on the steric and electronic properties of the metal centre.





Bite angle of a bidentate phosphine ligand, ω

Bite Angle, ω

CP100R (Strem: 97-0165) 81° Me-DUPHOS (Strem: 97-0096) 83° Xantphos (Strem: 15-1242) 107°



# Versatility of Phosphine Ligands - Example

**BINAPO** 



In this example, a larger bridge between the two donor atoms, improved enantioselectivity.



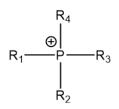
# Phosphorus in Flame Retardants



- Can be chemically bound in the material or used as an additive
- Liquid or Solid FR available
- Halogen-free systems

## **Phosphate**

## **Phosphonium**



## **Phosphonate**

$$O \longrightarrow P$$
 $O \longrightarrow R_3$ 
 $R_1 \longrightarrow O \longrightarrow R_2$ 

## **FR Product lines**

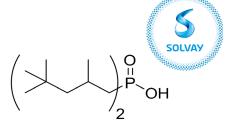
**PROBAN®** 

AMGARD®



# P Chemistry in Surface Engineering

- Flexible chemistry to manufacture a wide range of surface active materials;
- Phosphorus chemicals interact with a wide range of surfaces:
- Ability to chemically modify surfaces;
- Mono-molecular layers;
- Self assembly properties;
- Multiple process technologies allowing implementation at industrial scale developed;
- High thermal and hydrolytic stability (cf. organophosphates).



CYTOP® 501

(Strem: 15-7555)

**RHODAFAC® LPA 100P** 

(Strem: 97-1001)

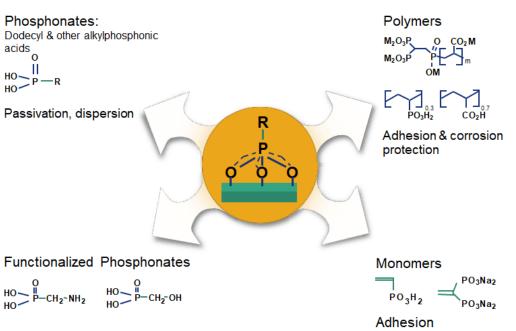
**RHODAPHOS® TEPA** 



# Functionalities in Surface Engineering



- Terminal functions give new properties to the surface:
  - Hydrophobic / hydrophilic;
  - Lubricant;
  - Anti-corrosive;
  - Self-cleaning;
- Advantages of monolayers:
  - Low volume of treatment required (1mg per 1m<sup>2</sup> of surface);
  - Straightforward process;
  - Long-lasting treatment.





# **Hydrophobicity - Contact Angle**



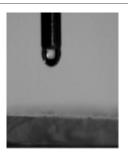
Treatment	None	C7 phosphonic acid	C8 phosphonic acid	C12 phosphonic acid (RHODAFAC® LPA 100P (Strem: 97-1001))	Phosphonylated mineral oil
Contact Angle	0°	127°	132°	134°	00









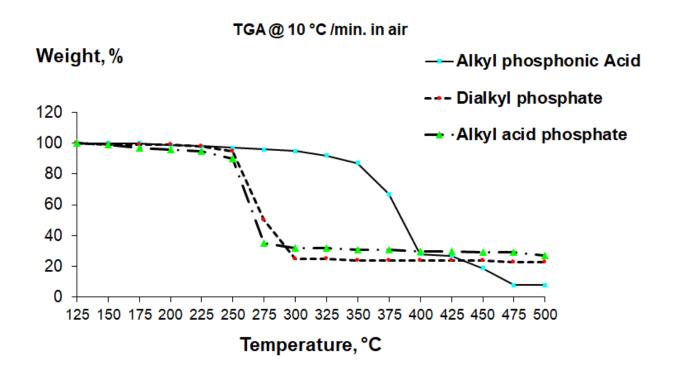


- TiO<sub>2</sub> coated by alkyl phosphonic acids shows obvious hydrophobicity (2 microL DI water);
- TiO<sub>2</sub> coated by phosphonylated mineral oil is not effective if MW is too high then coating is not effective.



# Thermal Stability

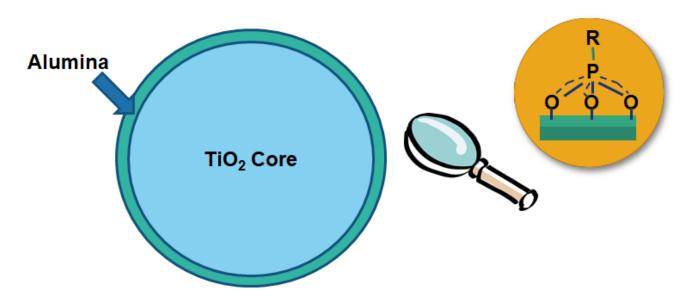






# Stabilization of Inorganic Particles





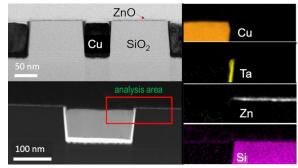
- Additives are used to stabilize nanoparticles, such as quantum dots and TiO<sub>2</sub>, in resin matrices;
- Polar head group for attaches to inorganic surface and long hydrocarbon chains promote favourable polymer interaction.

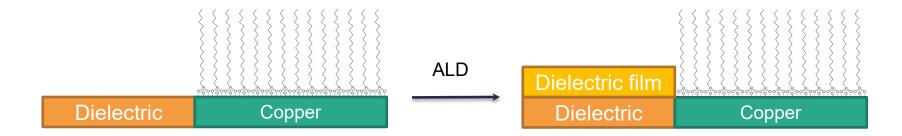


### Surface Protection & Adhesion



- Phosphorus materials can be used to selectively protect either dielectric or metal surfaces in semiconductor chip applications;
- For example, copper surfaces can be protected with ODPA allowing ALD or MLD to be performed selectively on the dielectric;
- In PCBs similar phosphorus derivatives are utilized as surface modifiers to improve adhesion under high heat stress of the copper foil to the resin / polymer / laminate in flexible CCLs.







## P in Electronics - Dopants





- Dopants for semiconductors:
  - High purity PH<sub>3</sub> gas as (n-type) dopant for various types of semiconductors (silicon, III-V compound semiconductor and TFT display manufacturing);
  - Alternative liquid dopants (improved safety);
- These semiconductors are used in a range of devices such as LEDs, logic, memory chips, photovoltaics and other display devices.

**CYTOP**® **142** (Strem: 97-0966)

**CYTOP**® **250** (Strem: 97-1003)

**CYTOP**<sup>®</sup> **266** (Strem: 97-1120)



## P in Electronics - Quantum Dots



- Quantum Dots are nanocrystals:
  - Diameters 2-10nm (10-50 atoms);
  - Composed of semiconducting materials (CdSe, InP, ZnTe for example);
  - Extremely high surface area to volume ratios;
  - Exhibit quantum mechanical properties;
- Applications derived from their ability to fluoresce with different colors depending on the size of the QD;





## P in Electronics - Quantum Dot Manufacture



- Applications for quantum dots in displays, transistors, solar cells, LEDs, medical imaging and in quantum computing;
- QDs are made by combining the semiconductor precursors, solvents and surfactants together at high temperature:
  - A number of phosphines are used in the manufacture of QDs such as TOP, TOPO, TOPS, TOPSe, DPP and TTMSP.



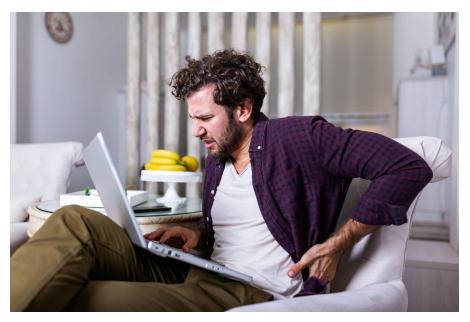


## Phosphorus in the Human Body



- Structural
  - Bones
  - Teeth
  - DNA
  - RNA
  - Phospholipids
  - ATP
  - Proteins and sugars
- Roles
  - Regulation of gene transcription
  - Activation of enzymes
  - Maintenance of extracellular pH
  - Intracellular energy storage

1-1.4% of fat free body mass!



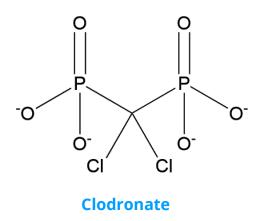


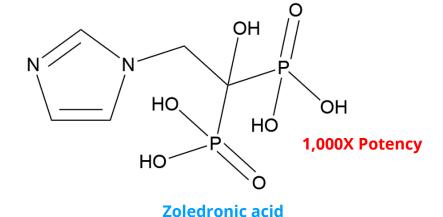
## **Bones - Osteoporosis Treatments**





- Main class of osteoporosis medications are bisphosphonates
- Reduce resorption of hydroxyapatite by:
  - Slowing formation of osteoclasts (inhibiting hydroxyapatite breakdown)
  - Inhibiting the activity of farnesyl pyrophosphate synthase (second generation nitrogen-containing bisphosphonates)



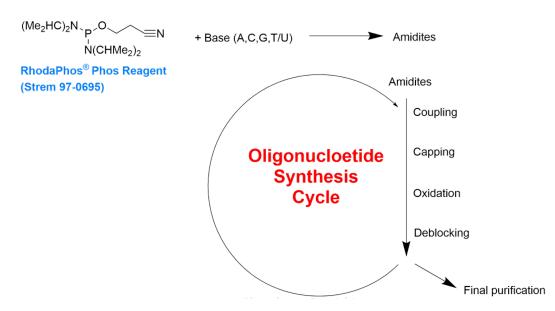




# DNA/RNA/proteins/phospholipids



- A modern approach to disease treatment involves synthetic oligonucleotides short single or double-stranded DNA and RNA molecules;
- Oligos are built in a stepwise fashion from bases and phosphorus reagents;
- Antisense and RNA-interfering oligos work through modulating gene and protein expression;
- Aptamer oligos act as 'chemical antibodies' to modulate the functions of proteins and other macromolecules.



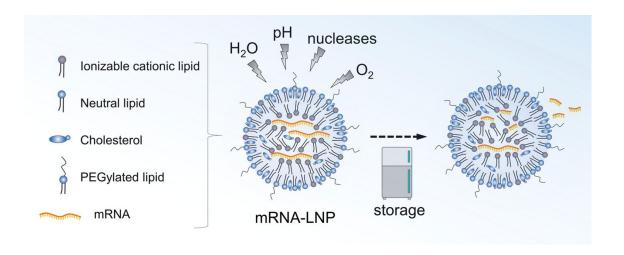




## mRNA & phospholipids



- Delivery of RNA/DNA based therapeutics is a major challenge in their development;
- mRNA vaccines break down very quickly in vivo;
- One approach is to encapsulate the mRNA in lipid nanoparticles;
- The mRNA-LNP vaccines also act as self-adjuvants;
- Approach used by BioNTech/Pfizer & Moderna for their COVID-19 vaccines.







### Disulfide Bond Reduction

# Solvay

#### **Gene Sequencing**

- DNA is fragmented, amplified, attached to a DNA sequence primer & affixed as a high-density array of spots on a glass chip.
- Array is subjected to reagents containing DNA bases modified with a dye and an end cap.

#### **CYTOP® 208** (Strem: 97-1002)

- tris(3-hydroxypropyl)phosphine ("THPP");
- CAS No. 4706-17-6;
- Quicker, more complete cleavage, no odor, stable over wide pH range

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Entry	Disulfide, 1a-1g	Thiol, 2a–2g	Reducing agent		
			THPP	TCEP	DTT
1	S S N 1a	HS O 2a	99°	77°	35°, 85 <sup>d</sup>
2	HO S-S OH <b>1b</b>	HO SH 2b	82 <sup>e</sup>	25 <sup>e</sup>	30e
3	HO OH	HS—OH—SH 2c	94 <sup>r</sup>	90 <sup>f</sup>	-



## Phosphorylation in Prodrug Synthesis

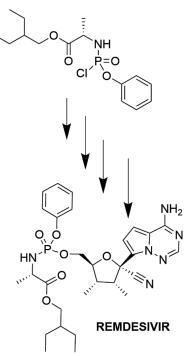
# SOLVAY

#### **Antiviral Remdesivir**

- Phenyl dichlorophosphate
- PDCP
- CAS No. 770-12-7



- Monophosphate nucleosides are important precursors to triphosphate metabolites as the first phosphorylation is often rate limiting;
- PDCP is often used as a phosphorylating agent for alcohols and amines.



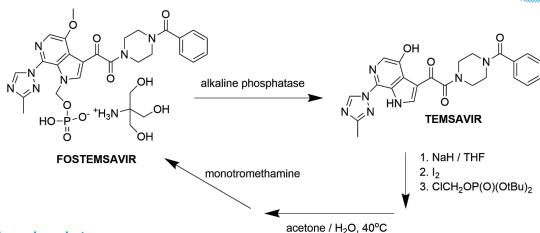


## Phosphorylation in Prodrug Synthesis

# SOLVAY

#### HIV-1 attachment inhibitor

- Temsavir has limited exposure at higher doses due to dissolution and / or solubility / absorption issues;
- Fostemsavir developed as prodrug to address this;
- Recently FDA & EMA approved for treatment of HIV in adults with few treatment options available.



- Di-t-butyl potassium phosphate
- DTBPOK
- CAS No. 33494-80-3

(1) Wang, T. et al. J. Med. Chem., 2018, 61, 6308-6327





## Global Manufacturing and R&I Support















1g - 1Kg

Laboratory investigations

100g - 25Kg

Manufacture of products in laboratory

5Kg - 10 tonnes

Pilot plant manufacture and data collection

10s - 1000s tonnes

Full scale manufacture on chemical plant

#### Facilities:

- Kilo scale prep labs
- Lab scale pressure PH3 autoclaves
- Fully inerted distillation facility
- Pilot plant
- State-of-the-art analytical equipment

#### Support for business line:

- Computational chemistry labs: DFT, MD, CFD
- Lab of the future "LOF"
- Corporate R&I





and derivatives platform



## **Custom Solutions - Critical to Sustainability**



- Each company has its own feedstocks, equipment, objectives, etc.
- Many situations require a custom solutions our specialty
- Solvay has over 60 years of experience providing customer-specific solutions
- We have the ability to partner with users and developers to create sustainable, cost-effective and value-added solutions
- Let's talk about your next targets!



### What Does **Your** Future Hold?



## Thank You

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#### Multi-kilo Samples available in the Strem Catalog



#### **Known Quality**

Quality is what sets us apart from the rest. Most of our products are high purity, typically 99%, with some at 99.9999% metals purity.



#### **Broad Portfolio**

~6,000 Specialty Chemicals with an emphasis on metals, inorganics, organometallics, and nanomaterials for R&D and commercial applications.



#### **Reliable Global Supply**

Expanded global supply network builds on world class service and reliability.

#### Industrial Scale from Solvay



#### Innovation:

160 years of know-how and innovation in phosphorus chemistry



#### Partnership:

We work closely with customers to translate their needs into concrete solutions



# Differentiated products and technologies:

We offer a wide range of phosphorusbased chemistry to meet precise application requirements