

CYTEC



CYANEX[®] 923 Extractant

Solvent Extraction Reagent

- Recovery of uranium from wet process phosphoric acid
- Cesium recovery
- Recovery of rhenium
- Acetic acid recovery from effluent streams
- Phenol extraction

2 | Table of Contents

INTRODUCTION

| | |
|---|---|
| Composition | 3 |
| Typical Properties | 3 |
| Suitability of Construction Materials | 4 |

POTENTIAL APPLICATIONS

ORGANIC SOLUTES

| | |
|------------------------------------|---|
| Carboxylic Acid Recovery | 5 |
| Phenol Recovery | 5 |
| Ethanol Extraction | 6 |

INORGANIC SOLUTES

| | |
|---|----|
| Impurity Removal From Copper Electrolytes | 7 |
| Uranium Extraction From Wet Process Phosphoric Acid | 9 |
| Niobium-Tantalum Separation | 10 |
| Cadmium Removal From Phosphoric Acid | 12 |

ANALYTICAL METHODS

| | |
|--|----|
| ANALYSIS IN ORGANIC SOLVENTS | 13 |
| ANALYSIS IN AQUEOUS SOLUTION | 14 |
| DETERMINATION OF WATER | 14 |

| | |
|---|-----------|
| TECHNICAL PAPERS AND PATENTS | 15 |
|---|-----------|

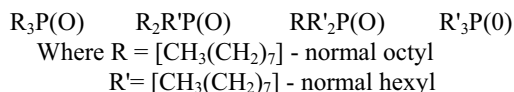
| | |
|------------------------------------|-----------|
| HEALTH AND SAFETY | 16 |
|------------------------------------|-----------|

CYANEX® 923 extractant is a liquid phosphine oxide which has potential applications in the solvent extraction recovery of both organic and inorganic solutes from aqueous solution, e.g. carboxylic acids from effluent streams and the removal of arsenic impurities from copper electrolytes.

The major advantage of CYANEX 923 extractant over similar extraction reagents, e.g. TOPO (trioctylphosphine oxide), is that it is completely miscible with all common hydrocarbon diluents even at low ambient temperatures. The major benefit of high solubility lies in the ability to prepare concentrated, stable solvents which can recover solutes (e.g. acetic acid) that are normally only weakly extracted by this type of reagent.

Composition

CYANEX 923 extractant is a mixture of four trialkylphosphine oxides as follows:



Average Molecular Weight = 348 (approximately)

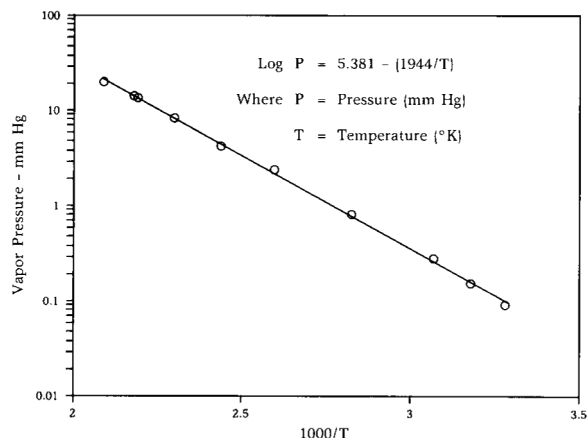
Typical Properties

| | | |
|--------------------------------------|---|--|
| Trialkylphosphine oxides | : | 93% |
| Appearance | : | Colorless mobile liquid |
| Specific Gravity | : | 0.88 at 25°C |
| Freezing Point | : | -5 to 0°C |
| Viscosity | : | 40.0 centipoise at 25°C 13.7 centipoise at 50°C |
| Flashpoint (Closed Cup Setaflash) | : | 182°C |
| Autoignition Temperature | : | 281°C |
| Vapor Pressure* | : | 0.09 mm. Hg at 31°C |
| Boiling Point | : | 310°C at 50 mm Hg |
| Solubility in Water | : | > 10 mg/l |
| CYANEX 923 extractant | : | 8 w/o |

| | | |
|----------------------|---------|---------------------------|
| Surface Tension | @ 25°C | 9.0 dynes/cm |
| | @ 100°C | 7.5 dynes/cm |
| | @ 150°C | 5.2 dynes/cm |
| Viscosity Kinematic | @ 25°C | 51.6 cSt |
| | @ 50°C | 18.9 cSt |
| | @ 100°C | 4.2 cSt |
| Specific Heat | @ 25°C | 0.45 cal/gm/°C |
| | @ 50°C | 0.47 cal/gm/°C |
| | @ 100°C | 0.51 Cal/gm/°C |
| Thermal Conductivity | @ 25°C | 0.000302 cal/cm/sec/°C |
| | @ 120°C | 0.000288 cal/cm/sec/°C |
| | @ 200°C | 0.000274 cal/cm/sec/°C |

* Shown as function of temperature in Figure 1

FIG. 1 — EFFECT OF TEMPERATURE ON VAPOR PRESSURE



4 Introduction

Suitability of Construction Materials

Samples of the following plastics and rubbers (in the form of tubing) were immersed for 200 hours at 50°C in glass vessels containing CYANEX 923 extractant.

The results are summarized below:

| Material | Remarks |
|---------------------------------|--|
| Butyl Rubber | Unsuitable. Rapid swelling and softening. |
| Teflon Fluorocarbon Film* | Suitable. No detectable effect. |
| Polypropylene | Suitable. No detectable effect. |
| Natural & Black Latex Rubber | Unsuitable. Complete dissolution in less than 192 hours. |
| PVC (Laboratory Grade) | Short-term suitability. Loss of plasticity in less than 192 hours. |
| PVC (Solvent Grade) | Suitable. Only a slight increase in dimension observed. |
| Red Gum Rubber | Unsuitable: Rapid swelling and softening. |
| Viton Fluoroelastometer* | Suitable. No detectable effect. |
| Silicone | Unsuitable. Disintegrated after 56 hours. |

Samples of the following metals in the form of coupons (approximate dimensions 50 mm x 20 mm. x 3 mm) were immersed for 1000 hours at 50°C in glass vessels containing CYANEX 923 extractant. The following observations were made.

| Metal | Remarks |
|-----------------------|--------------------------|
| Mild Steel | No detectable corrosion. |
| Stainless Steel (316) | No detectable corrosion. |
| Stainless Steel (304) | No detectable corrosion. |
| Aluminum | No detectable corrosion. |

**Product of E.L DuPont de Nemours & Co.*

ORGANIC SOLUTES

Carboxylic Acid Recovery

Processes in petrochemical plants, wood pulping mills, and other chemical facilities often generate aqueous effluent streams containing carboxylic acids; particularly acetic acid. Typically, these acids are present in concentrations between 1 and 50 g/l.

A solvent extraction plant to recover acetic acid from an effluent stream has been operated successfully by Lenzing A.G. in Austria since 1983. Briefly, the process involves extracting acetic acid with a solvent containing TOPO and stripping the loaded solvent by distillation.

The advantage of using CYANEX 923 extractant in this application, as opposed to TOPO, lies in the ability to prepare a concentrated, low freezing point solvent.

This leads to lower staging requirements in extraction and virtually eliminates the problem of plant freeze-up during periods when the ambient temperature is low.

The potential for CYANEX 923 extractant in this application is illustrated by the acetic acid extraction isotherms shown in Figure 2. The isotherms were plotted from the data in Table 1.

FIG. 2 — ACETIC ACID EXTRACTION ISOTHERMS

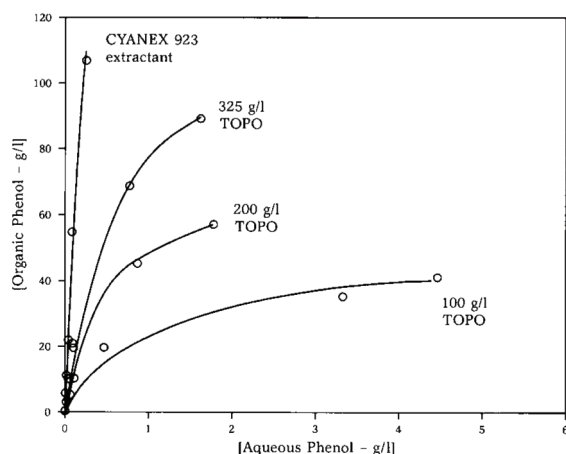


TABLE 1
Acetic Acid Recovery

| | | |
|--------------|---|---|
| Solvents | : | CYANEX 923 extractant undiluted) 150 g/l and 400 g/L TOPO in DPA diluent* |
| Aqueous | : | 10 g/l acetic acid (approx.) |
| Temperature | : | 50°C |
| Contact Time | : | 5 minutes |

Equilibrium Acetic Acid Concentration (g/l)

| A/O | 150 g/l TOPO | | 400 g/l TOPO | | CYANEX 923 extractant | |
|-----|--------------|------|--------------|------|-----------------------|------|
| | Org. | Aq. | Org. | Aq. | Org. | Aq. |
| 10 | - | - | - | - | 27.7 | 6.84 |
| 5 | - | - | - | - | 22.0 | 5.22 |
| 2 | 5.60 | 7.20 | 8.40 | 5.80 | 13.0 | 3.11 |
| 1 | 5.30 | 4.70 | 7.50 | 2.50 | 7.87 | 1.74 |
| 0.5 | 3.43 | 3.15 | 4.48 | 1.05 | 4.41 | 0.80 |
| 0.2 | 1.77 | 1.15 | 1.92 | 0.40 | - | - |
| 0.1 | 0.95 | 0.55 | 0.95 | 0.20 | - | - |

* DPA, a high boiling (330-379°C) diphenylalkene diluent, is a product of Conoco Chemicals Co. (a division of Conoco).

Phenol Recovery

Phenols, like carboxylic acids, are a common component of many aqueous effluents, e.g. waste streams produced during coal liquefaction, coal gasification (steel manufacture), and in the petrochemical industry.

Again, the potential benefit of recovering phenol by solvent extraction with CYANEX 923 extractant is the ability to construct plants with minimal staging requirements. Since phenol is strongly extracted by phosphine oxides, the advantages of CYANEX 923 extractant vs. TOPO are less marked than in the case of the more weakly extracted acetic acid. The major factor in choosing between the two in phenol systems will obviously depend upon the concentration of phenol in the effluent.

Phenol extractions isotherms are shown in Figure 3 and were plotted using the batch, shake-out data given in Table 2. Composition of the aqueous solution was chosen to approximate a real effluent. As with carboxylic acids, stripping is achieved by distillation.

Estimates indicate significant savings in capital and operating costs vs. the conventional Phenosolvan process.

6 Potential Applications

FIG. 3 — PHENOL EXTRACTION ISOTHERMS

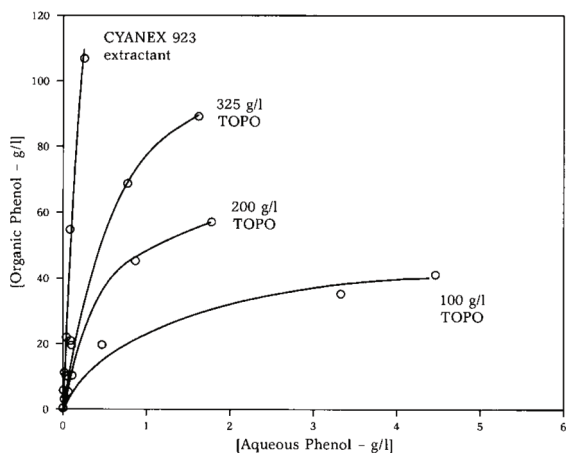


TABLE 2
Phenol Recovery

| | | |
|--------------|---|--|
| Solvents | : | CYANEX 923 extractant (undiluted) 100, 200 and 325 g/l TOPO in Nalkylene 500 diluent* |
| Aqueous | : | 10 g/l phenol (approx.) and 30 g/l Na ₂ SO ₄ . Initial pH = 5 (approx.) |
| Temperature | : | 50°C |
| Contact Time | : | 5 minutes |

Equilibrium Phenol Concentration (g/l)

| A/O | 100 g/l | | 200 g/l | | 325 g/l | | CYANEX 923 extractant | |
|------|---------|------|---------|------|---------|------|-----------------------|---------|
| | Org. | Aq. | Org. | Aq. | Org. | Aq. | Org. | Aq. |
| 10 | - | - | - | - | 88.8 | 1.65 | 107.2 | 0.28 |
| 7 | 40.0 | 4.48 | 56.6 | 1.79 | 68.2 | 0.79 | - | - |
| 5 | 34.3 | 3.34 | 45.0 | 0.87 | - | - | 54.6 | 0.089 |
| 2 | 19.4 | 0.47 | 19.6 | 0.10 | 20.9 | 0.08 | 21.0 | 0.028 |
| 1 | 10.1 | 0.10 | 9.84 | 0.04 | 10.5 | 0.04 | 11.0 | 0.013 |
| 0.5 | 5.07 | 0.05 | 4.93 | 0.02 | 5.25 | 0.03 | 5.50 | 0.005 |
| 0.25 | 2.54 | 0.02 | 2.46 | 0.01 | 2.63 | 0.02 | 2.75 | 0.002** |

* Nalkylene 500, a linear alkyl benzene diluent, is a product of Conoco Chemicals Co. (a division of Conoco.)

**Detection limit of the analytical method.

Ethanol Extraction

CYANEX 923 extractant exhibits a separation factor in ethanol/water solutions near the maximum useful limit for recovery from continuous fermentation broths, typically containing 5% ethanol. Higher values do not further reduce extractor size or energy required in the downstream distillation. This is illustrated in Figure 4 where separation factors for CYANEX 923 extractant and for other candidate extractants are shown in relation to the upper and lower limits. Extraction coefficients, and their effect on extractor size, are also plotted in Figure 4. The coefficient for

CYANEX 923 extractant is well into the flat part of the curve. This excess capacity can be exchanged for increased separation factor, if needed, by dilution with inert diluents.

The principle advantage of CYANEX 923 extractant lies in its very low solubility in water. This obviates or minimizes extra processing of raffinate that would be required by more soluble extractants. The solubilities in water of CYANEX 923 extractant and of other candidate ethanol extractants are compared in Table 3.

FIG. 4 — ETHANOL EXTRACTION

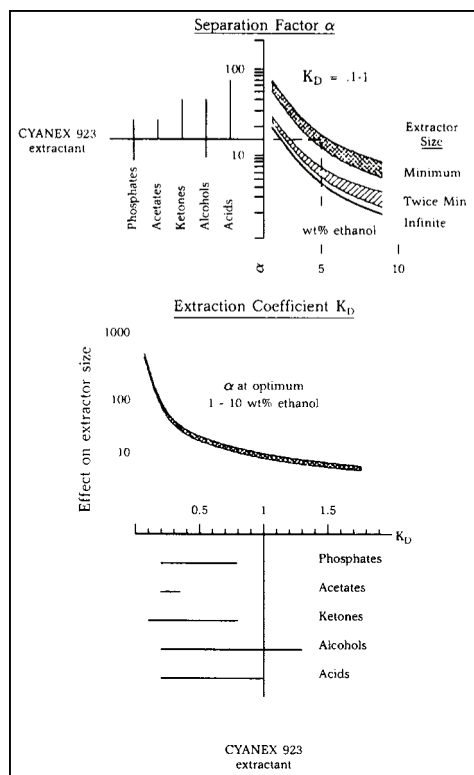


TABLE 3
Solubility in Water, WT%

| | Exptl ⁽¹⁾ | UNIFAC ⁽⁴⁾ |
|-------------------------------|----------------------|-----------------------|
| CYANEX 923 extractant | 0.001 ⁽²⁾ | |
| Phosphates | | |
| Tri-n-Butyl | 0.042 ⁽³⁾ | |
| Acetates | | |
| n-Butyl | 0.64 | |
| i-Butyl | 0.85 | |
| Ketones | | |
| Methyl Isobutyl | 1.9 | |
| Diisobutyl | 0.083 | |
| Isophorone | | 0.19 |
| Alcohols | | |
| 3-Phenyl-1-Propanol | | 0.15 |
| 2-Ethyl-1-Butanol | | 0.88 |
| 3-Methyl-3-Pentanol | 4.3 | |
| 4-Methyl-2-Pentanol | 1.6 | |
| 3-Ethyl-3-Pentanol | 1.7 | |
| 2,4-Dimethyl-3-Pentanol | 0.7 | |
| 1-Octanol | 0.051 | |
| 2,2-Dimethyl-3-Octanol | | 0.017 |
| 3,7-Dimethyl-3-Octanol | | 0.017 |
| 1-Nonanol | 0.013 | |
| 1-Decanol | 0.0037 | |
| 4-Decanol | | 0.016 |
| 1-Dodecanol | 0.00023 | |
| 1-Tridecanol | | 0.00072 |
| Acids | | |
| 2-Ethyl-4-Methyl Pentanoic | | 0.24 |
| n-Hexanoic | 1.1 | |
| 2-Ethyl Hexanoic | | 0.24 |
| n-Octanoic | | 0.24 |
| Neodecanoic | | 0.032 |

(1) J.M. Sorenson and W. Arlt, "Liquid-Liquid Equilibrium Data Collection," DECHEMA, Vol. V, Part 1 (1979)

(2) This work

(3) W.N. Schulz and J.P. Navratil, "Science and Technology of Tributyl Phosphate," CRC Press (1982)

(4) A. Fredenslund, et. al., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AICHE Journal* 21, No. 6, (1975), pp. 1086-1099.

INORGANIC SOLUTES

Impurity Removal from Copper Electrolytes

Briefly, the advantages of removing arsenic, antimony and bismuth impurities from copper electrolytes by so vent extraction rather than conventional processes consist of improvements in current efficiency, the quality of electrolytic copper, and in the productivity of the tankhouse. Minimizing the formation of arsine gas is also an important consideration.

Data on the extraction of arsenic, antimony and bismuth from a synthetic, nickeliferous copper electrolyte are given in Table 4. The corresponding arsenic and antimony extraction isotherms are shown in Figure 5. McCabe-Thiele interpolations indicated a reduction in the electrolyte arsenic concentration from 6 g/l to 1 g/l in two theoretical stages at O/A = 4. Under these conditions, the data indicated quantitative extraction of bismuth, 30-40% extraction of the antimony and a solvent loaded to 10-20 g/l H₂SO₄. High selectivity against copper and nickel extraction was observed. Copper loading in the solvents varied from 3 to 5 mg/l while no nickel extraction was observed.

Scrubbing sulfuric acid from the loaded solvent was readily achieved with water. The data in Table 5 and Figure 6 implied essentially quantitative removal in 3 theoretical stages at O/A=8 to produce a scrub liquor containing 130 g/l H₂SO₄ for recycle. The feasibility of a selective metal/acid scrub was also indicated.

Water proved to be an effective strip feed at a lower O/A ratio as shown by the data in Table 6 and the arsenic stripping isotherm plotted in Figure 7

Interpolations from the isotherm showed complete arsenic stripping in 5 stages at O/A = 2. Quantitative antimony stripping was estimated under these conditions while approximately 0.07 g/l bismuth remained loaded on the solvent.

Solubility losses of the extractant in this system varied from 1 mg/l in the electrolyte to 10 mg/l in the strip liquor.

8 Potential Applications

TABLE 4
Arsenic, Antimony and Bismuth
Extraction Isotherms

| | |
|--------------|--|
| Solvent | : 50 v/o CYANEX 923 extractant in Exxsol D-80 diluent* |
| Aqueous | : 31.3 g/l Cu, 8.4 g/l Ni (as sulfates), 7.30 g/l As, 0.35 g/l Sb, 1.10 g/l Bi, 167.4 g/l H ₂ SO ₄ |
| Contact Time | : 5 minutes |
| Temperature | : 50°C |

Equilibrium Metal Concentration (g/l)

| O/A | Arsenic | | Antimony | |
|-----|---------|---------|----------|---------|
| | Organic | Aqueous | Organic | Aqueous |
| 1 | 1.60 | 5.70 | 0.15 | 0.20 |
| 2 | 1.43 | 4.45 | 0.08 | 0.20 |
| 5 | 1.04 | 2.10 | 0.03 | 0.22 |
| 10 | 0.63 | 1.03 | 0.01 | 0.24 |

Bismuth quantitatively extracted at all O/A ratios

TABLE 5
Sulfuric Acid Scrubbing Using Water

| | |
|--------------|---|
| Solvent | : 50 v/o CYANEX 923 extractant in Exxsol D-80 diluent; loaded to 16.4 g/l H ₂ SO ₄ and 1.90 g/l As, 0.14 g/l Sb and 1.10 g/l Bi |
| Scrub Feed | : Distilled Water |
| Contact Time | : 5 minutes |
| Temperature | : 50°C |

Equilibrium H₂SO₄ Concentration

| O/A | Organic | Aqueous |
|-----|---------|---------|
| 0.5 | 0 | 9.1 |
| 1 | 0 | 17.4 |
| 5 | 0.7 | 78.4 |
| 10 | 5.4 | 110.0 |
| 20 | 9.9 | 130.2 |

* A product of Exxon Co., U. S. A.

TABLE 6
Arsenic, Antimony and Bismuth Stripping Isotherms

| | |
|--------------|---|
| Solvent | : 50 v/o CYANEX 923 extractant in Exxsol D-80 diluent; loaded to 1.38 g/l As, 0.061 g/l Sb, 0.19 g/l Bi |
| Strip Feed | : Distilled Water |
| Contact Time | : 5 minutes |
| Temperature | : 50°C |

Equilibrium Metal Concentration g/l

| O/A | As | | Sb | | Bi | |
|-----|---------|---------|---------|---------|---------|---------|
| | Organic | Aqueous | Organic | Aqueous | Organic | Aqueous |
| 0.5 | 0 | 0.71 | 0 | 0.033 | 0.01 | 0.09 |
| 1 | 0.28 | 1.10 | 0 | 0.061 | 0.02 | 0.17 |
| 2 | 0.53 | 1.71 | 0 | 0.14 | 0.08 | 0.22 |
| 5 | 0.89 | 2.45 | 0.009 | 0.26 | 0.14 | 0.26 |
| 10 | 1.08 | 3.05 | 0.029 | 0.32 | - | - |

FIG. 5 – ARSENIC AND ANTIMONY
EXTRACTION ISOTHERMS

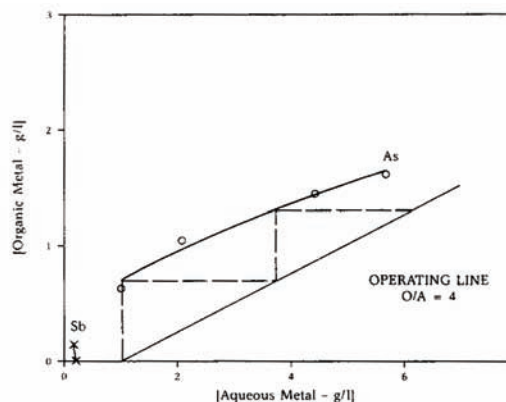


FIG. 6 – SULFURIC ACID SCRUBBING

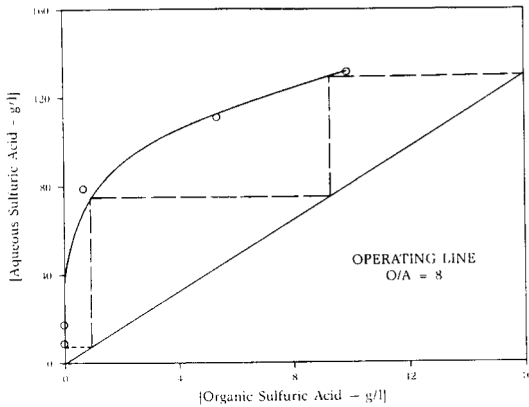
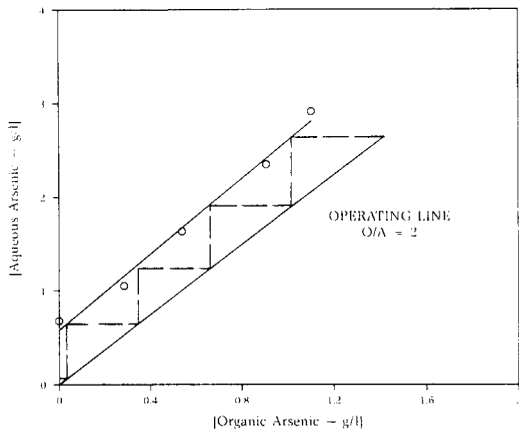


FIG. 7 – ARSENIC STRIPPING ISOTHERM



Uranium Extraction From Wet Process Phosphoric Acid

The conventional process for recovering uranium from wet process phosphoric acid involves extraction with a synergic mixture of D2EHPA and TOPO. CYANEX 923 extractant is a potential substitute for TOPO in this process and offers a materials handling advantage in that it is a liquid, while TOPO is a solid at normal temperatures (melting point approximately 50°C) and must be melted for ready removal from its container.

The feasibility of using CYANEX 923 extractant in this application is illustrated by the results of shake-out tests which are presented in Table 7 and Figure 8.

TABLE 7
Uranium Recovery from Wet-Process Phosphoric Acid Using Synergic Mixtures of Phosphine Oxides and D2EHPA

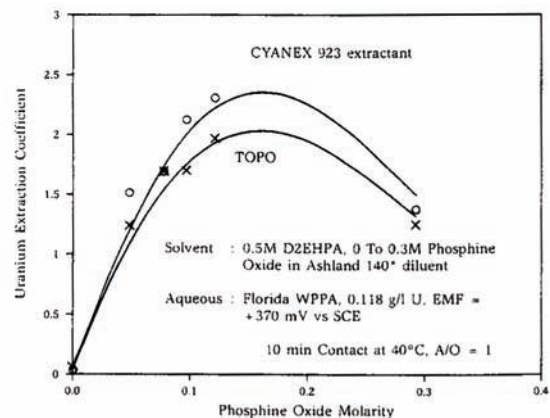
| | |
|--------------|---|
| Solvent | : All 0.5M D2EHPA in Ashland 140 diluent*. Varying in Phosphine Oxide concentration from 0 to 0.3M. |
| Aqueous | : Florida WPPA 0.118 g/l U, oxidized with H ₂ O ₂ to + 370 mV (vs.SCE). |
| A/O | : 1 |
| Temperature | : 40°C |
| Contact Time | : 10 minutes |

$$E_{A}^{O} = \frac{\text{Uranium Concentration In Solvent}}{\text{Uranium Concentration In Aqueous}} \text{ = At Equilibrium}$$

| Phosphine Oxide Molarity | TOPO | CYANEX 923 Extractant |
|--------------------------|------|-----------------------|
| 0 | 0.08 | 0.05 |
| 0.05 | 1.26 | 1.54 |
| 0.08 | 1.73 | 1.72 |
| 0.10 | 1.73 | 2.16 |
| 0.125 | 2.00 | 2.34 |
| 0.3 | 1.26 | 1.39 |

*Ashland 140, an aliphatic diluent, is a product of Ashland Chemical Co.

FIG. 8 – EFFECT OF PHOSPHINE OXIDE MOLARITY ON URANIUM EXTRACTION FROM WPPA



10 Potential Applications

Niobium - Tantalum Separation

Niobium - tantalum separation is normally effected using MIBK. The disadvantage here is the high aqueous solubility of the ketone (approximately 20 g/l) and the consequent need to treat the raffinate for recovery of the extractant. Recent work¹ has shown that TOPO has utility in niobium - tantalum separation and is reported to produce higher purity niobium oxide than MIBK.

The advantage of using CYANEX 923 extractant in place of TOPO is again related to its liquid state and higher organic solubility.

A strong diluent effect was observed in preliminary experiments on niobium extraction. This is illustrated by the results of extraction isotherms given in Table 8 and plotted in Figure 9. Aromatic 150* proved to be the superior diluent in comparison to both Aromatic 100* and Exxsol D-80.

The process for niobium - tantalum separation, as with MIBK and TOPO, consists of extracting both metals followed by a selective strip; first of niobium and then of tantalum. This is illustrated in Table 9 and Figure 10 where selective stripping of niobium from a niobium - tantalum loaded solvent was observed using a strip feed containing 0.1 N NH_4OH and 1% NH_4F . Tantalum was subsequently stripped using a more basic strip feed of 0.4 N NH_4OH and 4% NH_4F .

*A product of Exxon Co., U.S.A.

TABLE 8

The Effect of Diluent Type on Niobium Extraction

| | | |
|--------------|---|--|
| Solvent | : | 277 g/l (0.8M) CYANEX 923 extractant in the appropriate diluent. |
| Diluents | : | Exxsol D-80, Aromatic 100 and Aromatic 150 |
| Aqueous | : | 88.5 or 91.4 g/l Nb, 4N HF, 8N H_2SO_4 |
| Temperature | : | 24°C |
| Contact Time | : | 5 minutes |

Equilibrium Nb Concentration (g/l)

| O/A | EXXSOL D-80 | | Aromatic 100 | | Aromatic 150 | |
|-----|-------------|---------|--------------|---------|--------------|---------|
| | Organic | Aqueous | Organic | Aqueous | Organic | Aqueous |
| 2 | 43.8 | 66.6 | 38.7 | 72.0 | 61.3 | 60.7 |
| 1 | 36.6 | 51.9 | 39.7 | 51.7 | 61.9 | 29.5 |
| 0.5 | 36.6 | 15.3 | 36.5 | 18.5 | 44.8 | 1.86 |
| 0.3 | - | - | - | - | 27.2 | 0.73 |
| 0.2 | 17.4 | 1.53 | 18.2 | 0.30 | 18.2 | 0.56 |
| | 8.84 | 0.07 | 9.12 | 0.13 | 9.13 | 0.05 |

FIG. 9 — EFFECT OF DILUENT TYPE ON NIOBIUM EXTRACTION

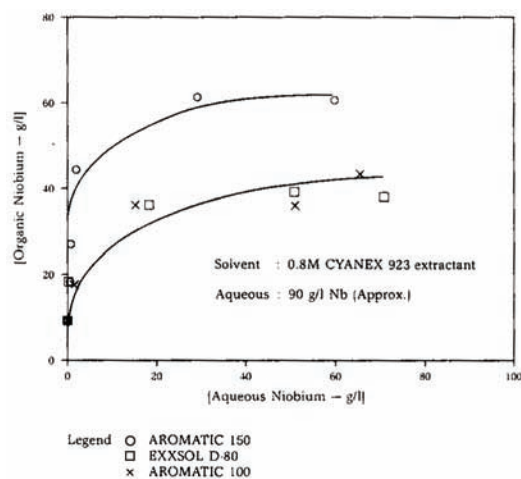


TABLE 9
Niobium Stripping From a Solvent Containing Niobium and Tantalum

Solvent : 277 g/l (0.8M) CYANEX 923 extractant in Aromatic 150 diluent. Loaded to 22.4 g/l Nb and 3.61 g/l Ta.
 Strip Feed : 0.1N NH₄OH, 1% NH₄F
 Contact Time : 5 minutes
 Temperature : 24°C

| Equilibrium Nb Concentration g/l | | |
|----------------------------------|---------|---------|
| A/O | Organic | Aqueous |
| 5 | 0 | 4.66 |
| 2 | 0 | 11.6 |
| 1 | 0 | 22.7 |
| 0.05 | 3.30 | 38.2 |
| 0.2 | 10.9 | 57.3 |
| 0.1 | 14.8 | 75.6 |

TABLE 10
Tantalum Stripping Isotherm

Solvent : 277 g/l (0.8M) CYANEX 923 extractant in Aromatic 150 diluent. Loaded to 6.78 g/l Ta.
 Strip Feed : 0.4N NH₄OH, 4% NH₄F
 Contact Time : 5 minutes
 Temperature : 24°C

| Equilibrium Ta Concentration g/l | | |
|----------------------------------|---------|---------|
| O/A | Organic | Aqueous |
| 2 | 0 | 3.39 |
| 1 | 0.61 | 5.93 |
| 0.5 | 0.74 | 11.6 |
| 0.2 | 2.66 | 19.4 |
| 0.1 | 4.71 | 18.3 |

FIG. 10 – NIOBIUM STRIPPING ISOTHERM

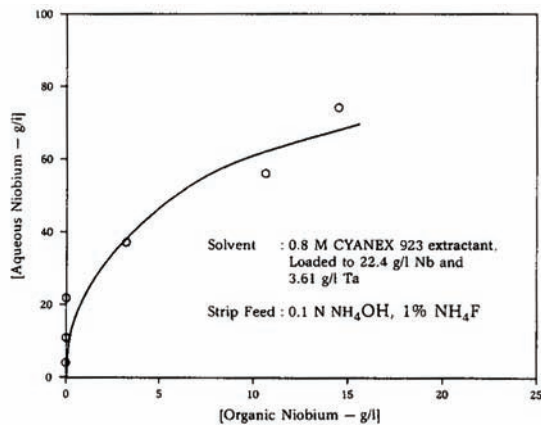
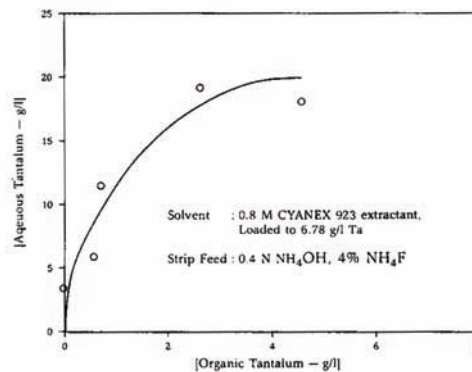


FIG. 11 – TANTALUM STRIPPING ISOTHERM



¹ R. Hahn and H. Retelsdorf, Production of Pure Niobium Using a New Extraction Process for Niobic Oxide and Optimal Reduction Processes. *Erzmetal*, 37, (9), 444-448 (1984).

12 Potential Applications

Cadmium Removal from Phosphoric Acid

Cadmium sometimes occurs as an undesirable impurity in phosphoric and other acids. The data given in Table 11 illustrate the ability of CYANEX 923 to readily reduce the concentration of cadmium from 10 mg/l to below a target of 2 mg/l; the specification in this particular application. McCabe-Thiele interpolations from the isotherm (Figure 12) indicate minimal staging requirements and that cadmium can be reduced from 10 mg/l to < 2 mg/l in two theoretical stages at A/O = 4.

Cadmium, as well as co-extracted acids, are efficiently stripped from the loaded solvent with water as shown by the data in Table 12. The stripping isotherm (Figure 13) again indicates minimal staging requirements.

TABLE 11
Extraction of Cadmium from HCl/H₃PO₄ Using 2.5 v/o CYANEX 923

| | |
|---------------|--|
| Solvent | : 2.5 v/o CYANEX 923 in Exxsol D-80 |
| Aqueous | : 10.2 mg/l Cd ²⁺ , 100 g/l HCl, 133 g/l H ₃ PO ₄ |
| Phase Contact | : 10 mins at 40°C |

Equilibrium Concentration

| A/O | Cd(mg/l) | | HCl (g/l) | | H ₃ PO ₄ (g/l) | |
|------|----------|---------|-----------|---------|--------------------------------------|---------|
| | Organic | Aqueous | Organic | Aqueous | Organic | Aqueous |
| 0.25 | 2.46 | 0.36 | 0.6 | 97.6 | 0.75 | 130 |
| 0.5 | 4.85 | 0.51 | 1.3 | 97.4 | 0.5 | 132 |
| 1 | 9.37 | 0.83 | 2.5 | 97.5 | 1 | 132 |
| 2 | 17.6 | 1.40 | 2.4 | 98.8 | 2 | 132 |
| 5 | 40.6 | 2.08 | 6.0 | 98.8 | 5 | 132 |

FIG. 12 - CADMIUM EXTRACTION ISOTHERM:
2.5 v/o CYANEX 923

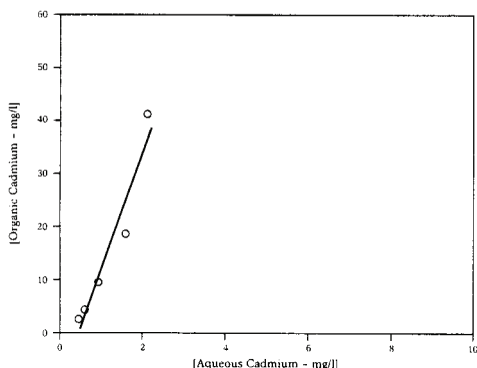


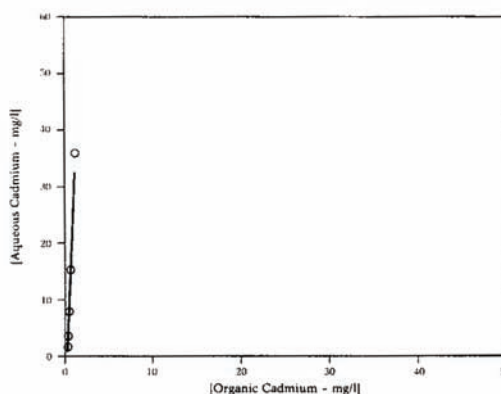
TABLE 12
Cadmium Stripping from 2.5 v/o CYANEX 923

| | |
|---------------|---|
| Solvent | : 2.5 v/o CYANEX 923 in Exxsol D-80 loaded to 8.05 mg/l Cd, 1.3 g/l HCl, 1.2 g/l H ₃ PO ₄ |
| Strip Feed | : Water |
| Phase Contact | : 10 mins at 40°C |

Equilibrium Concentration

| A/O | Cd(mg/l) | | HCl (g/l) | | H ₃ PO ₄ (g/l) | |
|-----|----------|---------|-----------|---------|--------------------------------------|---------|
| | Organic | Aqueous | Organic | Aqueous | Organic | Aqueous |
| 5 | 0.15 | 1.58 | 0 | 0.2 | 0 | 0.3 |
| 2 | 0.15 | 3.95 | 0 | 0.6 | 0 | 0.7 |
| 1 | 0.40 | 7.65 | 0 | 01.0 | 0 | 1.3 |
| 0.5 | 0.50 | 15.1 | 0 | 2.2 | 0 | 2.5 |
| 0.2 | 0.79 | 36.3 | 0 | 5.4 | 0 | 6.4 |

FIG. 13 - CADMIUM STRIPPING ISOTHERM:
2.5 v/o CYANEX 923



ANALYSIS IN ORGANIC SOLVENTS

As described, the gas chromatographic procedure is suitable for analyzing solvents containing approximately 120 g/l CYANEX 923 extractant. Other concentrations may be determined by diluting the solvent appropriately or adjusting the composition of the standard solution.

CYANEX 923 extractant is a mixture containing four major components, as follows: Trihexylphosphine oxide (1), dihexylmonooctyl-phosphine oxide (2), dioctylmonoheptyl-phosphine oxide (3) and trioctylphosphine oxide (4).

The method is based upon the fact that, within the limits of experimental error, the response factors for components 1, 2 and 3 are the same as for 4 and that 4 (TOPO) is readily available and may be easily purified to AR grade.

Reagents

1. Didecylphthalate (AR grade - internal standard)
2. TOPO (purified - see note 1)
3. Process diluent (e.g. Escaid* 110 diluent)

Calibration

1. Accurately weigh 1g (± 1 mg) of pure TOPO and 2g (± 0.1 g) of didecylphthalate into a 50 ml volumetric flask. Dissolve and make up to volume with the process diluent.
2. Analyze the above standard solution as described under "Gas Chromatographic Conditions" to determine the relative response factor of TOPO vs. didecylphthalate.

Procedure

1. Centrifuge the solvent to be analyzed or filter through PS paper" to remove entrained aqueous or suspended solids.
2. Accurately weigh 2g (± 0.1 g) of didecylphthalate into a 50 ml volumetric flask and pipette 25 ml of the clarified solvent into the same flask. Make up to volume with the process diluent.
3. Determine the relative response factor of each component of CYANEX 923 extractant vs. that of the internal standard as described under "Gas Chromatographic Conditions".

* A product of Exxon Co., U.S.A.

** Phase separation paper available from Whatman, Inc., Clifton, NJ

Calculations

Total Concentration of Trialkylphosphine Oxides (g/l)

$$\sum \left[\frac{R_{4S}}{R_{na}} \right] \times 2 \times C_{4S}$$

Where R_{4S} = Relative response factor for TOPO in the standard solution

R_{na} = Relative response factor for the n^{th} component in the analyte solution.

C_{4S} = Concentration of TOPO in the standard solution (g/l)

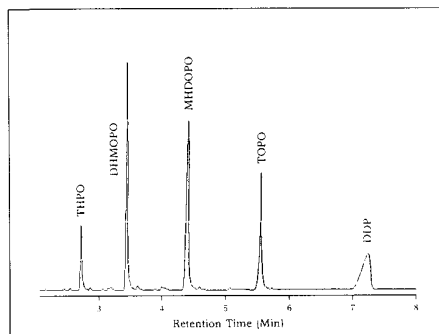
Gas Chromatographic Conditions

| | | |
|---------------------------------|---|---|
| Instrument | : | Perkin Elmer Sigma 115 or equivalent |
| Column | : | 30 in x 0.32 mm fused silica capillary column coated with 0.25 μm of DB1 |
| Detector | : | FID |
| Carrier Gas | : | Helium at 18 psig |
| Vent Flow | : | 100 ml/min |
| Column Flow | : | 4.3 ml/min |
| Split Ratio | : | 23/1 |
| Temperatures $^{\circ}\text{C}$ | | |
| Detector | : | 340 |
| Injection Port | : | 340 |
| Column | : | 220 to 330 at $10^{\circ}\text{C}/\text{min}$ |
| Sample Injection | | |
| Volume | : | 0.1 μl |
| Peak Areas | : | Determined by electronic integration |

Notes

1. A chromatogram of commercial CYANEX 923 extractant is shown in Figure 1A.
2. Pure TOPO (>99.5%) can be obtained by recrystallizing commercial grade TOPO from hexane (three recrystallizations are necessary).
3. Megabore columns may be used as an alternative to capillary columns. A thermal conductivity detector may also be used in place of an FID.
4. The method is based upon a single point determination. If required, a calibration curve can be constructed by varying the concentration of TOPO in the standard solution while maintaining a constant concentration of the internal standard.
5. This method has not been validated.

FIG. 2A — CHROMATOGRAM OF CYANEX 923 EXTRACTANT CONTAINING DIDECYLPHTHALATE (DDP) AS AN INTERNAL STANDARD



ANALYSIS IN AQUEOUS SOLUTION

The aqueous solubility of each component of CYANEX 923 extractant will normally be <2 mg/l. The method is based on analysis of the aqueous sample by gas chromatography. The response factors of the four active components are equal within the limits of experimental error.

Reagents

1. Tetrahydrofuran (THF). "Baker Analyzed Reagent, 100%."
2. TOPO (purified - see note 1.)

Calibration

1. Prepare a stock solution by accurately weighing (± 1 mg) approximately 0.5 g of TOPO into a 50 ml volumetric flask. Dilute to 50 ml with THF and dissolve the TOPO.
2. Dilute aliquots of the stock solution with distilled water to prepare standard solutions containing 2, 5, 10 and 30 mg/l of TOPO.
3. Analyze the solutions as described under "Gas Chromatographic Conditions."

Procedure

1. Filter the aqueous solution to remove entrained organic
2. Inject $3\mu\text{l}$ of the analyte solution and analyze as described under "Gas Chromatographic Conditions."

Calculation

1. *Response Factor for TOPO (R) =
$$\frac{\text{Conc. of TOPO in Standard (mg/l)}}{\text{Area of TOPO Standard Peak}}$$
2. Concentration of Component in Aqueous (mg/l) =
$$\frac{\text{Area of Component Peak (analyte)}}{\text{Area of TOPO Standard Peak}} \times R$$

*Response factor for the standard closest in concentration to the sample.

Gas Chromatographic Conditions

| | | |
|-----------------|---|--|
| Instrument | : | Hewlett Packard 5730A or equivalent |
| Column | : | 2 ft x 1/4 inch x 2 mm ID glass Column packed with 9% OV-17 and 12% SP2401 on 80/100 mesh Supelcoport |
| Detector | : | FID |
| Carrier Gas | : | Helium at 57 psi (Flowrate 40 ml/minute) |
| Temperatures °C | | |
| FID | : | 300 |
| Injection | : | |
| Port | : | 250 |
| Column | : | 230 (Isothermal) |
| Sample | | |
| Injection | | |
| Volume | : | 3 μl |

Notes

1. Pure TOPO can be obtained by recrystallizing commercial grade TOPO from hexane. (Three recrystallizations are necessary).
2. Retention time for TOPO is approximately 12 minutes.
3. Detection limit approximately 2 mg/l.
4. This method has not been validated.

DETERMINATION OF WATER

The method is based on distilling water from CYANEX 923 extractant in the form of an azeotrope with toluene. On contacting a condenser, the water and toluene separate and fall into a graduated trap. The volume of the distillate is then measured.

Apparatus

1. 500 ml round-bottomed, short-necked glass flask with a 40/50 ground glass fitting.
2. Water-cooled condenser. Cold-finger type.
3. Dean and Stark type trap. 10 ml capacity graduated in 0.1 ml divisions with a 40/50 ground glass fitting.
4. Heating mantle controlled by a rheostat.

Reagents

1. AR grade toluene (water-free)

Procedure

1. Weigh 50 g of the sample (± 0.5 g) into the 500 ml flask.
2. Add approximately 200 ml of toluene to the flask and assemble the apparatus.
3. Heat the contents of the flask to boiling and allow to reflux for 30 to 60 minutes or until the volume of water in the trap is constant.
4. Read the volume of water in the trap at room temperature.

Calculation

$$\% \text{ Water} = \frac{\text{Volume of Water in Trap (ml)}}{\text{Sample weight (g)}} \times 100$$

Notes

1. This method has not been validated.
2. Karl-Fisher titration is not recommended.

Technical Papers (listed chronologically)

1. **A Liquid Phosphine Oxide; Solvent Extraction of Phenol, Acetic Acid and Ethanol**
Watson, E.K.; et.al.
Solvent Extr. Ion Exch., 6, No. 2, Pages 207-20; (1988)
2. **Solvent Extraction Separation of Niobium and Tantalum at MHO**
Haesebroek, G.; et.al.
Process Metall., 7B, Pages 1115-20; (1992)
3. **Simulation of Countercurrent Multistage Extraction Process for Recovery of Titanium**
Kagaku Kogaku Ronbunshu, 19, No. 2,
Pages 214-19; (1993)
4. **Computer Modelling of Countercurrent Multistage Extraction for Titanium (IV) - Sulfuric Acid - CYANEX 923 System**
Technal. Rep. Kansai Univ., 35, Pages 59-67; (1993)
5. **Phenol Recovery with SLM using CYANEX 923**
Garea, A.; et.al.
Chem. Eng. Commer., 120, Pages 85-97; (1993)
6. **Computer Modelling of Countercurrent Multistage Extraction for Ti(4+) – H₂SO₄ CYANEX 923 System**
Int. Conf. Process. Mater. Prob.
Pages 521-4, Ed. Henein, H. Pub.
Miner. Met. Mater. Soc., Warrendale PA; (1993)
7. **Gold (I) Extraction Equilibrium in Cyanide Media by the Synergic Mixture of Primene 81R-CYANEX 923**
Coravaca, C.
Hydrometallurgy, 35, No. 1, Pages 27-40; (1994)
8. **The Phosphine Oxides CYANEX 923 and CYANEX 923 as Extractants for Gold (I) Cyanide Aqueous Solutions**
Alquacil, F.J.; et.al.
Hydrometallurgy, 16, No. 3, Pages 369-84; (1994)

Patents (listed chronologically)

1. **Liquid Phosphine Oxide Systems for Solvent Extraction**
Robertson, A.J. and Rickelton, W.A.
European Pat. Appl. EP 132700 A1 (1985)
2. **Procede de Separation des Terres Rares par Extraction Liquide-Liquide**
Dellaye, T.; et.al.
European Pat. Appl. 0284504 (1988)
3. **Recovery of Uranium from Wet Process Phosphoric Acid Using Asymetrical Phosphine Oxides**
Rickelton, W.A.
U.S. Patent 4778663 (1988)
4. **Process for Solvent Extraction Using Phosphine Oxide Mixtures**
Rickelton, W.A. and Robertson, A.J.
U.S. Patent 4909939 (1990)
5. **Recovery of Indium from Acidic Solutions by Solvent Extraction Using Trialkylphosphine Oxide**
Rickelton, W.A.
Canadian Pat. Appl. CA 2077601 (1994)
6. **Method for Recovering Carboxylic Acids from Aqueous Solutions**
Gentry, J.C.; et.al.
U.S. Patent 5399751 (1995)

As of July 26, 1995

16 | Health and Safety

The oral and dermal toxicity of CYANEX 923 extractant is low. CYANEX 923 extractant produces mild eye irritation and severe skin irritation upon contact. Repeated dermal exposure for 28 consecutive days produced severe skin irritation, but no systemic toxicity. CYANEX 923 extractant did not produce dermal sensitization in guinea pigs after

repeated dermal exposure. This product did not produce mutations in bacteria nor did it produce chromosomal effects in the mouse micronucleus or human lymphocyte aberration assays. CYANEX 923 extractant is highly toxic to fish and invertebrates and great care should be exercised to avoid environmental exposure.

• Email: custinfo@cytec.com Worldwide Contact Info: www.cytec.com US Toll Free 800-652-6013 Tel 973-357-3193 •

Cytec Industries Inc. in its own name and on behalf of its affiliated companies (collectively, "Cytec") decline any liability with respect to the use made by anyone of the information contained herein. The information contained herein represents Cytec's best knowledge thereon without constituting any express or implied guarantee or warranty of any kind (including, but not limited to, regarding the accuracy, the completeness or relevance of the data set out herein). Cytec is the sole owner or authorized user of the intellectual property rights relating to the information communicated. The information relating to the use of the products is given for information purposes only. No guarantee or warranty is provided that the product is adapted for any specific use. The user or purchaser should perform its own tests to determine the suitability for a particular purpose. The final choice of use of a product remains the sole responsibility of the user.

© 2008 Cytec Industries Inc. All rights reserved.

TRADEMARK NOTICE: The ® indicates a Registered Trademark in the United States and the ™ or * indicates a Trademark in the United States. The mark may also be registered, the subject of an application for registration or a trademark in other countries.

SPT-032-D