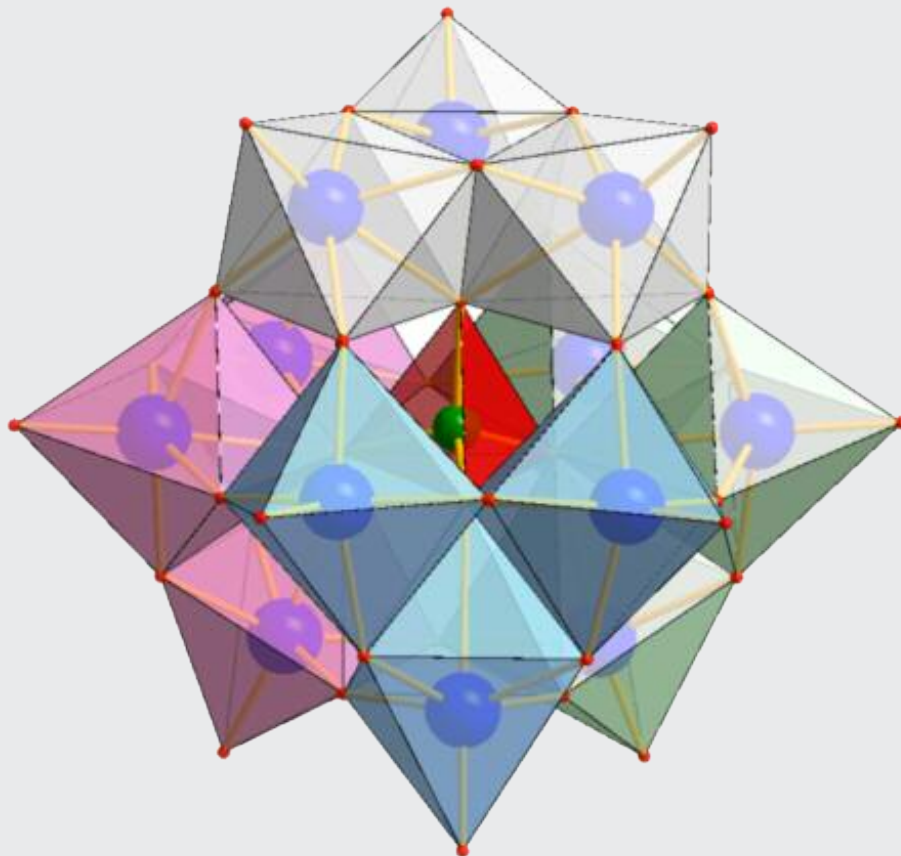


# Tungsten Chemicals and their Applications



J. Christian, R.P. Singh Gaur, T. Wolfe and J. R. L. Trasorras  
Global Tungsten and Powders Corp., Towanda, PA, USA

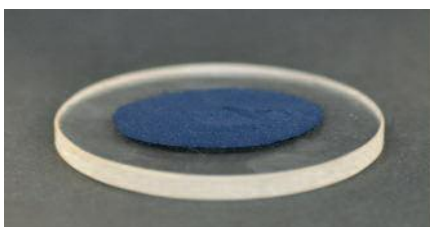
## HISTORICAL INTRODUCTION <sup>1</sup>

Since the dawn of tungsten chemistry at the end of the 18th century, colored W compounds have attracted people. The first to mention the beauty of the yellow tungsten oxide, Rudolph Erich Raspe (1737-1794), proposed to use it as artists color (*Figure 1*). However, no one did use it then, as in those days the color would have been too expensive – it also changes its color to green with time. Later, in 1824, Friedrich Wöhler (1800-1882) examined the group of colorful tungsten bronzes. These compounds found application as artists colors until they were substituted by organic colors.

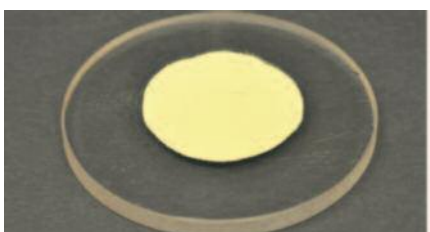
In 1847, a patent was granted to the engineer Robert Oxland related to “Improvements in Dyeing, certain parts of which Improvements are applicable to the Manufacture of Metallic Alloys”. This included the preparation of sodium tungstate, formation of tungstic acid, and the reduction to metallic form by oil, tar or charcoal. The work constituted an important step in modern tungsten chemistry, and opened the way to industrialization.



a) Tungsten violet oxide:  $WO_{2.72}$



b) Tungsten blue oxide:  $WO_{2.9}$



c) Tungsten trioxide:  $WO_3$

### Figure 1: Tungsten oxides.

(Courtesy of Global Tungsten and Powders Corp.)

*Rudolph Erich Raspe was already fascinated by the beauty of the tungsten yellow oxide in 1785; he proposed to use it as artists color.*

By the end of the 19th century tungsten salts were used to make colored cotton fast or washable and to make clothes used for theatrical and other purposes non-flammable. The tungstate of calcium and other metals were applied in preparing screens for X-ray work and tungsten sulphides found limited use in the lubricant industry.

In the 1930's new applications arose in the oil industry for the hydro-treating of crude oils, in particular for desulfurizing, and in the sixties new catalysts were invented containing tungsten compounds to treat internal combustion engine exhaust gases.

During all these early years, the amount of tungsten used for chemical applications was always small in comparison to steel, mill products and hard metals. However, tungsten chemicals are used today in the form of tungsten oxides, tungstates, tungstic acid, silicotungstic acid, phosphotungstic acid or tungsten sulfides across a broad range of applications in the oil, lubricants, electronics, medical, dental and mining industries.

### Maiden Blush: A Very Early Use of Tungsten that Wasn't

K.C. Li's book on “Tungsten” published in 1955 mentions a very early use of tungsten:

“It is of historical interest to note that the use of tungsten as coloring material for porcelain was practised in the reign of emperor Kang-his (A.D. 1662-1722). The Imperial Court of Emperor Kang-his ordered the best of the well-known porcelain kilns in the Province of Kiangsi at Ching Te Cheng (China) to manufacture eight forms of porcelain in the color of peach bloom. This peach-bloom color is particularly hard to produce in porcelain. It is neither pink nor red. It is a combination of pink and red with a suggestion of green. The Chinese call it Mei-Jen Chi, or maiden blush. As Chinese poets often compared “Maiden Blush” with peach bloom, the translation in English is peach bloom.

It is reported that 8,000 experiments on all kinds of minerals and metals were conducted before the tungsten color was discovered. The eight forms are as follows...

The first seven forms are on exhibit in the Metropolitan Museum of Art. In what form the tungsten was used is a mystery, but it has been proved by a German scientist, Dr. Paul Grünfeld, to be tungsten color...”

To confirm this early use of tungsten, Professor Wolf-Dieter Schubert of the Vienna University of Technology asked the Metropolitan Museum of Art in New York to make an analysis of several pieces of their collection. They agreed, and none of the specimens was found to contain tungsten. Probably, Dr. Grünfeld made an emission spectroscopy and used tungsten electrodes for making spark emission.

## MODERN APPLICATIONS

### TUNGSTEN IN CATALYSTS

The major modern day use of tungsten chemicals is in the area of catalysts. Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a *catalyst*. Unlike other reagents that participate in the chemical reaction, a catalyst is *not* consumed by the reaction itself. A catalyst may participate in multiple chemical transformations. Catalysts that speed the reaction are called positive catalysts.

Since the 1930's, the oil industry has been using tungsten in the catalysts for treating of crude oils. The four major catalytic reactions are summarised in [Table 1](#).

### Hydrocracking Catalysts

The hydrocracker is one of the most profitable units in a refinery as it converts heavy feedstocks to lighter more valuable products such as naphtha, diesel, jet-fuel, kerosene and feedstocks to lubricant units and kerosene plants. As refiners are pushed to operate at higher efficiency levels, at lower costs and with more stringent fuel specifications, the performance of their hydrocracking units becomes critical.

Various tungsten species are used to prepare catalysts for hydrocracking, hydrodesulfurization, hydrodenitrogenation, and hydrodearomatisation. These catalysts use tungsten and various other metal compounds supported on a ceramic carrier. The goal of these catalysts is to improve the yields of highly desirable organic components in gasoline, and reduce environmentally harmful by-products, such as sulfur and nitrogen compounds.



**Figure 2: Hydrocracking.**

The hydrocracker converts heavy feedstocks to lighter more valuable products such as naphtha, diesel, jet-fuel, kerosene and feedstocks to lubricant units and kerosene plants.

**Table 1. The Four Major Catalytic Reactions in the Treating of Crude Oil**

<p><b>DEHYDROGENATION</b> The dehydrogenation of naphthenes to convert them into aromatics. Example: conversion of methylcyclohexane (a naphthene) to toluene (an aromatic)</p>	<p><chem>CC1CCCCC1 &gt;&gt; Cc1ccccc1 + 3H2</chem></p>
<p><b>ISOMERIZATION</b> The isomerization of normal paraffins to isoparaffins. Example: conversion of normal octane to 2,5-Dimethylhexane (an isoparaffin)</p>	<p><chem>CCCCCCCC &gt;&gt; CC(C)CC(C)CC</chem></p>
<p><b>AROMATIZATION</b> The dehydrogenation and aromatization of paraffins to aromatics (commonly called dehydrocyclization) Example: conversion of normal heptane to toluene.</p>	<p>n-Heptane <math>\rightarrow</math> Toluene + 4 H<sub>2</sub></p> <p><chem>CCCCCCC + 4H2 &gt;&gt; Cc1ccccc1 + 4H2</chem></p>
<p><b>HYDROCRACKING</b> The hydrocracking of paraffins into smaller molecules. Example: cracking of normal heptane into isopentane and ethane.</p>	<p>n-Heptane + H<sub>2</sub> <math>\rightarrow</math> Isopentane + Ethane</p> <p><chem>CCCCCCC + H2 &gt;&gt; CC(C)CC + CC</chem></p>

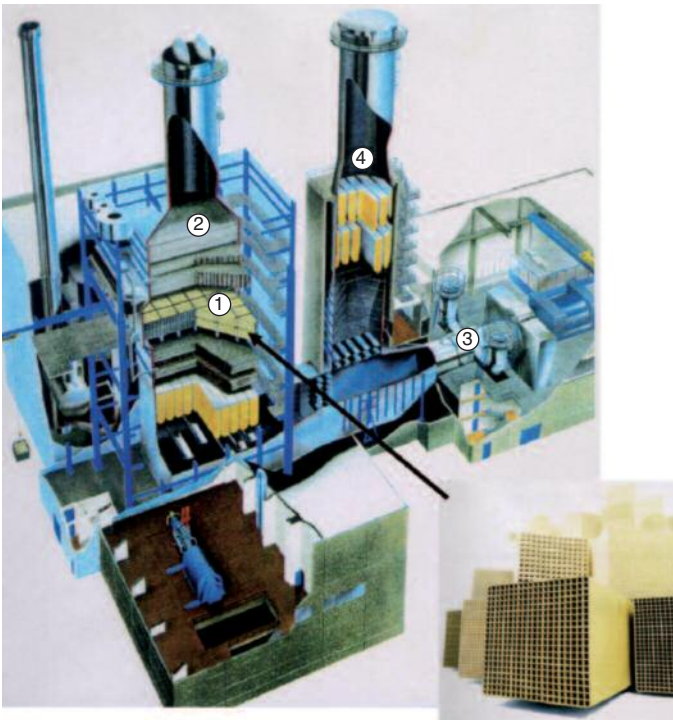


**Figure 3: Hydrocracking catalyst.**

TK-931 is a nickel-tungsten hydrocracking catalyst designed to produce very high yields of premium quality diesel and jet fuel or kerosene. (Haldor Topsoe)

## DE-NO<sub>x</sub> Catalysts

More recently, tungsten compounds have found increasing use as catalysts for the treatment of exhaust gases for the reduction of nitrogen oxide emissions. The term NO<sub>x</sub> is used to describe a mixture of nitrogen oxides NO and NO<sub>2</sub>, both gases, which are produced by fuel combustion. NO<sub>x</sub> gas is a major air pollution problem, causing acid rain and contributing to depletion of the ozone layer. “De-NO<sub>x</sub>” treatment aims to convert NO<sub>x</sub> gas to inert nitrogen gas. This conversion is a difficult process and catalysts are required to allow this to happen. Typical DeNO<sub>x</sub> catalysts are honeycomb-shaped TiO<sub>2</sub>WO<sub>3</sub>V<sub>2</sub>O<sub>5</sub> ceramics. De-NO<sub>x</sub> catalysts are used on the stack gases of power plants, chemical plants, cement plants and diesel engines. These catalysts use ammonia or urea to yield harmless products of nitrogen and water<sup>2</sup>:



**Figure 4: Electric power plant equipped with DeNO<sub>x</sub> catalyst elements containing tungsten oxide;**

1. catalyst modules, 2. waste heat recovery boiler, 3. gas turbine, 4. bypass stack. (Courtesy of Porzellanfabrik Frauenthal GmbH)

## Reforming Catalysts

Another emerging use of tungsten chemicals is in the manufacture of *reforming catalysts*. Reforming catalysts convert natural gas to hydrogen gas via a two-step process, called reforming and water-gas-shift. Ammonium metatungstate can be used to deposit tungsten on a catalyst support, then the tungsten is reacted in place to form a tungsten carbide or tungsten sulfide with very high surface area. Finding efficient reforming catalysts is critical to the fuel supply for hydrogen powered engines and fuel cells.

## Ammonium Metatungstate

Many of the above catalysts typically start with Ammonium Metatungstate (AMT), (NH<sub>4</sub>)<sub>6</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>]•xH<sub>2</sub>O, as the tungsten precursor. AMT is a wonderful molecule that allows tungsten to become highly soluble in water as metatungstate ion. At 25°C, 1.6 Kg of AMT is soluble per liter of water, with a density of about 2.5 g/mL. Once the AMT is impregnated into the ceramic substrate, it can be decomposed or converted to the appropriate tungsten species required for the catalytic reaction.

The metatungstate form is a Keggin structure as shown in **Figure 5**. This highly soluble form is also used for the preparation of other heteropoly acids and polyoxometallates (POM). Such compounds are attractive catalysts for many kinds of organic reactions.

**Figure 5: Structure of the Keggin molecule.**

This diagram of phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) shows the four trimer groups shaded pink, blue, green and white.

The phosphate group in the center is shown in red.

This illustration is a scale model of the molecule.

Chemists and Materials Scientists use drawings of atomic arrangements to help understand how atoms are arranged, and fit together like building blocks. This picture shows bonds between atoms and borders around the WO<sub>6</sub> groups to help visualize groups of atoms as building blocks. The atoms are drawn to scale except oxygen, which is in reality about three times larger than a single metal atom. (Courtesy of Global tungsten and Powders Corp.)



## Heteropoly Acid Compounds of Tungsten

Tungsten heteropoly compounds, or *polyoxometallates*, start from single WO<sub>6</sub> building blocks that form tungsten trimers (W<sub>3</sub>O<sub>13</sub>) that further combine to form a variety of polymerized metal forms. Four trimers combine around a central hetero atom (for example P) tetrahedron into the famous “structure of J. F. Keggin”. Keggin was one of the pioneers of deducing chemical structures. **Figure 5** shows the structure of phosphotungstic acid. Marignac<sup>3</sup> was the first to prepare



12-tungstosilic acid, a heteropoly compound of tungsten, in 1862 and recognized that such compounds are a distinct class of chemicals.

Today, the various polyoxometalate compounds are the subject of extensive research for energy, industrial and health applications<sup>1,2,4</sup>. They hold promise for catalysis, nanoscale magnets, drugs and drug delivery, insulin and metabolic control, separation science and technology, lignin separation for paper, and more recently in the decontamination of chemicals used in chemical warfare.

## PIGMENTS

Tungsten compounds are used for the manufacture of inorganic pigments for ceramic glazes and enamels.

- Tungsten trioxide  $WO_3$  is used for bright yellow glazes.
- Tungsten bronzes, i.e. partly reduced alkali and alkaline earth tungstates, are available in many bright colors.
- Barium and zinc tungstate are examples of bright white pigments.
- Colored organic dyes and pigments based on phosphotungstic acid and phosphotungsto-molybdic acid are made for paints, printing inks, plastic, rubber and other materials.



**Figure 6: A glazed vase made with tungsten oxide containing pigments.**

Photo by A. Bock



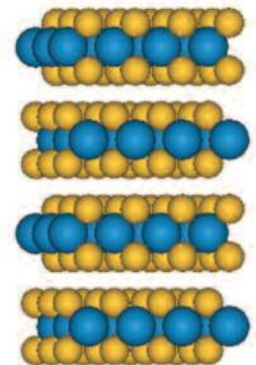
**Figure 7: inorganic pigments for ceramic glazes and enamels**

Tungsten bronzes, i.e. partly reduced alkali and alkaline earth tungstates, are available in many bright colors. China Tungsten (Xiamen)

## LUBRICANTS

### Tungsten disulfide

Tungsten disulfide,  $WS_2$ , is one of the most lubricous materials known to science with a dynamic coefficient of friction of  $\sim 0.03$ . It offers excellent dry lubricity that can be superior to that of molybdenum disulfide and graphite. It can operate in air up to  $583^\circ C$  and up to  $1316^\circ C$  under vacuum. Recent studies have shown that nano-sized Tungsten disulfide ( $WS_2$ )–zinc oxide (ZnO) composite is a candidate material that exhibits adaptive lubricant behavior. Adaptive lubricants undergo chemical changes with changing environment to provide lubrication in extreme environments<sup>5</sup>. **Tungsten Diselenide** is also being studied as a solid lubricant<sup>6</sup>. Lubrication by tungsten diselenide coatings is intended for reducing friction and wear. Dichalcogenides of refractory metals are of great importance in providing the reliability and increased life of different friction units. Tungsten diselenides have higher corrosive resistance in water and are capable of operating stably in water vapor as variations in the environment humidity and pressure have insignificant effect on their friction coefficients. Shortcomings of these solid lubricants from their oxidation and fatigue failure can be overcome by inserting gallium and indium in the diselenide coatings.



**Figure 8: Tungsten disulfide structure**

Tungsten disulfide exhibits a layer like structure and offers excellent lubrication under extreme conditions. When applied as a thin film on a clean surface it can create a molecular bond to the substrate.



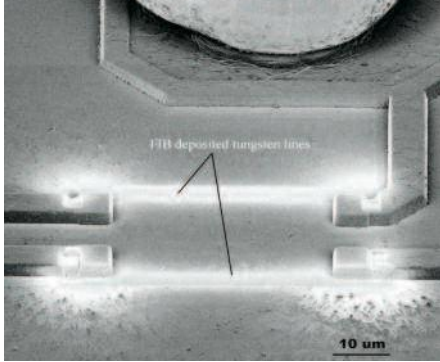
**Figure 9:**

**Tungsten disulfide is a high performance solid lubricant.**

Tungsten disulfide is increasingly used in automotive and aerospace applications. Typical applications include bearings, gears, valves, pump components, injection molding dies (ejection pins and part release). Dynacron®, Surcom Industries, Inc., Chicago.

**Metallizing of Semiconductors**

**Tungsten hexafluoride** is widely used in the semiconductor industry for depositing metal on semiconductor circuits and circuit boards through the process of chemical vapor deposition – upon decomposition, molecules of  $WF_6$  leave a residue of metallic tungsten. This layer serves as low-resistive metallic "interconnects."

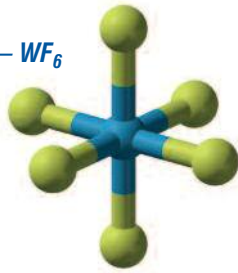


**Figure 10: Semiconductor metallization**

W lines deposited by Focused ion beam (FIB) assisted chemical vapour deposition. (University of Oulu)

**Figure 11: Tungsten hexafluoride —  $WF_6$**

Tungsten hexafluoride is the inorganic compound of tungsten and fluorine with the formula  $WF_6$ . This corrosive, colorless compound is a gas under standard conditions. With a density of about 13 g/L (roughly 11 times heavier than air).  $WF_6$  is one of the heaviest known gases under standard conditions.



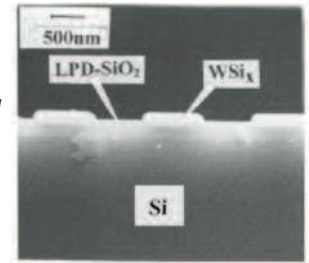
The expansion of the semiconductor industry in the 1980s and 1990s resulted in the increase of  $WF_6$  consumption, which remains at around 200 tonnes per year worldwide. Tungsten metal is attractive because of its relatively high thermal and chemical stability, as well as low resistivity ( $5.6 \mu\Omega \cdot \text{cm}$ ) and low electromigration.  $WF_6$  is favored over related compounds, such as  $WCl_6$  or  $WBr_6$ , because of its higher vapor pressure resulting in higher deposition rates. Since 1967, two  $WF_6$  deposition routes have been implemented, thermal decomposition and hydrogen reduction. The required  $WF_6$  gas purity is rather high and varies between 99.98% and 99.9995% depending on the application.

**Semiconductors**

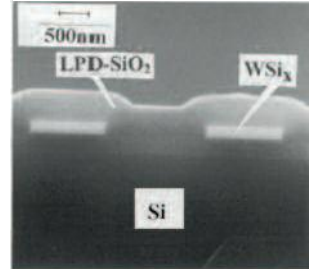
**Tungsten Disilicide ( $WSi_2$ )** is an electrically conductive ceramic material which can be categorized as a ceramic material, refractory material or a semiconductor material. The main applications of this compound are as a barrier between silicon and tungsten in semiconductors<sup>7</sup>.

**Figure 12: Tungsten Disilicide is a semiconductor material**

SEM cross-sectional views of blanket liquid phase deposition (LPD)  $SiO_2$  films deposited on patterned chemical vapour deposition (CVD)  $WSi_x$



a) after 1.5h LPD



b) after 3 h LPD

$WSi_2$  is used in microelectronics as a contact material, with resistivity  $60\text{--}80 \mu\Omega \cdot \text{cm}$ ; it forms at  $1000^\circ\text{C}$ . It is often used as a shunt over polysilicon lines to increase their conductivity and increase signal speed. Tungsten silicide layers can be prepared by chemical vapor deposition, e.g. using monosilane or dichlorosilane with tungsten hexafluoride as source gases. The deposited film is non-stoichiometric, and requires annealing to convert to more conductive stoichiometric form. Tungsten silicide is a replacement for earlier tungsten films. Tungsten silicide is also used as a barrier layer between silicon and other metals.

Tungsten silicide also finds use in microelectromechanical systems and for oxidation resistant coatings. Films of tungsten silicide can be plasma-etched using e.g. nitrogen trifluoride gas.

**SOLAR POWER**

**Tungsten Diselenide,  $WSe_2$**



**Figure 13: Tungsten Diselenide in Photovoltaic panels**

Non-stoichiometric tungsten diselenides ( $W_{1-x}Se_2$ ) are used as thin film coatings in photovoltaic cells.

Among potential thin-film materials for solar cells, tungsten diselenide has exceptional promise for photovoltaic applications<sup>8</sup>.

Investigations of electrical and optical properties<sup>9</sup> of WSe<sub>2</sub> proved that this compound is a semiconductor with a band gap ranging between 1.35 and 1.57 eV. Non-stoichiometric tungsten diselenides (W<sub>1-x</sub>Se<sub>2</sub>) are used as thin film coatings in photovoltaic cells, intercalated with indium, using tungsten diselenide (p-In<sub>0.5</sub>WSe<sub>2</sub>) as the semiconducting base layer for a film photocell.

## MEDICAL AND DENTAL APPLICATIONS

There are a number of tungsten chemicals that have been used in the medical and dental fields for X-ray shielding and conversely, X-ray opacity.

### Dental Filling Materials

Known tungsten compounds in dental composites are sodium tungstate, potassium tungstate, manganese tungstate, calcium tungstate, strontium tungstate, and barium tungstate. These various tungstates are added to give good definition in the dental X-rays. Interestingly, dental x-rays also use calcium tungstate as the X-ray intensifying phosphor to allow patients to receive smaller doses of radiation<sup>10</sup>.

### X-Ray Shielding

Tungsten compounds have been in use for the manufacturing of non-Lead radiation apparel. The advantage of non-Lead radiation apparel is that they are approximately 20% lighter than a corresponding lead version<sup>11</sup>.

**Figure 14: Lead-free radiation protection apparel.**

(Universal Medical)



## MINING AND MINERAL SEPARATIONS

Heavy liquids are dense fluids or solutions used to separate materials of different density through their buoyancy. Materials with a density greater than the heavy liquid will sink, while materials with a density less than the heavy liquid will float on the liquid surface<sup>12</sup>. There are several tungstate compounds (sodium polytungstate (SPT), lithium metatungstate (LMT)) that are used as safe and effective alternatives to traditional organic heavy liquids. Solutions of Lithium Metatungstate with a *specific gravity* of 3.7, (H<sub>2</sub>O = 1) are widely used as heavy liquids. LMT was originally developed and patented by BHP-Utah International Corp in the early 1990's. A recent addition to these

compounds has been the introduction of LST, a solution consisting of greater than 80% sodium heteropolytungstate.

In the mineral industry, heavy liquids are commonly used in the laboratory to separate the "light" minerals such as quartz and clay from the "heavy" minerals. The density used for this type of separation is about 2.85 g/mL, nearly three times the density of water. The introduction of heteropolytungstates has found great acceptance. Rio Tinto Exploration Pty Ltd and Iluka Resources Ltd were highly commended at the Year 2000 Australian National Safety and Health Innovation Award for using LST in place of the traditional organic heavy liquids.

Heavy liquid separations are carried out for varied reasons, depending on the industry. The mineral sands industry uses heavy liquid separations to check the grade of samples in their process, and to determine the efficiency of their industrial separations. The diamond exploration industry uses heavy liquids to separate the dense "indicator" minerals from sand and clay.



**Figure 15: Separation with Heavy Liquids**

(LMT Heavy Liquid, Idaho, USA)

Heavy liquids are dense fluids or solutions used to separate materials of different density through their buoyancy.

Another use of heavy liquids is in paleontology. Typically, these heavy liquid separations are conducted at a lower density (e.g. 2.2 g/mL) since the separation is not between minerals of different types, but between fossil bones and minerals.

## EMERGING APPLICATIONS

Emerging applications for tungsten chemicals center around two unique properties of tungsten oxides: intercalation and polycondensation. Intercalation is the ability of a tungsten oxide framework to hold other atoms in the spaces between framework atoms. Polycondensation is the formation of larger tungstate complexes that form single ionic molecules, called polyoxometalates. These two principles have led to a number of tungsten applications in medicine, fuel cell technology, and also to energy-saving "Intelligent Window" technology.



## FUEL CELLS

Fuel Cell technology holds great promise for the world, both in achieving higher fuel efficiency and to help realize the hydrogen economy – a world energy system where solar, wind, and fuel energy is stored as hydrogen and available on demand as electricity. Direct electricity from fuel cells eliminates large moving parts from electricity generation based on rotating generators. It also breaks the Carnot Cycle limitation on efficiency, especially at low temperatures, where the entropy loss of energy conversion is the lowest. In automobiles, fuel economy is projected to be 2 liter/100km (120 miles/gallon). This technology would drastically reduce energy requirements for transportation.

The main low-temperature fuel cell technology is the proton exchange membrane fuel cell (PEM or PEMFC). The fuel used is hydrogen, which can split into protons and electrons, then combine with oxygen to form water. The PEM cell uses two electrodes separated by a membrane to produce electricity (Figure 16). The membrane is a key component. The membrane must be electrically insulating, but conduct protons from one side to the other to complete the energy cycle.

There are three significant materials challenges for PEM Fuel Cells technology to succeed, the proton-exchange-membrane, the catalyst on the anode electrode, and the catalyst on the cathode electrode. The two catalysts are necessary to achieve the highest fuel efficiency, and each catalyst has unique requirements.

The fuel cell is arranged so hydrogen fuel is fed into one side, and air is fed into the other, as shown in Figure 16. In this Figure, the fuel

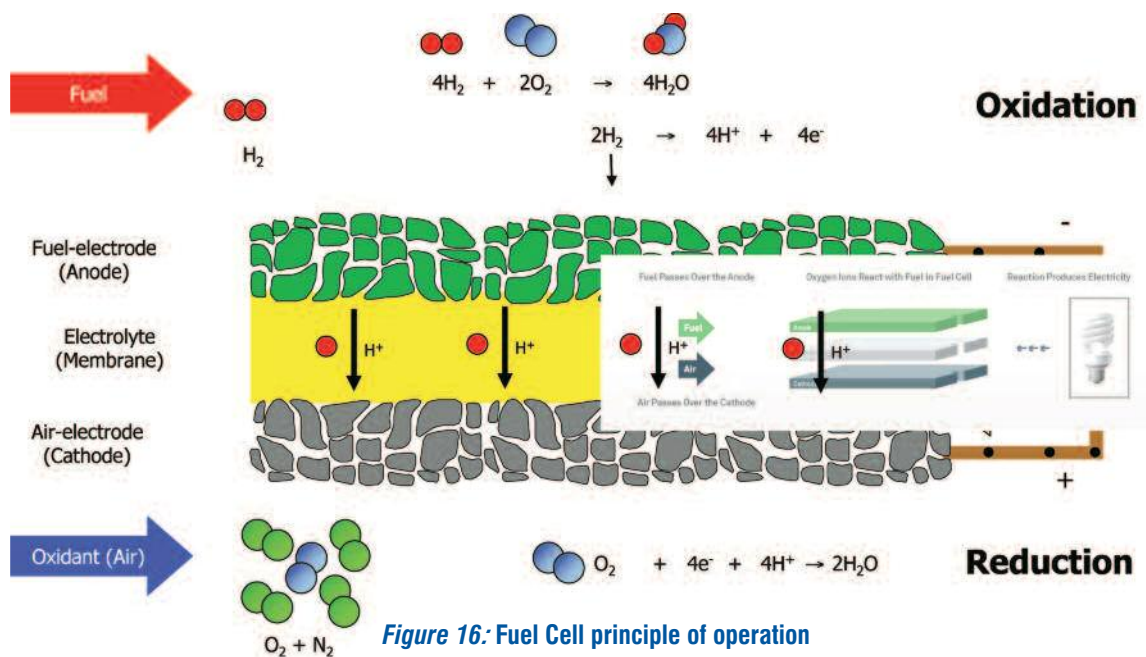
reaction proceeds from top to bottom. Each individual cell produces 1.2V at no load, and about 0.5V at working load. The cells are “stacked” to produce an appropriate voltage to power the device. Electronics use a stack of about 20 cells to produce 9V, autos require about 100 cells to produce 50V. While the number of cells determines the voltage, the available current is based on the area of each cell. Each square centimeter of cell area produces about 0.2 amperes of current. A typical auto requires about 70 kilowatts of power, requiring a fuel cell about the size of the auto’s tire. This cell can power a hybrid-electric drive vehicle, charging the battery and providing reserve power for acceleration and highway driving.

### Proton Conducting Membranes

Heteropolyacids are increasingly being investigated to replace proton conducting polymers. In particular, W heteropolyacids (HPAs) like 12-phosphotungstic acid (PWA) have the ability to form different protonic species and hydrogen bonds of different strength. The consequence of this is one of the principal properties of these compounds—high protonic conductivity,  $2 \times 10^{-2}$  to  $10^{-1}$  S  $\text{cm}^{-1}$  at room temperature—so that they belong to the group of superionic conductors<sup>13</sup>. Such ionic conductivity together with lower cost, with respect to polymer membranes, makes HPAs very attractive for fuel cells.

### Fuel Cell Catalyst Support

Tungsten is a promising replacement for high surface area activated carbons. Carbon is used as a catalyst support and electrode material for current fuel cell electrodes. In actual operation, the carbon powder corrodes over time. Because of the high acid resistance of tungsten

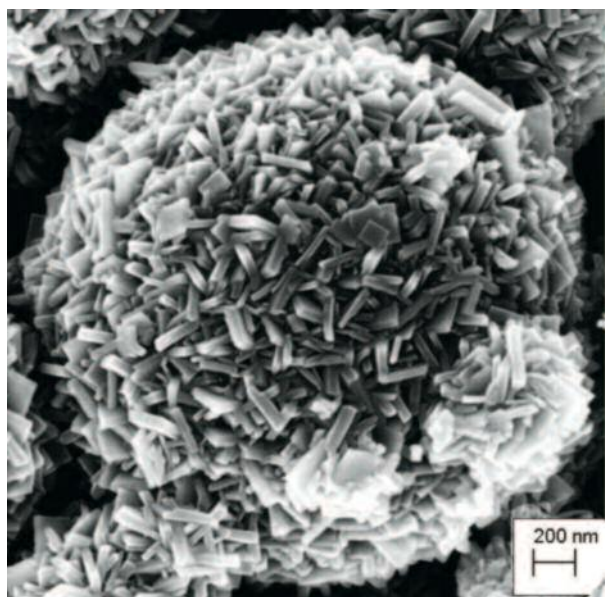


**Figure 16: Fuel Cell principle of operation**

Hydrogen fuel is ported to the anode electrode, where it catalytically is split to protons and electrons. Electrons travel through the electrical circuit, while protons migrate through the membrane to catalytically combine with oxygen to form water at the cathode.



oxide, using conducting tungsten oxides can increase the durability of fuel cells. **Figure 17** shows a high-surface-area tungsten oxide that is being used as a catalyst support.



**Figure 17: Catalyst Support**

(Courtesy of Global Tungsten and Powder Corp.)

Tungsten oxide high surface mesoporous catalyst support.

## Polymer Exchange membrane (PEM) Fuel Cell Cathode and Anode Catalyst

Platinum electrodes are the historical low-temperature electrode of choice for fuel cells. Platinum is an effective anode and cathode catalyst. However its high price has led a search for alternative materials. Tungsten compounds have been found to act as fuel cell catalysts. This includes tungsten bronzes, tungsten carbides, and reduced isopolytungstates. Since tungsten bronzes and tungsten carbides are non-stoichiometric compounds (i.e. not following a fixed chemical formula), materials synthesis is challenging to make reproducible electrode materials. Often, historical studies were confounded by contamination from platinum crucibles and platinum electrodes used for synthesis and testing – platinum migration caused low but catalytically effective levels of contamination. Still, tungsten compounds are promising catalyst materials. One recent study performed in a platinum-free environment found reduced isopolytungstates could achieve catalyst rates close to those of platinum, and even work in fuel with high levels of carbon monoxide, which poisons platinum catalysts<sup>14</sup>.

These same tungsten compounds have also been found to be beneficial co-catalysts with platinum metal to produce a bi-functional catalyst for anode or cathode applications. This is a promising application, since the well-known characteristics of platinum can be

combined with the beneficial effects of tungsten compounds for fuel tolerance and lower cost. Current research includes the use of tungsten carbides, tungsten bronzes, and polyoxometalates as co-catalysts with platinum to achieve better catalytic activity and durability.

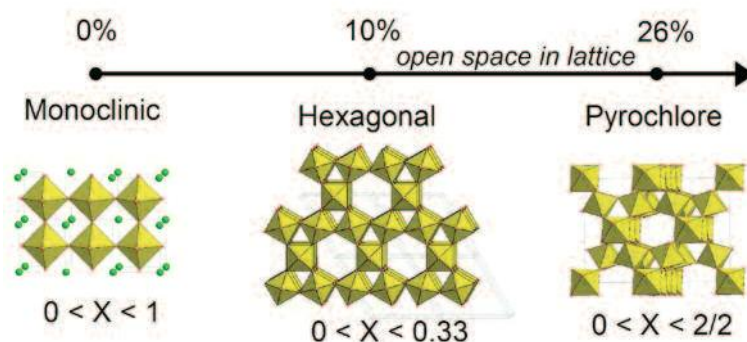


**Figure 18: Tungsten-Based materials for fuel cell applications**

Tungsten-based materials can play different roles in fuel cell systems; they can be used as catalysts, co-catalysts, catalyst supports and electrolytes in different types of fuel cells. W-based materials are being investigated for automotive proton exchange fuel cells.<sup>15</sup>

## GAS SENSORS

A unique property of tungsten oxide lies in the void spaces. The *pyrochlore* form of tungsten oxide has open spaces large enough to hold individual water molecules. When water fills the open spaces, a change in electrical properties occurs, making this material ideal for a stable humidity sensor with high physical stability. High accuracy humidity measurements are vital to proper performance of fuel cell engines, which have a delicate balance of water in and out for proper performance.

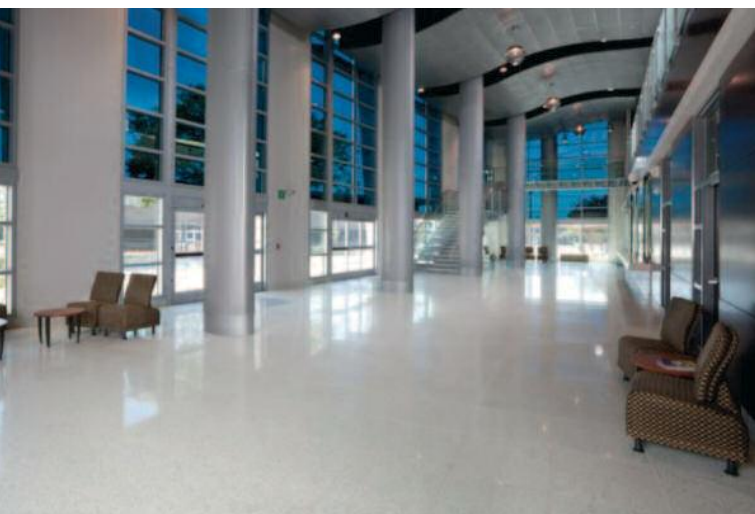
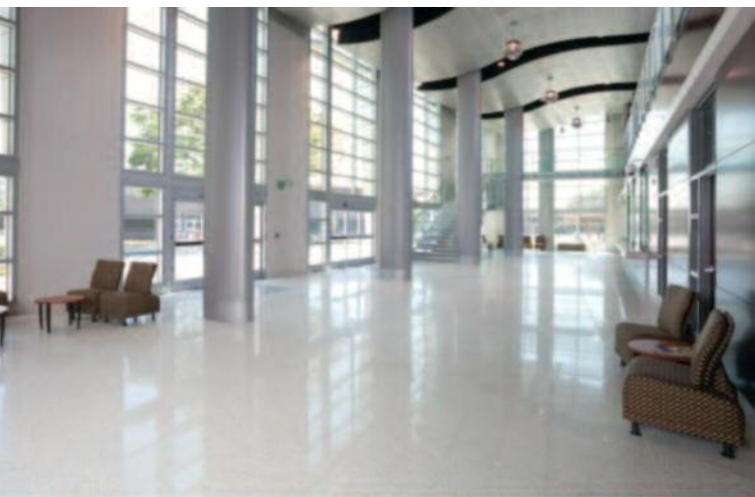


**Figure 19: WO<sub>3</sub>-based gas sensor materials**

Open spaces in the lattice change sensor properties.

## ENERGY SAVING INTELLIGENT WINDOWS

Another emerging technology for tungsten chemicals is for Intelligent Window Systems. With this technology, window glass can be darkened to reduce the heat from direct sunlight, and lightened to allow sunlight in based on weather conditions and occupancy needs. The energy saving potential is significant, especially for commercial space in warm climates that rely on air conditioning for occupant comfort.



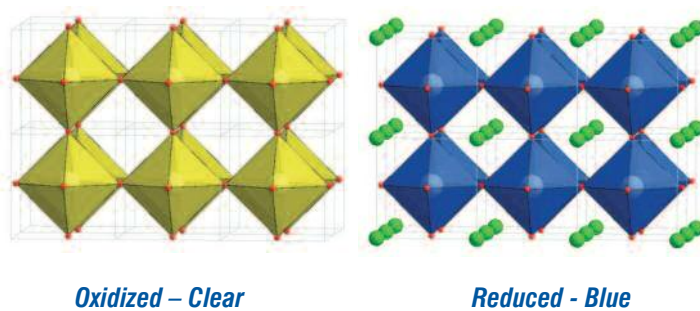
**Figure 20: Smart window**

(SAGE Electrochromics, Inc.)

Modulation of solar energy transmittance for energy-efficient architecture.

Electrochromic windows installed at Chabot College, Hayward, California

In this technology, a thin layer of tungsten is applied to the window glass, and connected to a control system. When current is applied, the tungsten layer darkens. When current is removed, the tungsten layer goes clear again. This effect is based on the property called intercalation, and creates an effect called *electrochromism*.



**Figure 21: Intercalation of Ions in the  $WO_3$  framework**

When current is applied, the tungsten layer darkens. When current is removed, the tungsten layer goes clear again. This effect is based on the property called intercalation, and creates an effect called *electrochromism*.

## MEDICAL APPLICATIONS<sup>16</sup> OF POLYOXOMETALATES (POMS)

The most active areas of medical POM research are antiviral and antitumoral. A third area of activity of POMs showing enhancement of antibiotic effectiveness against otherwise resistant strains of bacteria has also been demonstrated. In this activity, polyoxotungstates in combination with  $\beta$ -lactum antibiotics were studied. POM antiviral activity varies considerably not only with the structural class, composition, size and charge of the polyoxometalate anion but also with the virus and viral strain and the cell line at parity of virus strain.



**Figure 22: W Polyoxometalates (POMs) in Medicine**

W Polyoxometalates have found application as antiviral and antitumoral agents.

POMs have also shown enhancement of antibiotic effectiveness against otherwise resistant strains of bacteria.

Despite the numerous polyoxometalates reported and evaluated, the potential application of this class of compounds to medicine is still in its infancy. It is unfortunate that the first POM put into humans, HPA-23, was one of the most toxic polyoxometalate examined to date, as this retarded investigations of all biological research on POMs. Perhaps the most significant general medical property of POMs is their antiviral activity which is diverse but specific with efficacy *in vivo* not simply *in vitro*.

Tungsten polyoxometalates are also being investigated as an agent for insulin control. This discovery could help in treatment of diabetes as well as to develop new effective weight loss treatments.

## PROTECTIVE APPLICATIONS

Decontamination of Chemical Warfare Agents such as nerve gas (VX) and Sarin gas (GB) is reported by D. M. Mizrahi et al<sup>17</sup>, via an efficient heterogeneous and environmentally friendly degradation of a tungsten-based POM.

Efficient degradation of chemical warfare agents (CWAs) has been a major concern in recent years. Solid powders of ammonium 12-tungstophosphate, a Keggin type heteropoly compound of tungsten, could be used without the need of solvent for the degradation of VX and GB.

Because heteropoly ammonium 12-tungstophosphate works without solvent it could also be used in coating fibers to make protective clothing as well as being put in the formulation for developing skin protecting lotions.

Ammonium 12-tungstophosphate has also been used for the adsorption and separation of radioactive cesium from nuclear waste solutions.

## CONCLUSION

The largest use of W is in the form of cemented carbides (WC-Co). However, the family of W chemicals, ranging from oxides to heteropoly acids and polyoxometalates, offers a rich variety of chemical and physical properties that have driven the use of W chemicals over a wide range of applications. Starting in the late 18<sup>th</sup> century, W chemicals have been in use for over 200 years. New uses of W chemicals are constantly being explored and there are several emerging applications that are likely to propel the use of W chemicals for another hundred years.

## REFERENCES

- [1] Schubert, Wolf-Dieter and Erik Lasser, Tungsten, 2009, International Tungsten Industry Association.
- [2] Dai, Yongyang; Cui, Ying, 11th Int. Conf. on Electrostatic Precipitation, 606 – 610 (2008)
- [3] C. Marignac, J. Prakt. Chem., 77 (2), 417 (1862)
- [4] G. D. Yadav, "Synergism of clay and heteropoly acids as nanocatalysts for the development of green processes with potential industrial applications", Catalysis Surveys from Asia, vol. 9, No 2, pp117-137, May 2005
- [5] Husnu Emrah Unalan et al., IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 55, NO. 11, NOVEMBER, 2008
- [6] T. A. Lobova and E. A. Marchenko, "Modified Solid Lubricating Coatings Based on Tungsten Selenide," J. Friction & Wear, Vol. 28, pp. 193-199 (2007)
- [7] M. S. Chandrasekharaiah, J. L. Margrave, J. Phys. Chem. Ref. Data, V. 22, 1459-1468, 1993
- [8] Kim W. Mitchell, Ann. Rev. Mater. Sci. 12, 401-415,(1982)
- [9] J. Molenda and T Bak, Physica, Status Solidi (B), Vol 178, 205-214 (1993)
- [10] Neffgen, Stephan, et al., US Patent Application No 20100041789, 02/18/2010
- [11] Zuguchi, Masayuki; et al., Radiation Protection Dosimetry (2008), Vol. 131, No.4, pp. 532-534
- [12] Koroznika, L; et al., "The Use of Low-Toxic Heavy Suspensions in Mineral Sands Evaluation and Zircon Fractionation." The 6th Int. Heavy Minerals Conference 'Back to Basics', The Southern African Institute of Mining and Metallurgy, 2007
- [13] P. Staiti, et al., Journal of Power Sources, Vol. 90,(2000), pp. 231-235
- [14] J. B. Christian, et al., Electrochemistry Communications, Vol. 9, (2007), pp. 2128–2132
- [15] Antolini, E. and E.R. Gonzalez, Applied Catalysis B: Environmental, 96 (2010) 245-266.
- [16] J. T. Rhule, et al., Chem. Rev. 1998, 98, 327-357
- [17] D. M. Mizrahi, et al., Journal of Hazardous Materials, Vol. 179, (2010), pp. 495-499

### Publisher:

International Tungsten Industry Association  
1<sup>st</sup> Floor 454–458 Chiswick High Road, London W4 5TT, UK  
Tel +44 20 8996 2221 | Email info@itia.info | www.itia.info

### Editor in Chief:

Burghard Zeiler

### Copyright:

Agreement to cite text from the ITIA Newsletters must be requested in advance from ITIA. Permission to use the illustrations, however, must be sought direct from the owner of the original copyright.

### Disclaimer:

The International Tungsten Association (ITIA) has made every effort to ensure that the information presented is technically correct. However, ITIA does not represent or warrant the accuracy of the information contained in the Tungsten Newsletter or its suitability for any general or specific use. The reader is advised that the material contained herein is for information purposes only; it should not be used or relied upon for any specific or general application without first obtaining competent advice. ITIA, its members, employees and consultants disclaim any and all liability or responsibility of any kind of loss, damage, or injury resulting from the use of the information contained in this publication.