

SUMMARY OF DATA FOR CHEMICAL SELECTION

Tungsten Trioxide & Suboxides

BASIS OF NOMINATION TO THE NTP

Tungsten trioxide and its suboxides are brought to the attention of the Chemical Selection Working Group because of recent concerns that these substances may be fibrogenic in certain industrial settings. Previously, most information on tungsten compounds was from the cemented tungsten carbide industry. Although hard metal disease in this industry is well known, most effects have been attributed to cobalt.

Tungsten oxides were selected for review for several reasons. In the US, all sources of unrefined tungsten are presently imported for preparation of tungsten powder that is used to produce cemented tungsten carbide. Exposure to various tungsten oxides and suboxides occurs in the metallurgical processes used to produce tungsten powder. Recent studies in Sweden have shown that calcination of tungsten oxide (yellow oxide), ammonium paratungstate, and blue oxide ($WO_{2.90}$) results in the formation of asbestos-like tungsten oxide whiskers that are thought to be much more toxic than tungsten powder. Respirable tungsten oxide fibers with a diameter $<0.3 \mu\text{m}$ have also been found in dust from the hard metal industry. Tungsten oxide uses in the textiles, ceramics, and plastics industries, contribute further to potential worker exposure.

No adequate 2-year carcinogenicity studies of tungsten trioxide or its suboxides were found in the available literature. *In vitro* reports described the fibrous form of tungsten oxide as an inducer of hydroxyl radicals and a cytotoxic agent to human lung cells.

INPUT FROM GOVERNMENT AGENCIES/INDUSTRY

CSWG member, Dr. Yin-Tak Woo of the US Environmental Protection Agency (EPA) provided additional information on the toxicity of tungsten and tungsten compounds. This information, which was available to the CSWG members during their review of the tungsten oxides

nomination, is incorporated, as appropriate, into the final summary sheet forwarded to the NTP.

SELECTION STATUS: Selected

ACTION BY CSWG: 12/17/02

Studies requested:

Carcinogenicity

Priority:

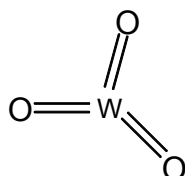
High

Rationale/Remarks:

- Tungsten is one of several metals that may form toxic fibrous “whiskers.”
- The carcinogenic potential of tungsten (vs cemented tungsten carbide) is not adequately characterized.
- Although most suboxide “whiskers” are generated by heat, blue oxide is a commercially available fibrous form of tungsten oxide.
- Width and aspect ratios are important criteria for selection of the fibrous oxide to be tested.

CHEMICAL IDENTIFICATION

<u>CAS Registry No.:</u>	1314-35-8
<u>Synonyms:</u>	Tungstic acid anhydride; tungstic anhydride; tungstic oxide; tungsten(VI) oxide; wolframic acid, anhydrous (ChemID, 2002; Lewis, 2002; Merck, 2001)

Structure, Molecular Formula, and Molecular Weight:WO₃

Mol. wt.: 231.84

Structural Class: Transition metal oxideChemical and Physical Properties:

<u>Description:</u>	Canary-yellow, heavy powder; dark-orange when heated, regaining original color when cooling; pseudorhombic crystal at room temperature, tetragonal above 700 °C (Lewis, 2002; Merck, 2001; Penrice, 1997)
<u>Melting Point:</u>	1473 °C (Lewis, 2002)
<u>Solubility:</u>	Soluble in caustic alkalies, very slightly sol. in acids, insol. in water (Lewis, 2002; Merck, 2001)
<u>Density/Specific Gravity:</u>	7.16 g/cm ³ (25 °C) (Lewis, 2002)
<u>Reactivity:</u>	Noncombustible (Lewis, 2002)

Technical Products and Impurities:

Tungsten trioxide (99.995%) is available from Sigma-Aldrich (Sigma-Aldrich, 2002b).

Several tungsten suboxides are formed as intermediates during the manufacture of metallic tungsten from tungsten trioxide. The best characterized of these suboxides is a whisker form, W₁₈O₄₉ (WO_{2.72}). Tungsten suboxide whiskers with a nominal composition of WO_{2.72} have been prepared in the laboratory by mixing tungsten trioxide with tungsten dioxide. These oxides (powder) were heated for 3 days in sealed silica capsules at 900 °C with a

moderate temperature gradient. The synthesized fibers of $W_{18}O_{49}$ had median length, width, and aspect ratios of 23.9, 0.96, and 26.14 Å, respectively (Leanderson & Sahle, 1995).

Another fibrous tungsten oxide is ‘blue oxide’, with a nominal composition of $WO_{2.90}$ ($W_{20}O_{58}$). This oxide is formed during the calcination of ammonium paratungstate (APT) as part of the final step in the production of tungsten powder. Blue oxide is also a raw material for the production of tungsten powder and can be obtained at >99.9% purity from Stanford Materials (International Tungsten Industry Association, 2002; Sahle *et al.*, 1996; Stanford Materials, 2002).

Table 1 summarizes the chemical composition, physical characteristics, and formation of tungsten trioxide and its best characterized suboxides.

Table 1. Composition and formation of tungsten trioxide and its suboxides.

Name/Molecular Formula	Nominal Composition	Use	Physical Characteristics of oxide/Formation
Tungsten trioxide (yellow oxide)	WO_3	Raw material for production of tungsten metal	Non-fibrous dust
Tungsten suboxide $W_{18}O_{49}$	$WO_{2.72}$		Fibrous dust, created during calcination of WO_3
Blue oxide $W_{20}O_{58}$	$WO_{2.90}$ or $WO_{2.90-2.97}$	Raw material for production of tungsten metal	Fibrous dust, created during calcination of APT

Sources: Leanderson & Sahle, 1995; Penrice, 1997; Sahle *et al.*, 1996; Stanford Materials, 2002

EXPOSURE INFORMATION

Production and Producers:

Manufacturing Process: Tungsten trioxide is obtained from the tungsten ores, scheelite and wolframite. These ores, which contain <1% tungsten trioxide, undergo crushing and grinding. Concentrates containing $\geq 65\%$ tungsten trioxide are then prepared by various separation steps (flotation, gravity, magnetic) and purification by acid leaching. Scheelite minerals are converted directly to tungstic acid precipitates by treating the concentrates with hot hydrochloric acid. Wolframite concentrates are fused with sodium carbonate to yield sodium tungstate that is extracted with hot water and treated with hydrochloric acid to form tungstic acid. The tungstic acid is dissolved with ammonia and evaporated to produce APT ($[\text{NH}_4]_{10}\text{W}_{12}\text{O}_{41}\cdot 5\text{H}_2\text{O}$) crystals. The APT crystals are calcined to yellow oxide (WO_3) or blue oxide ($\text{W}_{20}\text{O}_{58}$). The yellow oxides and blue oxides are reduced in pusher furnaces or in rotary furnaces to form tungsten metal powder (Christie & Brathwaite, 1996; International Tungsten Industry Association, 2002; Lewis, 2002).

Production/Import Level: Tungsten trioxide is listed in the US Environmental Protection Agency's (EPA's) Toxic Substances Control Act (TSCA) Inventory (ChemID, 2002).

The Port Import/Export Reporting Service (PIERS) reported tungsten trioxide imports with a cargo weight of 3,001,035 lbs over the 30-month period from March 2000 to September 2002. Exporting countries were China, Vietnam, Germany, Hong Kong, and the Netherlands. PIERS did not report tungsten trioxide exports during that period (Dialog Information Service, 2002).

In recent years, the primary tungsten raw material traded in the market is APT. Recycling is also an important source of tungsten. Approximately 30% of the world's tungsten supply is recycled (International Tungsten Industry Association, 2002). During 2001, the tungsten content of scrap found in processors and end users was estimated at 6,000 tons, representing about 43% of the apparent consumption of

tungsten in all forms (USGS, 2002).

US tungsten mines have been closed since 1994. In 1999, China and Russia were the largest suppliers of tungsten to the US, accounting for 66% of all imported tungsten. In 2001, a total of 10,400 metric tons (tungsten content) of tungsten minerals or concentrates were imported into the US. Of those, 2,400 metric tons were ore concentrates and 8,000 metric tons were other forms of tungsten. In 2001, eight US companies were known to process tungsten concentrates, APT, tungsten trioxide, or scrap (Shedd, 1999; USGS, 2002).

Producers and Importers: Twenty-one suppliers of tungsten trioxide are listed by Chem Sources USA (Chemical Sources International, 2002).

According to recent issues of chemical directories, tungsten trioxide is manufactured or distributed by Alfa Aesar/Johnson Matthey; Atlantic Equipment Engineers; CERAC Inc.; GFI Advanced Technologies, Inc.; Noah Technologies Corp.; Pechiney World Trade; Reade Advanced Materials; Spectrum Chemical Mfg. Corp. (Chemyclopedia Online, 2002; Hunter, 2001; Tilton, 2001).

Use Pattern: Yellow oxide and blue oxide are used primarily to produce tungsten metal powder (International Tungsten Industry Association, 2002; Lewis, 2002). The great majority of metallic tungsten is used to make cemented carbide parts, and the remainder is used in manufacturing components for lighting, electrical, electronic, heating, and welding applications; and in tool steels, alloys, catalysts, pigments, and high-temperature lubricants (Shedd, 1999; USGS, 2002).

Other uses of tungsten trioxide include:

- In the manufacturing of tungstates for x-ray screens and for fireproofing fabrics (Lewis, 2002; Merck, 2001)
- In textiles and in the plastics industry (ACGIH, 2001; Beliles, 1994)
- As a yellow pigment in ceramic glazes and enamels (ACGIH, 2001; International

Tungsten Industry Association, 2001; Lewis, 2002; Loehman, 1993)

- In electrochromic devices (ECD) used to manufacture ‘smart glass’ which is able to adjust the amount of light passing through it. Smart glass applications include night vision rear-view mirrors and automotive glass, eyewear, and ‘smart’ windows (Malvino Inc., 1999)
- As a catalyst in the production of propyl alcohols (Unruh & Pearson, 1996)
- In ozone monitoring sensors (Ropkins & Colvile, 2000)
- In lamps used in marine PEL (port entry light) sector lights (Vega Industries Limited, 2002)

Blue oxide ($W_{20}O_{58}$) is a catalyst and a promoter of catalysts in industrial chemical synthesis (Penrice, 1997).

Currently, 620 patents on file with the US Patents and Trademark Office mention the use of tungsten trioxide in some capacity. Several patents refer to the use of this material in coatings, films, gas sensors, and in catalyst compositions (US Patents and Trademark Office, 2002).

The total estimated value of tungsten consumed in the US in 2001 was \$350 million (USGS, 2002). Information on individual tungsten compounds was not found in the available literature.

Human Exposure:

Occupational Exposure: Workers may be exposed to tungsten compounds through inhalation of dust and dermal contact where these compounds are produced or used (HSDB, 2002a).

Tungsten oxide fibers were first detected in the environment of a Swedish hard-metal industry. All fibers were respirable, with about 80% being $\leq 0.3 \mu\text{m}$ in diameter. These fibers were measured in dust samples collected near a reduction furnace. The tungsten oxide fibers were usually very thin and short, either straight or curved. Both single fibers and aggregates were common. Gravimetric analysis of 32-hour samples collected

on Millipore filters showed total dust concentrations of 0.22 mg/m³, whereas fiber concentrations estimated by optical phase contrast microscope using generally accepted asbestos counting procedures ranged from 0.14-0.23 fibers/ml (Sahle, 1992; Sahle *et al.*, 1993).

In follow-up studies, Sahle and colleagues (1996) also detected respirable tungsten oxide fibers in static and personal samples collected at two Swedish factories where APT and blue oxide or yellow oxide were used to produce tungsten powder. In the first factory, at positions away from the calcination furnace, total and respirable dust levels were 0.15 and 0.13 mg/m³ with fiber levels of 0.003 f/ml (length $\geq 5 \mu\text{m}$) and 0.03 f/ml (length $\geq 0.5 \mu\text{m}$) when APT was used. Corresponding values for areas near the calcination furnace were ~ 0.14 and ~ 0.08 mg/m³ and 0.009 and 0.72 f/ml, respectively. Near the reduction furnace, total and respirable dust levels were 3.67 mg/m³ and 0.48 mg/m³, respectively, with fiber levels of 0.04 f/ml (length $\geq 5 \mu\text{m}$) and 1.23 f/ml (length $\geq 0.5 \mu\text{m}$).

In the second factory, when yellow oxide was used, the total dust level was 0.11-1.96 mg/m³ with respirable dust levels 0.1 ± 0.7 mg/m³. Mean fiber levels of 0.04 ± 0.03 f/ml (length $\geq 5 \mu\text{m}$) and 0.45 ± 0.16 (length $\geq 0.5 \mu\text{m}$) were measured using transmission electron microscopy. Personal samples ranged from 0.2-135.6 mg/m³ with fiber levels of 0.01 to 0.8 f/ml (length $\geq 5 \mu\text{m}$) and 0.06 to 4.9 f/ml (length $\geq 0.5 \mu\text{m}$). The highest levels were in charging of raw material, changing of the hammer, emptying and cleaning the cyclone and microfilters, and cleaning and maintenance of the furnaces (Sahle *et al.*, 1996).

Workers only wore respirators during extremely dusty operations, such as cleaning and maintenance of the furnaces. However, they were also exposed to airborne tungsten oxide whiskers during loading of raw materials, transporting, sieving, and handling of leftovers. When blue oxide was loaded in the calcination furnace, the dust generated was fibrous, while the dust originated from using APT or tungsten trioxide was not. However, the calcination of APT did generate tungsten oxide whiskers (Sahle *et al.*,

1996).

Tungsten was detected in the lungs of coal miners with concentrations varying from a low of 0.5 ppm to a high of 10 ppm. The tungsten concentration in the lungs of non-mining residents in the same area was comparable to those in the lungs of coal miners' lungs with the lowest values (Beliles, 1994).

Environmental Occurrence: Tungsten trioxide is found in mineral ores such as scheelite and wolframite at concentrations below 1%. Scheelite ores consist of a mixture of scheelite (CaWO_4) and powellite (CaMoO_4); wolframite is mostly ferberite (FeWO_4) and huebnerite (MnWO_4). These tungsten minerals are mostly found in deposits formed by hydrothermal fluids associated with intrusions of granitic composition, mainly skarns and wolframite-bearing quartz veins. Tungsten can also be produced as a co-product of some molybdenum mining operations (Christie & Brathwaite, 1996).

The average concentration of tungsten in the earth's crust is about 0.006%. The most stable oxidation state of tungsten is 6+ and tungsten occurs naturally in ores as tungstate (HSDB, 2002a).

The largest known tungsten deposits in the world are in China and Canada. Tungsten ores have also been found in the US, South Korea, France, North Caucasus, and South America (Christie & Brathwaite, 1996).

Tungsten may be found in negligible amounts in chrysotile asbestos and cement, while amounts in bituminous coal dust from Pennsylvania and Utah varied from insignificant to 0.32 ppm (Beliles, 1994).

Tungsten has been released into the atmosphere only at small concentrations, mainly from industrial emissions and nuclear fall-out. Its levels in air were reported to be $<1.5 \text{ ng/m}^3$. In another study, the concentration detected in a 24-hr urban air sample was $0.5 \text{ } \mu\text{g/m}^3$. In natural waters, tungsten is in the form WO_4^{2-} and other tungstate polyanions

(HSDB, 2002a; NIOSH, 1977).

Regulatory Status: The National Institute for Occupational Safety and Health (NIOSH) recommends a time-weighted average (TWA) for insoluble tungsten compounds of 5 mg/m³, measured as tungsten, for up to a 10-hr work shift in a 40-hr week (NIOSH, 1977).

The Mine Safety and Health Administration (MSHA) permissible exposure limit (PEL), the Occupational Safety and Health Administration (OSHA) PEL, and the American Conference of Governmental Industrial Hygienists (ACGIH)-recommended threshold limit value (TLV) for insoluble tungsten compounds is a TWA of 5 mg/m³, measured as tungsten (ACGIH, 2001; Beliles, 1994; Sigma-Aldrich, 2002a).

EVIDENCE FOR POSSIBLE CARCINOGENIC ACTIVITY

Human Data: No epidemiological studies or case reports specifically investigating the association of exposure to tungsten oxides and cancer risks in humans were identified in the available literature.

Two limited Russian studies examined some workers who were exposed to tungsten compounds in the early stages of cemented tungsten carbide production where cobalt and other materials had not yet been incorporated. Signs of pulmonary fibrosis were observed in 9 and 11% of these workers (NIOSH, 1977). In contrast, a 1966 letter from Union Carbide to the ACGIH reported that medical exams of workers with long-term exposure to tungsten or its insoluble compounds found no evidence of pneumoconiosis (ACGIH, 2001).

Patch tests in six hard-metal industry workers with dermatitis showed that these subjects did not react to tungsten oxides (NIOSH, 1977).

Animal Data: No 2-year carcinogenicity studies of any tungsten oxide were identified in the available literature.

Information on the acute toxicity of tungsten trioxide in laboratory animals is presented in Table 2.

Table 2. Acute toxicity of tungsten trioxide.

Species	Route	LD ₅₀
rat	oral	1,059 mg/kg
unspecified	oral	840 mg/kg

Sources: NIOSH, 1977; Sigma-Aldrich, 2002a

Two older studies examined the long-term consequences of a single intratracheal instillation of tungsten trioxide in animals. At 50 mg in rats, tungsten trioxide produced thickening of the walls between the alveoli and infiltration of macrophages around the blood vessels of the bronchi 4 months post-administration. The endothelium was swollen

and the walls of the small vessels were thickened. Sclerosis of the vascular walls and peribronchial areas was observed. Lesions surrounding the dust particles were characterized by fine, collagenous fibers. Cellular proliferation in the lung persisted 8 months after the instillation. No macroscopic alterations in other internal organs were observed at 4 or 8 months. Similar results were described in another study where rats were instilled intratracheally with a calcium-magnesium-tungstate phosphor containing 75% tungsten trioxide (HSDB, 2002b; NIOSH, 1977).

A single intratracheal instillation of a mixture of tungsten trioxide (47.5 mg) and silicon dioxide (2.5 mg) produced emphysema, enlarged lymph glands, and general fibrotic and sclerotic reactions in rats 8 months post-administration (Mogilevskaya, 1961).

Short-Term Tests: No studies of the genotoxic potential of tungsten trioxide or its suboxides were identified in the available literature.

Metabolism: The kinetics of radioactive tungsten trioxide following inhalation was determined in six beagle dogs. Anesthetized animals were exposed by facemask for 6 hours to an aerosol of tungsten trioxide ($^{181}\text{WO}_3$) with a specific activity of 98 $\mu\text{Ci}/\text{ml}$. The amount deposited in the respiratory tract ranged from 1.9 to 8.0 μCi , 60% of which was in the lower part of the tract. In the lung, 69% of the radioactivity was removed with a half-life of 4 hours, 23 % was removed with a half-life of 20 hours, 4.6% was removed with a half-life of 6.3 days, and 3% was removed with a half-life of 100 days. In contrast, 94% of the radioactivity in the lower body was removed with a half-life of 9 hours. The total body burden of radioactivity at 165 days post-inhalation was distributed among the skeleton (37%), lungs (31%), kidneys (15%), liver (9.7%), and skeletal muscle (5.7%) (Aamodt, 1975, cited in NIOSH, 1977).

A 1945 study in rats given tungsten trioxide in the diet (0.1% as tungsten) showed that the bone and spleen retained the most tungsten after 100 days while the liver, kidneys, and skin had only trace amounts (Kinard & Aull, 1945, cited in NIOSH, 1977).

Other Biological Effects: In an *in vitro* study, both tungsten oxide with a nominal composition $WO_{2.72}$, and crocidolite caused considerable dose-related hydroxyl radical formation, much greater than the amounts formed by anthophyllite asbestos. Tungsten oxide fibers were also more cytotoxic to human lung cells than crocidolite, however, crocidolite had a greater hemolytic effect on red blood cells than tungsten oxide fibers (Leanderson & Sahle, 1995).

Soluble mediators released from activated macrophages have been linked to the development of silicotic fibrosis. A study to investigate the fibrogenic effect of dusts was conducted in male Wistar rats. Intratracheal instillation of tungsten trioxide had no effects on the release of interleukin-1 to the bronchoalveolar lavage fluid (BAL). The *in vitro* proliferation of fibroblasts induced by BAL was the same in control and treated animals. These findings correlated with histological analysis of the lungs where tungsten trioxide produced no changes or variations in the content of lung collagen (Wang, 1994).

Structure-Activity Relationships: Toxicological data for tungsten carbide, and cemented tungsten carbide would not provide a meaningful structural comparison for tungsten trioxide and suboxide whiskers.

Epidemiologic studies on tungsten miners in China revealed a significantly higher incidence of mammary cancer mortality among both male (13.8-fold higher) and female (2.5-fold higher) workers. Lifetime exposure of mice to a trace level of sodium tungstate (5 ppm as tungsten) showed no evidence of carcinogenicity. A 30-week study in which rats were given drinking water containing sodium tungstate (100 ppm as tungsten) also showed no evidence of carcinogenicity. However, at 100-200 ppm, tungsten significantly enhanced the mammary carcinogenicity of nitrosomethylurea and countered the anticarcinogenic effect of molybdenum in rats. Two tungsten compounds, tungsten chloride and sodium tungstate were negative in an *in vitro* assay for potential to enhance viral cell transformation (Luo *et al.*, 1983; Wei *et al.*, 1985; Woo, 2002). The relevance of the information on soluble tungsten compounds to the carcinogenic potential of tungsten oxide whiskers is unknown.

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