

WHITE PAPER

Practical Toxicological Issues with Friction Materials and Brake Pads June 29, 2010 Dr. David Mohr

Performance Friction (PFC) Policy – Toxicology Issues in Friction Materials

- PFC's goal is to set the highest standard in the industry for toxicologically safe products, just as our goal is to be the best in product performance and safe stopping power.
- PFC's does not and will not use materials identified to be significant health risks in our products.
- In addition, PFC also excludes the use of material that transforms to a harmful material while in service, by action of heat or oxygen for example.

Disclaimer –

This paper is not intended to be all-encompassing or address all possible risks with materials used in friction materials. Please use as a starting point and resource for your own evaluations.

Also, practical issues of worker safety and best practices for working with these materials in a shop environment are not addressed. The whole purpose here is give the reader a starting point for assessing the risk associated with raw materials used in brake pads.

Background – Toxicology risks in the friction industry

The friction industry has a record of using potentially hazardous materials. This created potential harms to customers, end-consumers, and employees. As a result, the industry has undergone multiple lawsuits to compensate for their damages. This has placed a heavy burden on these organizations in terms of profitability and clouds their future.

Despite the government's encouragement to exclude known bad-actors from friction formulations, many suppliers continue to sell products containing hazardous materials such as:

- Asbestos
- Potassium Octatitanate whiskers
- Other ceramic fibers with high bio-persistence
- Lead compounds
- Antimony Sulfides (contain arsenic, and transform to antimony oxide in service)
- Chromium compounds
- Copper

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Some manufacturers choose to disregard ethical standards and continue to use these materials until the government bans them or their lawsuits become a greater liability than they are willing to bear.

This approach seems irresponsible to the public, the associated workforce, and to the long-term viability of companies using these materials.

Recent Legislation Changes the Landscape for Brake Pad Toxicology

Currently many states have either passed legislation banning the use of friction materials with significant toxic materials including copper (starting with Washington State Bill 6557) or are working on passing such legislation. Some details from SB 6557 follow:

- Under the legislation, passed in march 2010, all brake pads must contain less than 5-percent copper content starting in 2021 and, if proven feasible, the legislation could virtually eliminate copper from the pads altogether two years after that.
- Other toxic materials are eliminated January 1, 2014.

Text of the bill can be found at:

<http://apps.leg.wa.gov/documents/billdocs/2009-10/Pdf/Bills/Session%20Law%202010/6557-S.SL.pdf>

General Approach to Developing and Using Friction Materials: Assessing Risks:

An important step in sourcing any raw material lies in assessing the toxicological risk involved in using the material as supplied, as well as making an informed prediction concerning toxicological risks that may develop in service.

Friction materials in service often see relatively high temperatures at the rubbing interface. Brake pad temperature can reach 600-1000°F frequently in service and can get much hotter depending on the application. Because brake pad wear produces a very fine powder, lots of oxidation can occur at the surface.

Manufacturers should evaluate the toxicological risks associated with the raw material as purchased and after being in service.

One primary source for determining the status of raw materials can be found in:

The US Government: Welcome to TOXNET, a cluster of databases on toxicology, hazardous chemicals, and related areas
<http://toxnet.nlm.nih.gov/index.html>

Official Citation: Report on Carcinogens, Tenth Edition; U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, December 2002
<http://ehp.niehs.nih.gov/roc/toc10.html>

Also see Cal Prop 65, <http://www.calprop65.com/>; there are links to current lists on that web site.

Note: European and other regions maintain their own lists that may have to be assessed.

Also, OEM's and Tier 1 customers maintain their own lists that may change from time to time. **Examples:**

- GM: GMW3059
- Ford: WSS-M99P9999-A1. See https://fsn.ford.com/dbwf/docs/2003EnvGuide_v6.pdf
- BOSCH: Bosch Standard N2580
- IMDS system.

Discussion of specific risks

Asbestos, Potassium Octatitanate, and ceramic fibers with high bio-persistence:

Certain types of asbestos fiber are known to have negative health impacts. Other fibers, such as refractory ceramic fibers, that have the same characteristics can have the same adverse health effects.

International Agency for Research on Cancer (IARC) classifies some types of man-made fibers as carcinogens (IARC monograph Volume 43). Quoting an IARC document, "There is *sufficient evidence* for the carcinogenicity of glass wool and of ceramic fibers in experimental animals."

Meanwhile, over three million workers in the U.S. are estimated to have been exposed to asbestos, man-made mineral fibers, or silica (OSHA).

From EPA's IRIS 0647 report (<http://www.epa.gov/iris/subst/0647.htm>): "Refractory ceramic fibers (RCFs) are synthetic, vitreous, non-crystalline, aluminum silicate-based fibers. They are produced by melting kaolin clay, or a mixture of alumina (Al₂O₃) and silica (SiO₂), and then spinning or blowing the melt to form elongated particles at least 3 times longer than wide (aspect ratio >3). Up to 20% of zirconia (ZrO₂), and about 1-5% of other metallic oxides (TiO₂, Cr₂O₃, Fe₂O₃, MgO, etc.) are sometimes added in the process to produce specialty RCFs (e.g., zirconia RCF) for specific high-temperature applications. Fiber diameters and lengths vary within the products; the average diameters of most RCFs produced in the U.S. are 2.0-3.5 microns but can range from <1 micron to about 12 microns. Under some use conditions at temperatures above 1000 degrees C, crystalline silica may be generated from manufactured RCF products (IARC, 1988; U.S. EPA, 1988).

There is ample evidence from epidemiologic and animal studies that exposure to asbestos causes, in addition to lung cancer and mesothelioma, excess rates of lung fibrosis (asbestosis) and pleural changes. Many of these non-neoplastic pulmonary and pleural changes (e.g., pleural plaques) have been useful markers and most diagnostic for asbestos exposure. Refractory ceramic fibers (RCFs) are similar to asbestos in fiber sizes and many of their physical properties (e.g., durability), which are critical factors for their pathogenicity. Although no human data are available regarding cancer from exposure to RCFs, a

pulmonary morbidity study conducted on workers manufacturing RCFs and RCF products at five U.S. manufacturing facilities has shown an increased rate of pleural plaques among workers in the RCF industry (Lockey et al., 1991). Inhalation studies in rats (Davis et al., 1984) and hamsters (Carborundum, 1990) also showed that aluminum silicate RCFs caused pulmonary and pleural fibrosis (in addition to lung tumors and mesothelioma)."

Health effects seem to be related to the fiber size (length (L) and diameter (D)), ratio (L/D), bio-persistence, and perhaps the bio-activity of the fibers.

Fiber size is important because the fibers must be respirable to be active. Quoting an IARC document, "Man-made vitreous fiber products can release airborne respirable fibers during their production, use and removal." Typically, this refers to fibers with a diameter less than 3.5 microns and a length less than 50.

So, what is the status of various man-made fibers? Consider Potassium Titanate: A report by Adachi, et.al. From the Department of Public Health in Japan in "Industrial Health 2001, 39 (2): 168-74," lists Potassium Titanate whiskers as having about 23% of the carcinogenic effects of asbestos (UICC chrysotile B) in interperitoneal studies, with 77% developing mesothelioma by the end of the study when 10 mg of potassium titanate whiskers were administered. This was several times as high as the activity of several other refractory ceramic fibers. Note this would be affected by the fiber durability in lung tissue.

Bio-persistence is important because the longer a fiber stays in the lung, the more potential irritation it creates. Consequently, high bio-persistence may lead to more risk. Note the bio-persistence of some types of asbestos is quite high, and that different high temperature fibers vary in bio-persistence.

Important note: Using these factors (size and bio-persistence), fibers have been engineered that are not classified as carcinogens. Certain fibers such as calcium-magnesium-silicate wool (such as Thermal Ceramics Superwool 607 and 612) have low bio-persistence and are excluded from carcinogenic classification by European Commission Directive 97/69/EC.

Companies that use carcinogen fibers or fibers that may be carcinogens do so by choice, not necessity. Safer alternatives are available.

Antimony sulfide:

Our internal concerns with the antimony sulfides are three-fold:

1. Conversion of antimony sulfide to antimony trioxide in service.
2. Typical contaminants (arsenic, lead) present in antimony sulfide due to the raw material source.
3. Possible inherent toxicity of the material itself.

Note that U.S. Patent 6,303,545 B1 issued in 2001 to Chemetall (Austria) describes the effect of exposing antimony sulfide frictional heat plus atmospheric oxygen to form antimony oxide. This is described in lines 50-55 in the first column on page 2. Note that Chemetall has been a major supplier of metal sulfides, including antimony sulfide, to

European and other friction manufacturers for many years. They are technically the strongest company in the metal sulfide friction additive field.

Also note U.S. patent 3,944,653. This describes alternative methods for making antimony oxide, but cites the primary traditional route – heating antimony sulfide in air produces antimony oxide. The patent also describes a traditional problem with antimony sulfides derived from natural minerals like stibnite – they almost always contain significant contamination with arsenic and lead.

And as a reference, review excerpts from the International Agency for Research on Cancer (IARC) Summary and Evaluation, Volume 47 (1989) that discusses their findings at that time concerning antimony oxides and sulfides. Here, even the antimony sulfides may have shown potential carcinogenic activity – technically it was unclassifiable.

Also note a Swedish occupational standards report (2000). Most of the hazards cited were associated with antimony oxide, but the review also cited a troubling study where 6 of 125 workers exposed to antimony trisulfide resulted in sudden deaths. Additionally, 37 of 75 workers examined exhibited ECG changes. The review mentions that the purity in the antimony trisulfide was not mentioned in the study, so it is possible that the natural contaminants such as arsenic were to blame for the sudden deaths. Table one in this review also shows the results of several studies on oxides and sulfides.

Summarizing, this and similar information leads PFC to internally prohibit the use of antimony compounds.

Lead Compounds:

Lead and lead sulfide have been intimately linked with developmental effect in children. Quoting from the IRIS report for lead and lead compounds, "By comparison to most other environmental toxicants, the degree of uncertainty about the health effects of lead is quite low." It appears that some of these effects, particularly changes in the levels of certain blood enzymes and in aspects of children's neurobehavioral development, may occur at blood lead levels so low as to be essentially without a threshold." This means lead must be excluded from formulations as much as possible, even as a minor constituent to another raw material.

Chromium Compounds:

From IRIS: Chrome (VI):

"This RfD is limited to soluble salts of hexavalent chromium. Examples of soluble salts include potassium dichromate ($K_2Cr_2O_7$), sodium dichromate ($Na_2Cr_2O_7$), potassium chromate ($K_2Cr_2O_4$), and sodium chromate (Na_2CrO_4). Trivalent chromium is an essential nutrient. There is evidence to indicate that hexavalent chromium is reduced in part to trivalent chromium in vivo (Petrilli and DeFlora, 1977, 1978; Gruber and Jennette, 1978).

In 1965, a study of 155 subjects exposed to drinking water at concentrations of approximately 20 mg/L was conducted outside Jinzhou, China. Subjects were observed to

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have sores in the mouth, diarrhea, stomach ache, indigestion, vomiting, elevated white blood cell counts with respect to controls, and a higher per capita rate of cancers, including lung cancer and stomach cancer.”

Again from IRIS, Chrome (III) did not have the same level of known toxicity.

Copper:

The primary effect of copper in brake pads is caused by the effluent from wear debris on the water shed and aquatic life. For example, Washington State ecologists estimate that 318,000 pounds of copper are washed into the water system, 33% from cars and trucks.

Quoted from the Department of Ecology of the state of Washington
(<http://www.ecy.wa.gov/pubs/0903057.pdf>):

- Copper is highly toxic in aquatic environments and harms fish, invertebrates, amphibians and phytoplankton.
- Copper harms the sensory systems of threatened and endangered salmon. It reduces the ability of young salmon to escape from predators. It hinders adult salmon from finding their spawning streams. These toxic effects limit the abundance of salmon returning to our fisheries and spawning grounds.

Similar activity is cited in many other coastal areas and estuaries. California, Rhode Island, and others have legislation in process. EPA rules are driving many locations to consider similar legislation to control copper input at the source.

EPA document on Copper

<http://www.epa.gov/waterscience/criteria/copper/index.htm>