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De-mystifying Friction Material Terminology

Dr. David Mohr, Performance Friction Corporation

De-mystifying Brake Terminology:

Sometimes friction materials jargon can be like a foreign language. With many different materials being discussed and compare in the journals and magazines, it would be helpful to have a reference that explains some of the mystical nomenclature. This review will help you figure out what disc brake pad materials really are, how they are made, and some tips on what to look for (and what to avoid).

Disc Brake Pads: What are they made of?

Friction composites of several different ingredients are molded onto a steel backing plate to form disc brake pads (this process is called "integral molding"). However, there still are some brake pads out there that use the older method of riveting a friction "puck" onto a steel backing plate.

Asbestos based disc pad materials:

- Asbestos is a naturally mined ceramic fiber with a specific fiber length and diameter that has been linked to increased chances of lung cancer.
- Other fibers with similar chemical composition and sizes are likewise suspect.
- Note there are still some friction materials in the field (and some still being imported) that contain asbestos as well as other asbestos-like fibers. The use of such fibers in controlled or prohibited in some countries.
- These materials are typically asbestos fibers molded in a phenolic resin with conventional fillers.

"Ceramic" or NAO disc pads:

- These friction materials often called "ceramic" in the American aftermarket are the same materials that are also called "non-asbestos organic" (NAO) or organic pads. Historically NAO's were replacements for asbestos organic pads.
- Replacing asbestos, one-for-one, with other materials that have similar properties, originally developed the NAO pads.
- NAO's/Ceramic pads are an organic matrix composite containing organic and inorganic fillers that can be powders or fibers. These fillers may typically include barium sulfate ($.06 a lb.) wollastonite ceramic mineral fibers ($.10 a lb.), Kevlar or other aramid fibers, ceramic fibers, other mined mineral powders,
- A typical formulation follows:

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Figure 1. Chemical Analysis of a Typical NAO/Ceramic Friction Material

	Morse CMX 1/30/2003
Aluminum	0.56
Barium	1.67
Carbon	28.3
Calcium	1.54
Copper	**22.3**
Iron	0.36
Potassium	1.07
Magnesium	0.45
Sodium	0.37
Sulfur	3.15
Antimony	**9.84**
Silicon	18
Titanium	2.54
Fluorine	< 5
Insolubles	9.85
Sum	100

Note the two largest ingredients are carbon (not a ceramic) and copper (not a ceramic).

Figure 2. Electron Micrograph of Typical NAO/Ceramic

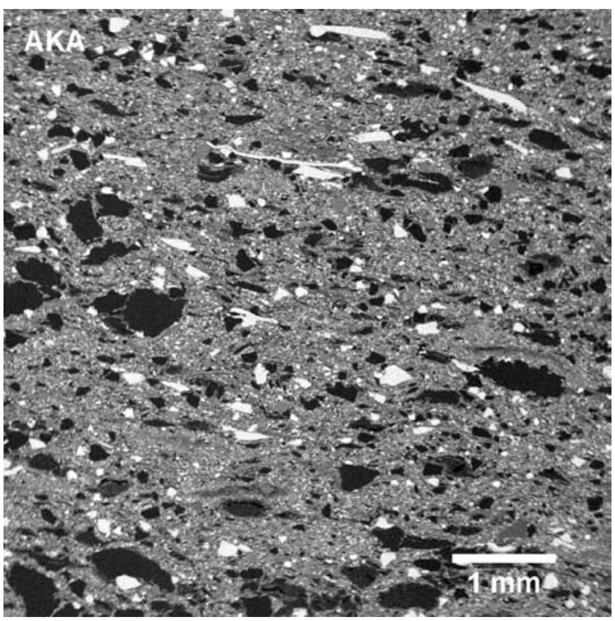

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Figure 3. Distribution of elements in NAO / Ceramic from electron microscope data. Note the presence of fine potassium titanate whiskers though much of the material.

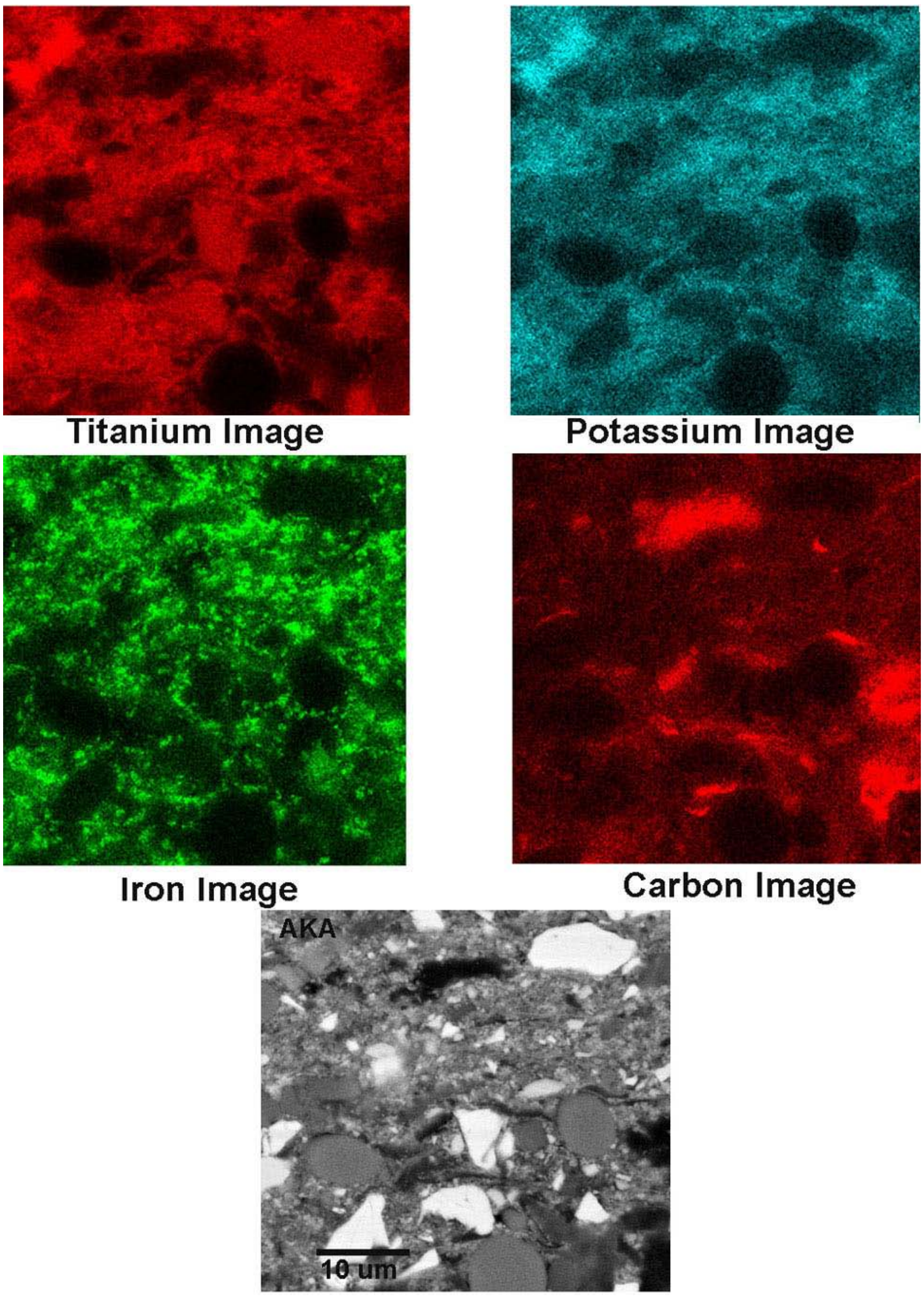

Figure 4. Higher magnification transmission electron microscope pictures show the needle-like shape of the potassium titanate.

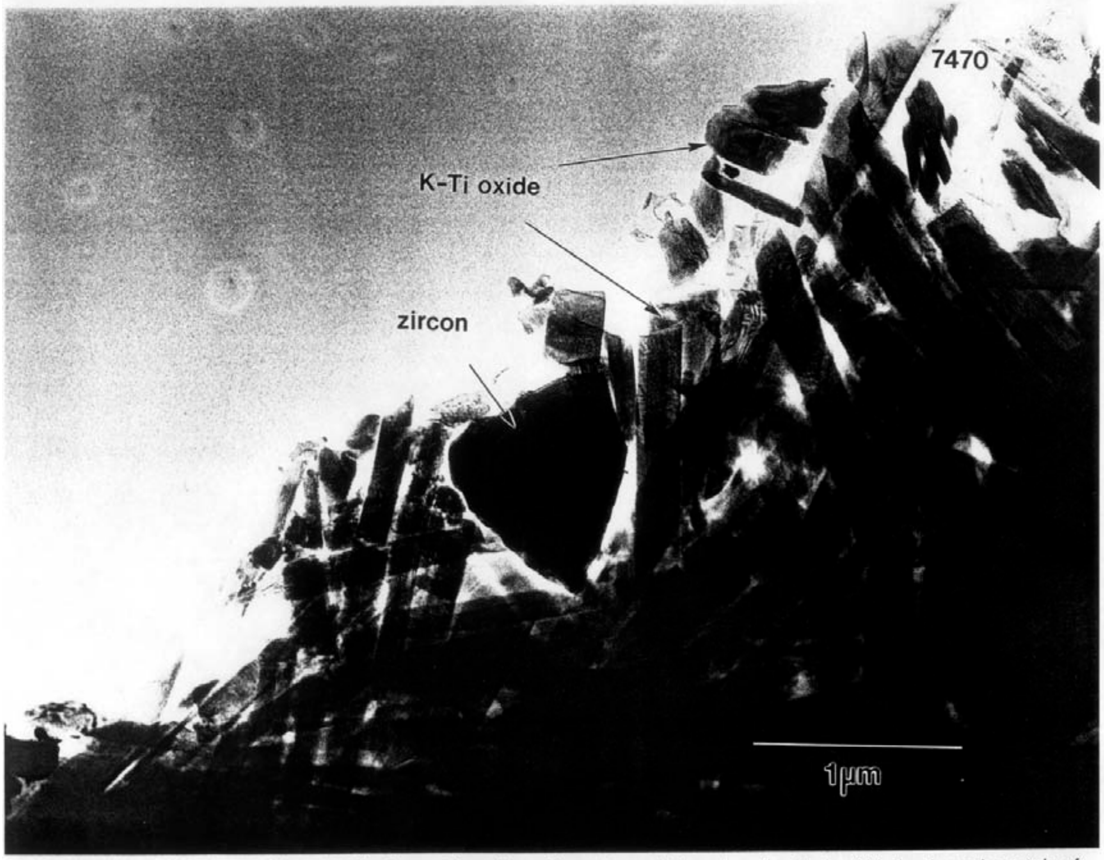

Figure 3. A TEM image (plate 7470) of a matrix region of layer 2 consisting almost entirely of blade-shaped crystals of the K-Ti oxide phase and a single inclusion of $ZrSiO_4$.

NAO's/Ceramics – continued

While NAO/Ceramic friction materials contain small to moderate amounts of ceramic powders or fibers, they are not "ceramic matrix materials or composites"; instead they are organic matrix composite molded using a phenolic or similar resin.

- NAO materials typically exhibit low friction and/or high wear rates at high temperatures. To counteract this behavior they sometimes contain many other raw materials (such as abrasives and metal sulfides) to maintain thermal stability.
- Metal sulfides generally provide lubrication and modify noise properties of these friction materials. Before toxicology concerns were understood these materials often contained lead sulfides and other materials (now banned by the automakers in new vehicles) in as effort to produce reasonable friction and thermal properties. Still some questionable materials like antimony sulfide are used.

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- While some toxic materials have been effectively replaced, “ceramic” or NAO friction materials still often contain fibers with many similar properties as asbestos, including potassium titanate in length and diameter, and/or friction additives like antimony sulfides that have questionable health implications as described below.

NAO/Ceramic Friction

- **Use – light duty applications**
- **Look for:**
  - **Increased compressibility/soft brake pedal under hot stopping conditions.**
  - **Increased wear at high temperatures**
  - **Large amounts of suspect/toxic materials like ceramic fibers and metal sulfides.**

Savvy technicians know that these “ceramic” brake pads are quite different than real ceramic brake components, such as ceramic composites brake rotors used on some high-end cars in limited quantities.

- Real ceramic composite brake rotors have a ceramic matrix, and usually contain reinforcing fibers or particles to improve toughness and reduce catastrophic cracking. NAO (“Ceramic”) pads have an organic matrix.
- Real ceramic composites have been used in rotors in a few exotic applications, but there are no known uses in brake pads.
- In real ceramic composites the fibers or fillers are combined in some way with a ceramic-forming material then heat-treated to form the matrix. Often it takes repeated cycled to reach good density and properties.
- The ceramic can be formed through a number of processes, including decomposition of special polymers; deposition of gas reaction products (chemical vapor deposition); reaction of gasses with a solid (reaction bonding); inorganic reactions in the melt phase; etc.
- Typically some type of organic disc pads is used with the ceramic matrix rotors.

So:

Aftermarket “Ceramic” Pads = Low Metallic Pads with Organic Resin Matrix
Real Ceramic Parts = Composites with real ceramic matrix.

Semi-Metallic friction materials:

Semi-Metallic friction materials were first seen as a high-performance alternative to asbestos materials as asbestos was being phased out.

- Typically a semi-met friction material is a mixture of steel fiber, iron powder, low cost carbon powder, phenolic resin and clay and organic fillers.

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- Fillers may be organic powders, fibers, rubbers, abrasives, lubricants such as graphite, inorganic powders, etc.
- Pads are usually formed onto steel backing plates using compression molding. Older processes sometimes rivet formed linings to the steel backing plates.
- Cure or the resin matrix is sometimes completed in a subsequent bake process.

Semi-Metallic Friction

Use – General friction applications
Look for – Trade-off in formulations – rotor wear for temperature stability.

Carbon Metallic® friction materials:

Carbon Metallic® (a Federally Registered Trademark of Performance Friction Corp.) brake pads are high-tech composites incorporating large volume amounts of special carbon materials (powders or fibers) in a metallic matrix that dramatically improves the thermal stability, stopping power, and noise characteristics of the friction material while yielding improvements in pad wear, and disc wear.

- Typically pads are molded using compression molding and Ionic Fusion® to the backing plate, followed by chemical and pressure controlled high temperature heat treatment to achieve optimal friction and wear properties.
- Technically advanced control of the molecular structure of the carbon and the layering of the composite attachment provide thermal stability, and exceptional noise and vibration characteristics.
- This technology has proven itself very effective at the highest levels of racing, capturing over 70% of the most prominent professional racing series pad sales.
- The characteristics of this product include good wear under all service conditions, good effectiveness and pedal feel, and low noise.
- This type of material is often specified by truck and police fleets due to favorable impact on the operating costs of the fleets: lower cost per mile.

<u>Carbon Metallic® Friction:</u>
Use – High-end applications like where you want good stopping power, noise and wear properties.
Look for – Firm pedal feel over broad range of stopping conditions.

Carbon-Carbon friction materials:

Carbon-Carbon (C-C) friction materials are used primarily in aerospace and industrial applications and specific racing series.

- The C-C composites usually contain carbon fibers in a matrix that is mostly carbon with minor additives.

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- C-C brakes have low cold friction, but once C-C gets hot it maintains good friction at high temperatures.
- The process to make these materials is both complex and expensive. A brief outline follows:
  1. Carbon powder and/or fibers are combined with a source of carbon (like phenolic resin, pitch or hydrocarbon gas) then;
  2. The composite is heated to very high temperature to drive off other materials as gasses, leaving only carbon behind.
  3. Often the "densification" process has to be repeated many times in order to get the part to have good properties.
  4. Further extreme high temperature heat treatments under vacuum or in the presence of inert gas provides carbon crystallization and densification of the composite.
- The process complexity and raw material cost, together with poor cold properties severely limits use of traditional C-C composites for road cars.

Carbon-Carbon Friction

Use – Racing / Aircraft
Look for – Low friction at low temperatures.

Sintered Metallic friction materials:

Sintered brake pads have a metallic matrix.

- Sintered brake pads are held together largely by a matrix of metallic particles that have been molded together using very high pressures using powder metallurgy techniques – followed by high temperature heating to densify or sinter the parts.
- Minor ingredients may include abrasives and lubricants.
- Composites contain very low carbon content, very high metal content.
- Thermal conductivity is very high for these materials.
- Highly abrasive, not generally suited for cast iron disc.

- **Use - Sintered materials are typically used in wet friction applications as well as minor uses in motorcycle and powersports applications, or industrial applications using steel disc rather than cast iron.**
- **Look for - These composites generally have very poor noise properties. Can be very abrasive, not generally suitable for cast iron disc.**

Responsible Recommended Prudent Practice for Friction Materials –

- Materials that have been identified as hazardous on recognized standards/lists such as proposition 65 should not be used in friction products.
- In addition, responsible friction manufacturers should monitor restricted materials lists from major customers as needed.
- Any new raw material incorporated into friction formulations should be reviewed and compared to such lists. Known bad actors should not be used.

- Also, if it is known that the raw material will produce a hazardous material in service due to the operating environment; these materials should also be banned. An example would be the transformation of antimony sulfide to antimony trioxide.

Background – Toxicology risks in the friction industry

The friction industry has a record of using potentially hazardous materials. You only have to look at the fall-out from asbestos to be wary. In addition to potential harm to customers, end users, and to employees, the industry has also paid a price in terms of lawsuits and damages. This has placed a heavy burden on these organizations in terms of profitability, and clouds their future. In addition, more recent laws seek to pass the responsibility down the supply chain to installers and retailers.

While a first step to addressing this would seem to be exclusion of known or suspected bad actors from friction formulations, many friction suppliers choose to sell products containing materials such as:

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

The attitude of some manufacturers seems to be that these materials will be used until the government bans them or the lawsuits build to such a level that their use becomes a sufficient liability to effectively ban them. This attitude is high risk considering upcoming cradle-to-grave environmental laws.

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

Assessing Risks:

An important step in picking any material lies in looking at the toxicological risk involved in using the material as supplied, as well as making a prediction concerning toxicological risks that may develop in service.

First you have to make sure you are looking for a reputable manufacturer that will list all real toxic materials in their MSDS (Materials Data Safety Sheet).

Once that is done, some primary sources 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

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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 California Proposition 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.

Discussion of specific risks

Fibers like Asbestos, Potassium Octatitanate, and ceramic fibers with high bio-persistence.

Research shows that some types of asbestos fiber can be linked to negative health effects. Other fibers, like refractory ceramic fibers, that have the same characteristics may have the same adverse health effects.

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

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

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

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

So what is the status of various man-made fibers? Consider Potassium Titanate: A report by Adachl, 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 interperotoneal 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 the fiber stays in the lung, the more potential irritation it creates. So 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 can have quite different bio-persistence.

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Antimony sulfide / Antimony Trioxide:

Concerns with the antimony sulfides are three-fold:

1. Conversion of antimony sulfide to antimony trioxide in service when exposed to high temperatures. Antimony Trioxide is listed as a carcinogen in Proposition 65.
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. Note Chemetall has been a major supplier of metal sulfides, among them antimony sulfide, to European and other friction manufacturers for many years.

Antimony oxide is a suspected carcinogen, and antimony sulfide can form antimony oxide with application of heat in air – like conditions during braking. This is a potential problem.

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 cited a troubling study where there were 6 sudden deaths of 125 workers exposed to antimony trisulfide. It added that 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 like arsenic were to blame for the sudden deaths.

Summarizing, this and similar information leads PFC to internally prohibit the use of these 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 (CASRN 7439-92-1), “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

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threshold." This means lead must be excluded from formulations as much as possible, even as a minor constituent to another raw material.

Chromium Compounds:

(Noticeable in materials by the color green.)

From IRIS: Chrome (VI) (CASRN 7439-92-1):
"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 have sores in the mouth, diarrhea, stomachache, 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.

Disc Pad Materials Conclusions:

- When working with the raw materials that some friction pads contain, caution and extensive research should be the guiding rule.
- Use caution when removing product of unknown origin.
- Try to select materials that are safe and avoid the potential for future problems and liability.
- Avoid breathing small fibers and exposure to heavy metals.