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**DRAFT**

**Health Hazards Manual  
for  
Cutting Oils  
Coolants  
and  
Metalworking Fluids**

**Risk and Reduction of Risk  
for the Machine Shop  
and Metalworker**

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Health Hazards Manual

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Cutting oils, also called coolants or metalworking fluids, are lubricating liquids used in metalworking, fabricating and machine shops to reduce friction during metal cutting, carry away the heat generated by the cutting process, and flush away metal chips. Fluid coolants are needed because more than 97% of the work involving metal cutting appears as heat. Lubricants prevent frictional welding, prevent tools from dulling prematurely due to buildup and wear, and thus prevent galling and breakage.

## What are Cutting Oils?

Gear hobbing, cutting, shaping and shaving

Turning

Boring

Facing

Grooving

Forming

Cutting off

Box turning

Trepanning

Milling

Drilling

Gum drilling

Counter boring

Spot facing

Counter sinking

Reaming

Broaching

Tapping

Thread cutting

Grinding

Sawing

## Cutting Tool Functions

Metalworking fluids may be chemical solutions (water-based), straight mineral oils, or soluble oils (emulsions of mineral oil in water). Generally the formulation includes a variety of additives as well which improve the performance of the oil or prolong its useful life. Health hazards may be caused by the oil itself, the additives, or both.

## Coolants and Additives

Oxidation inhibition

Corrosion inhibition

Detergency

Dispersive action

Extreme pressure

Film strength

Rust prevention

Pour-point depression

Viscosity improvement

Metal deactivation

Adhesion promotion

Foam inhibition

Foam inhibition

Bacterial growth suppression

Water repellency

Color stabilization

Color additives

## Functions of Additives

## How is the Metal- Worker at Risk from Cutting Oils?

Cutting fluids may be applied to the tool manually, by an air-carried mist, or by a continuous flood. When flooding is used, the oil is delivered by a pump, piping and nozzle to the cutting zone, and floods the tool, work and chip. (Used fluid is then collected in the chip pan and returned by gravity to the pump sump.) The metalworker can therefore be exposed to cutting oils by 2 basic routes of entry: *skin contact* and *inhalation*. The higher risk jobs tend to be those with high cutting speeds, heavy oil flow, and continuous contact which may result in the worker being splashed with oil on the skin or clothing. The oil may remain on the skin for some time and oil-soaked clothing may be worn all shift.

Inhalation of cutting oil mists may occur because of the nature of coolant delivery or because of the high temperatures and speeds generated at the cutting tool's working edge. When the mist stream method of coolant delivery is used, much of it evaporates on contact with the hot tool, workpiece or chip. In addition to the intentional production of oil mists, vaporized oil can also be generated by the forces of the rapidly spinning workpiece or tool or by the vaporization of the fluid from the heat of the cutting process.

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## Basic Types of Cutting Fluids

Since the nature of the health hazard of a cutting fluid is determined by the fluid's composition, we will first take an overall look at the 3 basic types of cutting fluids: straight mineral oils, soluble oils and synthetics. (We will look at composition in more detail later when we discuss product substitution as a means of reducing risk.)

1. Straight oils with additives ("neat" oils): These contain no water and are made from highly refined base oils (mineral oils) blended with appropriate additives. ~~They typically represent about 45% of the metalworking fluids used today.~~ Straight oils tend to be used when heavy cuts are taken or fine finishes are required.

Mineral oil was used in pressworking in the early 1900s to prevent punches from prematurely wearing and breaking, but drawbacks included limitations in the depth that the metal could draw and poor die life. A new development, mixing soaps with animal fats to produce a paste, increased lubricity, ("slip") and produced a higher film strength than straight mineral oil, allowing the metal to flow more easily under drawing pressure. This led to the addition of fats to oil and to the development of lard oils. Powders were added to improve the deep draw capability (extreme pressure characteristics) of the lubricant; such as mica, talc, whiting, calcium carbonate, and aluminum stearate.

During the 1920s, '30s and '40s, paste was used for drawing and lard oil for stamping. However, pigmented paste tended to be difficult to clean off, would build up on presses and dies, and (more recently) is difficult to dispose of under the Resource Conservation and Recovery Act. In the 1950s, lubricants containing sulfur, chlorine and phosphate were developed; these additives do not depend upon viscous lubrication or film strength to separate tool and work. Instead, they react with the metal surface of the tool and workpiece to produce a metallic oxide coating, which in turn becomes the bearing surface. These metallic oxides have high resistance to frictional welding, keeping punches from dulling prematurely due to buildup and wear, and thus preventing galling and breakage.

Straight cutting oils may be corrosive or non-corrosive. "Corrosive" or "active" means that the product contains active sulfur which can react with copper to form copper sulfide.

a. Non-corrosive straight cutting oils: These have additives including sulfurized non-active fats, polychlorinated paraffins, antirust agents and fatty esters.

b. Corrosive straight cutting oils: These have additives which include sulfurized base oils, sulfurized active fats, sulfurized/phosphorized hydrocarbons, fatty esters, polychlorinated paraffins and antirust agents.

2. Emulsions ("emulsifiable" or "soluble" oils): Soluble cutting oils are made from higher viscosity base stocks than straight cutting oils. Prior to use in the machine shop, these oils are mixed with anywhere from five to over a hundred parts water to one part oil. These contain a surface active emulsifying agent (such as a soap or detergent) so that, on dilution with water, the emulsified oil and water stays mixed. Soluble oils make up about 50% of all metalworking fluids. They were developed to combine the cooling properties of water with the lubricating properties of oil. These water-based fluids are often used in higher speed cutting operations with their greater rate of heat generation: The higher specific heat of water makes it a better coolant than oil.

Water-soluble oils for drawing and stamping metal developed from a breakthrough in additive formulations which occurred in the 1960s. Before that, the amount of chlorine from chlorinated additives which was stable in an emulsion ranged from 8 - 12%. The development of several new emulsifiers allowed that to increase to 20%, which enabled the use of soluble oils in deep-draw metalforming. Currently, other additives (anti-wipe, lubricity, polarity) and a chlorine content up to 40% enable the manufacture of a range of products of

of varying water mixes which can do about 85% of all drawing and stamping jobs, replacing the paste and straight petroleum-based oil compounds.

Soluble oils consist of:

Mineral Oil (60-90%)  
Emulsifiers (sodium and amine soaps, sodium naphthenates, rosinate, sulfonates)  
Coupling agents (alcohols, glycol ethers, glycols)  
Rust inhibitors (amines, fatty oils, sodium nitrite, sulfurized fatty oils)  
Water  
Biocides (such as chlorophenols, formaldehyde releasers, hexachlorophene, quaternary ammonium compounds).

The presence of some additives seems to necessitate the presence of other additives: so what begins as a simple idea - a coolant with the desirable characteristics of both water and oil - rapidly becomes more complex. Since oil and water do not mix, emulsifiers such as soaps or detergents/surfactants are added to keep the product from separating. But these additives are biodegradable, so a bactericide is needed to prevent spoilage. Since water can corrode metal, corrosion or rust inhibitors are needed. Emulsifiers (soaps, detergents) can cause foaming, thus anti-foaming agents are required. Since hard water can form curds or films when mixed with soaps, water conditioners are needed to deal with water hardness. As we shall see shortly, adverse health effects may be due to one or more of these components.

**3. Synthetic fluids:** These are soap-polymer-based solutions with additives, diluted with water, and used for specialty application in place of soluble oils. These are still being developed and tested, but are becoming more popular due to several definite advantages: their ability to outperform chlorinated soluble oils at the same or weaker dilutions, the advantage of tailoring their composition for a specific task, and a greater ease of meeting energy conservation and pollution control regulations.

The types of synthetic fluids include:

- a. Semisynthetic: contain small amounts of oil
- b. Water-based synthetic fluids: contain no oil.

Additives may include ethanolamines and their fatty acid salts, sodium nitrite, colorants, antirust additives and biocides. Since water is also in use here, corrosion inhibitors are needed. Those formulations which contain oils require emulsifying agents (soaps or detergents) to keep the oil from separating. To prevent spoilage of the emulsifying agent, bactericides are needed. Anti-foaming agents are added to prevent the foaming of the soap or detergent. Water conditioners are required to prevent soap curds from forming. So, once again, the product's formulation becomes complex.

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In later chapters, we will look in greater depth at the base oils, additives, and other aspects of the cutting fluid's composition to assist you in understanding and eliminating health hazards using product substitution.

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Next--

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**Oil Components and Potential Health Hazards from Skin Contact**

Tools with high cutting speeds, heavy oil flow, and continuous contact tend to involve greater risks because the worker can be splashed with oil or oil mists, principally on the hands, forearms and face. Some of the resulting skin problems are due to the means the skin uses to try to protect itself, such as a tendency to thicken and produce a horny surface layer to act as a barrier. This layer is quite impenetrable to water-soluble materials, but is less resistant to fat or oil-soluble materials or to alkaline fluids.

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**Trauma and Skin Cuts**

As a cutting fluid is used, metal slivers contaminate the oil; these can cause skin cuts and abrasions as well as increase the possibility of infection and other skin disorders discussed below. This problem could be minimized by filtration of metal slivers from the oil as a part of the coolant system.

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**Irritation and Sensitization**

Irritation and sensitization (allergic) reactions depend greatly upon whether the oil is a plant, animal or petroleum product. Natural animal, fish and vegetable oils tend to be well tolerated by the skin, although weak irritant reactions may occur from unsaturated fatty acids (such as oleic acid) or from acids contained in rancid oils. Lanolin, used in anti-corrosion greases, may be a sensitizer for some people. Petroleum-derived oils (mineral oils) appear to act as primary irritants and rarely as sensitizers. The irritancy of oils tends to lessen with increasing boiling point (something to look for on the product's MSDS), although all oils may be irritants on damaged or abraded skin.

Besides the base oil, the additives can cause irritant and/or allergic dermatitis (as well as other health effects). Also, some additives can facilitate the movement of other additives into the skin. Below are some additive types associated with irritation or sensitization effects on the skin:

- Anticorrosive agents: allergic sensitization
- Anti-wear additives: phosphates such as tricresylphosphate
- Emulsifying agents
- Pour-point depressants
- Detergents: petroleum sulphonates, alkyl phenates, metallic alkyl salicylates (such as calcium alkyl salicylate)
- Deodorizers: sensitization from odor disguising agents; such as terpenes in pine oils (turpentine) and pine tar
- Plasticizers
- Dyes: allergic sensitization from petroleum azo dyes or the para-phenylene diamine quinone group of dyes.

(continued)



- Extreme-pressure lubricants
- Anti-misting polymers: reduce mechanically produced mist
- Anti-oxidants: potential sensitizers; amines (such as diphenyl amine and phenyl-alphanaphthylamine), hydroxy compounds (such as phenols, calcium octylphenol or naphthols), phenothiazines, alkyl sulfides and disulfides; organic phosphorus (such as zinc diethyl dithiophosphate and other metallic compounds using arsenic, antimony, selenium or tellurium)
- Anti-microbials (discussed at length in Chapter 3).

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These conditions are usually more evident from insoluble cutting oils (straight mineral oils). They tend to start as a chemical irritation of the skin's hair/sebaceous follicles. When the cutting oil plugs the pores of the skin, glandular secretions (natural body oils) are retained in the pores and cannot reach the skin surface to be excreted. This stimulates the formation of keratin (a tough protein of which the hair and fingernails are composed) and the pores are blocked by keratin plugs. The result can be boils, sterile folliculitis (non-infective inflammation of hair follicles), comedones (blackheads), and papules (small, solid bumps). These occur on the hands, fingers, extensor sides of forearms, elbows, arms and thighs; and are especially prevalent wherever oil-soaked clothing rubs on the skin. Bacteria in the oils (see Chapter 3) do not cause the folliculitis, but may be responsible for secondary infections (usually by Staphylococcus or Pseudomonas organisms).

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**Oil Acne and Folliculitis**

The skin may darken in color as the areas about the hair follicles become hyperpigmented (melanosis). This darkening may be due to irritation by the oil or as a secondary effect to folliculitis. Sunlight may contribute to this reaction since some coolant additives may cause photosensitization, a condition in which the skin becomes more sensitive to light.

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**Melanosis**

This is caused by chlorinated materials; in cutting fluids these are the chlorinated naphthalenes and chlorinated diphenyl oxides used as extreme pressure additives. These chemicals cause acne-like lesions on exposed skin. Chronic exposure may result in liver damage.

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**Chloracne**

This appears as redness, swelling and water blisters in acute effects; that is, the result of short-term exposure. Subacute and chronic effects (long-term exposure) include redness, scaling, cracking, and thickening of the skin. In its early stages, the skin eruption appears as tiny blisters on the sides of the fingers, in the finger webs, and over the backs of the hands. This dermatitis may be due to damage to the skin's effectiveness as a

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**Irritant or Eczematous Contact Dermatitis**

barrier layer due to repeated cycles of wetting and evaporative drying with the coolant; these cycles can be more harmful than prolonged immersion in the coolant fluid. Irritant dermatitis may occur from soluble cutting oils (due to their defatting action on the skin), synthetic coolants, or from components such as bactericides, extreme pressure additives, rancid fatty oils, low boiling distillates, acrolates from over heated oil, amines and chlorinated solvents.

This dermatitis can be aggravated by contributing factors such as inadequate skin cleansing to remove the oil; excessive use of water less cleansers; using solvents, abrasives or harsh alkaline soaps for washing; or inadequate drying of the hands in the winter. Also associated with this condition are abrasions and cuts from oily wipe rags contaminated by metallic swarf, inadequate cleaning of sumps, hot working conditions and bacterial contamination of the coolant.

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**Allergic Contact Dermatitis**

This is a dermatitis due to sensitizers such as bactericides and/or their breakdown products, corrosion inhibitors, emulsifiers such as ethylenediamine and triethanolamine, formaldehyde, anti-foaming agents (such as pine oil), nickel salts from machined metal or chromates. Some rare allergic reactions can be caused by mineral oil itself.

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**Xerosis**

Some cutting fluids contain solvents which remove the skin's oily protective layer. Also, synthetic metal-working fluids are potent skin defatting agents.

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**Miscellaneous Irritation**

Disinfecting agents (see Chapter 3) may be skin irritants. Chlorinated sulfurized cutting oils may react with water to release hydrochloric acid which can irritate or burn the skin. Therefore, oils should not be mixed with one another; straight cutting fluids should be kept separate from emulsions. Also, machines should be cleaned thoroughly between fluid changes so that no water residues from emulsions can contaminate a new oil.

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**Skin Cancer Hazard**

Skin exposure to cutting oils has been related to the development of skin cancer, particularly squamous cell carcinoma. Cutting fluids have been found to contain suspect carcinogens of the skin and the scrotum with the scrotum as the most common site. Scrotal cancer has a high potential for malignancy and a poor prognosis unless detected early. It first appears as a small painless, itchy sore, wart, pimple or lump on the scrotum (most frequently on the left side) which may bleed as a result of scratching. When the lesion grows so as to penetrate the scrotal wall, it may become painful. Drainage tends to follow, generally complicated by infection. Growth of the lesion may become rapid and it

can metastasize (spread) to the groin via the lymphatic system quite early. Treatment involves surgical removal of the primary lesion and lymphatic nodes draining the area, with further removal of scrotal contents depending upon the individual case.

Mineral oils which appear chiefly implicated in causing skin cancer are those in the boiling range 350 - 400C (662 - 752F) and which contain polycyclic aromatic hydrocarbons (PACs) with 4-5 fused rings. Generally, oils which are solvent-refined are less carcinogenic and those which are soluble and used as an emulsion have the least risk. Thus, the potential skin cancer hazard might be reduced by the use of oils from which the carcinogens have been removed by solvent extraction.

However, this issue may be complicated by the use of oil additives. Some additives may possess co-carcinogenic activity; that is, they may work with other oil constituents to cause cancer. Suspect carcinogens, such as the nitrosamines, may be formed by the reaction of amine additives (such as triethanolamine) with nitrite additives to form N-nitrosamines. Nitrite may be added to soluble cutting oil while preparing it for use even if it is not one of the original additives. Cutting fluids containing nitrites were first used in the 1950s and were mostly removed from the market in the late 1970s.

Six cases of squamous-cell carcinoma of the skin occurred at a single machine operating plant. In these cases, the sites of exposure were scrotum or forearm. The man with the scrotal carcinoma worked at a horizontal broacher, a machine which regularly splashed oil towards the lower abdomen of the standing operator. The soluble cutting oil in use in this plant was later used in a series of animal experiments involving skin painting to determine tumor production and carcinogenicity. The cutting oil in use was a 50-50 blend of sulfurized and filtered straight-run distillates of a crude mineral oil. The cutting oil proved to be a more potent carcinogen than its base oil alone, so it was concluded that one or more of the additives may act synergistically with the mineral oil. Moreover, the studies indicated that the highly diluted oil was also carcinogenic; it only required a longer induction period.

The generation of oil mists from high speed machines or by vaporization due to the heat produced by metal-working produces the second route of exposure to cutting oils - inhalation of the coolant mist. Oil mist particles are respirable since their diameters range in size from < 1 to 10 um; particles smaller than 5 um reach the alveoli of the lungs. Synthetic and soluble oil metal-working fluids are less prone to fuming and misting than

#### Case History

#### Oil Components and Potential Health Hazards from Inhalation of Cutting Oil Mists

straight mineral oils, although they do carry a greater risk of dermatitis. Anti-misting additives in a metalworking fluid may help to reduce this inhalation hazard.

The inhalation of emulsions contaminated with bacteria or fungi could cause lung infections or transfer them between workers.

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### Occupational Asthma

Asthma has been caused by cutting oil mist exposure, as illustrated by this case history:

A toolsetter/machine operator with 43 years experience was exposed to cutting oil mist. He had a ten year history of unproductive cough, wheeze, airway obstruction and progressively worsening shortness of breath; but he tended to improve on weekends and holidays. X-rays showed that the lungs were clear and there were no macrophages (eosinophiles) in his sputum. Testing indicated that after 30 minutes of exposure to the oil vapors, he had headache, muscular aches and chest tightness. Investigation of exposure to the cutting oil constituents showed considerable reaction to the reodorant (pine oil) and to colophony (residue from distilling turpentine from pine resin) which was a constituent of the emulsifier. Although his work involved grinding, and thus exposure to dusts containing cobalt and tungsten, he showed no response to these. (Occupational asthma in hard metal workers typically is caused by cobalt.) Since the worker responded to unused emulsified oil at room temperature, this ruled out causes such as bacteria, endotoxin and dissolved metals.

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### Lipoid Pneumonia

When oil enters the lungs, the initial reaction is inflammation: the capillaries become engorged by increased circulation of blood and numerous phagocytic cells (macrophages) appear to attempt to clean it up. Elimination of oil from the lungs can occur by expectoration or, if the oil is a vegetable or animal product, it may be metabolized (digested by the macrophages) and removed. But, true mineral oil (a petroleum product) is inert and indigestible by macrophages; it acts as a foreign body in the lungs and accumulates there. The resulting condition is pulmonary paraffinoma, an advanced lipoid pneumonia. This condition can mimic lung cancer clinically; in fact, the lesions (collections of oil-filled macrophages and oil globules) have been misdiagnosed as lung cancer tumors or as tuberculosis. In some cases, radical surgery (removal of an entire lung) has been performed when removal of a lobe would have sufficed. The symptoms of lipoid pneumonia may be nonexistent or may include chronic cough with or

without sputum, blood in the sputum, a low-grade fever, frequent lower respiratory infections, or shortness of breath on exertion.

An aircraft mechanic, exposed to a spray of half kerosene and half cleaning agent containing 50% vegetable oil soap for a year and a half, developed lipid pneumonia. Six months after his condition had been diagnosed and exposure ceased, his condition had steadily improved and his chest x-rays showed that almost no oil remained since the vegetable oil could be engulfed and destroyed by macrophages.

## Case History

Studies of the inhalation of oil mists as reported in the scientific literature do not appear to be in agreement on whether there is a significant hazard for respiratory cancer of fatal nonmalignant respiratory disease. Workers exposed to oil mist have shown squamous metaplasia in the mucous membranes of the respiratory tract, which is thought to be one possible pathway toward malignancy. Many long-term exposure studies have been performed; some show an increased lung cancer hazard, others do not. A major difficulty in dealing with these studies is the lack of information on the types and compositions of the cutting oils involved.

## Lung Cancer Hazard

However, comparisons of observed and expected numbers of deaths from specific cancer sites of workers exposed to oil mist show higher than expected deaths from cancers in the gastrointestinal tract. This underscores the fact that we swallow so much of the contaminants which we inhale due to the respiratory system's normal clearance mechanisms by which we swallow mucus, etc. Cutting oil exposure appears to produce an increase in risk for sinonasal cancer; this may be linked to the oil's content of polyaromatic hydrocarbons. A higher risk of bladder cancer is also a possibility and may be related to aromatic amines additives used as antioxidants.

The principal difficulty with the scientific literature is that studies generally do not indicate the types of cutting oils to which the workers were exposed. It is easy to see that not all studies would indicate a significantly increased cancer risk since oils differ in carcinogenic potential and types of additives. As we have already seen, there is an enormous variety in oil types and components. We shall see shortly that there are not only possible carcinogens in the base oils themselves but also potential carcinogens or co-carcinogens present as contaminants. Information on the cutting oil itself is needed to see what workplaces are at risk from a particular oil, which oils are safer, etc. based upon their

constituents.

### **Teratogenesis**

The International Agency for Research on Cancer has stated that there is sufficient evidence from studies in humans to conclude that mineral oils (containing various additives and impurities) that have been used in occupations such as metal machining are carcinogenic to humans.

This area of health effects is under review; but so far the evidence does not yet show an increased risk of cancer in the children of parents exposed to cutting oils as machinists.

## Chapter 3

Unused cutting oils may consist of as many as 15 intentional ingredients; but may contain more unintentional components. These additional constituents may be due to chemical reactions between ingredients; they may be closely related chemicals which were not removed during refining; they could be by-products of the production process; or they may simply be contaminants, residuals or trace substances.

### The Problem of Unintentional Components

A lathe operator with 15 years experience developed a rash on hands, elbows and lips which cleared when away from work but relapsed more severely each time he resumed work; eventually appearing within minutes of entering the workshop. Patch tests to the coolant and to 1:10, 1:50 and 1:100 dilutions indicated that a potent allergen was present. The 14 constituents of the coolant were tested individually, but results were negative. The cutting oil was manufactured in 5 stages; the manufacturer supplied samples of each and these were patch-tested. All samples produced an allergic reaction - so the allergen was being manufactured in the first stage of product when the triethanolamine and caprylic acid were mixed to produce a soap, triethanolamine caprylate. Such amine soaps are recognized as allergenic. In this case a reaction product was the allergen.

Products stored before use under a variety of conditions can react to form other substances. High temperatures and pressures at the cutting tool's cutting edge, along with agitation and aeration, can cause further chemical reactions. Levels of the carcinogen benzo(a)pyrene in cutting oils have been found to increase with use. Heavy metals generated during the cutting process become contaminants. The working fluid may be heated to retard spoilage, which may generate chemicals not produced at ambient temperatures.

N-Nitrosodiethanolamine has been found at levels of 5-20 mg/kg in emulsions, but not in straight cutting oils. The combination of nitrite and amines which leads to the formation of these nitrosamines has been eliminated in many products. The reaction of nitrite additives with diethanolamines or triethanolamines produces mutagens such as N-nitrosodiethanolamine and lesser amounts of other volatile N-nitrosamines. These are the following:

N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodipropylamine, N-nitroso-dibutylamine, N-nitrosopiperidine, N-nitrosopyrrolidine, and N-nitrosomorpholine.

Studies of mutagenicity (using the Ames test) indicate that both water-soluble and water-insoluble cutting oils can contain direct and indirect-acting mutagens. Concentrations of N-nitrosodiethanolamine have been found which exceed 2000 ppm. Such mutagens cause changes in chromosomes called point mutations. Chromosomal abnormalities have been found in blood from tool and die workers.

The coolant may be reclaimed and recycled several times with the entire system subject to attack by microorganisms. Re-refined oils and synthetic fluids may differ in constituents, including those that are carcinogenic, from the original oil. Perylene and chrysene have been identified in reprocessed straight oil; other polynuclear aromatic hydrocarbons (known or suspect carcinogens) may be present in used or new oils.

When ready for disposal, cutting oil may have become a toxic waste; yet it is possible that it has been a toxic waste for some time before it is to be discarded.

#### **Problems Related to Bacteria and Preservatives**

Soluble oil emulsions are a breeding ground for bacterial. Bactericides are added to soluble cutting fluids to prevent decomposition and odor formation, not for prevention of skin infections. Dermatitis is especially likely to occur after contact with rancid oils. Microbial growth reveals itself as slimes and sediments, objectionable smells and darkening color of the oil. Continuously used well-aerated systems at close to ambient temperatures degrade quickly and are dominated by aerobic bacteria.

Systems which are not well-aerated, are intermittently used, or have a slow rate of turnover will also contain anaerobic and facultative aerobic or anaerobic organisms. These are responsible for producing 2,6-dimethyl-3-methoxypyrazine and other similar compounds with a sickening, clinging smell - the so-called "Monday morning odors", musty, "foul drains" or "sour dishcloths". Sulfur may be reduced to hydrogen sulfide which smells like rotten eggs. Rolling oil emulsions maintained at elevated temperatures tend to suppress the growth of organisms found in cooler systems, but encourage others to flourish.

Although, theoretically, many of the hydrocarbons and fatty acids can be converted to carbon dioxide and water, oil breakdown tends to take place in many minor steps; this can be seen by a drop in coolant pH from markedly alkaline to near neutrality. If yeast and fungi proliferate, pH may drop as low as 4.0. Although



monitoring pH can serve as a warning that the oil is being broken down by microorganisms, developing acidity may be masked by ammonia from degrading nitrogenous component additives.

Emulsion oil-wetted skin encourages Candida fungal infections. Infections can complicate cuts, burns, oil acne and exzematous dermatitis. The bacterium Pseudomonas aeruginosa causes green discoloration of nails and secondary infections of wounds, accompanied by ulceration.

**Phenolics:** *concentrates are potential irritants to skin and eyes; may be skin sensitizers*

o-benzyl-p-chlorophenol  
o-phenylphenol  
sodium salt of o-phenylphenol

**Formaldehyde "donors" or "releaser":**  
*may be skin sensitizers*

2-hydroxymethyl-2-nitro-1,3-propanediol:  
*concentrate not a primary irritant*  
hexahydro-1,3,5-tris-2-hydroxyethyl-(s)-triazine:  
*concentrate non-irritating*  
hexahydro-1,3,5-tri-ethyl-(s)-triazine: *potential irritant*  
1-(3-chlor allyl)-3,5,7-triaza-1-azonia-  
adamantane: *concentrate not a primary irritant*  
5-ethyl-1-1-aza-3,7-dioxabicyclo-3,3,0-octane:  
*potential sensitizer*  
4-(2-nitrobutyl)morpholine: *potential sensitizer*  
4,4'-(2-ethyl-2-nitromethylene)-dimorpholine:  
*potential sensitizer*

**Salicylanilides:** *produce photosensitivity to skin*

3,4',5-tribromosalicylanilide (76-88%) and 3,5-dibromosalicylanilide (12-24%): *Concentrate not a primary irritant*  
3,4',5-tribromosalicylanilide (98-100%):  
*Concentrate not a primary irritant*

**Isothiazolines:** *sensitizers (allergic contact dermatitis)*

5-chloro-2-methyl-4-isothiazolin-3-one  
2-methyl-4-isothiazolin-3-one

## Types of Cutting Fluid Preservatives

Excerpted from: Brown, N. J. 1988. Health hazards manual for cutting oils, coolants, and metalworking fluids. Cornell University. Chemical Hazard Information Program. 120 Delaware Ave. Rm. 232. Buffalo, NY 14202.

#### PROTECTION AND PREVENTION:

1. SUBSTITUTION of "safe" oils for oils which are carcinogenic or have other health problems associated with them. This is probably not practical at present since carcinogens not yet precisely identified, but some minimization of risk may be possible by lowering exposure to mineral oil containing products. Some of these health problems might be solved by the use of products which have a defined, specific composition, such as synthetic lubricants, rather than using crude distillation fractions derived from petroleum which constitute mineral oils.
2. SAFE WORKING PROCEDURES and ENVIRONMENTAL CONTROLS such as the use of closed systems or at least protective shields or splash guards on machines and good housekeeping. Regular testing of cutting fluids for pH (under 10), low bacterial count (chiefly in soluble oils), and proper viscosity. To control the infection of coolant systems, drain and clean (chemically and physically) the cooling system, and sterilize the system between changes. Providing adequate exhaust for fumes; leaks in tanks and pipes should be sealed by welding. Proper waste oil handling. Education of workers and foremen on hazards and proper handling of cutting fluids and operation of machines.
3. USE OF PROTECTIVE CLOTHING and barrier creams: use special protective clothing such as polyvinyl plastic aprons, gloves, and sleeves. Change work clothing daily and have double lockers, one for work clothing and the other for street clothing. Do not place oilsoaked wipe rags in trouser pockets. Barrier creams which block the pores may prevent oils from entering the skin by this route; however, they have proved of little value in preventing chloracne and may, in fact, enable carcinogenic components to enter the skin more easily.
4. ~~PERSONAL HYGIENE and cleanliness~~: Use waterless hand cleaners or soap; no harsh cleansers or raw solvents. Wash hands at all breaks in work, both before and after visiting the toilet, and avoid transferring oil from the hands to the underclothing. Daily shower with lots of soap and hot water. Wash hands and arms with good hand cleaner at least four times daily during the shift.
5. EDUCATION and instruction on the health hazards to all workers concerned on the shop floor. Ultraviolet light can be used to show the presence of oil on skin and clothing and is useful for instructing workers in the best methods of cleansing and in cleansing efficiency.
6. Encouragement to carry out SELF-INSPECTION and examination by the worker of his own body and to report any significant finding to the doctor; for example, small warts or ulcers.
7. ROUTINE MEDICAL EXAMINATION for high risk/heavily exposed groups of

workers.

#### REDUCING HAZARDS/RISKS USING PRODUCT SUBSTITUTION:

As we have seen in the previous chapters, much of the risk involved in working with cutting oils derives from the use of mineral oils: they have poorly defined chemical compositions, impurities from refining processes, and contaminants produced by the heat of the cutting tool, etc. As a result, it is possible to reduce some health risks by substituting with coolants having a lower mineral oil content, such as changing from a neat oil to a soluble oil. The irritancy of oils lessens with increasing boiling point.

Another alternative is to switch to a synthetic lubricant since these have a known composition. If you look only at initial cost of purchase, synthetic lubricants may appear more expensive than straight mineral oils or soluble oils. This difference may disappear when you consider energy costs and the expense of disposing of the used oil. Consider products which can be recycled or cleaned rather than reclaimed to avoid the possible buildup of polynuclear aromatic compounds from reclamation. Consider burning used oil for heat.

Cleaning methods for coolant include:

- Settling tanks, with or without heat
- Centrifuges
- Filtration
- Vacuum dehydration without heat
- Vacuum distillation with heat, at high or low temperatures
- Low vacuum distillation at low temperatures (140 - 150 F)

Low temperature cleaning methods do not oxidize the oil.

Parts produced with a synthetic may only require cleaning in a mild alkaline solution at less than 100 F or may not need to be cleaned at all if the synthetic does not interfere with subsequent processing (mastic bonding, welding, painting, etc.). Also, the disposal of water-soluble products may cost more than the original price of the compound. (Remember, although you buy the product as a concentrate in a small volume, you must dilute it with water to put it into usable form -- this generates a large volume of liquid for disposal.) Some synthetics are highly biodegradable and thus may require little pretreatment before discharge into a municipal sewer system. Biological treatment of synthetics may be accomplished using biological reactors, including fluidized bed processes. Pretreatment may require little more than separation of tramp oils before dumping and many synthetics are formulated to kick tramp oil to the surface where it can be easily skimmed and collected for disposal. Although synthetic lubricants may not do the toughest job in the shop, they might do the majority of the other jobs which are the principal operations of the business.

Look at the parts after machining to see if they tend to corrode quickly or have poor surface finishes. See if machines show short tool life, fouling

of grinding wheels or wheel burn. See if the coolant must have additional oil or concentrate or biocide added to maintain its lifetime or its emulsion strength. These types of problems may be good reasons for having more frequent oil changes and better maintenance of the coolant system -- dirty fluids are costly. Consider what happens to coolants over the holidays or during plant shutdowns.

Where allergic reactions to a biocide are a problem, switch to a product using a different family of biocides altogether. For example, don't change from one formaldehyde-releaser to another but to a preservative with a different mechanism of action, such as a isothiazolinone.

Find out what kind of base oil is used in your cutting oil and, if possible, what kind of oils were used in your shop in the past -- this is important to look at long-term health risks. If poor records were kept on cutting fluid types, start keeping these records now for future use! Unfortunately, so many of the health studies looking at long term exposure to cutting oils have no information on the kind of oil or its refining process. As we saw earlier, it was difficult to conclude about lung cancer risk because the type of oil to which the workers were exposed was not well defined. Below is a classification of base oils based upon refining processes; find out if your oil was solvent-extracted, hydrotreated, etc. from the material safety data sheet or the manufacturer.

#### TOXICOLOGICAL CHARACTERISTICS OF REFINERY STREAMS USED TO MANUFACTURE LUBRICATING OILS:

Although predominantly hydrocarbons, finished base oils contain some organic sulfur, oxygen, and nitrogen compounds and traces of metal compounds. The hydrocarbons themselves are a mixture of various chemical structures (aromatics, naphthenes or cycloparaffins, and paraffins); the proportions of these structures in any one oil are what give the oil its unique characteristics. Higher molecular weights (that is, larger hydrocarbon molecules) produce more viscous oils. The refining process separates the crude petroleum into its constituent oil fractions, separates the various chemical structures, and also determines the content of polynuclear aromatic compounds (PACs) in the finished base oil. As we saw earlier, the PACs can be carcinogenic; so the refining process is a major determining factor in the cancer-causing ability of the cutting oil.

I.A.R.C. categories of base oils classified by increasing severity of processing or refinement:

Oils may also be described as "highly refined" or having had "limited refining." The term "highly refined" tends to mean severely hydrotreated and/or severely solvent refined or oleum-treated (treated with fuming sulfuric acid). "Limited refining" indicates those oils subjected only to sulfuric acid/clay treatment, mild solvent refining, or mild hydrotreatment. (See the attached figure illustrating base oil refinement processes.) Machine-tool lubrication oils tend to be medium-viscosity, highly refined, paraffinic oils: the base oils from classes 3, 4, or 5, the (base oil + additives) in class 7.1. Cutting oils have a similar formulation or are emulsifiable oils used with water, also class 7.1.

Other metal-forming oils may be similarly classified or may contain a significant portion of light petroleum distillates (such as white spirit or kerosene) or other volatile solvents (also class 7.1) or solid or semi-solid lubricants which are not greases (also class 7.1). Although this group may include base oils which have had limited refining (insufficient to reduce the aromatic hydrocarbon content as low as that of normal solvent refining), this is now only a small portion of the current production. Generally, these have been replaced with base oils from classes 1, 2 or mildly treated 3, 4.

- Class 1: Vacuum distillates (May have subsequent finishing steps such as caustic neutralization, dewaxing, clay treatment and/or mild hydrotreatment; but not acid-treated or solvent-extracted.)  
IARC - sufficient evidence for carcinogenicity in animals.
- Class 2: Acid-treated oils (May have subsequent finishing steps such as caustic neutralization, dewaxing, clay treatment and/or mild hydrotreatment; but not solvent-extracted.) Treatment with fuming sulfuric acid (oleum) can remove aromatics, including PACs, almost completely.  
IARC - sufficient evidence for carcinogenicity in animals.
- Class 3: Solvent-refined oils or raffinate (May have undergone subsequent finishing steps such as dewaxing, clay treatment and/or mild hydrotreatment.) Removes PACs and total aromatics. Impurities include traces of solvent such as phenol, furfural, etc.  
IARC - sufficient evidence for carcinogenicity in animals for mildly solvent-refined oils, but NO evidence for severely solvent-refined oils. It would appear that excessive solvent refining is a purifying process which removes many carcinogenic constituents.
- Class 4: Hydrotreated oils. Severe hydroprocessing reduces PACs and total aromatics.  
IARC - sufficient evidence for carcinogenicity in animals for mildly hydrotreated oils, but INSUFFICIENT evidence to evaluate the carcinogenic potential of severely hydrotreated oils.
- Class 5: White oils and petrolatums suitable for food and/or medicinal use  
IARC - NO evidence for carcinogenicity in animals (except by injection into the body cavity upon repeated experiments).
- Class 6: Aromatic oils  
IARC - sufficient evidence for carcinogenicity in animals.
- 6.1 Solvent extracts
- 6.2 Catalytically cracked oils
- Class 7: Miscellaneous materials
- 7.1 Formulated products (Mineral oils from other classes with additives were placed here.)

IARC - health hazards of these products will depend upon their base oils and additives; however, there is limited evidence for the carcinogenicity of some cutting oils in animals.

#### 7.2 Used oils

IARC - health hazards of these products will depend upon their base oils, and additives, and conditions of use.

Class 8: Petroleum-derived materials not otherwise classified or insufficiently described to permit assignment to other classes

Overall, the IARC concluded that there is sufficient evidence from studies in humans to conclude that mineral oils (containing various additives and impurities) that have been used in metal machining are carcinogenic to humans.

#### WHAT TO LOOK FOR ON A CUTTING FLUID MATERIAL SAFETY DATA SHEET:

If the MSDS is not as detailed as you would like, ask the manufacturer for more specific information or for the results of actual health studies. (See the attached sample MSDSs.)

     What is the type of fluid? Neat oil, soluble oil, or synthetic?

     If mineral oil or petroleum oil is present, how was it treated or refined? Is the base oil listed with a CAS number? (See the attached figure listing the CAS#s for base oils.) What is the content of polynuclear aromatic compounds? What is the boiling point or boiling range of the oil? (The product may be described as a neat oil or mineral oil product, but may not list mineral oil as a hazardous ingredient because the manufacturer doesn't consider it to be hazardous -- that's why it is important to ask.)

     Are both nitrites and some kind of amine present in the product? Or will one of these ingredients be added later before use in the machine?

     Are any chlorinated additives present? What are they? What are their health effects?

     Are any glycol ether emulsifiers or coupling agents present? Such as cellosolves, ethoxy or methoxy ethanols?

     Are any preservatives present?

     What is the pH of the product?

     Have colors or odorants been added? Consider whether you really need these ingredients.

     Has the final product been tested for contaminants such as nitrosamines, polynuclear aromatic compounds, etc.?

Has the manufacturer performed any animal studies or human epidemiological studies on the health effects of this product?

What is the proper use of the coolant: appropriate dilutions, maintenance of the system, cleaning of the system when changing oils, etc.?

When is the coolant to be changed?

How do you dispose of the coolant? Is it reclaimable or biodegradable?

TABLE II  
Composition of Insoluble Oil  
(Straight Cutting Oil)

1. Mineral oil base (paraffinic or naphthenic), 60-100%.  
If 100%—straight mineral oil; otherwise a blend with fatty oils such as lard oil and sperm oil.
2. Bactericides, sometimes added to prevent rancidity.\*
3. Extreme pressure (EP) additives.\*
  - a. Sulfur, free or combined with base oil or fats. 1-3%.\*
  - b. Chlorinated fats and paraffin oils. 1-3%.
  - c. Sulfochlorinated fats, 1-3%.

\*Additives, not present in all formulations.

TABLE III  
"Soluble" Oil (Emulsifiable Oil, "Soup,"  
"Suds")

Depending on intended use, concentrate is diluted 1:5 to 1:50 by adding to water, pH 8-9.

1. Mineral oil, 60-85% of concentrate.
2. Emulsifiers, e.g., petroleum sulfonates, soaps.
3. Bactericide (germicide, antiseptic, disinfectant), e.g. cresylic acid, orthoohenvylphenol, tris (hydroxymethyl) nitromethane, 0.1-2% of use concentration. Recharged as needed.\*
4. Corrosion (rust) inhibitors, e.g., hydroxyl amines.\*
5. Extreme pressure additives.\*
6. Anti-foaming agents, e.g., silicones.\*
7. Dyes, e.g., fluorescein.\*
8. Water-used in pre-formed emulsions and also for dissolving water soluble ingredients.
9. Water conditioners, e.g., polyphosphates, trisodium phosphate, borax, sodium carbonate (soda ash). Added to water before formation of emulsion.\*

\*Additives, not present in all formulations.

TABLE IV  
Synthetic (Chemical) Coolant

An aqueous solution—contains little or no emulsified oil. Concentrate is diluted 1:10 to 1:200 depending on intended use, pH 8-10.

1. Corrosion inhibitors, e.g., hydroxyl amines, inorganic and organic nitrites, nitrates for nitrite stabilization.
2. Soaps and wetting agents.\*
3. Blending agents, e.g., glycols.\*
4. Bactericides.\*
5. Water conditioners, e.g., phosphates and borates.\*
6. Anti-foaming agents, e.g., silicones.\*
7. Dyes.\*