



**INDEPENDENT
LUBRICANT
MANUFACTURERS
ASSOCIATION**

May 31, 1996

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VIA OVERNIGHT COURIER
Ms. Diane Manning
Education and Information Division
National Institute for Occupational
Safety and Health
4676 Columbia Parkway
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Cincinnati, OH 45226-1998

**Re: "Criteria for a Recommended Standard:
Occupational Exposures to Metalworking Fluids"**

Dear Ms. Manning:

The Independent Lubricant Manufacturers Association submits the enclosed comments (two copies) on the February 23, 1996 draft of the above-referenced document.

Sincerely,

Richard H. Ekfelt
Richard H. Ekfelt
Executive Director

cc: ILMA Health and Safety Task Force (w/encl.)
Jeffrey L. Leiter, Esq. (w/encl.)
Brenda Boutin (NIOSH) (w/encl.)

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**COMMENTS
OF THE
INDEPENDENT LUBRICANT MANUFACTURERS ASSOCIATION
ON THE
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH'S
"CRITERIA FOR A RECOMMENDED STANDARD: OCCUPATIONAL
EXPOSURES TO METALWORKING FLUIDS"**

May 31, 1996

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I. INTRODUCTION

The Independent Lubricant Manufacturers Association ("ILMA") submits the following comments regarding the National Institute for Occupational Safety and Health's ("NIOSH" or "Agency") draft "Criteria for a Recommended Standard: Occupational Exposures to Metalworking Fluids" ("Draft Criteria Document") (February 23, 1996).

A. The Independent Lubricant Manufacturers Association

ILMA, established in 1948, is a national trade association of 147 regular member companies, consisting largely of small businesses, ranging in size from fewer than 10 to more than 200 employees. As a group, ILMA member companies blend, compound and sell over 25 percent of the United States' lubricant needs and over 75 percent of the metal removal fluids utilized in the country.

A lubricant is a liquid or solid substance used to reduce the friction, heat and wear between solid surfaces. ILMA members manufacture automotive, truck, marine, aircraft and industrial engine oils; transmission fluids; hydraulic fluids; greases; general industrial oils; power equipment oils; process oils; metal removal, treatment, protecting and forming lubricants; and rolling oils.

In order to manufacture a lubricant, ILMA member companies purchase oil and synthetic lubricant base stocks and a wide range of additives. ILMA member companies then compound and blend the base stocks with the correct additives in the proper proportions to produce a lubricant with the desired characteristics for a particular job.

ILMA members are diverse. A large proportion manufacture automotive lubricants for original equipment manufacturers and for the retail market, either under their own labels or through contract packaging arrangements. Many produce lubricants for metalworking and heavy

industrial machines, while others supply lubricants for mining, textiles, food processing, electronics, as well as many other industries.

Independent lubricant manufacturers by definition are neither owned nor controlled by companies that explore for or refine crude oil to produce lubricant base stocks. Base oils are purchased from refiners, who are also competitors in the sale of finished products. Independent lubricant manufacturers succeed by manufacturing and marketing high-quality, often specialized, lubricants. Their success in this competitive market also is directly attributable to their tradition of providing excellent, individualized service to their customers.

B. ILMA's Interest in the Draft Criteria Document

ILMA, in addition to its members' product stewardship, has a longstanding involvement and leadership role relative to metal removal fluid issues. The Association submitted comments and information to NIOSH on the Agency's 1990 request for data on exposures to cutting fluids and on the 1994 draft hazard review document. ILMA's request to meet with NIOSH led to the Agency's unprecedented November 1994 public meeting in Cincinnati, Ohio to discuss metal removal fluid matters.

The Association cooperated closely with the American Automobile Manufacturers Association ("AAMA") and others in conducting the November 1995 metalworking fluids symposium, "The Industrial Metalworking Environment: Assessment and Control."

ILMA also is working with the Occupational Safety and Health Administration ("OSHA") and the Environmental Protection Agency ("EPA") as these agencies investigate whether there are adverse health effects from workers' exposures to metal removal fluids that may need to be regulated or that may cause existing regulations or standards to be revised. The Association has

and will continue to provide credible and useful information and data to NIOSH and to these other agencies.

C. NIOSH and Its Reader-Audience

ILMA believes that it is important for NIOSH, as part of the Draft Criteria Document, to consider and remain focused on the reader-audience, particularly given the Agency's recommendations of an exposure limit, safety and health program, and medical surveillance. According to the "14th American Machinist Inventory," 68 percent of all metalcutting machine tools are in plants with less than 100 workers (23 percent are in workplaces with 19 or fewer employees, while 45 percent are in the 20 to 99 worker range). Moreover, the 14th Inventory also indicates that 60 percent of metalcutting machine tools in use are more than 10 years old. See "14th American Machinists Inventory," *American Machinist*, November 1989 (Attachment A).

Table 1 — Metalcutting Machine Tool Distribution

<u>Age (years)</u>	<u>Percent</u>	<u>Shop Size (Employees)</u>	<u>Percent</u>
0 - 4	16	1 - 20	23
5 - 9	24	20 - 99	45
10 - 19	34	100 - 499	21
20 >	26	500 >	11

Source: "14th American Machinists Inventory," *American Machinist*, November 1989.

The prevalence of the country's manufacturing equipment in small-sized plants and businesses needs to be a significant concern to NIOSH, even though the Agency may not be required to consider cost-benefits or cost-effectiveness. These employers and their employees, at a minimum, have to be able to obtain, read and understand the Draft Criteria Document when

it is finalized and published. This will be no easy task, even with the help of ILMA and others involved in the distribution of metal removal fluids. Further, NIOSH cannot overlook the cost implications to these small shops, particularly those associated with the Agency's proposed medical surveillance program. Moreover, the age distribution of metalcutting machine tools is significant when "phase-ins" are viewed. Accordingly, in making revisions and other changes suggested by ILMA and other commenters, NIOSH should make such revisions and changes in a manner that will make the final document understandable to and usable by the reader-audience — that is, the overwhelming number of small-sized shops using metal removal fluids.

II. EXECUTIVE SUMMARY

After years of information collection, NIOSH released in 1994 a draft hazard review document on occupational exposures to metalworking fluids. NIOSH subsequently concluded that information and public comments supported the development of a "criteria document," instead of the more limited "hazard review." The Draft Criteria Document was released in February 1996, and is the subject of these comments.

In the Draft Criteria Document, NIOSH has not adequately supported its Recommended Exposure Limit ("REL") for occupational exposures to metal removal fluids — either on a technical or a legal basis. Because of this lack of justification, and for the reasons discussed below, NIOSH should correct the scientific and legal inadequacies in its document and should publish the final version as a "hazard review" without a REL.

A. ILMA's Technical Concerns

The following summarizes ILMA's principal technical concerns with the Draft Criteria Document and supports the Association's position that the document should be finalized as a hazard review without a REL:

- NIOSH is responsible for drawing its conclusions based on sound science that has been peer-reviewed and that has been made available to the public. NIOSH has not adhered strictly to this responsibility. Much of the respiratory effects section (three out of four papers) is based upon "non-binding, peer-review" by "[the Occupational Health Advisory Board ("OHAB")]"^{1/} of papers that have not been published. NIOSH should not rely upon the OHAB-reviewed data to draw any respiratory effects conclusions for two reasons: (1) a non-binding OHAB review should not substitute for "traditional, peer-reviewed, published articles"; and (2) ILMA and other interested parties are at a distinct disadvantage in commenting on the technical aspects of the studies. ILMA members, as well as other interested parties, rely upon peer-reviewed, published articles for confidence in the results and proper interpretation because many Association members and these other interested parties lack qualified staff and sufficient resources to conduct an appropriate peer review.

^{1/} OHAB is sponsored by General Motors ("GM") and the International Union, United Automobile, Aerospace & Agricultural Implement Workers of America ("UAW"). This GM-UAW group, consisting of six to seven university scientists, conducts joint health and safety activities and solicits and funds research projects by academic institutions. OHAB's peer review of research reports is non-binding on the investigators.

- NIOSH incorrectly utilizes highly-specific and technical terms. The Draft Criteria Document generically uses the term "metalworking fluids," when, in fact, NIOSH actually is referring to "metal removal fluids." Metal removal fluids are a distinct subset of metalworking fluids, rather than interchangeable terms. The studies relied upon by NIOSH generally deal with metal removal fluids, rather than metalworking fluids as a whole. Further, these studies do not justify the inclusion of all metalworking fluids in the Draft Criteria Document. These and other technical terms must be used properly in order to avoid both confusion and the inappropriate application and use of information released by NIOSH.
- Once in use, metal removal fluids are not static. Many changes may and do occur to these fluids during use, including: (1) component concentration and depletion; (2) tankside additions of chemicals (*e.g.*, bactericides, fungicides and pH buffers); (3) chemical contamination; (4) microbial (bacterial and fungal) contamination; (5) metallic contamination; and (6) housekeeping and other (*e.g.*, cigarette, human waste and food) contamination. As a result, efforts to quantify occupational exposures must differentiate between metal removal fluid effects and those resulting from the presence of contaminants.
- Alleged associations between specific cancers and out-of-service and obsolete metal removal fluid formulations are unproven and suspect at best. Moreover, these alleged associations cannot be extended to today's products. NIOSH has avoided temporal considerations when relating its conclusions about cancer risks to exposures to metal removal fluids. Conclusions that arguably may be relevant

to the 1950s, but not the 1990s, should be identified. Metal removal fluids' composition and use characteristics have changed substantially in the past 15 to 20 years.

- NIOSH's statement that "[t]he thoracic fraction comprises approximately 2/3 of total particulate mass . . ." is inaccurate and misleading. Particle size character of metal removal fluid aerosols is dependent largely upon both the type of metal removal fluid used and the specific metal removal operation (or machine type).
- The Draft Criteria Document goes well beyond the limits of objective scientific analysis of the available epidemiological data. Statements by NIOSH that exposures have resulted in various cancers and that exposure to "machining fluids" is strongly associated with cancer ignore accepted standards for adequate evidence. The conditions for establishing a relationship between an exposure and a disease were set forth by Hill (Hill, Bradford, *The Environment and Disease: Association or Causation?* (1965)). These conditions for establishing relationships are characterized under the following headings: (1) strength; (2) consistency; (3) specificity; (4) temporality; (5) biological gradient; (6) biological plausibility; (7) coherence; (8) experiment; and (9) analogy. NIOSH should subject the available epidemiological data to a rigorous analysis of the relationship conditions set forth by Hill.
- If cancer hazards were present as a result of workers being exposed to a metalworking environment, these hazards will have specific, assignable causes. These causes may be due to the presence of a carcinogen in: (1) a metal removal

fluid formulation; (2) a contaminant that enters a metal removal fluid; or (3) some other material present in the workplace. This being the case, epidemiological studies would give inconsistent results depending on whether the causative agent(s) were present in the workplace. Further, the specific, assignable causes would be the agents appropriate for regulation.

- NIOSH's comment that a confounding exposure is less likely than the exposure to metal removal fluids to be the assignable cause of an increased risk of pancreatic and other cancers is disingenuous.
- Deaths from lung cancer were by far the greatest for any category in the Eisen study, and the standard mortality ratio ("SMR") for lung cancers was 1.0. The lung is a primary exposure site to fluid mists; therefore, if a cancer risk were present, it is reasonable to predict that the incidence of lung cancer would reflect this fact.
- NIOSH states on page 50:

However, since there [are] little epidemiological data to support the association of any of these factors with the cancer risks observed in earlier cohorts, there is insufficient evidence to conclude that these changes will have prevented any further risks.

The virtual elimination of carcinogenic polynuclear aromatics ("PNAs") from base oils, the reduction of potential *N*-nitrosamine formation through both the removal of nitrites and the reduction in use of secondary amines, and the elimination/reduction in use of carcinogenic chlorinated paraffin species from metal removal fluid formulations must have some impact upon reduced cancer risk. It would be more more accurate statement for NIOSH is to acknowledge that

these re-formulation activities do indeed reduce the perceived carcinogenic potential of metal removal fluids, but quantification of the risk reduction is not yet possible. The only supportable conclusion is that the combination of a significant reduction in exposure with a significant reduction in impurities in metal removal fluids has reduced and will continue to reduce any future possible carcinogenic risks, to the extent that these risks actually were present.

- ILMA is confident that the use of triethanolamine ("TEA") does not present a significant health risk. There have been many studies of TEA which have shown the chemical to have very low toxicological and carcinogenic tendencies. From a human standpoint, perhaps the greatest endorsement for the safety of TEA comes from cosmetics manufacturers. Cosmetics have contained TEA for decades with no ill effects to the users.
- Animal skin painting studies of 11 synthetic fluids containing varying levels of *N*-nitrosodiethanolamine ("NDELA") failed to find any significant increases in tumors in any organ or tissue that could be attributed to the presence of NDELA.
- ILMA supports implementation of an exposure limit of less than 5 mg/m³, and has earlier suggested to OSHA an exposure limit of 2 mg/m³. However, the Association also believes that users of metal removal fluids would be better served by a restriction on short-term exposures to protect workers' health in addition to a time-weighted average exposure limit. Furthermore, as more data become available, a biologically-based exposure limit may be required. Users of metal

removal fluids would not be well served by only limiting average exposures to levels so low as to be achieved only at great expense.

- Any short-term exposure standard should seek to assure that exposures shall not exceed the specified level for more than a predetermined period of time with 95 percent confidence. As long as all observers can reach that conclusion from their measurements, the actual values measured and the methods used are moot. If measured exposures are near the specified level, then precision and accuracy become important.
- NIOSH's recommendations for an occupational safety and health program are unsupported by the data. Such a program would be extremely difficult and costly to implement, particularly for small businesses, with little or no health and safety benefits.
- ILMA questions why workers exposed to aerosol concentrations at half the REL should be under medical surveillance. Irritation can occur only at much higher levels, and there is substantial evidence to indicate that the irritation is caused by biological contamination and not by the fluid itself. The high cost of medical monitoring would put an unnecessary burden on businesses of all sizes, particularly small and medium-sized companies.

B. ILMA's Legal Concerns

ILMA also has legal concerns with the issuance of a criteria document based upon inadequate scientific support. These legal concerns, in part, form the basis for the Association's recommendation that NIOSH publish a hazard review that would not include a REL.

Section 22(d) of the Occupational Safety and Health Act, 29 U.S.C. § 671, authorizes NIOSH to conduct research "for the development of criteria for new and improved" OSHA standards. Generally, NIOSH recommendations must be formally adopted by OSHA through a rulemaking before they are effective. However, a NIOSH criteria document, and more specifically, a REL, can become the basis of a section 5(a)(1), "general duty clause" violation. 29 U.S.C. § 654(a).

The test for whether a REL may be the basis for a general duty clause violation requires more than general recognition within the industry. Under the case law, OSHA has the burden of demonstrating a general duty clause violation and must prove: (1) a condition or activity in the workplace presents a hazard to an employee; (2) the condition or activity is recognized as a hazard; (3) the hazard is causing or is likely to cause death or serious injury; and (4) a feasible means exists to eliminate or materially reduce the hazard. *National Realty and Construction Co. v. OSHRC*, 489 F.2d 1257 (D.C. Cir. 1973).

Notwithstanding this burden, companies that use metal removal fluids should not be exposed to potential legal liability based upon a REL that is unjustified and lacks scientific foundation. In addition, "loose" use of technical terminology, such as using "metalworking fluids" interchangeably with "metal removal fluids," may create many unintended consequences. NIOSH, and ultimately OSHA, have a responsibility to avoid creating legal liabilities where none should exist. Therefore, NIOSH should redraft the Draft Criteria Document as a hazard review without a REL, as well as fix the loose terminology, and the Agency should base its conclusions on the following specific comments.

III. SUBSTANTIVE COMMENTS ON DRAFT CRITERIA DOCUMENT

ILMA submits the following substantive comments on NIOSH's Draft Criteria Document. The Association's comments are ordered according to the chapters in the Draft Criteria Document.

A. Chapter 1: Introduction

NIOSH's stated intent of the Draft Criteria Document is threefold: (1) to identify populations potentially exposed to metal removal fluids and assess those worker exposures; (2) to examine adverse health effects associated with such exposures; and (3) to recommend a total particulate exposure limit and an occupational safety and health program. The third goal can only be completed after the first two goals have been thoroughly and scientifically analyzed using the most up-to-date information available. ILMA is concerned that NIOSH has recommended an exposure limit prematurely, certainly prior to a rigorous review by all interested parties of all information relied upon by NIOSH. NIOSH is responsible for drawing its conclusions based on sound science that has been peer-reviewed and is available to the public. NIOSH has not strictly adhered to this responsibility.

ILMA has been and will continue to be an active participant in the reevaluation of current exposure limits, available data, and methodologies; however, until there is a scientific basis that is well understood, it is premature for NIOSH to recommend an exposure limit. Additionally, NIOSH needs to recognize that, until an economic justification for additional regulatory controls also has been made, customers who purchase products from ILMA members will resist being forced to spend millions of dollars to comply with command-and-control mandates that may not prove to have any significant health and safety benefits.

B. Chapter 2: Background

ILMA questions the technical accuracy of the background section that forms much of the basis for the Draft Criteria Document. A principal concern is that NIOSH has consistently and has incorrectly interchanged the terms "metalworking fluids" and "machining fluids." In fact, what NIOSH has studied in the Draft Criteria Document are technically referred to as "metal removal fluids."

Metal removal fluids are used in the machining, grinding and honing of metal parts. Metalworking fluids are a significantly larger group of lubricants, many of which are not subject to the NIOSH study. In order to avoid confusion or inappropriate application of the Draft Criteria Document, NIOSH must clarify that its study applies only to metal removal fluids or, in the alternative, NIOSH must define the scope or application of the study. Further, NIOSH should revise Table 2-2 by moving "honoring" from "forming fluids" to "Removal Fluids." (*See page 10^{2/}*).^{3/}

Other examples of technical questions or inaccuracies associated with the background section include:

^{2/} Hereinafter, unless otherwise stated, all page numbers refer to the Draft Criteria Document.

^{3/} NIOSH relied upon information from ILMA in preparing Table 2-2. Information in the source document was incorrect and has been corrected by the Association. For a thorough review of the composition and use of metalworking fluids and the relationship between metal removal fluids and other metalworking fluids, *see* Howell, J.K.; Lucke, W.E.; Steigerwald, J.C. "Metalworking Fluids: Composition and Use." In *The Industrial Metalworking Environment — Assessment and Control: Proceedings of the Symposium in Dearborn, Michigan, November 13-16, 1995*, by the American Automobile Manufacturers Association. Washington, D.C.: AAMA, 1996, pp. 13-22. (Attachment B.)

- The Draft Criteria Document states (page 3) that metal removal fluids "may be manually applied to the cutting zone of the tool and the work or they may be delivered as a mist in a high velocity air stream." These are not the typical methods for metal removal fluid application. Metal removal fluids usually are applied by a stream of machining removal fluid to the tool/workpiece interface by flooding or, alternatively, through the tool itself.
- The definitions in Section 2.4 (page 4) should be replaced with the following:
 - "Straight oils" are metal removal fluids which typically consist of a severely-solvent refined petroleum oil, a severely-hydrotreated petroleum oil, or other oil of animal, marine, vegetable or synthetic origin used singly or in combination, or with other additives. These products are not designed to be diluted with water before use.
 - "Soluble oil" (or emulsifiable oil) is a combination of between 30 to 85 percent severely-refined lubricant base oil and emulsifiers and which may include other performance additives. Such products are supplied as concentrates which are diluted with water at ratios of one part concentrate to five to 40 parts water.
 - A "semi-synthetic metal removal fluid" contains a lower amount of severely-refined base oil; for example, five to 30 percent in the concentrate. These products also contain a higher proportion of emulsifiers, as well as 30 to 50 percent water, resulting in a transparent concentrate, and are typically transparent or translucent when they are diluted with 10 to 40 parts water.

— "Synthetic metal removal formulations" do not contain any petroleum oil.

They may be water soluble or water dispersible.

- Table 2-1 (page 5) should refer to "straight oils" not "insoluble oils," and a water component should be added to the table as a "diluent."
- NIOSH should note at the end of Section 2.4.1 (page 7) that, in "modern" oils, both sulfur and chlorine compounds have been reduced or eliminated from formulations. NIOSH also should footnote that, when moving from one product to a substitute, all health effects of the substitute may not be known. Formulation substitution is an effort to assure safety; however, the level of knowledge concerning the substitute may be less. Finally, substitutes often do not work as well and can result in increased production costs.
- Section 2.4.2 should be amended to indicate that "highly refined mineral oils. . . of soluble metal removal fluids" may be blended from high-viscosity oil base stocks or insoluble oils.
- Section 2.4.5 should recognize that severe hydrotreating will remove most PNAs from mineral oils.

NIOSH should add two tables to the Draft Criteria Document — Table 2-4, Industrial Lubricants and Table 2-5, In-Process Cleaners (Attachment C) — and should expand the section to include additional information regarding fluid changes during use by adding the following to Section 2.5 (page 9):

Table 2-4, Industrial Lubricants, illustrates the many types of industrial lubricants used in and around machine tools, all of which may leak into and contaminate the metal removal fluid. Table 2-5, In-Process Cleaners, describes the several types of in-process

cleaners used. As shown in Table 2-3, surface preparation is included as a common metalworking process and there are often many intermediate cleaning steps in a component manufacturing process.

As discussed below, metal removal fluids undergo change as they are used. Metal removal fluids, particularly water-miscible metal removal fluids, as used in the shop, are not static. These fluids' changes are due in large part both to the environment in which they are used and how they are used. Further, because the characteristics (*e.g.*, sump size, make up, water quality, metal removal operations, and contaminants) of individual central systems vary widely, even the same product may have a different "composition" after one or more years' use in one central system versus another. While metal removal fluids have a shorter "life" in stand-alone machine tools, such fluids also change as they are used. Stand-alone machines comprise approximately two-thirds of machine tools.

The changes or differences in metal removal fluids occur largely for two reasons: (1) increases of some and decreases of other components of the fluid occur over time; and (2) there is an effect from contaminants that arise from a variety of sources. It is generally understood, for example, that alkanolamines will tend to increase in concentration in a system over time, relative to other components. Additionally, because of the constant addition of water to circulating systems, increases in concentrations of metal salts also are likely to occur. Such salts, particularly in hard water areas, tend to destabilize semi-synthetic and soluble metal removal fluids as these salts build up in the system.

Some components, most notably corrosion inhibitors (particularly organic acid salts) and biocides, decrease over time because they are depleted during use. Most times, addition of the product concentrate on a routine basis (based on a regular program of chemical testing and

analysis) will keep metal removal fluid components in "balance." Sometimes, however, supplementary additions of these specific components are required to keep the fluid's performance at the desired level.

In addition to changes in component concentration, contaminants can have deleterious effects. As noted above, industrial lubricants find their way into circulating metal removal fluid systems. So-called "tramp oil," whether it be from leaking hydraulic or spindle oils or from slideway or gear lubricants, add to the complexity of the situation by contaminating the metal removal fluid with components that are emulsifiable or miscible with the metal removal fluid, but yet are not part of the fluid as it was formulated or first used. Poorly-maintained machine tools can leak a significant amount of hydraulic oil, for example, adding far more oil than might otherwise be provided through addition of "make-up" metal removal fluid.

Virtually all water-miscible metal removal fluids become contaminated with bacteria, sometimes through disposal of materials, such as food waste, in the fluid itself. Aside from degrading components of the fluid, most notably fatty acids, contamination of fluids with high levels of bacteria may increase the risk from opportunistic pathogens. More recently, endotoxins have been identified as a potential risk from exposure to metal removal fluids. Fungal contamination appears to occur less frequently than bacterial contamination.

Depending on the machining process and the type of metal or alloy machined, contamination of the metal removal fluid by both particulate and dissolved metals occurs. Several metallic contaminants — for example, nickel and cobalt — can have potentially deleterious health effects. Particulate contamination, usually the result of poorly functioning or absent filtration systems, increases the risk of dermatitis. A recent study identified build-up of alumina

in the fluid as a contaminant in the machining of automotive aluminum alloys. A recently-published ASTM document (E-1497-94) suggests guidelines for safe use of water-miscible metal removal fluid (Attachment D).

Housekeeping and other contaminants — for example, floor sweepings, cigarette butts, and human waste — are found in used metal removal fluids and also can cause or can explain changes. Accordingly, NIOSH's efforts to quantify occupational exposures must differentiate between effects of exposures to metal removal fluids and effects resulting from exposures to contaminants.

C. Chapter 3: Occupational Exposures to Metal Removal Fluids

ILMA member companies are producers of metal removal fluids and, while familiar with many applications of metal removal fluids, do not claim to be experts in occupational exposures experienced by all end users of metal removal fluids. However, the Association agrees with OSHA's data in Table 9-1 (page 169) that occupational exposures have reduced over time.

Nevertheless, ILMA believes that Section 3.4 should be rewritten. The statement regarding "(t)he thoracic fraction comprises approximately 2/3 of the total particulate mass. . . ." is inaccurate and misleading. Chan *et al.*, (App. Occup. Environ. Hyg. 5:162-170, 1990) and Woskie *et al.*, (Appl. Occup. Environ. Hyg. 9:612-621, 1994) have demonstrated clearly that the particle size character of metal removal fluid aerosols is dependent largely upon both the type of metal removal fluid used and the specific metalworking operation (or machine type). The use of different machining fluids for the same operation or in the same machine can produce workplace aerosols of different size characters. The same is also true of aerosols from the same fluid generated by different machine types or operations.

Further, NIOSH should caution that, even if this sentence were correct at the generation point, it will change as the mist circulates throughout the workplace.

D. Chapter 4: Occupational Health Risks for Workers Exposed to Metal Removal Fluids

Chapter 4 is perhaps the most significant chapter in the Draft Criteria Document. This chapter reviews the relationship between metal removal fluids and various types of cancer. This chapter is one that, because of its importance, should be closely scrutinized by the most stringent scientific and peer review. Conclusions that assume causal relationships between worker exposures and resulting cancers, without definitive cause-effect analyses and scrutiny, should be eliminated or identified as hypothetical in nature.

The Draft Criteria Document goes well beyond the limits of objective, scientific analysis of the epidemiological data. Statements that exposure has resulted in various cancers and that exposure to metal removal fluids is strongly associated with cancer ignore accepted standards for adequate evidence. The conditions for establishing a relationship between an exposure and a disease were set forth by Hill (Hill, Bradford, *The Environment and Disease: Association or Causation?* (1965)):

Strength: If the ratio of the number of observed cases to the number of expected cases is large (>10), the association is strong. If the difference is twofold, the association is weak. The ratios in the cited studies are only rarely greater than two, and then only in isolated subsets of the data. Moreover, no overall increases of cancer are found for those exposed to metal removal fluids; the alleged excesses are found only in selected subgroups. There obviously would be some subgroups with apparent decreases in occurrences of cancer that would bring the overall average to 1.0. Neither extreme should be considered significant.

Consistency: Similar studies of similarly-exposed populations should find the same relationships. The incidence of reported cancers vary widely from plant to plant. If strong toxic effects were present, such effects should be observable in all cases. This does not happen.

Specificity: The types of cancer reported are common in unexposed populations. It is impossible to associate digestive cancers with exposure to machining fluids only, especially when the study designs do not control for confounding factors, such as ethnic origin, diet, or smoking.

Temporality: Exposure to the causative agent must precede the onset of the disease. For carcinogens, the exposure should occur 20 to 30 years prior to onset. This is not established in the studies. This would be especially true in the case of nitrosamines which would have been present between 1950 and 1985. If nitrosamines were, in fact, a cause of cancer in machinists, there should have been a noticeable increase in cancer (especially cancer of the liver) sometime after 1970. No study has found such an effect.

Biological Gradient: Greater exposure should be reflected in a greater incidence of the disease. Again, this is not consistently found in those studies where a dose/response relationship can be tested.

Biological Plausibility: A suspected association is credible if a biological mechanism for the origin of the disease can be suggested. In the case of metal removal fluids, the principal routes of exposure are by skin contact and inhalation. It would be reasonable, therefore, to expect that skin and lung cancers would be in excess. Further, one of the more frequently proposed carcinogenic agents in such fluids is the PNA fraction of mineral oils. While some of these chemicals are known to cause skin cancer (and only skin cancer), no excess of skin and

lung cancers are reported by any recent study which would reflect exposures to metal removal fluids processed after 1950.

Another proposed carcinogen, N-nitrosodiethanolamine ("NDELA"), is a powerful liver carcinogen. Excesses of liver cancer are not found in machinists.

Coherence: The association of exposure to metal removal fluids with cancer should be consistent with the known properties of the fluids and the natural history and biology of the disease. This is not true for metal removal fluids. The chemical component used in the greatest amount of fluids is mineral oil. All the oils presently supplied to the market have been tested for carcinogenic potential through skin painting studies. They are monitored on a regular basis using the modified Ames test of the DMSO-extractable fraction (ASTM E-1687-95) or through chemical analysis for PNA content. The other major market for many of the components used to formulate metal removal fluids is in formulations of personal care products; there is no substantiated question of their safety. *In short, there is no identifiable causative agent for the alleged cancers in metal removal fluids.*

Experiment: There are no data from true experiments on humans (randomized control trials) that would support a conclusion that exposure to metal removal fluids is a cause of cancer. There is indirect evidence that the introduction and removal of a suspected hazard did not result in an increase or decrease in incidence of cancer (*see* discussion of nitrosamines above).

Analogy: The most commonly cited analogous case is that of poorly-refined mineral oils, which have been associated with skin cancer. However, changes in refining practices have made this analogy irrelevant.

In the absence of any strong evidence for a cause-and-effect relationship, the argument that exposure to metal removal fluids is a cause of cancer rests on observations of apparent excess numbers of cancer deaths. This reduces to statistical inference; often conclusions are drawn without proper regard for statistical rigor. As noted by Korelitz (1988):

If many studies are conducted in populations where a disease is not related to an exposure, it is still highly probable that, in several of the studies, SMR's greater than 1.0 will be observed, resulting in an apparent, but fallacious, confirmation of an association between exposure and disease.

Finally, NIOSH must avoid blinding itself to temporal variations and the advances in worker protection and metal removal fluids reformulations over the past 50 years. In many of the subsections that analyze potential or suspected carcinogenic effects from metal removal fluids, NIOSH draws conclusions that are written in present tense but actually refer to past exposures and activities that are not relevant with regard to today's industrial practices. For example, Section 4.1.3.1 concludes (page 24):

. . . the large number of case reports, the cancer incident study, and the case-control study suggest that primarily straight [metal removal fluid] exposure is associated with an increased risk for skin and scrotal cancer.

NIOSH should understand that such a conclusion is based on metal removal fluids from before the 1970s. NIOSH's token statement that current exposures to straight oils may have substantially reduced risk is insufficient to reflect accurately that skin and scrotal cancer findings and conclusions resulted from studies of exposures which occurred between the 1940s and 1970s. The lack of temporal reference is confusing and misleading.

The following specific comments should serve as examples for NIOSH reevaluating and revising its conclusions based upon Chapter 4:

1. Cancer Risks for Workers Exposed to Metal Removal Fluids

a. Skin Cancer Link More Tenuous Over Time

The bulk of the evidence for an association of straight oil exposure with skin cancer is based primarily upon case reports. This type of report generally suffers from poor or inadequate exposure assessment. Consequently, definitive cause-effect relationships are difficult to establish; thus, case reports should not be given the same weight as more thorough and detailed epidemiological studies.

As indicated above, the conclusion of Section 4.1.3.1 should begin with a temporal discussion. Emphasis should be placed on the substantially reduced risk of skin or scrotal cancer based on current exposures and industry practices, including advances in petroleum refining techniques.

b. Stomach Cancer Link Inconsistent

In Section 4.1.3.2, the study by Rotimi *et al.* (1993) reports excess mortality due to stomach cancer primarily among workers hired prior to 1955. In order to interpret properly this finding, it is critical to take into consideration the substantive differences between current metal removal fluid formulations and those before 1955. It is equally important to consider the differences in workplace exposure conditions that exist now versus pre-1955 in terms of both metal removal fluid aerosol/mist exposure levels, as well as concomitant exposure to other airborne materials. The marked improvements in present general workplace conditions compared to prior decades and the impact upon occupational hazards cannot be overemphasized.

In the study by Silverstein *et al.*, (1988), the greatest association with stomach cancer was among workers employed 10 years or more. This study was based on an evaluation of mortality

data between 1950 and 1982; however, the affected workers were likely exposed prior to the 1970s when one considers the usual latency period for cancer (*i.e.*, 10 or more years). Again, the issue raised above regarding prior formulations and prior exposure conditions should be taken into consideration by NIOSH.

Among the studies that were negative with respect to stomach cancer are the reports by Eisen *et al.* (1992) and Tolbert *et al.*, (1992), which are acknowledged as the "largest and best designed" studies. Despite the statistical power of these studies, no statistically significant association with stomach cancer was found, even upon analysis by Poisson modeling. Thus, the discussion speculating support for the association with stomach cancer from the data presented in these studies should be stricken. These studies did not meet the criteria established on pages 21 and 22 for a "positive" study. NIOSH inappropriately uses the data from these studies. Therefore, the section should conclude that there is no association between metal removal fluids and stomach cancer among the largest and best studies.

c. Pancreatic Cancer Link Questionable at Best

In Section 4.1.3.3, the inclusion or classification of the study by Acquavella *et al.*, (1993) as "significant" is questioned because it did not meet the criteria for significance defined on pages 21 and 22 (the lower bound of the 95 percent confidence interval was 0.9). Moreover, this study involved only white workers, whereas the study by Rotimi *et al.*, included both black and white workers, but reported significant pancreatic cancer excess among black workers only. In addition, the highest risk for pancreatic cancer reported in the Acquavella study was among assembly workers, who are not likely to have metal removal fluid exposure. The race-related inconsistency, as well as the excess cancer risk among the control subjects (assembly workers),

needs to be addressed. The lack of consistency between Vena *et al.* and Mallin *et al.* also casts suspicion upon the significance and relevance of the results.

ILMA also questions NIOSH's statement (page 29) that:

Tolbert *et al.*, (1992) found excess pancreatic cancer among black workers exposed to soluble oils at Plants I and II in Michigan (SMR = 1.6, 95% CI = 1.0, 2.5).

Again, the lower bound 95 percent confidence interval (0.98 as reported in Table 4.1-4 and not 1.0 as cited on page 29) fails to meet the criteria set for significance. In addition, the statement discussing the Poisson regression analysis in this study is misleading. The study authors themselves reported the Poisson analysis results in the following context:

The Poisson models indicated an unstable [emphasis added] evaluation of risk in the highest exposure group for synthetic machining fluid; and

The Poisson regression (but not the SMR analysis) provided limited evidence of an association between pancreatic cancer and exposure to synthetic fluids.

Moreover, once again, the lower bound 95 percent confidence interval of the Poisson analysis (0.88) does not meet the significance criteria established on pages 21 and 22. Thus, the presentation of the work by Tolbert *et al.*, relative to pancreatic cancer and synthetic metal removal fluids, should either be removed or rewritten to convey properly the significance of the findings throughout the Draft Criteria Document.

The studies by Vena *et al.*, (1985), Mallin *et al.*, (1986), and Silverstein *et al.*, (1988) involved evaluation of mortality data between 1970 and 1979, 1970 and 1982, and 1950 and 1982, respectively. Assuming a 10 years or greater latency, the critical exposure period of the study subjects to metal removal fluid aerosols occurred during the 1960s and 1970s (or earlier).

Again, the consideration of exposure to prior metal removal fluid formulations and prior workplace exposure conditions is needed to evaluate properly the significance of these results with respect to current metal removal fluid formulations and workplace exposure scenarios.

For the study by Silverstein *et al.*, (1992), there is a minor discrepancy between the p-value cited for 10 or more years exposure (page 30) and the values in Table 4.1-4.

In conclusion, it is important to remember that metal removal fluids are a broad category of chemical mixtures, blended from many ingredients. If cancer hazards were present as a result of workers being exposed to a metalworking environment, these hazards will have specific, assignable causes. These causes may be due to the presence of a carcinogen in: (1) a metal removal fluid formulation; (2) a contaminant that enters a metal removal fluid; or (3) some other material present in the workplace. This being the case, epidemiological studies would give inconsistent results depending on whether the causative agents were present in the workplace. Further, the specific, assignable causes would be the agents appropriate for regulation. NIOSH's comment that a confounding exposure is less likely than the exposure to metal removal fluids to be the assignable cause of an increased risk of pancreatic and other cancers is disingenuous.

d. Laryngeal Cancer Association Confounded by Major Risk Factors

In Section 4.1.3.4, information regarding the study by Rotimi *et al.*, (1993), cited in the text on pages 31 and 32, does not appear in Table 4.1-5. Table 4.1-5 also does not accurately reflect the study by Eisen *et al.*, (1994). The significant association should identify clearly exposures to straight oils. In addition, the results showing no association of laryngeal cancer with soluble oil exposures in the same study should be reported in the table. Moreover, biocides are a broad category covering many different molecular species. To consider such a broad class as

a possible confounding factor is much too simplistic. The same can be said for the other classes in the list.

Smoking and alcohol are well-documented major risk factors for laryngeal cancer and the inability to control or adjust for these two major risk factors is a significant shortcoming of the study by Eisen *et al.*, (1994). The study authors attempt to address this issue by evaluating the incidence of death due to smoking (lung cancer) and alcohol (cirrhosis) and report neither risk factor increased with increasing exposure to straight metal removal fluids (*i.e.*, the incidence of death due to lung cancer and liver cirrhosis is similar between metal removal fluid exposure groups). The subsequent suggestion, however, that there is no association between straight metal removal fluid exposure and smoking or alcohol is inaccurate and misleading. This indirect approach provides no information about whether smoking and/or alcohol compromise or predispose individuals to the onset of laryngeal cancer upon exposure to straight metal removal fluids. Thus, the potential confounding effects of smoking and alcohol consumption cannot be addressed adequately and should be duly noted by NIOSH in the proper context. As suggested previously, the concluding statements (*i.e.*, sentences beginning with "In conclusion") should be modified to show the time-frame when the exposures to metal removal fluids occurred.

e. Rectal Cancer Studies

In Section 4.1.3.5, the discussion of the study by Gerhardsson de Verdier *et al.*, (1992) and the result of adjusting the analysis for other exposures should indicate not only the lowered risk of rectal cancer, but should also reflect the absence of statistical significance when the adjustments are made.

Again, as noted above, the concluding statements (second paragraph 2 on page 35) should indicate the time-frame when exposures to metal removal fluids occurred among the study subjects.

f. Lung Cancer - Notable Absence of Increased Risk

Deaths from lung cancer were by far the greatest for any category in the Eisen study and the SMR for lung cancers was 1.0. The lung is a primary exposure site to fluid mists. Accordingly, if a real cancer risk were present, it is reasonable to predict that the incidence of lung cancer would reflect this. In Section 4.1.3.10, the discussion concerning the suggestion by Tolbert *et al.*, (1992) that the negative association between metal removal fluid exposure and lung cancer is due to endotoxin merely perpetuates speculation and should be stricken. There is no scientific evidence of any such "protective" effect from endotoxin exposure. It is much more likely that the apparent deficits in lung cancer deaths in specific subsets of exposed workers indicate the degree of statistical variation to be found in this type of analysis and serve as a "reality check" for conclusions based on apparent excesses.

Inhalation exposure is one of the two primary routes of exposure to metal removal fluids. ILMA suggests that the lack of an SMR greater than 1.0 for lung cancers in the Eisen study — the largest population studied to date and at a time when exposures were higher and potentially hazardous ingredients might have been present — creates strong doubt on the association of cancer with any exposure to metal removal fluids.

g. Genetic Effects Linked to Contaminants, Not Metal Removal Fluids

In Section 4.1.4, it should be stated clearly that NDELA is a *contaminant* in metal removal fluids rather than an intended component. Clarification of this point is important,

because nitrosamine contamination of metal removal fluids is not discussed until later in the document (Chapter 6).

h. Improper Generalizations Regarding Aerosol Particle Size Distribution

The work of Chan *et al.*, (1990) and Woskie *et al.*, (1994) demonstrate clearly that both the aerosol concentration and the specific particle size characteristics of metal removal fluid aerosols are dependent largely upon the metal removal fluid type and the type of machinery or operation. Thus, generalizations regarding the particle-size character of metal removal fluid aerosols without consideration of machine type and fluid type are inappropriate. Therefore, NIOSH should amend or strike the sentence (page 47):

Eisen *et al.*, (1994) report that approximately one third of the total particulate material was in the extra thoracic fraction.

i. Cancer-Causing Effects, Conclusions

Nitrosamines and PNAs are not fluid constituents; they are contaminants. For water-diluted fluids, contaminants, especially tramp oils, are often present in greater amounts than is the metal removal fluid concentrate. Jenkins, *et al.* (in review, draft attached as Attachment E) have surveyed air in a non-metalworking environment and have reported on particulates, metals and volatile organics that are part of the workplace background. Again, the consideration of exposure to prior metal removal formulations and prior workplace exposure conditions is needed to evaluate properly the significance of these results with respect to current metal removal fluid formulations and workplace exposure scenarios.

Reductions in nitrosamine levels in the 1980s were the result of industry actions, not EPA. EPA published an Advanced Notice of Proposed Rulemaking in 1983, but never took further

action because industry reductions were well underway by that time. *See* 58 Fed. Reg. 27940 (1993).

The speculation by Tolbert, *et al.* that emulsification may alter a supposed carcinogenic agent is less credible in explaining inconsistencies between straight oil and soluble oil results than speculation that there is no carcinogen present. ILMA agrees that concerns over respiratory irritation justify a reduction in OSHA's current permissible exposure limit. ILMA, however, does not agree with NIOSH that there is substantive, credible evidence to associate cancer in any organ or tissue with exposures to current metal removal fluid formulations as a class of products.

NIOSH makes the statement (page 50):

However, since there is little epidemiological data to support the association of any of these factors with the cancer risks observed in earlier cohorts, there is insufficient evidence to conclude that these changes will have prevented any further risks.

The virtual elimination of carcinogenic PNAs from base oils, the reduction of potential *N*-nitrosamine formation through both the removal of nitrites and the reduction in use of secondary amines, and the elimination/reduction in use of carcinogenic chlorinated paraffin species from metal removal fluid formulations must have some impact upon reduced cancer risk. A more accurate statement is to acknowledge that these re-formulation activities do indeed reduce cancer potential of metal removal fluid, but quantification of the risk reduction is not yet possible.

Finally, NIOSH concludes (pages 50 and 51):

The substantial evidence that [metal removal fluids] in commercial use prior to the mid 1970's is associated with cancer at several sites, and the possible potential for current [metal removal fluids] to pose a similar carcinogenic hazard, support the recommendation based on respiratory disease risks for a reduction in allowable airborne MWF exposures. (Emphasis added.)

This is purely speculative with regard to current metal removal fluids. The only supportable conclusion is that the combination of a significant reduction in exposure, coupled with a significant reduction in impurities in metal removal fluids, has reduced and will reduce any future possible carcinogenic risks.

2. Non-malignant Respiratory Effects

a. General Background

NIOSH has made a noticeable change in policy in its review of non-malignant respiratory effects in comparison to its review of possible carcinogenic effects resulting from exposures to metal removal fluids. In its "cancer" section, NIOSH generally relied upon published and peer-reviewed data that are readily accessible to ILMA members and other interested parties. However, much of the "non-malignant respiratory effects" section (three out of four papers) is based upon "non-binding, peer-review" by OHAB of papers that have not been published. NIOSH should not rely upon the OHAB-reviewed data to draw any respiratory effects conclusions for two reasons: (1) a non-binding OHAB review should not substitute for "traditional, peer-reviewed" articles; and (2) ILMA and other interested parties are at a distinct disadvantage in commenting on the technical aspects of the studies. ILMA, as well as other interested parties, rely upon peer-reviewed, published articles for confidence in the results and proper interpretation because many Association members and these other parties lack qualified staff and sufficient resources to conduct their own appropriate peer review.

NIOSH must support its statements that all the listed materials (*e.g.*, chlorine) can, in fact, cause or aggravate asthma at the concentrations typically found in metal removal fluids. Also, in the first paragraph on page 73, NIOSH needs to include references to support the last sentence:

Increasing evidence suggests that an individual's occupational asthma is more likely to become chronic (*i.e.*, irreversible airflow limitation) the longer the worker continues to be exposed.

b. Asthma - Case Reports and Observations from Surveillance Programs

Only one of the eight studies reviewed or cited by NIOSH provides information regarding exposure levels and duration of employment and exposures (*i.e.*, latency period). This information also is not provided or indicated for the surveillance programs from New Jersey and Massachusetts. If this information is not reported by either the authors or surveillance agencies, then NIOSH should note the data/information gap. Some discussion regarding the impact of the absence of this information upon the assessment of possible cause-effect relationship(s) and potential risk also is needed, especially in the context of current occupational exposures. Sound exposure assessment and hazard identification are both critical requirements for proper risk assessment.

c. Asthma - Summary

The first sentence in the section is misleading (page 82):

The studies summarized above provide substantial evidence of an elevated risk of asthma among workers exposed to [metal removal fluid] aerosol exposure concentrations currently found in large [metal removal fluid] shops and well below the OSHA PEL of 5 mg/m³ for mineral oil mist.

First, many of the references cited by NIOSH provide no exposure data or information regarding exposure levels or conditions. Second, the OSHA PEL pertains to total mineral oil mist suspended in air, whereas three of the six studies listed in Table 4-1 (page 84) provide only the airborne concentration of the thoracic or inhalable fractions. Moreover, two of the remaining three studies in Table 4-1 indicate total aerosol exposure concentrations of <4.0 mg/m³ and 2.6

mg/m³. ILMA questions whether it is accurate to characterize these exposure levels as "well below the OSHA PEL." No exposure information was provided in the remaining study listed in Table 4-1.

d. Symptoms of Airways Disorders - Summary

As in the preceding comment, ILMA questions the accuracy of the phrase ". . . well below the current OSHA PEL for mineral oil mist of 5 mg/m³" (page 94). As noted above, OSHA's PEL is based upon total mineral oil mist. In Table 4-2, only the studies by Greaves *et al.*, (1995), and Kriebel *et al.*, (1994) report exposure levels which can be construed as "well below the OSHA PEL." Once again, however, the authors of these studies do not report total oil mist concentration, but rather only the thoracic or inhalable fraction of the total airborne oil mist.

e. Cross-sectional Studies of Lung Function - Summary

Similar to the preceding two comments, the statement ". . . well below the OSHA PEL for mineral oil mist . . ." (page 106) is misleading and inaccurate. For the four studies listed in Table 4-3, the reported aerosol exposure concentrations respectively are: 5 - 99.5 mg/m³ (total mist), 2.6 mg/m³ (total mist), 0.41 - 0.55 mg/m³ (thoracic fraction), and 0.22 mg/m³ (inhalable fraction).

Reports of respiratory responses at low exposure levels (0.2 mg/m³) are based on the time-weighted average ("TWA") exposure level. Data collected by "real time" techniques show that peak mist levels can be well above the average for a substantial portion of the work day (Ball, in review, draft attached as Attachment F). This commonly occurs when the doors of an enclosed machine are opened to change workpieces. The TWA may be a poor predictor of actual exposure

potential, and metal removal fluid mists may not be as irritating as NIOSH's review suggests. Thus, a PEL based on TWA alone may not provide the best protection for the operator.

ILMA supports the implementation of an exposure limit of less than 5 mg/m³ and has earlier suggested to OSHA an exposure limit of 2 mg/m³. The Association, however, also believes that users of metal removal fluids would be better served by a restriction on short-term exposures to protect workers' health in addition to a TWA exposure limit. Furthermore, as data become available, a biologically-based exposure limit may be required. Users of metal removal fluids would not be well served by limiting average exposures to levels so low as to be achieved only at great expense.

E. Chapter 5: Selected Potentially Hazardous Chemical Ingredients or Additives

The value of Chapter 5 to the Draft Criteria Document is suspect. The introduction identifies significant variables and unknowns regarding chemical ingredients or additives and disclaims an intent to characterize all potential chemical health risks. Individual chemicals are discussed relative to a number of animal studies, yet the chapter concludes that NIOSH relies on epidemiologic data in deciding on a REL for metal removal fluids. With this in mind, ILMA submits the following comments:

1. Triethanolamine

TEA is added to metal removal fluids; however, TEA is not a surfactant. TEA would not be considered a surfactant by the normal definition of "surfactant"; but, TEA would be expected in analyses of metal removal fluids. TEA is undoubtedly the most commonly-used alkanolamine in metal removal fluids. Therefore, it would be more of an oddity in the Kenyon, Eisen, and Woskie studies if TEA were not found in exposure samples.

The NTP studies indicate a sensitivity to TEA by some specific test groups of rats and mice, but some of these groups were shown to have other health problems which may have skewed the results. The overall preponderance of the data did not show increased tendency for carcinomas from exposures to excessive doses of TEA.

ILMA is confident that the use of TEA does not present a significant health risk. There have been many studies of TEA which have shown the chemical to have very low toxicological and carcinogenic tendencies. From a human standpoint, perhaps the greatest endorsement for the safety of TEA comes from cosmetic manufacturers. Cosmetics have contained TEA for decades with no ill effects to the users.

2. Mineral Oil

The dermal carcinogenic potential of mineral oil is strongly related to the PNA content, which is directly related to the degree of refining. This has been well documented. ILMA members' base oil suppliers have been very responsive in converting to lower PNA mineral oils as data became available. In 1985, there was a massive effort by these suppliers to complete the conversion to the production of more highly-refined, lower-PNA mineral oils. This involved extensive reformulation work by ILMA members because the more highly-refined mineral oils do not easily emulsify. These highly-refined mineral oils are classified as severely hydrotreated, meeting OSHA's guidelines of ≥ 800 PSI and $\geq 800^\circ\text{F}$, or are severely solvent refined. Today, suppliers to the industry provide skin painting studies, modified Ames test assays (ASTM E-1687-95) and other short-term test results to show the lack of dermal carcinogenic potential.

3. Biocides

All biocides go through extensive toxicity testing under regulations implementing the Federal Insecticide, Fungicide and Rodenticide Act (*see* Pesticide Assessment Guidelines, 40 C.F.R. § 158.20) prior to being approved by EPA for use in metal removal fluids. At recommended levels, these biocides should not cause health problems.

Table 5-1 is not correct. Sodium omadine, Proxel CRL, Kathon 886, and Dowicide 1 are not formaldehyde-release biocides. Although Bioban P-1487 is a formaldehyde condensate, there has not been any evidence to show that it releases formaldehyde in use.

Non-formaldehyde biocides are generally more effective against fungi than bacteria. Effectiveness depends solely on the product's chemistry. Of the non-formaldehyde biocides listed, Proxel CRL, Givgard DXN (not DNX), and DBNPA are all better bactericides than fungicides.

Although OSHA requires labelling and training at levels of greater than 0.1 PPM formaldehyde, the PEL is 0.75 PPM and the STEL is 2.0 PPM. Many areas cited in the Cohen studies have shown background levels of greater than 0.1 PPM formaldehyde where no formaldehyde-release biocides are used (*e.g.*, office areas). Cohen, Howard J. *A Study of Formaldehyde Exposures from Metalworking Fluid Operations Using Hexahydro-1, 3, 5-Tris (2-Hydroxyethyl)-S-Triazine* (1994). There is also much doubt as to the accuracy of the test method at this low level of formaldehyde.

As stated, there is potential for nitrated biocides to release nitrite in use which could combine with amines to form nitrosamines. However, there currently are no data published to indicate that potentially dangerous levels of nitrosamines form in metal removal fluids by this process.

4. Chlorinated Paraffins

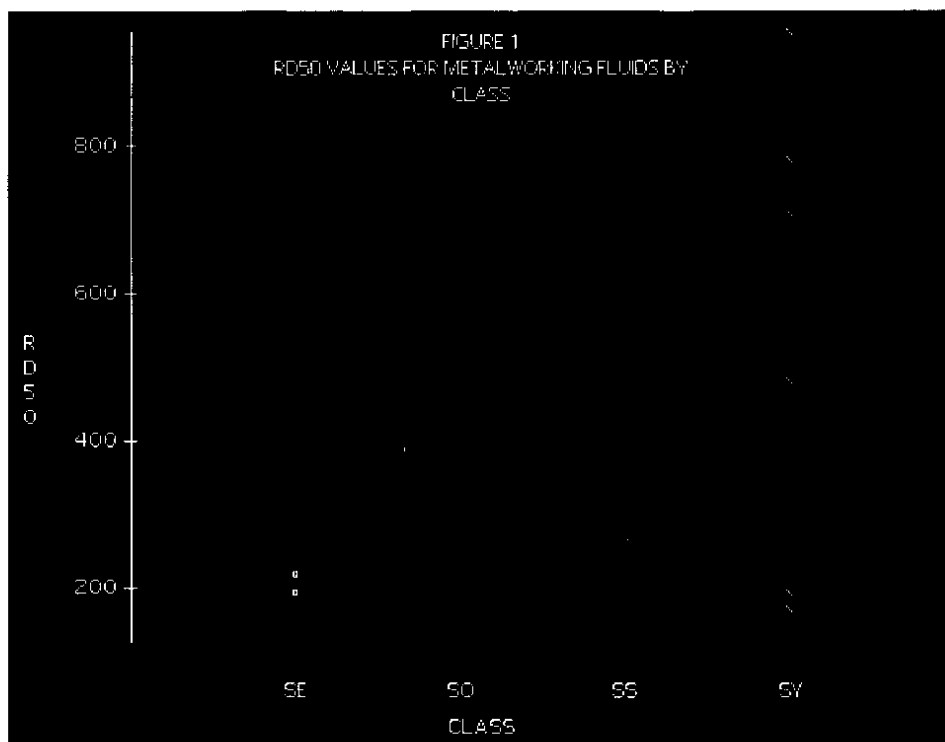
NTP has studied only two chlorinated paraffins: C₂₃, 43 percent chlorine, and C₁₂, 60 percent chlorine. There are many other long and short-chain paraffins with varying chlorine levels besides the ones listed. Thus, NIOSH's statement (page 134) should read "(o)ne long chain chlorinated paraffin and one short chain chlorinated paraffin (C₂₃, 43 percent chlorine and C₁₂, 60 percent chlorine) were selected by the National Cancer Institute ("NCI") for toxicity and carcinogenicity evaluation." Metal removal fluid manufacturers have eliminated the two studied chlorinated paraffins from formulations when the information was released by NTP and chlorinated paraffin suppliers subsequently have removed these chlorinated paraffins from the marketplace.

In November 1994, EPA promulgated a final rule expanding the list of toxic chemicals subject to Section 313 reporting under the Emergency Planning and Community Right-to-Know Act ("EPCRA") that included limited chlorinated paraffins (*see* 59 Fed. Reg. 61432 (November 30, 1994)). In its rulemaking, EPA concluded that "there is insufficient evidence to list long-chain chlorinated paraffins on the EPCRA Section 313 list." *Id.* at 61462.

In fact, EPA only added short-chain (10-13 carbon) polychlorinated alkanes (*i.e.*, chlorinated paraffins/alpha-olefins) to the EPCRA Section 313 list. EPA made the determination to add these polychlorinated alkanes not because it could prove such chemicals cause cancer in humans, but because the standard for addition to the EPCRA Section 313 list is informal enough to add chemicals that can "reasonably be anticipated to cause an effect listed under EPCRA Section 313(d)(2)(B)." *See* Summary and Response to Public Comments, Docket No. OPPTS-400082, page 157. These effects include: cancer; reproductive dysfunction; neurological disorders; inheritable genetic mutations; or, other chronic health effects. However, despite the need for further scientific studies on short-chain polychlorinated alkanes to determine their specific detrimental effects, if any, on humans, ILMA members began eliminating short-chain polychlorinated alkanes from their formulations.

5. Potential Sensory or Polmonary Irritants

The Schaper generalization of relative irritation of metal removal fluid classes is based on a comparison of only 10 metal removal fluids and does not hold up when more metal removal fluids are included (Ball, *et al.*) (*see* Figure 1, below).



The use of RD₅₀ values to set exposure limits does not give values that can be supported by workplace experiences. The calculated values, especially for straight oils, are much higher than operators will tolerate, even with the generous safety factor built into the calculation. In actual use, tall oil fatty acids ("TOFA") and sulfonic acids ("SA") do not exist in metal removal fluids. These components are always neutralized by some source of alkalinity to form salts. They do not exist as the free acids in metal removal fluids. Thus, any data or conclusions from this study would be highly questionable as to how they relate to metal removal fluids in use.

6. Conclusions

The mouse bioassay is not a good model for human exposure. ILMA supports NIOSH's decision to base recommendations on actual human data.

It has been and continues to be the policy of ILMA member companies to be good product stewards and to consider the health, safety, and environmental impact of the metal removal fluids they manufacture. As data have become available, ILMA members have made every effort to remove metal removal fluid components which have been shown to be potentially hazardous.

As noted above, many of the components typically used in metal removal fluids also are used in personal care products. The Cosmetic, Toiletry and Fragrance Association tests continually such components and publishes an annual compendium of its research findings.

F. **Chapter 6: Potentially Hazardous Contaminants**

ILMA understands that metal removal fluid end users may handle, store or use metal removal fluids in such a way that the metal removal fluids may be contaminated with hazardous constituents. With regard to such possible contamination, ILMA submits the following comments on particular suspected contaminants:

1. Nitrosamines

Lucke, *et al.* (Attachment G) have shown that, for metal removal fluid concentrates, the sole determining factor in the level of nitrosamine formed is the amount of diethanolamine ("DEA") present. No evidence for significant levels of nitrosation of TEA or other amines or catalysis by formaldehyde-release biocides was found. Tertiary amines can be nitrosated in acidic

media, but the reaction does not proceed at a significant rate at pH 10-11 levels typical of metal removal fluid concentrates.

Primary amines do not react with nitrosating agents to form stable nitrosamines. These are further nitrosated to form unstable diazonium salts, which immediately lose nitrogen. The reaction products of nitrous acid and ethanolamine ("MEA") are ethanol and nitrogen. This is a well-known reaction used to characterize primary amines.

NDELA is not formed from TEA in metal removal fluids.

Rounbehler *et al.* [*N-Nitroso Compounds in the Factory Environment*, NIOSH contract 210-77-0100, June 1983] have shown that nitrosamines are rapidly degraded in used metal removal fluids. The reduction of nitrosamines by zinc dust is a classical test for classification of nitrosamines; a similar reaction with nascent iron surfaces formed during machining or grinding quickly strips NDELA from the fluid. Nitrosation of DEA apparently does occur during use; however, at low levels of DEA, the destructive reaction is faster than the formation.

Animal skin painting studies of 11 synthetic fluids containing varying levels of NDELA failed to find any significant increases in tumors that could be attributed to the presence of NDELA. [*Machine Oils and Nitrosamines Study for Carcinogenesis in Mice*, NIOSH contract 210-77-0136, September 1982.]

Monarca, *et al.* [*Biological Monitoring of Workers Exposed to NDELA in the Metal Industry, Environmental Health Perspectives, 104: 78-82, 1996*] report that only workers exposed to NDELA in metal removal fluids at levels greater than 5 mg/L excreted trace levels of NDELA in their urine. No differences were found between urine excretion of mutagens, urinary D-glucaric acid, or lymphocyte sister chromatid exchange for a high-exposure group (>5 mg/l

NDELA), a low-exposure group (<5 mg/L NDELA) and an unexposed group. The use of coffee and tobacco did cause changes in these biomarkers. High-exposure subjects had a higher mean value of thioethers in their urine than the other groups. This was interpreted as possible detoxification of the NDELA by reaction with endogenous glutathione.

NDELA levels found in fluids in 1977 were in the parts per hundred range. No adverse effects of exposure to those fluids have been demonstrated by animal studies or by epidemiological studies. NDELA levels of modern fluids are reported in the parts per billion range and are of questionable reliability. Adverse effects of nitrosamine exposures in current metal removal fluids would be expected to be reduced to the same extent.

The reported presence of *N*-nitrosodimethylamine ("NDMA") in metal removal fluids is in itself reason to question the validity of the finding of low levels of nitrosamines in current fluids. Dimethylamine is not a component or a foreseeable contaminant of metal removal fluids. The NDMA is clearly an analytical artifact. Trace level finds of nitrosamines should always be questioned and verified before being accepted.

2. Microbial Contamination

ILMA agrees with NIOSH's comments on the proper use of biocides to prevent microbial growth as opposed to attempts to remediate contaminated systems. There is laboratory evidence that the formaldehyde release biocides can neutralize endotoxins by crosslinking the cell wall (Rossmoore, *et al.* reference, *see* Attachment H). Limited field experience seems to confirm this prediction.

G. Chapter 8: Sampling and Analytical Methods^{4/}

ILMA agrees that sampling and analytical methodology should address operations where exposure to both metal removal fluid and non-metal removal fluid material is present. In such cases, two exposure limits would appear to be in effect: 0.5 mg/m³ for the fluid mist and 5 mg/m³ for other respirable particulates. This could well happen in areas where wet and dry operations take place near each other. It will be important to be able to have a consistent, objective means of apportioning the collected mass between the two classes. The reliability of the assignment should approach that of the measurement, if the limit is to be enforceable.

Current gravimetric methods give only an average value to represent operator exposure. ILMA is not satisfied that a TWA gives an adequate measure of fluid mist exposures. Operators of enclosed machines must open the enclosures to remove finished parts and mount new workpieces for processing. At these times, exposures can be many times that of the average value. It seems likely that the respiratory effects reported at time-weighted averages of less than 0.5 mg/m³ actually result from short-term exposures rather than to peak levels well above the overall average. In ILMA members' experience, respiratory complaints are always associated with at least some exposure to high mist levels during the work day. ILMA supports implementation of an exposure limit of less than 5.0 mg/m³, but believes that users of metal removal fluids would be better served by a restriction on short-term exposures rather than by limiting average exposures to levels so low as to be achieved only at great expense.

^{4/} ILMA has no comments on Chapter 7, Current Occupational Recommendations and Standards.

Short-term exposure limits assume the availability of adequate measurement methods. Instruments, like the RAM-1, have proven capable of collecting reproducible measurements under metalworking conditions in real time. Results are in general agreement with more conventional gravimetric methods. In this situation, absolute accuracy is not needed. It is important to be able to determine that a mist level is or is not greater than 1.0 mg/m^3 than it is to be able to distinguish between 0.95 and 0.98 mg/m^3 . The standard should be drafted to assure that exposure shall not exceed that specified level for more than a set period of time with 95 percent confidence. As long as all observers can reach that conclusion from their measurements, the actual values measured and the methods used are moot.

H. Chapter 9: Basis for a Recommended Exposure Limit ("REL")

Chapter 9 begins with a recapitulation of the steady decline in worker exposures to metal removal fluids over the past 20 to 30 years. Yet, temporal relations seem to be ignored in NIOSH's review of effects from exposure (Section 9.2). This leads to NIOSH drawing several incomplete or inconsistent conclusions. For example, Section 9.2.1 states that "the use of mineral oils treated by appropriate refinery methods should eliminate or reduce the risk of skin carcinogenesis." However, NIOSH does not point out that severely-refined mineral oils have been in general use for decades and exclusively used since 1985. NIOSH should note that the significantly reduced PNA content of mineral oils that have been severely refined are likely to reduce occurrences of cancer at sites associated with exposure to metal removal fluid formulations from decades earlier.

NIOSH needs to note (on the top of page 170) that grinders work the same in small shops as in large shops. As a result, exposures associated with older machine tools are not likely to be lower, but rather the same or higher.

Throughout the chapter, NIOSH should indicate when it is referring to studies based on exposures to antiquated metal removal fluids. Specifically, ILMA suggests:

- NIOSH needs to reemphasize (at the top of page 171) that "studies of workers exposed to [metal removal fluids] in use decades ago indicate an association between [metal removal fluid] exposure and risk." NIOSH should also add at the end of this paragraph a note that, as noted earlier, exposures have declined significantly in recent years.
- NIOSH needs to recognize that there is no evidence to associate exposure to current formulations with any increased risk of cancer and, as a result, change the sentence on page 172 to read, "The specific constituent(s), additive(s), and/or contaminant(s) of [metal removal fluids] that might have been present and possibly responsible for the elevated risk for the various site-specific cancers remains to be determined." Similarly, the tense in the last sentence of the first paragraph on page 172 needs to be changed from "found in certain [metal removal fluids] are considered carcinogenic" to "that may have been present in older formulations of [metal removal fluids] . . ."
- NIOSH's discussion of life-style factors (page 172), such as tobacco and alcohol consumption, is inadequate and needs to be significantly expanded.

- NIOSH's conclusion on page 173, "Because changes in [metal removal fluid] composition and reduced airborne [metal removal fluid] exposures may not be sufficient to eliminate the cancer risks associated with [metal removal fluid] exposures, the reductions in airborne [metal removal fluid] exposure recommended in this chapter are warranted," is unfounded and should be deleted. NIOSH has not taken into account the substantial information presented to NIOSH by ILMA over the last six years. Formulators, many of whom are ILMA members, have taken significant steps to eliminate carcinogens or suspected carcinogens from metal removal fluid compositions. Moreover, as discussed elsewhere in the chapter, in the last 15 years alone, exposures to metal removal fluids have been significantly reduced.
- NIOSH's statement (page 174) that, "A variety of components, additives, or contaminants of [metal removal fluids] are sensitizers or irritants known to induce new-onset asthma, aggravate pre-existing asthma, and/or irritate airways of non-asthmatic individuals . . . are . . . known . . ." is inappropriate without documentation. Documentation should be provided.
- NIOSH suggests (page 175) without adequate documentation that "various other agents . . . may cause a high proportion of [metal removal fluid]-associated asthma." In contrast to the statement made, NIOSH should note the sensitizers mentioned in the references [Savonious, *et al.*, 1994; Hendy, *et al.*, 1985] and should not speculate on what "various other agents" may or may not do.

- NIOSH's conclusion (page 176) that a two-fold increase of asthma among machinists exposed to soluble or synthetic metal removal fluids at average aerosol exposures of 0.2 - 1 mg/m³ deserves further clarification. A direct quotation from the cited references to support NIOSH's conclusion is required.
- NIOSH's conclusion (page 177) that, "the observed reduction in pulmonary function may be acute and reversible, but their stronger relationship with past rather than current exposures suggests that these effects are probably substantially chronic and irreversible," [Greaves *et al.*, 1995a] is completely unfounded. There is no evidence that links the observed acute and reversible pulmonary function changes resulting from metal removal fluid exposure to "chronic and irreversible effects."
- NIOSH's reading (page 177) of Greaves, *et al.*, 1995a, that associates (with a dose related increase) adverse effects attributable to aerosol concentrations in excess of 0.5 mg/m³ (thoracic fraction) argues strongly for a higher REL.
- NIOSH's conclusions (page 177) that "acute reactions are likely manifestations of newly developed but not yet diagnosed asthma" is without foundation. Further, while Becklake [1995] may have demonstrated that "other occupational agents" may give a biologically plausible explanation that "repeated modest and apparently acute airways effects may ultimately lead to irreversible impairment and chronic pulmonary disability," NIOSH has no evidence whatsoever that any metal removal fluid components or contaminants might cause a similar response.

- While ILMA agrees with NIOSH's assertion (page 178) that there is "uncertainty about specific etiologic components/contaminants," NIOSH's conclusion that "limiting exposure based on gravimetric measurement and reduction of [metal removal fluid] aerosol would have substantial prevention benefit" is insufficiently documented.
- NIOSH's discussion (page 180) of prevalence rates of dermatitis of 14 to 67 percent are vastly higher than reported by others. While ILMA agrees that contact dermatitis is a concern of users of metal removal fluids, presentation of that data gives the reader the impression that one-out-of-five to two-out-of-three workers suffer from dermatitis, a totally and unrealistically high estimate. Further, while ILMA agrees with other NIOSH preventative measures for dermatitis, NIOSH must note that formulators do not purposely add allergens to metal removal fluid formulations, the use of certain biocides tankside notwithstanding.
- NIOSH's discussion (page 183) of the potential impact of endotoxin inhalation is too short and inadequate. While NIOSH freely speculates and inadequately supports conclusions in many other sections of the document, it does not draw into the discussion NIOSH's own comments on endotoxins in Chapter 6.2, such as the known adverse effects of endotoxin exposure to the levels observed in in-use, water-miscible metal removal fluids nor Gordon's [Gordon, T., 1993] work associating endotoxin exposure in metal removal fluids with adverse health effects in animals. Further, while there may be insufficient data at this time to support a biologically-based REL, NIOSH fails its reader-community by not mentioning

- at least directionally — that good microbiological control helps to reduce exposure to endotoxins found in in-use water miscible metal removal fluids.
- ILMA earlier commented and disagrees with NIOSH's conclusion (page 185) that "acute reactions" [to occupational exposure to metal removal fluid aerosols] are likely manifestations of newly-developed, but not yet diagnosed, asthma. Further, ILMA earlier commented on and now suggests again that NIOSH's conclusion that reversible acute lung effects, in fact, lead to irreversible lung impairment is inaccurate and unacceptable. Finally, NIOSH's statement that it is a "distinct possibility" that "long-term exposure to [metal removal fluids] could contribute substantially to the development of chronic obstructive lung disease in an unknown fraction of the exposed work force" is totally inappropriate. There is no evidence to support the conclusion.
 - ILMA believes that no one in the potentially affected community would argue that the current PEL for oil mist exposure as it applies in facilities that use machining fluids that contain oil should not be lowered, and ILMA had earlier suggested to OSHA a PEL of 2.0 mg/m³ would be acceptable, at least as a first step. On page 186, NIOSH discusses the relationship between thoracic exposure and total particulate exposure. While ILMA acknowledges that Kennedy *et al.*'s earlier research indicates reversible lung impacts at concentrations as low as 0.2 mg/m³ thoracic particulate, the percentage of workers so affected is low and there may be other life-style impacts occurring here as well. Based on the data presented, NIOSH also could have recommended an exposure level of 0.7-0.8 mg/m³ total

particulate. ILMA agrees that, while thoracic particulate measurements would be most desirable, it understands that the more common total gravimetric measurement method can be used as a surrogate. However, NIOSH has disregarded its own distinction in differentiating between aerosols as measured by thoracic or total particulates.

- ILMA not only agrees with NIOSH's statement (page 192) that, "not all work places may be able to control exposures to [metal removal fluids] to 0.5 mg/m³ for all operations," but, in fact, believes that it is not technologically feasible to control metal removal fluid exposures to that level in the majority of shops where metal removal fluids are used today, given the age of many machine tools still in use in the country, as well as size and configuration of many individual machines. While some automotive shops have demonstrated thoracic exposures between 0.2 and 0.55 mg/m³ (0.3-0.8 mg/m³ total particulate), it is not likely that other shops with older machine tools could achieve such levels, because NIOSH also shows [Hands, 1996] data that retrofitting older machines reduces exposures approximately 10 percent.
- As noted earlier, ILMA disagrees sharply with NIOSH's assertion (page 193) that present day formulations pose a cancer risk. Based on the data presented, ILMA believes that a higher REL (total particulate) is more reasonable and certainly more achievable than 0.5 mg/m³ as an eight-hour time-weighted average. ILMA also believes, as noted above, that the respiratory effects which are observed may, in fact, be due to the occasional excursion that occurs when an operator opens a

cabinet door on a machine tool to remove a part or adjust a tool. These peak exposures, and the possibility that effects might arise from these exposures, need to be quantified further and those results included in the process of determining a REL that might include a short-term exposure level for such peak exposures.

I. Chapter 10: Recommendations for an Occupational Safety and Health Program

ILMA member companies and, to the best of ILMA's knowledge, companies that use metal removal fluids produced by ILMA member companies, already have extensive OSHA safety and health programs. Many of these programs include core elements of NIOSH's recommendations in Chapter 10. However, NIOSH's recommended practices are unsupported by the data and would be extremely difficult and costly to implement, with little or no health and safety benefits.

For example, Section 10.3 recommends an environmental sampling strategy that is extremely onerous, particularly for small businesses. According to Table 9.1, one could expect that 70 percent of machinists would be exposed to levels higher than 50 percent of the REL. Thus, based on these figures, one could expect over 800,000 annual tests to be conducted industry-wide. Not only would the cost of such a sampling program be significant, there is some question whether the resources — hygienists and laboratory capacity — are available to support such a program. In addition, significant annual sampling must occur simply to determine whether a machinist is exposed to 50 percent of the REL. If sampling is to be required at all, facilities should only be required to conduct initial screenings to establish exposure levels, and then rescreen if they exceeded the REL or if their operations are significantly altered.

In addition, Section 10.4.1 requires that metal removal fluids and additives concentrations be monitored continually so that components and additives may be added as needed. Yet, some water-extendible metal removal fluids can contain greater than 10 ingredients, several of which themselves are complex mixtures. Small businesses should not be expected to monitor all of these concentrations. Only specific additives "of concern" should be monitored, if at all. The paragraph further recommends selection of non-irritating or sensitizing metal removal fluids. NIOSH should realize that the irritation potential of fluids change with use. Mechanisms and preventable measures for these changes are not fully understood and/or even controllable. Some possible irritants will not be detected using the total particulate method (*e.g.*, H₂S, CH₂O, and SO_x).

In Section 10.4.2, ILMA would recommend aeration of metal removal fluids during shut downs to prevent changes caused by anaerobic conditions. There is evidence that formaldehyde releasing biocides can denature endotoxins and mitigate their health effects. Thus, the use of such biocides in some situations may be beneficial.

Finally, the recommendations made in Sections 10.4.3 and 10.4.4 would be financially disastrous to small businesses. For example, creating "isolation" by retrofitting old machines is marginally effective and is more costly than new machines. *See* page 191, Hands, 1996 reference (New = 0.21 mg/m³; old - retrofit = 0.44 mg/m³; old - no retrofit = 0.5 mg/m³). Moreover, using Kramer's estimate of \$8.5 million per million square feet of plant with annual maintenance costs of \$500,000, ILMA questions whether estimated costs for ventilation systems for small businesses of \$8.50 per square foot is understated and whether NIOSH appropriately has considered installation and maintenance costs for small-sized businesses.

J. Chapter 11: Medical Monitoring of Exposed Workers

ILMA does not accept that asthma and other adverse, non-malignant respiratory health effects are associated with the exposures to metal removal fluids. Because NIOSH has proposed a low REL, ILMA finds it difficult to understand the need for a medical monitoring program given the fact that a new standard would limit the exposure of workers to metal removal fluids. There is a very high cost associated with medical monitoring that would put an unnecessary burden on all businesses, particularly small and medium-sized companies. NIOSH estimates that there are 1.2 million workers potentially exposed to metal removal fluids. Based on data presented by OSHA, approximately 840,000 workers are exposed to levels greater than 0.3 mg/m³. For these workers, annual physicals would be required by health care professionals trained in NIOSH's lung spirometry standard. In addition, other medical and surveillance tests not specified by NIOSH, could be incorporated into a medical monitoring program. Further, 588,000 of the 1.2 million workers are employed by companies with less than 100 persons in the shop. This illustrates the potential cost problems for smaller companies.

ILMA questions why workers exposed to aerosol concentrations at half the REL should be under medical surveillance. How is this level justified? ILMA believes that irritation can occur only at much higher levels, and there is substantial evidence that the irritation is caused by biological contamination and not by the fluid itself. Surveillance, if needed, should be triggered by a parameter other than a very low mist level.

K. Chapter 12: Research Needs

ILMA agrees with NIOSH that more research on metal removal fluids is needed. However, the Association suggests that, because resources are limited, NIOSH should prioritize such research needs. ILMA suggests the following priority:

- Sampling and analytical methods need to be developed for detecting and monitoring metal removal fluids. NIOSH should include research to verify and validate test methods for short-term exposures.
- Potential worker exposures and health effects due to bacterial and fungal contamination, endotoxins and other metabolic products should be investigated.
- Methods of biomonitoring exposed workers, including biomarkers, should be developed as an effective means to measure worker exposure to chemical and biological contaminants and potentially hazardous ingredients and additives.
- Bioassays or other methods should be developed to measure respiratory or dermatologic irritancy of metal removal fluids. There presently are no valid screening tests to allow formulators to predict or compare the expected irritation potential of their metal removal fluid formulations.
- Epidemiological and industrial hygiene evaluations are needed of the workers exposed to current metal removal fluid compositions, ingredients, additives, contaminants and other metal removal fluid worksite exposures.

IV. CONCLUSION

NIOSH has not adequately supported its proposed REL in the Draft Criteria Document for occupational exposures to metal removal fluids. For the reasons discussed in these comments,

NIOSH should correct the scientific and legal inadequacies and should publish the final version as a "hazard review" without a REL.

As an initial matter, NIOSH needs to use the correct term for the metal removal fluids it has reviewed. The Agency should be referring to "metal removal fluids," rather than the larger class of "metalworking fluids."

NIOSH has not adhered to its strict responsibility to rely on scientific results that have been peer reviewed and that are available to the public. The Agency has abandoned this responsibility in relying on three of four papers studying respiratory effects which have not gone through a binding, peer-review process and which have not been published. NIOSH's reliance on the OHAB review process is misplaced.

Alleged associations between specific cancers and obsolete metal removal fluid formulations are unproven and suspect at best. These alleged associations cannot be extended to today's products. Moreover, NIOSH has avoided temporal considerations when relating its conclusions about cancer risks to exposures to metal removal fluids. The Draft Criteria Document goes well beyond the limits of objective scientific analysis of the available epidemiological data.

ILMA supports an exposure limit of less than 5 mg/m³; however, the Association believes that users of metal removal fluids would be better served by a restriction on short-term exposures in addition to a time-weighted average exposure limit. Further, as data become available, a biologically-based exposure limit also may be required.

* * * *

ILMA appreciates this opportunity to comment on the Draft Criteria Document. The Association is available to answer any questions its comments may have raised. ILMA has and will continue to participate in the reevaluation of exposure data and the development of new exposure limits.

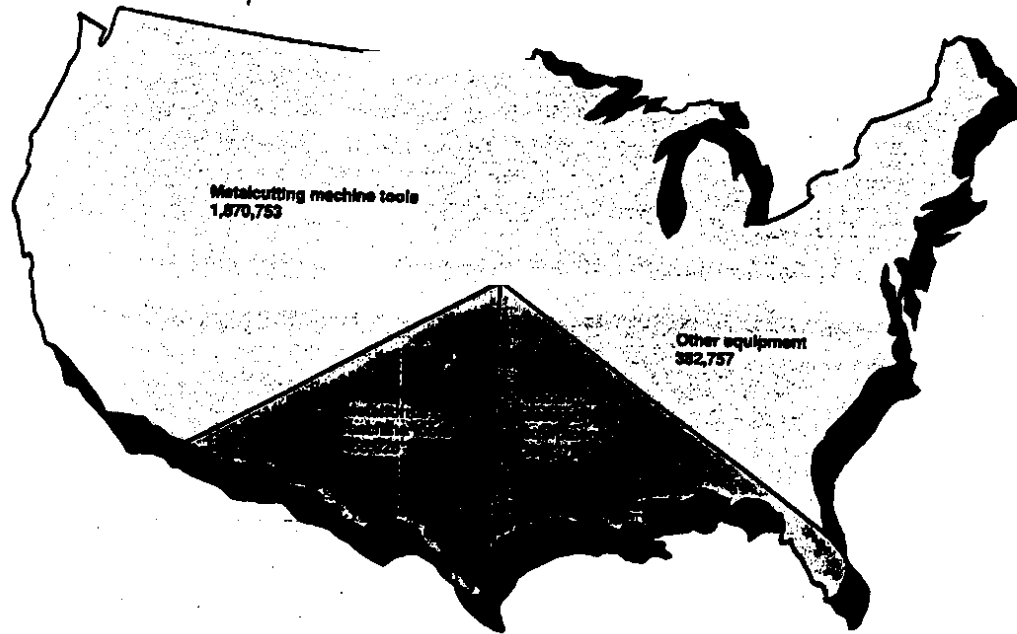
SPECIAL REPORT 808

Big gains for smaller plants

Unique database depicts machinery in actual use in US. Highlights, unveiled here, show equipment concentration doesn't necessarily follow employment size. NC equipment types make expected gains

THE TOTAL NUMBER of numerically controlled machine tools installed in metalworking plants in America has more than doubled in the last six years to 221,101 units, according to the new *American Machinist Inventory of Metalworking Equipment*. This happened while the total number of machine tools (NC and non-NC) remained about static, at 1,870,753 metalcutting machines and 456,028 metalforming machines.

The equipment America manufactures with



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Metalworking Fluids: Composition and Use

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ABSTRACT

Metal removal fluids, used to cool and lubricate the tool and workpiece being machined or ground, are complex mixtures. Depending on the fluid type, *straight oil*, *soluble oil*, *semisynthetic*, or *synthetic*, the composition of the fluid will vary depending on the application for which it is intended. Each type has advantages and disadvantages. As new health effects questions about fluid components are raised, manufacturers have reformulated their products to address these concerns about operator health and safety, consistent with then-available toxicological information. Petroleum oils, nitrites, chlorinated paraffins, and alkanolamines are examples of issues that have been raised over the last twenty years. Water-miscible metal removal fluids in particular change during use as specific components increase or decrease, other contaminants increase, and as microbial action occurs. Dermal contact and inhalation are the two primary routes of exposure to metal removal fluids. Inhalation exposures have been recently documented and observed short term health effects suggest lowered exposure standards are appropriate.

INTRODUCTION

Metalworking fluids have been used for almost 100 years to aid the process of metal cutting.⁽¹⁾ Over the years, as demands for higher productivity, quality, and worker health and safety have increased, metalworking fluid technology has changed to meet these changing requirements. In the following paragraphs, we will understand why metalworking fluids are used, what they consist of, how fluid formulations have changed over the years, how fluids themselves change as they are used, and what routes of exposure are most commonly encountered.

WHY USE METALWORKING FLUIDS?

Metalworking fluids include a broad range of products designed for many specific applications. Independent Lubricant Manufacturers Association ("ILMA") recently⁽²⁾ developed several matrices which show the interrelationships among these several types of fluids and how they are used. As shown in Figure 1, metalworking fluids include the category known as metal removal fluids. Other types of metalworking fluids include those used for metal *forming*, metal *protecting*, and metal *treating*. In this discussion, we will focus on that category known as metal removal fluids, which include those products designed for machining or grinding. Figure 2 shows the relationship of *machining* to other processes and operations common to producing finished parts such as an automotive engine or transmission. Figure 3 describes the many types of *industrial lubricants* used in and around *machine tools*, the actual machines which do the machining or grinding. It is important to note that the types of industrial lubricants described in Figure 3 often leak into machining or grinding fluids, contaminating them in the process. Figure 4

describes the several types of *in-process cleaners* used. As shown in Figure 2, cleaning and surface preparation is included as a common metalworking process and there are often many intermediate cleaning steps in a component manufacturing process. Each one provides an opportunity to further contaminate the metal removal fluid in the next operation.

Metal removal fluids have two primary functions: to *cool* and to *lubricate*. The metal cutting process - whether it be machining or grinding - develops a tremendous amount of heat which must be dissipated if proper part geometry and desired finish is to be achieved. Additionally, the cooling effect provided by a metal removal fluid extends cutting tool or wheel life and prevents burning and smoking.

Lubrication - at the tool-part interface - is the second primary function of a metal removal fluid. Lubrication may be either *physical*, *boundary*, or *chemical*. Physical lubrication is provided by a thin film of lubricating component, such as a severely solvent refined or hydrotreated mineral oil or an inverse soluble nonionic surfactant above its cloud point. Boundary lubrication occurs when a specially included component, for example a polar material such as a naturally occurring vegetable fat or ester attaches itself to the surface of the metallic part being machined, such as an aluminum casting. Chemical lubrication occurs when a component of the machining or grinding fluid, such as sulfur, reacts with the metallic component being machined, resulting in improved tool life, better finishes, or both.

Besides the primary functions of cooling and lubricating, metal removal fluids have a number of secondary functions. Among these are to provide corrosion protection for the part and machine, assist in the removal of chips or swarf from the machining or grinding process, lubricating the machine tool itself, rancidity control, and, when the fluid has reached the end of its economic service life, ease of disposal. For example, almost all machine tools include at least some amount of steel or brass which could rust or corrode. For that reason, components are included in water-miscible metal removal fluid formulations which retard or prevent such corrosion. Additionally, every metal removal operation involves formation of at least some swarf or metal chip. Metal removal fluids - and the circulating systems which carry the fluid within the machine tool or from machine tool to a central filter - are designed to carry that swarf or chip to a filtration device that will remove most, if not all, of those contaminants prior to the fluid being recirculated back to the machine tool.

Despite being designed for long life and despite the care normally given to fluids by users to maintain them, metal removal fluids do not always perform as intended. The causes are many but any list would include rust or corrosion of the machine tool or of the part produced, rancidity due to failure to control bacteria in water-miscible formulations, growths of fungus which impede or block fluid flow, failure at the workpiece tool interface (for example, burning of the part due to excessive heat build-up), foam, and dermatitis. Understanding how fluids are formulated, what components tend to increase in concentration with use, what components tend to deplete with use, what contaminants enter into the system and accumulate, and how microbial action can affect the performance and longevity of a fluid are all essential to understanding why fluids fail.

COMPOSITION

ILMA recently compiled a list of components which are commonly used in metal removal fluid compositions.⁽³⁾ Metal removal fluids are commonly identified as one of four types: *straight oils* or *neat oils*; *soluble oils*; *semisynthetics*; and *synthetics*. Foltz⁽⁴⁾ defined these four types of fluids in a recent publication. Straight oils are metal removal fluids which typically consist of a

severely solvent refined petroleum oil, a severely hydrotreated petroleum oil, or other oil of animal, marine, vegetable or synthetic origin used singly or in combination, or with other additives. These products are not designed to be diluted with water before use. Historically, the oldest class of engineered metal removal products, straight oils provide excellent lubricity, good rust control, and long sump life. Depending on the intended application, straight oils may have:

- "oiliness agents" such as the vegetable oils identified above or polyol esters
- extreme pressure additives such as sulfurized fatty materials or chlorinated paraffins
- antioxidants, such as an alkylated phenol
- a metal passivator, such as a triazole
- other corrosion inhibitors, such as a calcium sulfonate
- an antimist agent, such as a polymethacrylate polymer
- dispersants
- odorants
- a dye.

Some lower viscosity straight oil products, such as those designed for an application such as honing, will use middle distillate petroleum fractions, rather than the more viscous vacuum distilled fractions.

In 1984, the International Agency for Research on Cancer ("IARC") reviewed lubricant base oils and products derived from them.⁽³⁾ IARC noted in their review that "the processes used to produce lubricant base oils and, correspondingly, product formulation have changed considerably over the years. Until about 1940, processing consisted of acid refining with clay finishing and subsequent dewaxing by chilling. Solvent refining (and solvent dewaxing) was first introduced into the USA and in Europe in the 1930s. Hydrotreating, as a newer, more severe process than 'hydrofinishing' was introduced in the 1960s. The trend has been to more highly refined oils with associated removal of impurities including polynuclear aromatic compounds." In the USA, the advent of implementation of the Hazard Communication Standard in 1985, required chemical producers to label products and amend material safety data sheets ("MSDS") if they were determined to be carcinogenic or if they contained more than 0.1% of an identified carcinogen; to the extent that any oil that was not highly refined had been used prior to 1985, such use was discontinued by manufacturers at that time.

Soluble oil (or emulsifiable oil) is a combination of between 30-85% severely refined lubricant base oil and emulsifiers and which may include other performance additives. Such products are supplied as concentrates which are diluted with water at ratios of one part concentrate to five to forty parts water. In addition to the base oil, soluble oils can contain:

- oiliness agents, such as an ester
- extreme pressure additives, such as a chlorinated olefin or ester or sulfurized fatty material
- emulsifiers, very typically including a sodium petroleum sulfonate, salts of fatty acids, and/or nonionic surfactants
- alkanolamines to provide "reserve alkalinity"
- a biocide, such as a triazine or oxazolidene
- a "coupler," such as a fatty alcohol
- a defoamer, such as a long chain organic fatty alcohol or salt
- possibly, corrosion inhibitors, antioxidants, dyes, and/or metal passivators, such as may be found in straight oils as previously described.

"Reserve alkalinity" is a term used to describe alkaline materials present in a composition that are available to react with, for example, short chain organic acids produced by bacteria.

Soluble oils as a class provide good lubrication as well as improved (as compared to straight oils) cooling. On the other hand, soluble oils sometimes have poor corrosion control, are sometimes "dirty" (i.e., machine tool surfaces and adjacent areas become covered with oil or difficult-to-remove product residues), may smoke (because of insufficient ability to cool), and may have poor mix stability or short sump life. Distinction needs to be made between "commodity" soluble oils, containing few if any performance enhancing additives, and "premium" soluble oils, which offer the user higher performance and extended fluid life.

A *semisynthetic* metal removal fluid contains a lower amount of severely refined base oil, for example, 5-30% in the concentrate. These products also contain a higher proportion of emulsifiers as well as 30-50% water, resulting in a transparent concentrate, and are typically transparent or translucent when they are diluted with ten to forty parts water. Perhaps the most complex of metal removal fluid formulations, semisynthetics offer good lubrication, good heat reduction, good rust control, and have longer sump life and are cleaner than soluble oils. Conversely, this class of products have a greater tendency to foam in softer water and can be unstable in hard water. Comprised of many of the same ingredients as soluble oils, semisynthetics will contain a more complex emulsifier package, often including fatty amides, additional corrosion inhibitors such as an amine salt of boric acid, and sometimes a chelator, such as a salt of ethylenediamine tetraacetic acid ("EDTA").

Straight oils, soluble oils, and semisynthetics may contain chlorinated paraffins as extreme pressure (EP) lubricants. These are typically made by chlorination of various straight chain hydrocarbon C_{10} - C_{30} feedstocks, most commonly paraffins or olefins. Chlorine contents range from thirty to seventy percent of the molecular weight.

Two chlorinated paraffins (C_{23} , 43% chlorine; C_{12} , 60% chlorine) were evaluated by the National Toxicology Program ("NTP") in two-year gavage studies.^(6,7) Under the conditions of the studies, NTP found clear evidence of carcinogenicity for male mice and equivocal evidence of carcinogenicity for female mice and rats for the longer chain material and clear evidence of carcinogenicity of the shorter chain material for both sexes of both species. NTP included the shorter chain material in their *Fifth Annual Report on Carcinogens*⁽⁸⁾.

More recently, EPA made all polychlorinated alkanes with chain lengths of C_{10} - C_{13} and chlorine content of forty to seventy percent subject to the reporting requirements⁽⁹⁾ of the Toxics Release Inventory ("TRI") because of aquatic toxicity concerns.

Fluid manufacturers have replaced the chlorinated paraffins with other performance additives not subject to labeling or reporting requirements to the extent possible. When this is not possible, the appropriate information is included on the MSDS.

Synthetic metal removal formulations do not contain any petroleum oil. Among the four classes of fluids, they are the cleanest, offer the best heat reduction, have excellent rust control and long sump life, are transparent (allowing the operator to see his or her work), and are largely unaffected by hard water. On the other hand, synthetics offer poor physical lubrication, can be more difficult to waste-treat, and can foam in some applications. Like the other classes of water-miscible fluids, synthetics are designed to be diluted with water, from ten to forty parts per part of fluid concentrate. Besides water, synthetics can contain ethylene oxide - propylene oxide polymers, amides, and /or organic esters as lubricants, amine salts of mono- and dicarboxylic and boric acids as corrosion inhibitors; alkanolamines to provide reserve alkalinity; a plasticizer, such

as a glycol ether, and, as in other classes of water-miscible fluids, chelators, defoamers, odorants, biocides, and or dyes can be optionally included.

Virtually all synthetics and semisynthetics, as well as many soluble oils contain alkanolamines. These materials - which typically include both ethanolamines and isopropanolamines - are present to provide reserve alkalinity as well as being present as the alkaline portion of carboxylic acid and boric acid salts included to provide corrosion protection. Each of the three ethanolamines, monoethanolamine, diethanolamine ("DEA"), and triethanolamine ("TEA") are or have been used in metal removal fluid formulations, depending on the application and other requirements. Both TEA and DEA have been or are being evaluated by NTP in shorter ninety-day and in longer two-year studies. Prior to 1985, and particularly prior to 1976, water-miscible metal removal formulations often included sodium nitrite as a corrosion inhibitor. Nitrite - even under alkaline conditions - was determined to have the potential to react with secondary amines to form N-nitrosamines, many of which are identified animal carcinogens.⁽⁸⁾ Despite the fact that formulators no longer included sodium nitrite in formulations, beginning as early as 1977 and no later than 1985, evidence of contamination of fluid concentrates with N-Nitrosodiethanolamine ("NDELA") was reported as late as 1990,⁽¹⁰⁾ with mean NDELA concentrations of 0.07 ppm for soluble oil-, 1.5 ppm for semisynthetic-, and 11.4 ppm for synthetic-fluid concentrates reported. Since that time, concern over liver and kidney target organ effects in animals has caused use of diethanolamine in metal removal formulations to decline,⁽¹¹⁾ since it has been shown that the amount of NDELA formed is related to the amount of DEA present,⁽¹²⁾ it is likely that contamination of fluids with NDELA has decreased even further. Nonetheless, it may be that carry-over of nitrite-containing in-process cleaners into a metal removal fluid containing a secondary alkanolamine may be responsible for the small amount of NDELA observed. In May, 1993, the US. Environmental Protection Agency issued a *Significant New Use Rule* for alkali metal nitrites intended for use in metal removal fluids.⁽¹³⁾

Most water-miscible metal removal fluids contain a biocide to provide protection from microbial degradation. Perhaps the most commonly used biocide is "triazine," hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine. A member of the so-called class of biocides known as formaldehyde-release-agents, triazine used in metal removal fluid operations was the subject of an industrial hygiene survey in 1993 that sought to quantify release of formaldehyde. The results indicated that background levels at a number of facilities and uncertainty in the measurement process allowed for the possibility that results of both area and personal monitoring for formaldehyde may at times exceed 0.1 ppm as a time-weighted average, but that this exposure could not be attributed to the use of triazine.⁽¹⁴⁾ No workplace values exceeded the 0.5 ppm "action level," set in the Formaldehyde Standard⁽¹⁵⁾. Formaldehyde, under the Standard, has a Permissible Exposure Level of 0.75 ppm.

HOW METAL REMOVAL FLUIDS CHANGE AS THEY ARE USED

Metal removal fluids, particularly water-miscible metal removal fluids, as used in the shop, are not static systems; indeed, they are very dynamic systems. This is due in large part both to the environment they are in and how they are used. And, because the characteristics of individual central systems vary widely, even the same product may have a different "composition" after one or more years use in one central system versus another. Why is this the case? It is largely due to two reasons: one, increases of some and decreases of other components of the fluid over time; and, two, addition of and effect from contaminants that arise from a variety of sources. While

much of the information is considered to be proprietary by the manufacturers of metal removal fluids, it is generally understood that alkanolamines will tend to increase in concentration in a system over time, relative to other components. Additionally, because of the constant addition of water to circulating systems, increases in concentrations of metal salts is also likely to occur. Such salts, particularly in hard water areas, tend to destabilize semisynthetic and soluble oil fluids as they are used. On the other hand, some components, most notably corrosion inhibitors (particularly organic acid salts) and biocides decrease over time since they are depleted during use; most times, addition of the product concentrate on a routine basis (based on a regular program of chemical testing and analysis) will keep fluid components in balance. Sometimes, however, supplementary additions of these specific components are required to keep fluid performance at the desired level.

In addition to changes in component concentration, other contaminants can have deleterious effects. As noted above, industrial lubricants find their way into circulating metal removal fluid systems. So-called "tramp oil," whether it be from leaking hydraulic or spindle oils or slideway or gear lubricants, add to the complexity of the situation by contaminating the fluid with components that are emulsifiable or miscible with the metal removal fluid, but yet are not part of the fluid as it was formulated or first used. Poorly maintained machine tools can leak a significant amount of hydraulic oil, for example, adding far more oil than might be otherwise provided through addition of make-up metal removal fluid.

Virtually all water-miscible metal removal fluids become contaminated with bacteria,^(16,17) sometimes through disposal of materials such as food waste in the fluid itself. Aside from degrading components of the fluid, most notably fatty acids, contamination of fluids with high levels of bacteria may increase the risk from opportunistic pathogens;⁽¹⁸⁾ more recently, endotoxins have been identified as a potential risk from exposure to metal removal fluids.⁽¹⁹⁾ Fungal contamination appears to occur less frequently than bacterial contamination.

Depending on the machining process and the type of metal or alloy machined, contamination of the metal removal fluid by both particulate and dissolved metals occurs. Several metallic contaminants, for example, nickel and cobalt, can have potentially deleterious health effects.⁽²⁰⁾ Particulate contaminants, usually the result of poorly functioning or absent filtration systems, increase the risk of dermatitis. A recent study⁽²¹⁾ identified build-up of alumina in the fluid as a contaminant in the machining of automotive aluminum alloys. A recently published ASTM document suggests guidelines for safe use of water-miscible metal removal fluids.⁽²²⁾

Straight oils are less affected by component depletion or by contamination. On the other hand, there has been concern expressed about potential increase in polycyclic aromatic compounds ("PCA") as a straight oil is used. Evans, *et al.*⁽²³⁾ studied a 91,000 liter straight oil system and found that PCAs increased with time for three years, then stabilized. Despite the increase, there was no evidence of carcinogenic potential demonstrated over the 249 week life of the study. Additionally, Mckee, *et al.*⁽²⁴⁾ evaluated the epidermal carcinogenic potential of cutting fluids formulated with solvent extracted paraffinic and naphthenic base oils and found no evidence for dermal carcinogenicity even after simulated industrial usage.

ROUTES OF EXPOSURE

Dermal contact and inhalation are the two most common routes of exposure to metal removal fluids. Although automated part handling on large transfer lines and machining centers has reduced the opportunity for dermal exposure of a machinist to the fluid, there are still many

older machine tools that require parts to be manually loaded and unloaded resulting in a machinist with his or her forearms and hands more or less continuously wet with fluid. Dermatitis is the most commonly reported medical situation involving metal removal fluids.^(23,26) It has been estimated⁽²³⁾ at various times that between 0.3 and 1 % of machinists have either contact dermatitis or allergic contact dermatitis. Under normal conditions, exposure to fluids does not in itself cause dermatitis. The underlying route cause of skin problems usually involves one or more of the following:

- rich concentrations
- filter malfunction
- abrasive soaps
- poor personal hygiene
- use of solvents
- dirty shop rags
- off job activities
- seasonal conditions
- contamination of the fluid by dissolved metals, abrasive particulates, or alkaline materials.

In most cases, dermatitis situations are managed through a combination of efforts by the fluid manufacturer, user, and medical personnel.

Exposure through inhalation is the second most common route of exposure and one that can be reduced through engineering controls and practices. Several recent studies have given an indication of exposures. For example, in automotive transmission facility, Kennedy, *et al.*⁽²⁷⁾ determined total aerosol exposures to be between 0.16 and 2.03 mg/m³ for machine operators, determined the fractions above, between, and below 9.8 and 3.5 µm and noted that exposure levels were very similar across different machining fluid types. Chan, *et al.*⁽²⁸⁾ determined area total and respirable particulate concentrations in an automotive transmission facility and found total particulate concentrations of between 0.71 and 2.99 mg/m³, with differences noted between fluid types. Woskie, *et al.*^(29,30) found an average total particulate exposure of 0.7 mg/m³ and used statistical analysis to investigate the factors which contribute most significantly to the variability in exposures to large and small particles. Kenyon, *et al.*⁽³¹⁾ determined ethanalamine exposures in an automotive parts facility and found that air levels of TEA in personal samples were related in an operation-specific manner with TEA in the bulk machining fluid formulations, but found no consistent relationship between TEA and particulate mass. And, Ball⁽³²⁾, in a survey of eight plants determined a median exposure level of approximately 1 mg/m³. Kennedy, *et al.*'s finding that a cross-shift decrease in forced expiratory volume with increasing exposure levels above approximately 0.20 mg/m³ caused them to suggest that allowable exposure levels to metal removal fluid aerosols were too high.

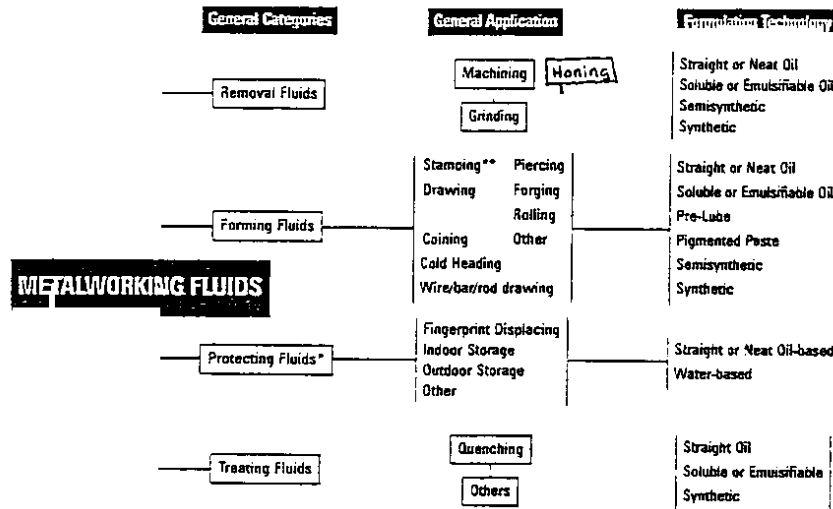
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Figure 1. Metalworking Fluids



*Note: Protecting Fluids are shorter-term and are to be differentiated from the longer term protection offered by passivated metal surfaces and coatings.
 **Note: Protecting Fluids are often brought in on sheet steel products, particularly in stamping operations.

Figure 2. Metalworking Process Flow Chart

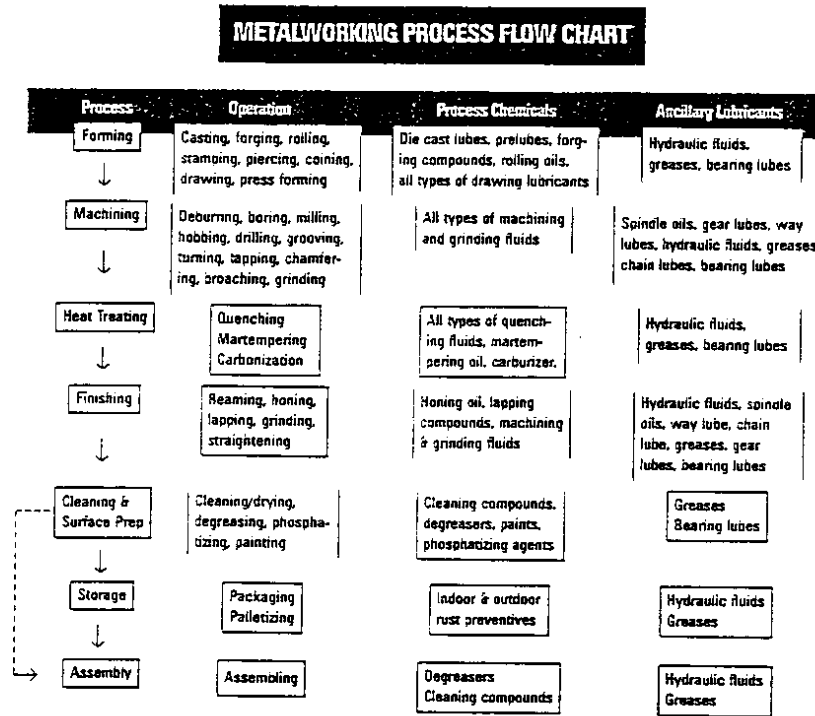


Figure 3. Industrial Lubricants

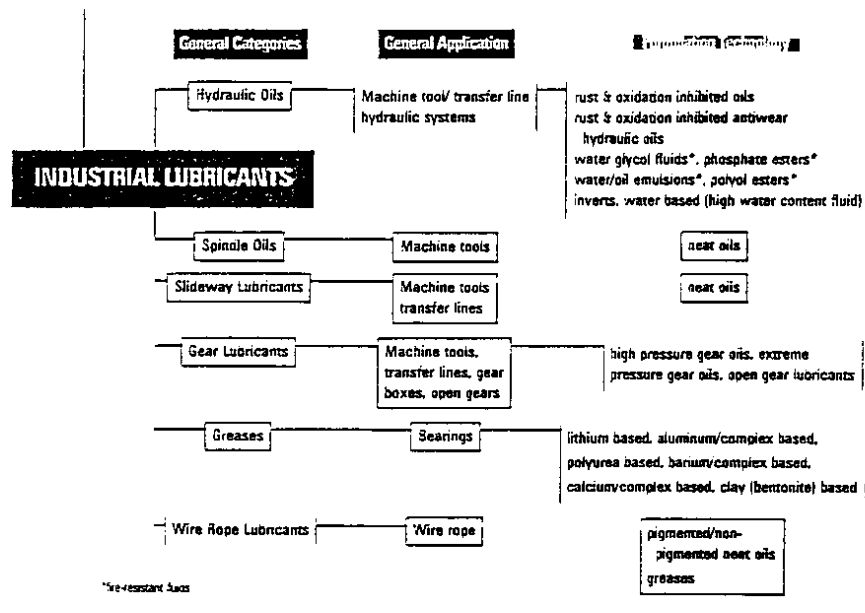


Figure 4. In-Process Cleaners

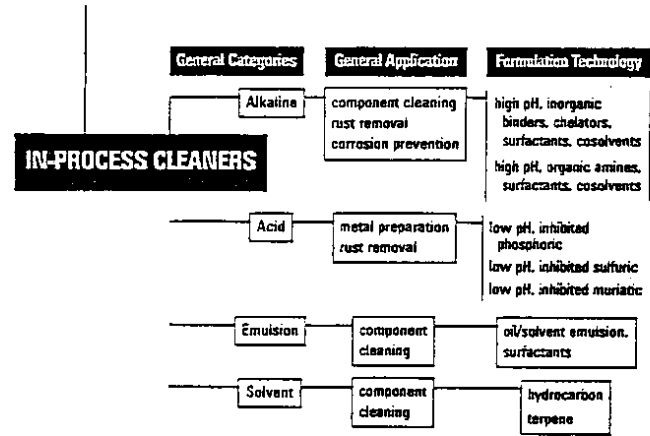


Figure 3. Industrial Lubricants

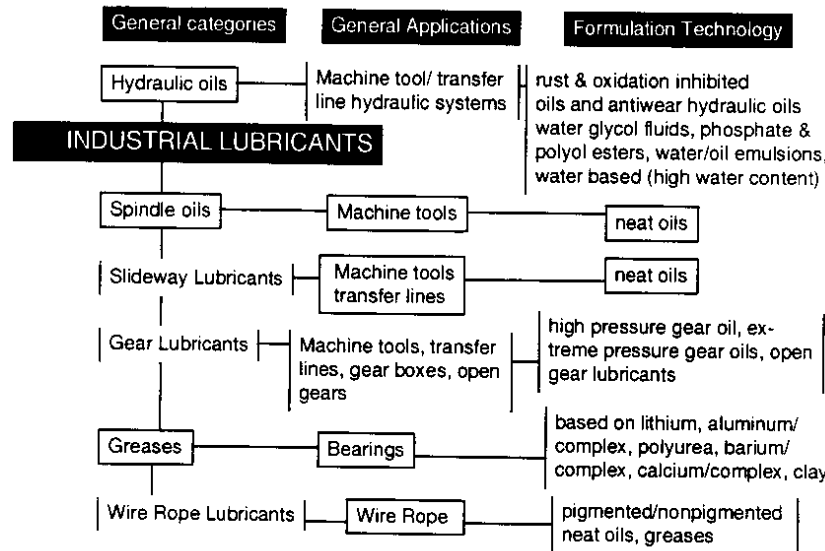
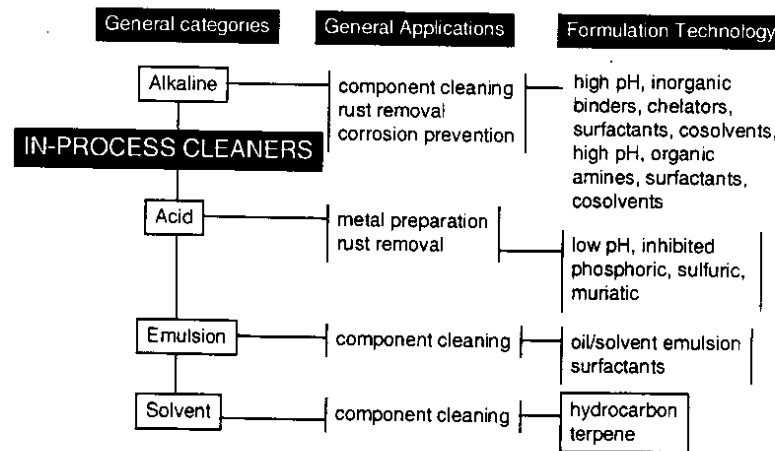


Figure 4. In-Process Cleaners





Standard Practice for Safe Use of Water-Miscible Metalworking Fluids¹

This standard is issued under the fixed designation E 1497; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice sets forth guidelines for the safe use of water-miscible metalworking fluids. This includes product selection, storage, dispensing, and maintenance.

1.2 Although water-miscible metalworking fluids are typically used at high dilution, dilution rates vary widely. Additionally, there is potential for exposure to metalworking fluid as manufactured and exposure to concentrated and diluted metalworking fluid additives and biocides.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

E 1302 Guide for Acute Animal Toxicity Testing of Water-Miscible Metalworking Fluids²

D 3946 Test Method for Evaluating the Bacteria Resistance of Water-Dilutable Metalworking Fluids³

E 686 Test Method for Evaluation of Antimicrobial Agents in Aqueous Metalworking Fluids⁴

2.2 OSHA Standard (Occupational Safety and Health Administration):

29 CFR 1910.1200 Hazard Communication⁵

29 CFR 1910.134 Use of Respirators in the Workplace⁵

3. Significance and Use

3.1 Use of this practice will reduce occupational hazards associated with use of water-miscible metalworking fluids.

4. Routes of Metalworking Fluid Exposure and Effects of Overexposure

4.1 Routes of exposure to metalworking fluids include dermal contact, eye contact, inhalation and ingestion. Exposure may be direct through contact with the fluid or indirect by contact with airborne fluid mists or fluid residue on machinery and on parts.

4.2 Prolonged or repeated dermal contact may cause dry and cracked skin, rash, redness, burning, or itching. Skin

abrasions can intensify the effects. Some metalworking fluids and additives may also cause a sensitizing reaction.

4.3 Eye contact may cause mild to severe irritation.

4.4 Inhalation may cause respiratory irritation.

4.5 Ingestion may cause gastrointestinal disturbances.

5. Product Selection

5.1 Potential health hazards can be minimized by careful material selection and substitution. See Guide E 1302.

5.2 The metalworking fluid manufacturer's material safety data sheet (MSDS) and toxicological data on metalworking fluids, ingredients, and additives shall be reviewed in order to evaluate potential hazards and establish appropriate control procedures.

5.3 Additives, including rust inhibitors, product stabilizers, biocides of all types, odorants, and dyes shall be reviewed for their impact on the metalworking fluid mixture to which they are added. Additives shall only be used with the agreement of the metalworking fluid manufacturer.

5.4 As supplied, biocides and other additives for tankside addition may present greater health and safety risks than the metalworking fluid. Further, additives and biocides are less likely to be handled automatically, or with special delivery equipment, than metalworking fluid concentrate so greater care and attention are required to reduce risks of exposure.

5.5 The metalworking fluid should perform as intended while providing the safest working conditions. The selection of a metalworking fluid for each different operation must fit the inherent limitations of the product. Product recommendations and performance information should be obtained from the metalworking fluid manufacturer.

5.6 All applicable disposal criteria must be met.

6. Water Quality and Treatment

6.1 Water constitutes more than 90 % of the diluted metalworking fluid mixture. Water shall be evaluated for hardness, alkalinity, high conductivity, turbidity, corrosivity, biological contaminants, and other factors that may lead to increased use of metalworking fluid concentrate, additives, or biocides, or a combination thereof. Good water quality is fundamental to proper metalworking fluid use and will help minimize use of additives and biocides.

6.2 Where suitable water is not available, water treatment shall be designed to produce enough water of sufficient quality for metalworking fluid use. Treated water shall be readily available from holding tanks large enough to meet anticipated daily requirements. Treated water quality must be monitored. Tests performed depend on the type of water treatment used. Guidance on water quality and water treatment may be obtained from the metalworking fluid manufacturer.

¹ This test method is under the jurisdiction of ASTM Committee E-34 on Occupational Health and Safety and is the direct responsibility of Subcommittee E34.50 on Health and Safety Standards for Metalworking Fluids.

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² Annual Book of ASTM Standards, Vol 11.03.

³ Annual Book of ASTM Standards, Vol 05.02.

⁴ Annual Book of ASTM Standards, Vol 11.04.

⁵ Code of Federal Regulations available from United States Government Printing Office, Washington, DC 20402.

**Characterization of Aerosols From a Tube Milling and Welding
Operation Quenched with Metalworking Fluid**

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The particle morphology and composition of ambient aerosols collected near a tube milling and weld quenching operation were complex. Indoor air characterization was prompted by incidents of eye irritation reported by tube milling operators. Total suspended particulate levels in the breathing zone fluctuated from less than 0.5 mg/m³ to approximately 14 mg/m³ as measured by filter entrainment and real time monitoring. These levels were below the OSHA

threshold limit value (TLV) of 15 mg/m³ for an 8 hour time weighted average (TWA). Particle size characterizations indicated bimodal distributions, with the major portion of the particle mass having a mass median diameter of less than 10 μm. The largest particulate mass fraction was metallic in nature, perhaps due to welding fumes in the immediate vicinity of the weld quenching operation. Species present in particulates were: aluminum, calcium, and iron with traces of sulfur, chlorine, and manganese. Vapor phase organic levels found near tube milling operations were about 1000 fold lower than the TLV for selected substituted aromatics. Tentatively identified species were characteristic of internal combustion emissions. Formaldehyde was present in ambient aerosols, at levels as high as 40 μg/m³. Weld quench liquid was comprised of a commercially available semi-synthetic metalworking fluid formulated with a formaldehyde condensate biocide, at equivalent formaldehyde concentrations up to 150 ppm. Aerosol formaldehyde concentrations did not exceed the TLV of 370 μg/m³. The NIOSH formaldehyde recommended exposure level (REL) of 19.6 μg/m³ for an 8 hour TWA was exceeded possibly due to accelerated biocide breakdown by the welding process. A different quenching fluid formulation is recommended.

INTRODUCTION

Metalworking fluid constituents can undergo chemical reactions during fluid use and aging or coolants may become contaminated with tramp oils, metal particles, or grinding debris. Fluid contamination with microorganisms can also occur causing difficulties in maintaining clean working environments⁽¹⁾. Work place air characterization in industry is often necessary to ascertain whether the health of workers is being affected by exposure to byproducts of industrial processes. These species may also be sensory irritants and could reside in the fluid, vapor or particulate phases. Additionally, industrial metalforming environments may contain airborne contaminants as solid or liquid particulates, dusts or mists respectively. Human exposure to airborne contaminants in the metalworking industry can occur by inhalation or skin contact^(1,2) of coolant fluid, vapors, dusts, and mists generated during industrial processes.

Anecdotal reports of mild irritation of the eyes and mucosal membranes were associated with a coolant weld quenching operation at an industrial metalforming facility. This prompted the mist characterization work described here. Symptoms of irritation reported by workers was consistent with the expected effects of human exposure to aldehydes. A sampling protocol was

developed to determine if aldehydes, acrolein in particular, were present in the coolant fluid and the resulting mists⁽³⁾. Formaldehyde was also a targeted constituent; however, the presence of formaldehyde⁽⁴⁾ at low concentrations was not thought to be a health concern. The sampling protocol also employed more general collection techniques to determine the presence of certain inorganic species, volatile organic compounds, and to measure particulate size distributions of any aerosols or mists produced by this operation. These techniques were used in an effort to identify other sources of irritation^(5,6,7,8). Certain welding techniques, even without quenching, also produce particulates with complex morphologies and organic pollutants, some of which are known irritants^(9,10,11,12). The intention of this work was to affect a more comprehensive characterization of the physical and chemical constituents occurring in the particulates and vapors generated as a result of this weld quenching/metallforming operation.

MATERIAL AND METHODS

Description of Operation

This study focussed on characterizing possible irritants produced by a metal tube forming and welding operation. A large tube milling machine was located toward one end of a large industrial bay area in which various other metal fabrication processes were being performed. This large building was equipped with large doors which were usually open so that trailer trucks and other vehicles could drive directly into the facility for routine materials delivery and shipment. The tube mill, a machine about 50 feet long, converted flat steel stock into finished tubes cut to manageable lengths. This feed-through process involved flat stock bending, tube forming, automated tube seam welding, weld quenching, and cutting the finished tube to desired lengths. Quenching the hot, newly-welded tube stock was accomplished by spraying dilute metalworking fluid onto the welded tube as it was fed through a coolant trough equipped with many nozzles. A mist was typically observed above the quenching tank during tube milling operations. This aerosol was a mixture of welding fume, metalworking fluid condensation and spray, background particulates from other fabrication processes in the shop, and

background resulting from engine emissions.

Total Particulate Sampling and Analysis

Industrial shop mist concentrations were determined gravimetrically by collection of mists on filters utilizing high flow rate Staplex® sampling pumps (The Staplex Co., New York, NY). Particulates were collected on 4 inch diameter Pallflex® T60A20 Teflon coated glass fiber filters (Pall Corp., Putnam, CT), at flow rates up to 60 ft.³/min. These were collected at several specific locations clustered around the tube forming weld quenching operation described above. Analyses of organics on filter entrained particulates involved solvent extraction of the filters with acetonitrile followed by high performance liquid chromatography (HPLC) analyses of the particulate extracts. Sample extracts were analyzed using a Zorbax ODS 4.5 by 150 millimeter (mm) HPLC column. Chromatographic conditions were: typical injection volume of 10 µl eluted with isocratic mobile phase 50/50 percent acetonitrile/water at about 0.3 mL/min. flow rate with ultraviolet-visible detection at a wavelength of 254 nanometers (nm). A portion of one particulate sample and selected particle size distribution samples were also

tested to determine the presence of metal constituents by X-ray fluorescence elemental analysis with an HNU X-RAY System 5000. Scanning Electron micrographs of particulates at magnifications ranging from 350 to 7500x were obtained with a JEOL JSM-5300 scanning electron microscope (SEM).

Ambient total particulate levels were also monitored in real time near and around the weld quenching operation. Data was acquired with a DataRAM® (Monitoring Instruments for the Environment, Inc., Billerica, MA), real time aerosol monitoring device placed in several stationary locations near the tube mill. Data acquisition parameters were set to store total particulate concentration readings in 10 second increments. Particulate concentration data was later downloaded in Lotus 1-2-3® spread sheet format and analyzed off line.

Particle Size Distribution Measurements

Particulates were collected with Mercer® cascade impactors (IN-TOX Products, Albuquerque, NM), for particle size characterization of mists resulting from the tube mill operation. Sampling durations of 3 to 6 hours at flows up to

1400 mL/min. were necessary to obtain sufficient sample loading for analysis. Impacted particulates were collected on 22 mm diameter glass microscope cover plates. Sample particulate extracts were measured by ultraviolet-visible fluorescence using a Perkin-Elmer LS-5B Luminescence Spectrometer at an excitation wavelength of 281 nm. Fluorescence emission was measured at the 360 and 430 nm spectral peak maxima. Particulate distributions of selected inorganic species were measured by X-ray fluorescence elemental analysis with an HNU X-RAY System 5000. Resulting data was then plotted on logarithmic versus probability coordinates to determine the particulate mass median aerodynamic diameter (MMAD) of the aerosol size distribution.

Vapor Phase Sampling and Analysis

Work place vapor phase constituents were collected by utilizing Pallflex T60A20 Teflon coated glass fiber filters to screen out air particulates. The vapor phase sampling arrangement involved filters placed first in the air sampling stream followed by glass impingers containing distilled water to collect polar vapor phase constituents. This arrangement also employed triple sorbent traps (TST),

downstream of the impingers, for effective collection of more nonpolar vapor phase organics. Air sampling flow rates were controlled below 900 mL/min. with Dupont® P4000 sampling pumps (E. I. du Pont de Nemours & Co., Wilmington, DE). Air sample volumes of up to 0.25 m³ were collected. No quantitation was performed on the filters and impingers, which were utilized to remove species which would be difficult to recover from TST.

Triple sorbent traps were manufactured in-house of stainless steel tubes 6 mm OD by 76 mm long (with a 1 mm wall thickness) packed with three sequentially loaded beds of sorbents, Carbotrap C, Carbotrap, and Carbosieve S-III (Supelco, Inc, Bellefonte, PA), each 14 mm in length. Thermal desorption gas chromatography/mass spectrometric analyses were performed on a Hewlett-Packard 5995 gas chromatography mass spectrometry detection (GC/MSD) system. Triple sorbent traps were placed in a tube furnace and heated to 400°C. Thermally desorbed constituents were then purged with helium onto a cryogenic loop. The GC oven was held at 10°C for 10 min, then increased to 230°C at a rate of 3°C/min. Mass spectral data were acquired at a scan rate of 266 amu/sec over a mass range of 35 to 300 amu. The GC/MS was calibrated by thermally desorbing multi-sorbent traps (TST) which had been loaded with a mixture of vapor phase standard.

Work place mist vapor phase samples were also collected with passivated stainless steel SUMMA® canisters (Graseby, Smyrna, GA), evacuated to less than 20 Torr and equipped with inlet filters. Samples were collected by opening the canister inlet valves thus allowing canister pressures to increase to ambient atmospheric pressure. Filter and impinger samples were analyzed by HPLC with the Beckman Model 110A instrument described above. Canister samples were subjected to analysis by gas chromatography/mass spectrometry using a Hewlett Packard Model 5972 GC/MS. The procedure entails transferring the sample from a canister using a pressure differential device onto an external loop where it is collected using liquid nitrogen as the cryogen. Analyses were performed using a 60 meter RTX-5 column (0.32 mm ID, 1.0 µm film thickness from Restek Corp., Bellefonte, PA). The GC oven was held at 10°C for ten minutes before ramping at 2°/min to 230°C. Mass spectral data was acquired over a mass range of 15 to 300 amu. Constituents were tentatively identified by mass spectral library matches and quantitated utilizing approximate response factors for aromatic and aliphatic hydrocarbons.

Carbonyl-Specific Air Sampling and Analysis

Industrial shop mists were collected on SKC sorbent tubes (SKC Inc., Eighty Four, PA), comprised of 2,4-dinitro phenylhydrazine (2,4-DNPH) coated on silica gel. Formaldehyde, acrolein and other aldehydes or ketones present in shop mists and metalworking fluid were derivatized in situ during sampling by reacting with 2,4-DNPH to yield the respective 2,4-dinitro phenylhydrazone derivatives. Air (mist) samples were collected for several hours on each sorbent tube with Alpha 2 sampling pumps (E. I. du Pont de Nemours & Co., Wilmington, DE). Flow rates were held to below 700 milliliters per minute (mL/min.) in all cases. Sampling volumes ranged from 0.05 to 0.23 cubic meters (m³).

Metalworking coolant concentrate was added twice to the tube mill coolant reservoir during air sampling operations. The tube mill metalworking fluid reservoir was also sampled 4 times during this time period. Carbonyl species in tube mill coolant fluid samples were converted to their 2,4-dinitro phenylhydrazone derivatives by spiking metalworking fluid directly onto sorbent tubes. Fluid spike volumes were from 50 to 100 microliters (μl) on each tube. Aldehyde standards were also derivatized by spiking 100 μl of each standard solution onto sorbent tubes.

All DNPH sorbent tubes were eluted with approximately 5 mL acetonitrile each. The 2,4-DNPH derivatized sample eluates were analyzed using HPLC with a Zorbax ODS 4.5 by 150 millimeter (mm) HPLC column. Chromatographic conditions were: typical injection volume of 15 μ l eluted with isocratic mobile phase 60/40 percent acetonitrile/water at about 0.3 mL/min. flow rate with ultraviolet-visible detection at a wavelength of 360 nanometers (nm). Selected samples were also analyzed under similar conditions with a Hewlett Packard Series II 1090 Liquid Chromatograph with diode array detection to obtain ultraviolet-visible spectra of targeted component peaks. These constituents have not been confirmed with independent mass spectrometric analyses, however; comparisons were made of ultraviolet-visible spectra of derivatized sample and authentic standard formaldehyde.

RESULTS AND DISCUSSION

Total air particulate concentrations, as measured by high volume filtration, ranged from 1.3 to 4 mg/m^3 (see Table I). These levels are well below the OSHA standard⁽¹³⁾ threshold limit value (TLV) for total suspended particulates (TSP) of 15 mg/m^3 for the 8 hour time weighted average (TWA). Time averaged results of

particulates entrained on filters agreed reasonably well with real time particulate concentration data, which fluctuated from less than 0.5 mg/m³ to spikes of up to approximately 14 mg/m³ (Figure 1). Ambient total particulate levels, as measured in real time with DataRAM® near the weld quenching/metalforming operation, were usually below 1 mg/m³. Several episodes of higher readings up to about 2 mg/m³ were noted as the real time aerosol monitoring probe was moved to different stationary locations within approximately 20 ft. of the welding zone (see Figure 1). Increased particulate levels are apparently a result of spacial as well as temporal effects of the weld quenching operation. The particulate concentration spikes of about 30 sec. duration, ranging from about 7 to 14 mg/m³, represent events during which the monitoring device was placed very close to the welding arc. The mean of these real time results is still below the OSHA standard for the respirable particulate fraction (RSP) which is 5 mg/m³ for the 8 hour TWA.

Particulate size distributions of the aerosol organic fraction collected near the tube mill welding operation were determined by ultraviolet-visible fluorescence. Cyclic aromatic hydrocarbons would be among the species detectable with this analytical technique. Distributions appeared to be bimodal, with MMAD of 0.7 and 1.2 µm. Determination of the size distribution of the inorganic species in the collected particulates was performed using energy

dispersive X-ray (EDX) as the quantification tool. The analysis indicated the presence of aluminum, calcium and iron with traces of sulfur, chlorine and manganese. It should be noted that volatile components in the particulates would not be present during elemental analysis because the samples are analyzed under vacuum. Results from EDX analysis (Figure 2), suggests that the relative composition of the measured inorganic species changes as a function of particulate size. These inorganic species were not detected on blank samples of the filter media used for collecting particulates. Iron, calcium and aluminum predominate in the larger size particulates as judged from the relative abundances on each impactor stage. Manganese, sulfur/molybdenum and chlorine are apparently slightly enriched in the fine particles. The distribution of the inorganic species yielded a somewhat larger MMAD, in the 1.3 to 2 μm range, than the distribution of organic species. According to particle size results, the major portion of the particulate mass was found to be less than 10 μm in diameter, and therefore within the inhalable particle size range. Approximately 20% of the total particulate mass was determined to be larger than 4 μm . Electron micrographs of the particulates also confirms this (Figure 3). Particles larger than 10 μm in diameter were also observed. The majority of the particulates appear to be within the OSHA defined RSP range, which has a 3.5 μm cutoff.

The diverse particulate morphology and composition shown in Figure 3 shows that the aerosols found near tube milling operations are quite complex and not exclusively derived from the tube milling and welding process. It appears reasonable to hypothesize that spherical particles composed primarily of iron originate from welding fumes⁽¹⁰⁾. The origin of irregularly shaped particulates comprised primarily of iron is not clear. Presumably these species could be produced by other fabrication processes occurring in the shop, possibly grinding or metal cutting and stamping operations. Silicon containing and other nonspherical nonmetallic particulates are probably not related directly to any manufacturing activity. These particulates apparently are from background shop dusts which were ubiquitous on exposed surfaces.

Vapor phase air samples were determined to contain large numbers of aromatic and aliphatic hydrocarbons in easily detectable quantities. Estimated concentrations of individual volatile species present in indoor air at the manufacturing facility ranged from 0.01 to 0.2 mg/m³ in the vicinity of the tube milling operation. The complexity of the chromatogram presented in Figure 4, and the number of species which have been tentatively identified and for which concentrations have been estimated (Table II) suggests the complexity of the composition of the vapor phase organics near the weld quenching operation. The

presence of toluene, xylene, and other substituted aromatic and aliphatic hydrocarbons normally found in gasoline suggests that other contaminant sources such as internal combustion engines contribute to the complexity of the environment near the tube milling operation. This was confirmed by visual observation. The vapor phase levels found near tube milling operations were about 1000 fold lower than the OSHA TLV-TWA and short term exposure limits (STEL) for toluene and xylene⁽¹³⁾.

Vapor phase samples collected in SUMMA® canisters confirmed results obtained from air sampled near the tube milling operation on multisorbent traps. Ambient air collected immediately outside the manufacturing facility contained total vapor phase organics at levels of less than 0.01 mg/m³. Air sampled immediately downwind of the welding operation was determined to contain total organics estimated at 2 mg/m³. Therefore, the ambient air outside the facility contributes little to the very low vapor phase occupational exposure occurring inside the facility. Large bay doors were usually kept open during warm weather allowing adequate cross ventilation of the facility with outside air thus diluting the emissions generated indoors. Exposure to vapor phase organics in this facility appears not likely to exceed the OSHA TLV as long as the plant remains well ventilated.

Carbonyl-specific analysis of ambient vapors and mists near the tube mill indicate the presence of formaldehyde at relatively low concentrations.

Formaldehyde levels increased in mists during tube production from approximately 10 to 40 $\mu\text{g}/\text{m}^3$ (see Table III). Analytical error associated with the methodology was estimated to be approximately 9 to 17% by comparison of standards; therefore, changes detected in ambient formaldehyde levels were genuine.

Formaldehyde was also detected in the metalworking fluid utilized to quench the hot tube weld (see Figure 5). This semi-synthetic metalworking fluid contained triazine, a formaldehyde condensate biocide, accounting for the presence of formaldehyde in the fluid samples and possibly also in the resulting mists.

Metalworking fluid concentrate was added periodically to the tube mill coolant reservoir to achieve proper machining specifications. This apparently caused formaldehyde concentrations to increase in the fluid during tube production, from about 5 to 150 ppm. Increasing formaldehyde concentrations in the metalworking fluid apparently correspond with increased formaldehyde levels observed in aerosols near tube milling operations. These aerosol concentrations ranging up to 40 $\mu\text{g}/\text{m}^3$ did not exceed the formaldehyde OSHA standard⁽¹⁴⁾ which is a TLV of 370 $\mu\text{g}/\text{m}^3$. However, the NIOSH recommended exposure level (REL) of 19.6 $\mu\text{g}/\text{m}^3$ for an 8 hour TWA was exceeded in some cases. This brings into question

whether a metalworking fluid formulated with a formaldehyde condensate biocide is the proper quench liquid for use with an arc welding operation. The addition of fluid concentrate to the tube mill coolant reservoir was necessary to achieve desired metalforming characteristics. As a result, the REL for formaldehyde was sometimes exceeded. This may have been due to accelerated breakdown of triazine, the formaldehyde releasing biocide, from contact with the hot weld. It would seem prudent to conduct weld quenching with a material not likely to generate formaldehyde from thermal or chemical decomposition.

The presence of acetaldehyde, retention time 14.7 min., in the coolant or mist was suspected but was not confirmed. The component eluting at approximately 7.8 min. was excess 2,4-DNPH reagent eluted with solvent from sorbent traps along with the derivatives (Figure 5). Certain other unidentified components, present in the mist and metalworking fluid, were observed initially at relatively high quantities which became depleted while formaldehyde concentrations increased.

CONCLUSIONS

Airborne aerosols and vapors present in the ambient air near a tube milling

and weld quenching operation were complex regarding particulate morphology and airborne species detected. Time averaged TSP levels entrained on filters ranged up to 4 mg/m^3 . This agrees with real time TSP concentration data which fluctuated from less than 0.5 mg/m^3 to spikes of up to approximately 14 mg/m^3 . These levels are below the OSHA standard TLV for total suspended particulates of 15 mg/m^3 for the 8 hour TWA. Particle size characterizations suggest bimodal distributions, with the major portion of the particle mass having a mass median diameter of less than $10 \text{ }\mu\text{m}$. The largest fraction of the particulate mass is inorganic or metallic in nature, perhaps due to welding fumes in the immediate vicinity of the weld quenching operation. Among the species present in particulates are: aluminum, calcium, and iron with traces of sulfur, chlorine, and manganese. Vapor phase organic levels found near tube milling operations were about 1000 fold lower than the OSHA TLV-TWA and STEL for selected substituted aromatics. Tentatively identified compound classes include alkanes, alkenes, and substituted aromatic species characteristic of internal combustion emissions, the estimated sum of which are approximately 1.5 mg/m^3 . Exposure to vapor phase organics in this facility appears not likely to exceed the OSHA TLV provided the plant remains well ventilated. Formaldehyde was present in the ambient air, at levels as high as $40 \text{ }\mu\text{g/m}^3$, and in the weld quench mixture

comprised of water and a commercially available semi-synthetic metalworking fluid formulated with triazine, a formaldehyde condensate biocide. Aerosol formaldehyde concentrations did not exceed the OSHA standard TLV of 370 $\mu\text{g}/\text{m}^3$. The NIOSH formaldehyde REL of 19.6 $\mu\text{g}/\text{m}^3$ for an 8 hour TWA, was exceeded possibly due to accelerated breakdown of triazine by surface contact with hot tube weld. It would appear prudent to perform weld quenching with a material less likely to generate airborne toxic species.

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TABLE I
Summary of High Capacity Total Particulate Sample Collection

Sample Location	Sampling Duration, min [†]	Particulate Concentration,
Front side of tube mill	52	4.0
Near pipe bending operation,	108	1.4
Down wind of tube mill, east	63	1.9
Southeast of welding operation	49	2.0
Southeast of welding operation	70	1.3

*Particulate mass collected ranged from 125 to 155 mg

†Mean sampling flow rate ranged from 20 to 50 ft³/min

TABLE III
Temporal Variations in Aerosol Formaldehyde Levels
Observed Near Tube Milling and Welding Operations

Sampling Time Midpoint	Formaldehyde
10:15	8.6
11:05	25.5
17:42	38.9

* Analytical error associated with the methodology was estimated to be approximately 9 to 17% by comparison of standards.

Figure Caption List:

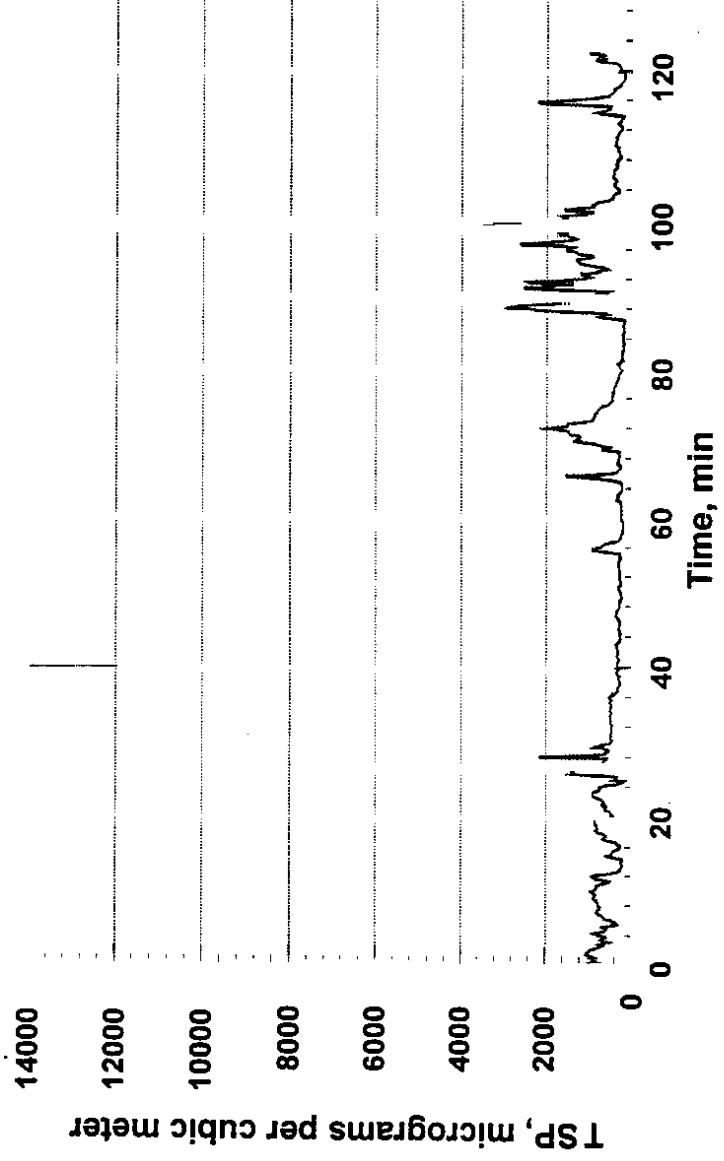
FIGURE 1. Ambient particulate levels as a function of time, near tube milling and welding operation quenched with metalworking fluid. Real time data acquired with DataRAM®.

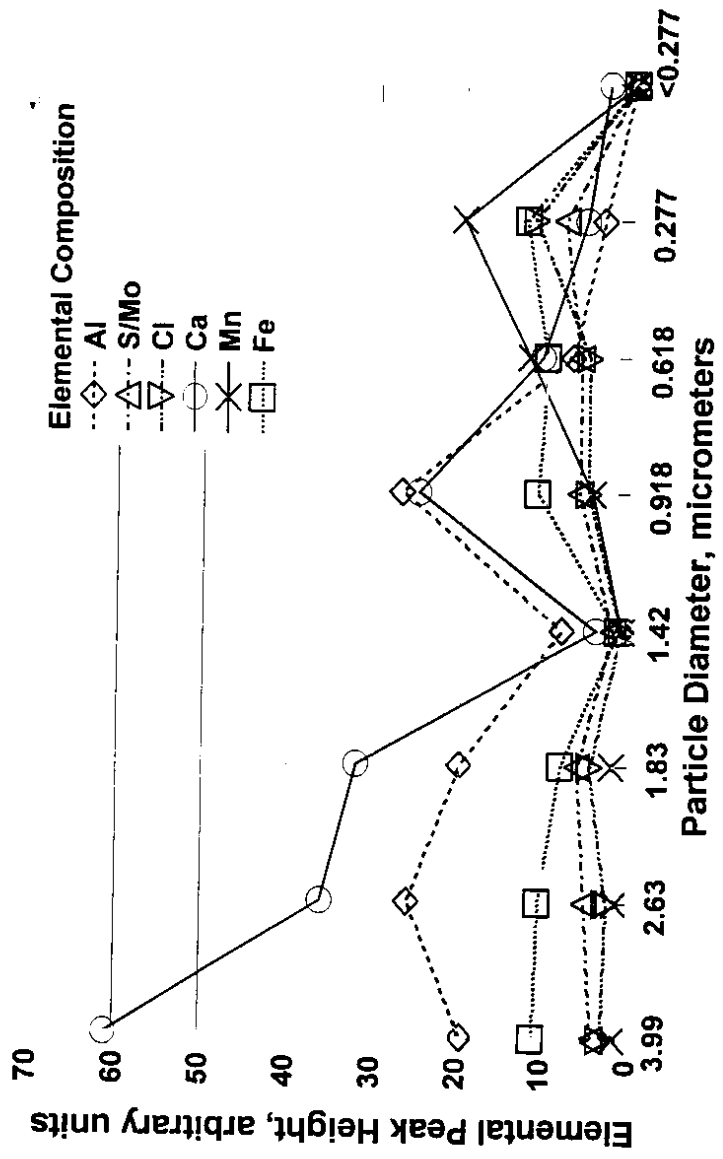
FIGURE 2. Elemental peak height as a function of particle diameter for six inorganic constituents.

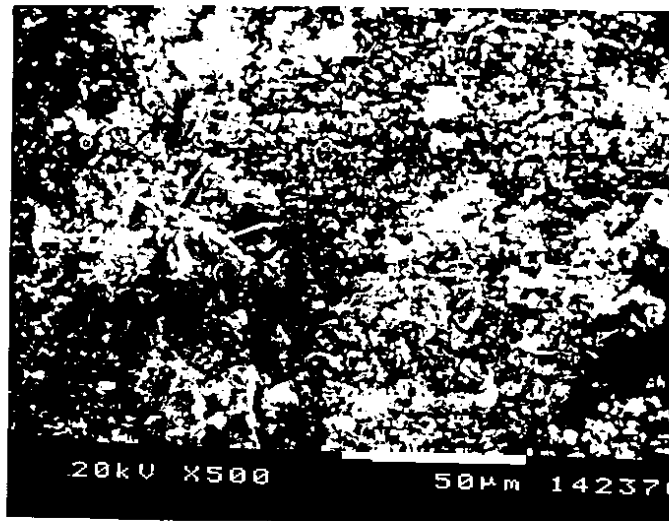
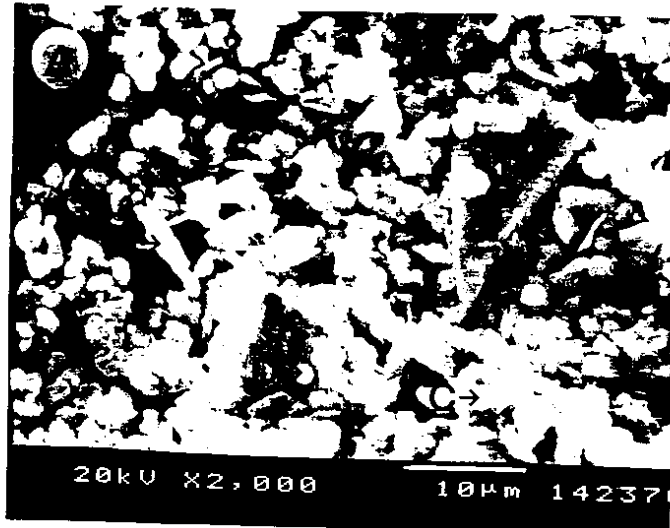
FIGURE 3. Scanning electron micrographs at two magnifications illustrating diversity of particulate morphology and composition. Particulate compositions are as follows: selected particle A, iron; B, silicon; C, calcium and iron; D, iron and manganese; and E, iron and silicon.

FIGURE 4. Total ion chromatogram of tentatively identified compounds from ambient air near weld quenching operation. Air was sampled on carbonaceous multisorbent traps, sampling volume was approximately 0.25 cubic meters.

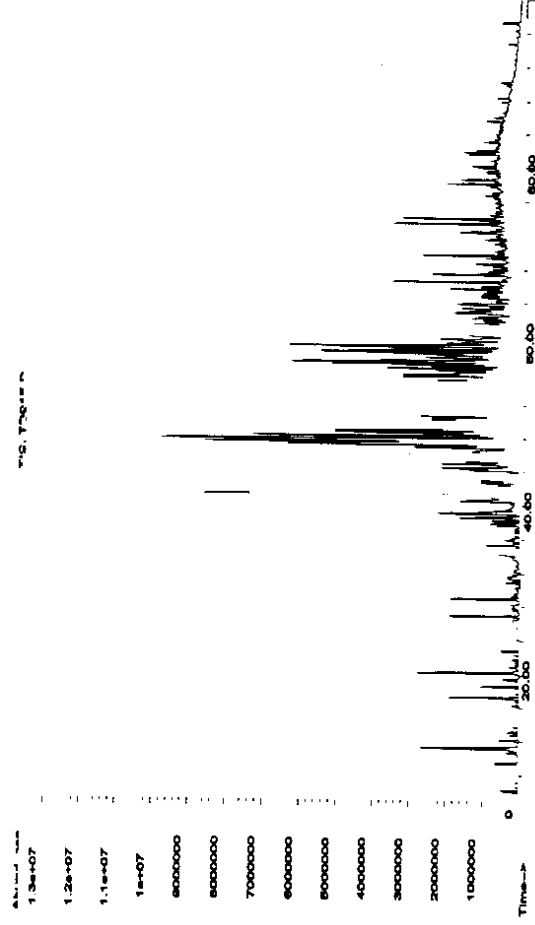
FIGURE 5. HPLC of coolant and mists generated from tube milling and welding operation. Formaldehyde was detected in used coolant and mists resulting from this operation, aldehyde standards included for comparison.

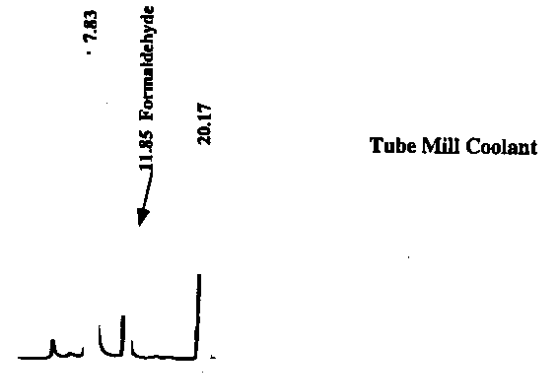
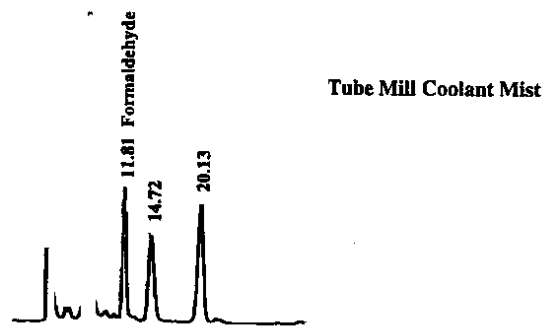
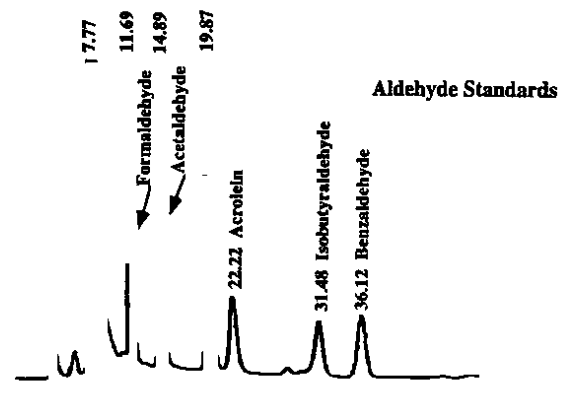






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Instrument : 8972 - In
Sample Name: 42288LPHITD\WGCTET889.TST-4
Misc Info : 6L HE REMOVE H2O.85001-A21.883.10(10)2303
Vial Number: 1





A Survey of Metalworking Fluid Mist In Manufacturing Plants

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Key Words:

Mist, Metalworking Fluid, Mist Levels

Abstract

Metalworking fluid mist levels in eight manufacturing plants were surveyed using a RAM-1 or a DataRAM, light scattering device. Most levels fell in the 1 to 2.50 mg/m³ range, well within the present standards set by OSHA and ACGIH. Variation in observed mist levels were not determined by metalworking fluid type but by variables such as ventilation, temperature, humidity, fluid flow rate, and mist collection systems.

Introduction

There are many contaminants that get into the air of a manufacturing plant. These can be categorized into four general areas;

1. Metalworking fluids (removal, forming, protecting and treating fluids). These fluids may be straight oils, soluble oils, semi synthetic, or synthetic.
2. Industrial Lubricants (hydraulic oils, spindle oils, slideway lubes, gear lubes, greases and wire rope lubes). Formulation types include neat oils, lithium based, aluminum based, rust inhibited oils, polyol esters, inverts, and greases.
3. In-Process Cleaners (alkaline, acid, emulsion and solvent based). These may be high pH, inorganic binders, high pH, organic amines, surfactants, low pH inhibited phosphoric, inhibited sulfuric, oil/solvent emulsion, surfactants, hydrocarbon and terpene.
4. Miscellaneous Contaminants which may include diesel exhaust fumes, mold, bacteria, endotoxins, welding smoke, and paint fumes.

Exposure is not limited to metalworking fluids alone. Particulate in the workplace air actually come from many individual complex substances that combine into one "unknown" complex mixture.

Recent studies of health effects associated with occupational exposure to this complex have increased concern about workplace mist exposure for various types of manufacturing operations. Kennedy *et al*¹ concluded that changes in FEV₁, (Forced Expiratory Volume, 1 second) observed over the work week in automotive component manufacturing workers were induced by metalworking fluid mist. Schaper and Detweiler² have found that metalworking fluid aerosols are both respiratory and pulmonary irritants in mice. Thorne³ and Gordon⁴ have found evidence that respiratory irritation in machinists may have a microbial origin as well as a chemical origin.

Potential for exposure is not determined solely by the properties of the fluid. The type of operations present in a plant, machine set up, distance between machines, ceiling height and design and condition of HVAC and mist collection systems all may contribute to the amount of mist and other air contaminants found in a workplace.

The UAW has petitioned OSHA to reduce the permissible exposure level (PEL) for mist levels within plants from 5 mg/m³ to 0.5 mg/m³ citing the results of studies^{5,6} conducted by the Harvard School of Public Health under the sponsorship of General Motors and the UAW. In the resulting

dialog, it became apparent that there was little data available on the actual exposure levels present in the workplace.

The data reported in this study were compiled over a five year period after surveying eight manufacturing facilities which utilized various metalworking fluid types (synthetic, semi-synthetic, soluble oil) in machining and grinding operations with varying degrees of enclosure and guarding. Mist levels were evaluated to compare plant conditions to regulatory limits, collect data in a real world environment, conduct risk assessments, determine efficiency of mist control devices and address employee concerns.

The sampling protocol used measured the mist present in a defined area. Industrial hygiene studies typically measure the exposure of a specific individual. Personal sampling is focused on the operator's actual exposure and regulatory limits are based on these data. Area sampling on the other hand is focused on the process and estimates worst case exposures. Area samples are more useful in making comparisons of the effects of process changes since their focus is on the process. Both types of data serve a purpose; but when extending these results to industrial hygiene issues, the differences must be considered.

A side study conducted to evaluate mist levels between highly enclosed and non enclosed machines is also included.

Apparatus

Mist levels were monitored using a Real Time Aerosol Monitor (RAM-1) or a DataRAM, manufactured by Monitoring Instruments for the Environment, Inc., Billerica, Massachusetts. The RAM-1 is a light scattering instrument capable of measuring aerosol concentration over a range of 5 decades, approximately 0.001 mg/m^3 to 200 mg/m^3 . When the RAM-1 was utilized a personal data logger (PDL) was connected so that mist concentration data could be continuously logged. The PDL is a single channel analog data acquisition unit for continuous data storage. The DataRAM is a high sensitivity monitor that has internal data logging capabilities. It's measurement span ranges from 0.0001 mg/m^3 to 400 mg/m^3 . Data from the DataRam were downloaded from the instrument as comma separated (CSV) files which were imported into Microsoft Excel© for analysis and presentation. Statistical analysis was performed using Data Desk (Data Presentation Inc., Ithaca, NY).

Procedure

Test areas were selected, generally, on a worst case basis by plant personnel. Site determinations were conducted prior to sampling during plant walkthroughs. Notes were taken for each site during the walkthrough and at the time of sampling with specific interest given to type of machine, proximity to air vents and fans, fluid used, and mist collection systems.

The sites were sampled with the RAM-1 or DataRAM at a location in the worker's exposure envelope around the machine, approximately five to six feet from the floor. The instrument was placed so that the workers normal routine would not be disrupted. Each site was monitored continuously, for approximately thirty minutes, collecting data throughout the time period. Measurements were for the total mist particulate, not just the respirable fraction.

Total mist particulate was measured in mg/m^3 at one sample/second. At ten minute intervals, the minimum, maximum, and average levels for the prior 600 data points were calculated and recorded.

Results

- Overall, the data showed that mist levels were well within the current standards set by OSHA⁷ and ACGIH⁸
- The overall mean value for the 180 measurements taken in the eight plants was $0.85\text{mg}/\text{m}^3$. (Fig. 1).
- Almost all the observations were less than $2\text{ mg}/\text{m}^3$.
- The highest reading recorded was taken near a parts washer in an automotive plant. This particular washer had provision for mist collection and the washer itself was not well maintained; operators in the area complained of irritating rancid odors.
- Mist levels were not dependent on metalworking fluid type. Variables of ventilation, temperature, humidity, fluid flow rate, and mist collection were found to have an effect on observed mist level. Similar observations were made by Woskie *et al*⁹.
- Mist levels were higher for grinding operations than for machining operations.
- Gravimetric measurements of mist level are determined as the weight of mist collected from a known volume of sampled air during the sampling period and expressed as the time weighted average mist level. No information is collected on the dynamic range represented by the sample. The sampling frequency of the RAM-1 and the DataRam allows collection of this type of information. For example, Fig. 2 presents maximum, average and minimum mist levels for each sampling interval for data collected from three areas in Plant H. Average mist levels were similar in the three areas ($1.7\text{-}1.9\text{ mg}/\text{m}^3$). However, peak levels in Area 5 clearly are higher than those in the other areas and there is a greater potential for exposure in this area. Further, there are short periods of time in Areas 2 and 6 when levels are higher or lower than at other times. These intervals can be correlated with process operations to suggest how control measures might best be applied. This information would not be available from gravimetric data.

All the data for each plant surveyed are presented in Fig. 3.

- **Plant A** had 12 locations tested over three separate visits. Majority of the machines were individual, enclosed machining centers with mist collectors connected at several of the machines.

- **Plant B** had 35 locations tested on two occasions. The majority of the machines were enclosed with fluid supplied from a central system. Most operations in the facility were machining. There were no mist collectors used in the plant.
- **Plant C** had 24 location surveyed on two occasions. Operations tested included turning, machining, and some grinding. Most of the fluid was supplied by central systems but some machines were set-up on individual sumps. The plant was comprised of three phases. The oldest phase had air supplied by roof vents and windows; the newest section was fully air conditioned with mist collectors on the machines.
- **Plant D** had 8 locations tested. The machines were all grinders with no mist collection used.
- **Plant E** had 23 locations tested on two occasions. Machines included enclosed machining centers, and 2 grinders. Mist collection was used on the enclosed machine centers during the second monitoring period.
- **Plant F** had 30 locations doing various operations. There were mist collectors on many machines but not all were operational.
- **Plant G** had 3 enclosed turning centers monitored. No mist collection systems were utilized.
- **Plant H** studied 6 locations, all grinding machines. The plant had low ceilings and no mist collectors were used.

The effects of seasonal changes can be seen from Company A data that was collected on three occasions during, spring, summer and winter. As may be seen from **Fig. 4**, mist levels during the winter are slightly higher than during warm weather.

In a side study, mist was measured around an enclosed and a non-enclosed grinding machine, comparing values to see how enclosures affected mist emission. Other variables that were evaluated in this portion of the study included; use of a mist collector vs no collector, the effects of operator location operator side vs infeed side and the effects of machining vs grinding. **Fig. 5** shows that on an enclosed machine no difference in mist level was observed at the operator location with the use of a mist collector, it does reduce the level of mist given off at the infeed side though. **Fig. 6** compares three different operations; throughfeed grinding, in-feed grinding and turning. The in-feed grinding operation had mist levels three times higher than throughfeed and almost six times higher than the turning operation.

Discussion

The combined data are well-described by a log-normal distribution, slightly skewed towards low values (skewness = -1.3). Extending that distribution to metalworking operations in general, the average mist level would be expected to be 0.89 mg/m^3 , the median would be 0.95 mg/m^3 . Ninety five per cent of the mist levels would be less than 1.4 mg/m^3 , only 5% would meet the PEL

proposed by the UAW, but that limit would apply to personal samples, not area samples. These data do not speak to the achievability of the proposed limit.

Practical field experience suggests that when average mist levels are kept below 3 mg/m^3 , the number of mist related complaints will be eliminated. Clearly, the current levels of 15 mg/m^3 for total particulate, 5 mg/m^3 for oil mist and 5 mg/m^3 for respirable particles are too high. On the other hand, the 0.5 mg/m^3 level would require major corrections by almost every employer with no proven benefit to employees. A level of 1 mg/m^3 is obviously well within the capability of the industry and would provide some safety factor to allow for momentary exposures to higher levels.

Conclusions

The type of metalworking fluid used in the plants surveyed did not influence the mist levels suggesting that non-fluid factors must be addressed to realize mist reductions. The significant factors include operation type, ventilation, fluid flow rate, machine guarding, placement of enclosed machines with respect to the flumes and fan placement. Overall process design must be addressed as changes are made (i.e. machines are added or replaced, changes in fluid application, etc.). If mist collection systems are used or are being added they need to be properly engineered for the operation and enclosures used. The plant needs to maintain overall good housekeeping and consider non-machining sources of mist to achieve an overall decrease in total mist.

It is important to consider peak values obtained over the work day to properly assess and address the nuisance potential for mist in any particular location.

Acknowledgments

I would like to thank Bill Lucke for his assistance with statistical analyses and in fine tuning this manuscript. Also, many thanks to Melody Lequire for helping keep my work under control while I was away doing sampling for this study.

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A Survey of Metalworking Fluid Mist In Manufacturing Plants
Ann Ball

List of Fig. numbers and titles.

Fig. 1: Log Normal Histogram For Mist Data

Fig. 2: Mist Level Variation For Three Areas With A Similar Overall Average in Plant H

Minimum, Maximum & Average points shown for each sampling interval

Fig. 3: Mist Levels by Company

Fig. 4: Mist Levels by Season

Fig. 5: Effect of Sampling Site and Mist Collector on Level

Fig. 6: Effect of Operation on Mist Level at Operator Position

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60 -
Log Normal Histogram of Mist Data

Fig. 1

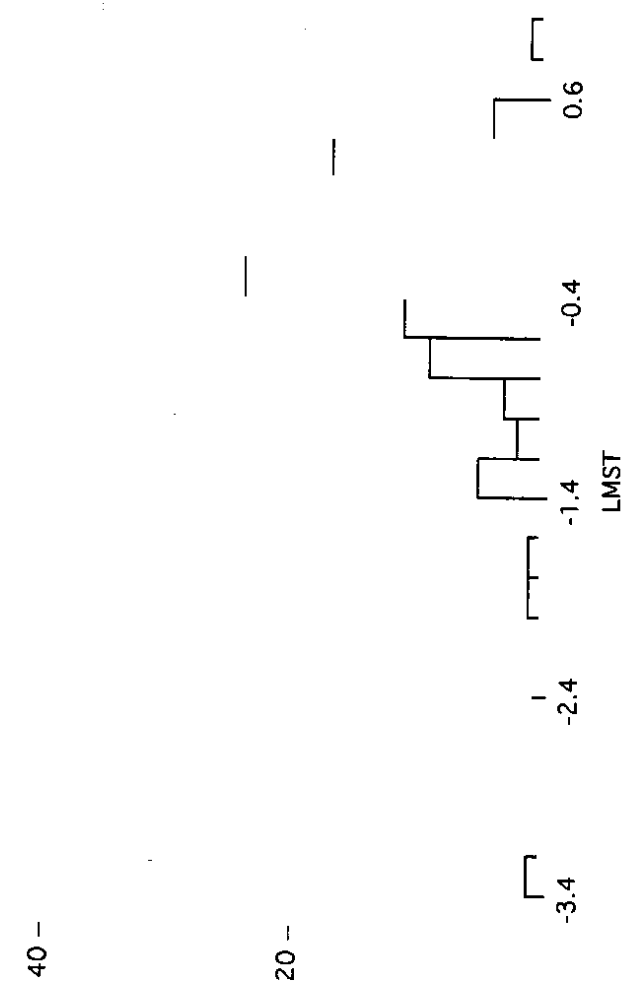
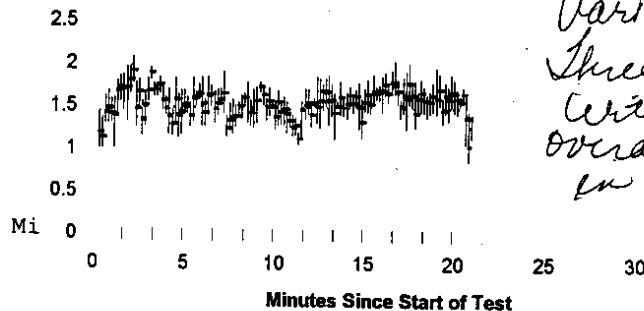
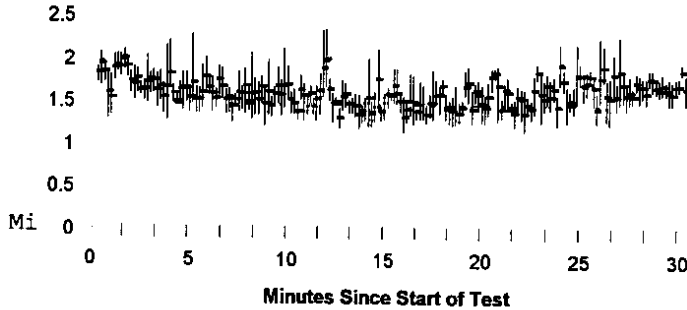


Fig 2
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mist level
variation for
three areas
with a similar
overall average
in Plant H

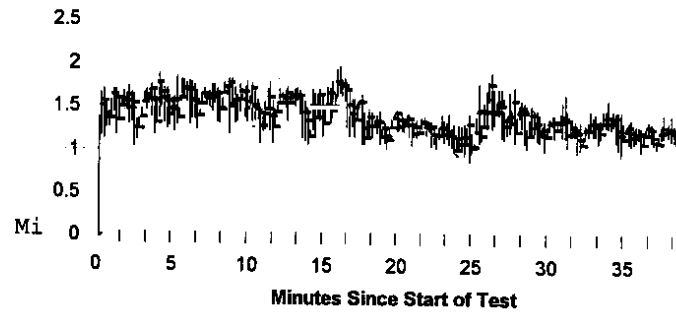
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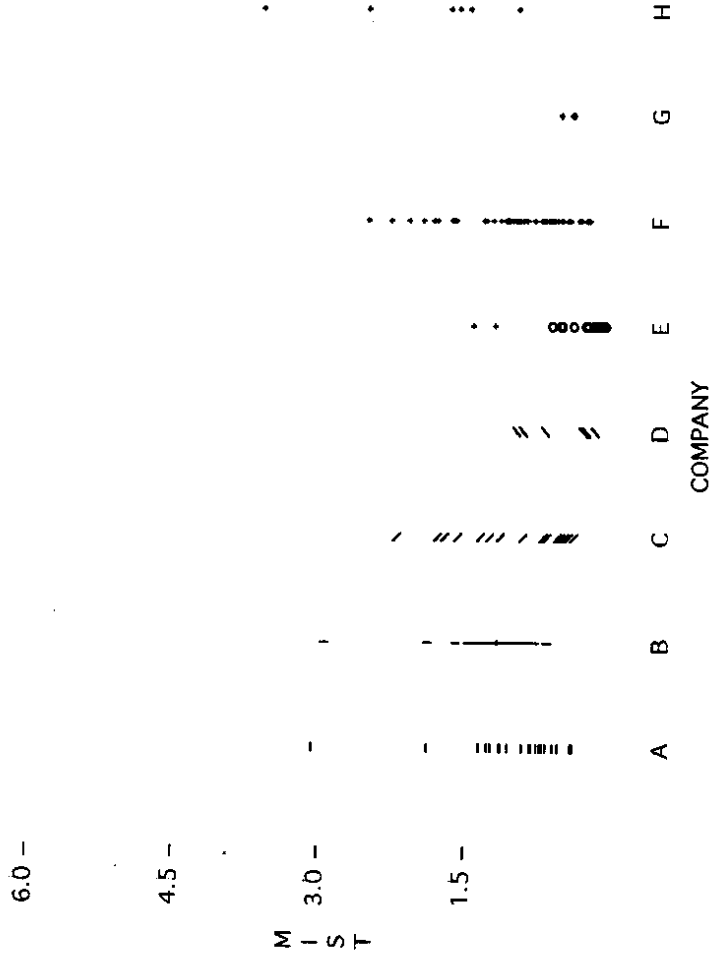
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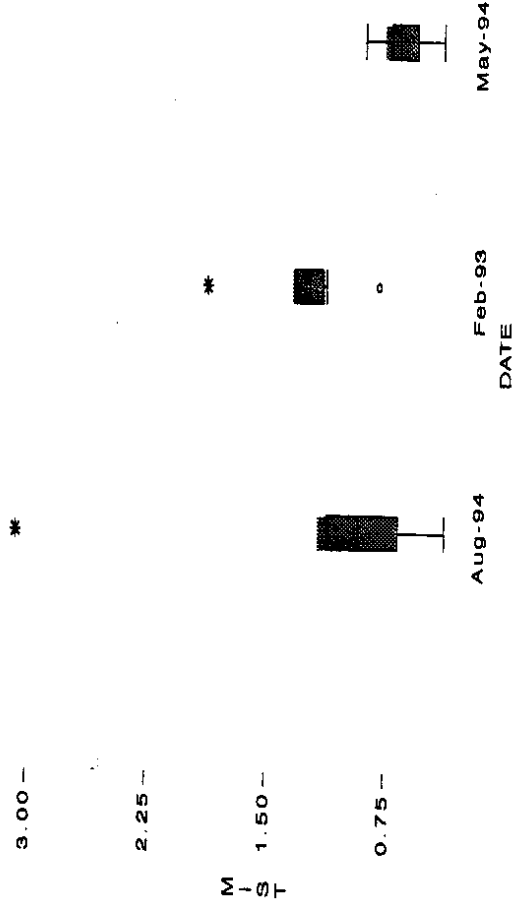
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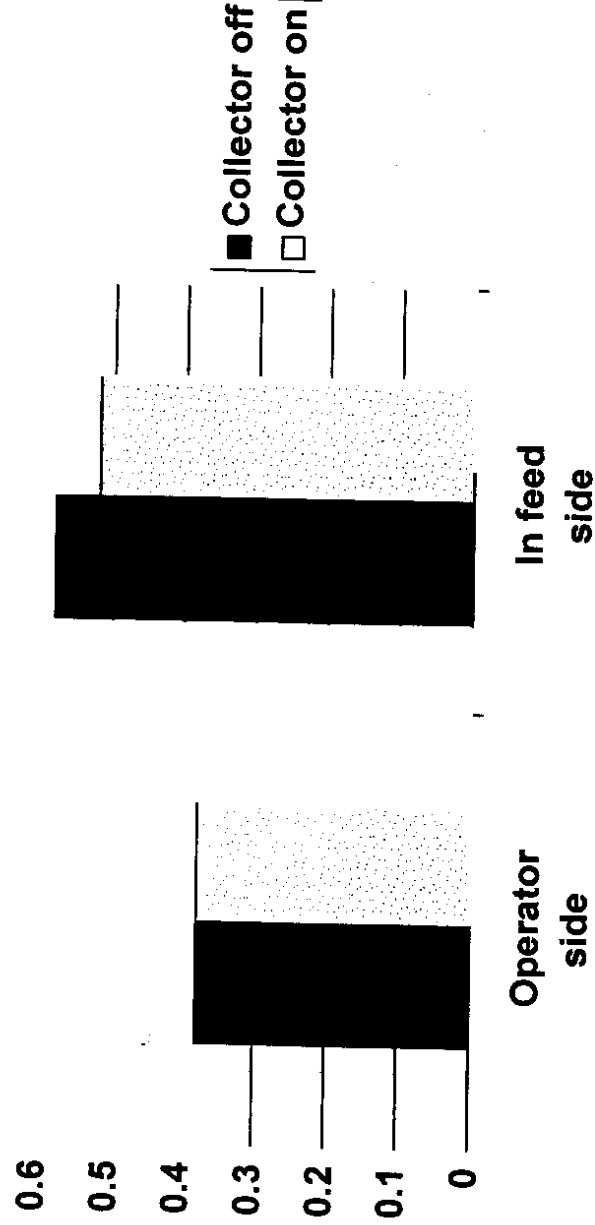
Distribution of Mist Levels by Company



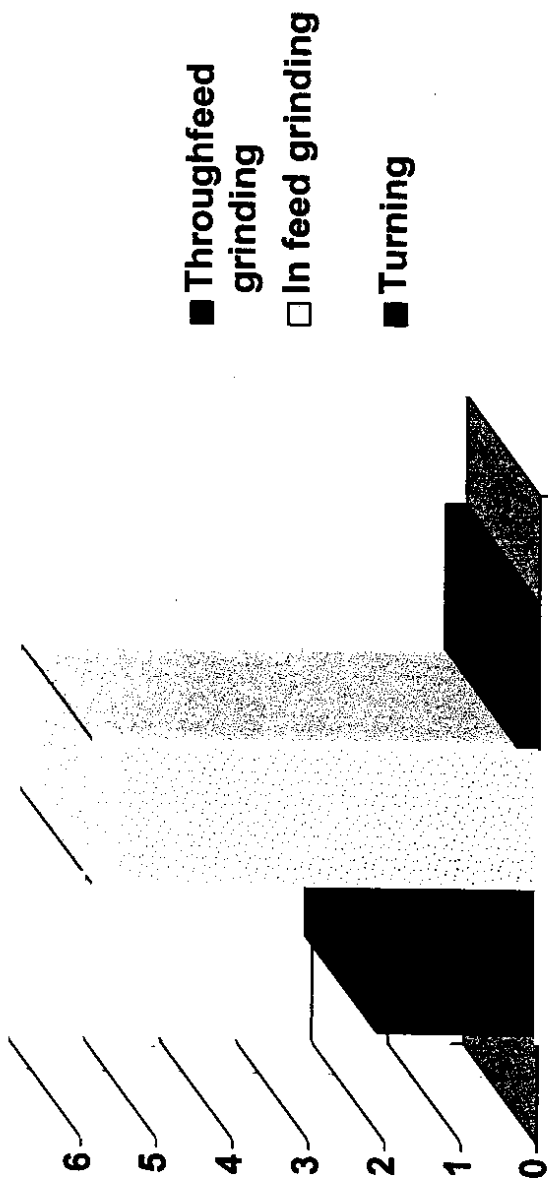
Mist Levels by Season



Effect of Sampling Site and Mist Collector on Level



Effect of Operation on Mist Level at Operator Position



**FORMATION AND PRECURSORS OF
NITROSAMINES IN
METALWORKING FLUIDS[©]**

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Formation and Precursors of Nitrosamines in Metalworking Fluids[®]

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Extensive analysis of representative nitrite-containing metalworking fluids for N-nitrosodiethanolamine suggests that the levels of NDELA formed are related to the amount of diethanolamine originally present. There is no evidence that nitrosation of triethanolamine occurs.

BACKGROUND

Synthetic coolants are commonly used in the metalworking industry to cool workpieces during metal removal operations. Sodium nitrite in combination with monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) was commonly used prior to 1985 as a corrosion inhibitor for these products. While it was known that nitrites and secondary amines could react to form a class of compounds known as nitrosamines (R_2NNO) and that these compounds were often carcinogenic, it was commonly believed that this reaction only took place at acidic pH levels. (1) Since metalworking fluids were alkaline, the possibility of nitrosamine formation in these products was discounted. In 1976, the availability of sensitive, selective analytical methods led to the discovery that this assumption was incorrect, and that in fact the reaction product of nitrite and diethanolamine, nitrosodiethanolamine (NDELA), could be found in many commercial products at the parts per hundred level. (2) NDELA has been reported to be one of the most potent liver carcinogens ever tested. (3) In view of the projected exposure of an estimated 750000 machinists to these products, a substantial risk was assumed to exist, leading to the ultimate removal of amine-nitrite fluids from the market place.

EXPERIMENTAL METHODS

NDELA Content of Metalworking Fluid Concentrates

Nitrosamines in metalworking fluids are present at relatively low levels in a complex matrix of oils, surfactants,

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biocides and other chemicals, so a means of isolating them for analysis is necessary. Isolation is complicated by the need to avoid artifact formation during the process. Simple removal of water from a mixture of diethanolamine and sodium nitrite at alkaline pH by vacuum distillation or lyophilization was found to result in the formation of nitrosamines. A modification of the procedure developed by Fine, et al (2) was used for the results reported here.

Thus, a 1 ml portion of fluid concentrate was mixed for 15 to 30 minutes with 10 g of calcium sulfate, and extracted with 10 ml of ethyl acetate. The solid was removed by filtration and washed twice more with 10 ml of ethyl acetate. The filtrates were collected and evaporated to dryness at 50° C under vacuum. The residue was dissolved in 1 ml dry pyridine and was treated with 0.25 ml hexamethyldisilazane and 0.1 ml trimethylchlorosilane. This solution was analyzed by gas-liquid chromatography.

Chromatography was carried out using nitrogen as the carrier gas at a flow rate of 20 ml/min at 50 psi. The flame ionization detector was operated at 375° C with a hydrogen flow rate of 35 ml/min and air at 250 ml/min. One of two columns was used, depending on interferences for each product. A 6 ft. × 2 mm glass column with 3% OV-1 on 100/120 mesh Chromosorb W-AW-DMCS or a 6 ft. × 2 mm glass column of 10% SP-2330 on the same support was used for separations. In each case, the initial oven temperature of 90° C was held for two minutes, followed by a temperature increase of five degrees per minute to final temperatures of 350° C for OV-1 or 275° C for SP-2330. The upper temperature was held for 10 minutes. Recoveries of standards were 70 percent, in agreement with previous work.(4).

NDELA Content of Used Fluids

The GLC method proved unsuitable for the analysis of used, diluted metalworking fluids, owing to the large volumes of sample needed to isolate sufficient nitrosamine to exceed the detection limit. Analysis of used mixes became possible with the development of solid phase extraction techniques and electrochemical liquid chromatographic detectors which could be optimized to detect only the nitroso group, simplifying the process of removing the sample matrix.

25. Evaluation of endotoxin–biocide interaction by the *Limulus* amoebocyte lysate assay

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SUMMARY

Previous reports of neutralization of endotoxin pyrogenicity and systemic shock by a formaldehyde condensate biocide suggested that the interaction might be a generalized one related to formaldehyde activity. This study utilized *Limulus* amoebocyte lysate (LAL) as the indicator system for endotoxin activity. Purified *Escherichia coli* endotoxin was mixed with several levels of commercially available industrial biocides at doses comparable to those in actual use. Of those tested, compounds with known available aldehyde neutralized LAL endotoxin effect (i.e., no gelling) while those with no aldehyde had no effect.

INTRODUCTION

Endotoxins, the lipopolysaccharide portion of the outer membrane of gram-negative bacteria, are capable of eliciting a large number of pathophysiological effects in their hosts including decreased spirometry, pulmonary inflammation, fever, septic shock, and a range of hyper-immune responses. Considering the ubiquitous nature of gram-negative bacteria, the detection and neutralization of endotoxins are of significance.

In 1964, Levin and Bang described the ability of endotoxins to coagulate the lysate of amoebocytes of the horse shoe crab, *Limulus polyphemus* [8, 9]. Since that time, the *Limulus* amoebocyte lysate (LAL) assay has become the 'method of choice' in detecting the presence of endotoxins [10]. Although there is no certainty that the LAL assay measures the same aspects as the rabbit pyrogen bioassay (RPB), the official test of endotoxin screening, excellent correlation has been shown between these

two assays [5]. The U.S. Food and Drug Administration has established guidelines for the LAL assay to be used as an alternative method for the RPB [11]. This is of considerable advantage since the LAL assay is simpler, more rapid, reproducible, and economical as a method of endotoxin screening.

In a series of studies by Brown et al. [1–3], two substances – noxythiolin (oxymethylene methylthiourea) and taurolin (*bis*-[1,1-dioxo-perhydro-1,2,4-thiadiazinyl-4] methane) – have been effective in the treatment of bacterial peritonitis. The chemotherapeutic effect of these substances has been attributed to their ability to undergo slow decomposition, releasing free formaldehyde.

Pfirrmann and Leslie [12] investigated changes in the mean rectal temperature of rabbits injected with endotoxin and determined that the pyrexia and lethal effects of endotoxins can be dramatically reduced if administered with taurolin. In the same article, the mitigation of endotoxin lethality in mice