

## **Presentation to the WATCH Committee, York, 24<sup>th</sup> February 2011.**

### **Introduction.**

This information has been prepared on behalf of the Metalworking Fluid Product Stewardship Group (MWFPSG) of United Kingdom Lubricants Association. Formed from suppliers of metalworking fluids, additives and raw materials, the MWFPSG promotes high ethical standards, safety and regulatory compliance in the formulation and use of metalworking fluids, working closely with the Health and Safety Executive.

My name is David Neadle. I am a chemist. My working life began in the research department of a manufacturer of organic chemicals, after which I joined the Medical Research Council, carrying out chemical analysis and synthesis linked to the chemical pathology of mental disorders. Following a further one year as a hospital biochemist, I returned to industry and have worked with lubricants for 42 years. I am now retired except for my role as chair of the MWFPSG which I am due to vacate in the Autumn. My presentation today is on the types, composition and regulatory aspects of metalworking fluids. I will provide a transcript of this presentation, together with related documents.

### **Applications of metalworking fluids.**

Metalworking fluids are used in a vast range of metal removal (cutting and grinding) and metal forming processes. Fluids which are used for washing components, although not classified as metalworking fluids, may also need to be considered in relation to the health issues under discussion.

### **Types of metalworking fluids.**

There are two main types of Metalworking Fluids:

- Neat oils which are used as supplied
- Water-Mix metalworking fluids which are mixed with water before use.

There are three broad types of Water-Mix Metalworking Fluids:

- Soluble oils, sometimes called conventional milky fluids, macro-emulsions or even suds or slurry oils.
- Semi-synthetic fluids.
- Synthetic fluids.

Metalworking fluids are complex products with up to 20 individual components in water-mix fluids. Soluble oils (conventional/milky fluids) and Semi-synthetic fluids form oil-in-water emulsions. Synthetic water-mix fluids may form emulsions or solutions when diluted in water, depending on their composition.

**General composition of neat oils:**

Highly refined mineral oil or synthetic hydrocarbon or natural or synthetic ester.  
Lubricity additives (sometimes called boundary lubricants),  
Extreme pressure additives.  
Anti-mist additive.  
Metal passivator.  
Corrosion inhibitor.  
Antioxidant.  
Dye/reodorant.

Neat oils, depending on their intended applications, have a wide range of viscosities. This can have important implications for exposure for both the respiratory system and the skin.

**General composition of oil-containing water-mix metalworking fluids (soluble oils and semi-synthetic fluids):**

Highly refined mineral oil.  
Emulsifiers.  
Lubricity additives (sometimes called boundary lubricants).  
Extreme pressure additives\*  
Corrosion inhibitors.  
Coupling agent.  
Buffers/pH stabilisers.  
Biocide/preservative.  
Metal passivator.  
Antifoam.  
Chelator\*  
Dye/reodorant.  
Water.  
\* more usual in semi-synthetic fluids.

**General composition of synthetic water-mix metalworking fluids.**

Lubricants.  
Corrosion inhibitors/wetting agents.  
Plasticiser (in some products).  
Chelator.  
Metal passivator.  
Biocide/preservative.  
Antifoam.  
Water.

The constituents of neat oils generally do not react with each other during manufacture which is essentially a blending process. In the case of Water-Mix Metalworking Fluids, some components remain unaltered in the manufacturing process, whilst others undergo reactions, principally between acids and bases. In cases where reactants have a hazard classification, it is our experience that the products are either unclassified or of lesser hazard. The MWFPSG has developed a protocol for predicting the chemicals formed e.g. the strongest acids and bases would react first. In the end it is the responsibility of individual manufacturers to determine the substances present in their products

### **Regulation and health/environmental concerns.**

The MWFPSG does not specify or control formulations which are developed by individual manufacturers, based on their own technology and experience. Our group aims to identify and communicate regulatory requirements or concerns, as a result of which members may determine a need to modify formulations.

An early issue arose during the late 1960's (long before the formation of the group) when it became known from the results of research that base oils with a high content of polycyclic aromatic hydrocarbons could cause skin cancer. Working practices during the 1940's and 1950's are likely to have contributed to the problem, which resulted in a large number of cases of scrotal cancer among tool setters, particularly in the Birmingham area. During the early 1970's the lubricants industry introduced modified formulations containing base oils which were solvent refined or treated in alternative ways to effect a major reduction in the polycyclic aromatic hydrocarbon content. Another early example is the removal from metalworking fluids (and other lubricants) of sperm whale oil, owing to considerations of animal cruelty. Other examples of substances which have given rise to concerns include:

Sodium nitrite (formation of nitrosamines in combination with secondary amines).

2, 2', 2''-(Hexahydro-1,3,5-triazine-1,3,5-triyl) triethanol biocide (skin sensitising properties).

Nonyl phenol ethoxylates (hormone mimicking characteristics).

Certain chlorinated hydrocarbons (health and environmental issues).

A current issue, under REACH, concerns boric acid and certain borate salts. Boric acid and sodium borates are being classified as Category 1B reproductive toxins for fertility and developmental effects. For boric acid present in mixtures the concentration limit is 5.5%. More detailed information can be found in Brian Tuohey's article on page 10 of the December 2010 issue of LUBE.

A new Biocide Directive will come into force on 1<sup>st</sup> January 2013 and will incorporate the active involvement of the European Chemicals Agency.

The European Regulation on Classification, Labelling and Packaging of chemical substances and mixtures (CLP) implements the Globally Harmonised System. Under CLP manufacturers and importers of chemical substances are required to notify them to ECHA, together with their classification, for inclusion on the Classification and Labelling Inventory.

Waste management has been identified as a priority by the European Union, based on the principles of waste prevention, recycling/reuse and improving final disposal/monitoring.

Christian Eyler, in his article on page 6 of the December 2010 issue of LUBE believes that the impact of the various regulatory requirements will include reduced variety of metalworking fluids, higher costs for raw materials and finished products and apparently more dangerous labelling of products for the same formulation.

### **Metalworking fluids in use.**

I would first draw your attention to the article on Control and Maintenance of Metalworking Fluids printed in the December 2010 issue of LUBE which is provided with this presentation. Metalworking Fluids undergo changes in service which may have an effect on the health of those who work with them, particularly machine operators.

The characteristics of fresh fluids are altered by service. The changes may be slight or significant and are likely to be progressive unless appropriate corrective actions are taken. The rate of change in fluids depends on their conditions of use.

In the case of water-mix fluids, concentration usually increases and pH falls in service. Contaminants may enter both neat oils and water-mix fluids, for example lubricating and hydraulic oils, solvents, greases and metals in dissolved or particulate form\*.

Oxidation can also lead to deterioration of fluids. In neat oils, oxidation can result in the development of acidity and formation of sticky deposits which interfere with the operation of machine tools. Dissolved metals derived from the machining process accelerate the deterioration process (iron and copper are strong pro-oxidation catalysts).

Concentrations of several hundred parts per million of dissolved lead can build up in neat oils. Cobalt can become dissolved in water-mix fluids used for grinding hard metals if specially formulated fluids are not selected.

A Condition Monitoring Programme can be very effective in detecting changes in metalworking fluids in service and identifying trends and sudden events. Water-mix fluids in service would typically be tested for concentration, pH value, corrosion resistance and contamination by lubricants, metals and micro organisms. The tests for neat oils could include viscosity, flash point, infra-red analysis, acid value, elemental analysis and particulate content.

Routine testing for micro organisms in water-mix fluids is usually carried out using slides coated with nutrient media. The slides are dipped into the fluid in use and incubated before being examined for growth of colonies in comparison with standards. Determination of more specific information about the types of micro organisms present and their significance requires the special expertise of the microbiologist.

\*When examined microscopically, metal particles generated in cutting and grinding operations are found to be very sharp. They can inflict damage upon the skin, especially when embedded in wiping cloths or work wear. The resulting disruption of the skin's outer protective layers facilitates further penetration of oils and chemicals. Damage to the skin produced in this way is progressive and healing can be very slow and problematic.

### **The aftermath of Powertrain.**

Investigations following the Powertrain outbreak led to the conclusion that the respiratory diseases were associated with exposure to mists from contaminated water-mix metalworking fluids (and possibly cleaning fluids) and the presence of micro organisms.

Following the outbreak of respiratory diseases at Powertrain, the HSE published new guidance including the following recommendations:

- A risk assessment should be carried out

- Metalworking fluids in use should be monitored and controlled (monitoring to include testing for micro organisms)

- Exposure to metalworking fluids and the mists, fumes and vapours from them should be controlled

- Health surveillance should be provided for those exposed to metalworking fluids.

As we all know the Health and Safety Executive is promoting awareness of these issues through fieldwork and the Health and Safety Laboratory is carrying out research with the objective a reaching a deeper understanding of the causes of the respiratory diseases.

There is a vast amount of literature available on the association between metalworking fluids and respiratory diseases. Unfortunately the reports from different sources do not allow of meaningful comparisons and conclusions. However, there does appear to be a strong linkage between the presence of high numbers of micro organisms (or substances derived from them) and respiratory ill health.

### **Constituents of metalworking fluids.**

Appendix 1 provides information on the constituents of the various types of metalworking fluids. Any individual manufacturer would be unlikely to use the whole range of materials in their products and some producers of specialised fluids may utilise other constituents. In some cases I have not been able to identify specific molecules because there may be differences between the raw materials selected by individual manufacturers and some of the materials are naturally derived and do not consist of a single molecular formula. Many of the constituents of metalworking fluids are multifunctional, for example an emulsifier may contribute to anti-corrosive properties There are various listings available for the components of metalworking fluids and I have used my best judgement in making this compilation.

Relevant chemical lists already exist, for example the List of Substances for Cooling Lubricants in accordance with DIN 51385 for Metalworking and the Global Automotive Declarable Substance List (GADSL).

### **A word about safety data and hazard classification.**

Although any hazards associated with a given constituent must appear on its safety data sheet and defines the classification of the substance, the classification may or may not carry through to that of a preparation containing the substance. This depends on the applicable concentration limits (which depend on the particular hazard classification). Furthermore, the hazard classifications for Water-Mix Metalworking

Fluids relate to the concentrate and not to the diluted fluid in use, normally within the range 2% to 10%.

In recent years, a number of substances have received newly-assigned hazardous classifications and in companies where I have worked a great deal of development effort has been devoted to modifying formulations so as to eliminate such substances.

Whilst some raw materials are classified as being hazardous, I am not aware of any which are classified as respiratory sensitisers (R42).

D. J. Neadle.

8<sup>th</sup> February 2011.

## **APPENDIX 1**

### **Typical constituents of the main types of metalworking fluids.**

#### **NEAT OILS.**

##### **Highly refined mineral oil.**

Paraffinic or naphthenic mineral oil.

Synthesised hydrocarbon.

##### **Lubricity additives.**

Natural esters of animal or vegetable origin including lard oil and rapeseed oil.

Synthetic esters.

Fatty acids including oleic acid.

##### **Extreme pressure agents.**

Sulphurised natural or synthetic esters.

Polysulphides.

Chlorinated hydrocarbons.

Phosphate esters.

Zinc dialkyl dithiophosphate (multifunctional including corrosion inhibition).

##### **Anti-mist agent.**

Methacrylate

Polybutene.

##### **Metal passivator.**

Triazole derivative.

##### **Corrosion inhibitor.**

Calcium sulphonate.

##### **Antioxidant.**

Alkylated phenol.

## **SOLUBLE OIL (CONVENTIONAL/MILKY FLUID).**

### **Highly refined mineral oil.**

Paraffinic or naphthenic mineral oil.

### **Emulsifiers.**

Petroleum sulphonates.

Synthetic sulphonates.

Salts of fatty acids including tall oil fatty acids and oleic acid.

Nonionic surfactants.

Alkanolamides.

### **Lubricity additives.**

Fatty/vegetable oil esters.

### **Metal passivator.**

Triazole derivative.

### **Corrosion inhibitors.**

Petroleum or synthetic sulphonates.

Alkanolamine esters.

Alkanolamides.

Alkanolamines (for reserve alkalinity).

### **Coupling agent.**

Fatty alcohol.

Glycol ether.

Glycols.

**Biocide/Preservatives** to help retard the effects of microbiological spoilage on the metalworking fluid, for example:

Oxazolidines.

Isothiazolinones.

Sodium Omadine (2-pyridinethiol-1-oxide, sodium salt).

### **Antifoam.**

Long chain fatty alcohol.

Polisiloxanes.

### **Reodorants and dyes.**

### **Note.**

Some Conventional/Milky Fluids also contain extreme pressure additives of similar types to those shown for Semi-synthetic fluids.

## **SEMI-SYNTHETIC FLUID.**

### **Highly refined mineral oil.**

Paraffinic or naphthenic mineral oil.

### **Emulsifiers.**

Petroleum sulphonates.

Synthetic sulphonates.

Salts of fatty acids including tall oil fatty acids and oleic acid.

Nonionic surfactants.

Alkanolamine fatty acid esters.

Alkanolamides.

### **Lubricity additives.**

Fatty/vegetable oil esters.

Synthetic lubricants including polyglycols and esters.

### **Extreme pressure additives.**

Sulphurised natural or synthetic esters.

Chlorinated hydrocarbons.

Phosphate esters.

### **Metal passivator.**

Triazole derivative e.g. benzotriazole.

### **Corrosion inhibitors.**

Petroleum sulphonates.

Synthetic sulphonates.

Alkanolamine/boric acid compounds.

Alkanolamides.

Alkanolamines (for reserve alkalinity).

**Biocide/Preservative** to help retard the effects of microbial spoilage on the metalworking fluid, for example:

Oxazolidines.

Isothiazolinones.

Sodium Omadine (2-pyridinethiol-1-oxide, sodium salt).

### **Coupling agents.**

Fatty alcohols, glycol ethers, glycols.

### **Antifoam.**

Long chain fatty alcohols, polysiloxanes, waxes.

**Chelators.** (derivatives of ethylenediamine tetra acetic acid).

**Reodorants, dyes, water.**

## **SYNTHETIC/MINERAL OIL FREE.**

### **Lubricants.**

Polyglycols/other glycolic compounds.

Amides.

Organic esters.

Phosphate esters.

### **Corrosion inhibitors/Wetting Agents.**

Amine salts of monocarboxylic and dicarboxylic acids.

Amine/boric acid compounds.

Alkanolamine fatty acid esters.

Alkanolamides.

Nonionic surfactants.

### **Plasticiser.**

Glycol ethers.

### **Chelators.**

Derivatives of ethylenediamine tetraacetic acid.

### **Metal passivator.**

Triazole derivatives.

**Biocide/Preservative** to help retard the effects of microbiological spoilage on the metalworking fluid.

Examples:

Oxazolidines.

Isothiazolinones.

Sodium Omadine (2-pyridinethiol-1-oxide, sodium salt).

### **Antifoam.**

Polysiloxanes.

Long chain fatty alcohols.

Waxes.

### **Reodorants and dyes.**

### **Water.**