METALWORKING FLUIDS

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The Chemistry of Metalworking Fluids

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I. INTRODUCTION: FLUID TYPES

Throughout the twentieth century, metalworking chemistry has evolved from simple oils to sophisticated water-based technology. The evolution of these products is shown in Fig. 1. Between 1910 and 1920, soluble oils were initially developed to improve the cooling properties and fire resistance of straight oils. By emulsifying the oil into water, smoke and fire were greatly reduced in the factories, thus improving working conditions. With the presence of water in the fluid, tool life was extended by reducing wear since the fluid kept the tools cool. However, water-diluted fluids caused rust on the workpiece, thereby creating the need for rust inhibition.

Synthetic fluids were first marketed in the 1950s because of better cooling and rust protection compared to soluble oils in grinding operations. In the early 1970s, oil shortages encouraged compounders of cutting fluids to formulate synthetic oil-free products that could replace oil-based fluids in all metalworking operations. Synthetic fluids offer benefits over soluble oil technology. These benefits include better cooling and longer tank life because of good hard-water

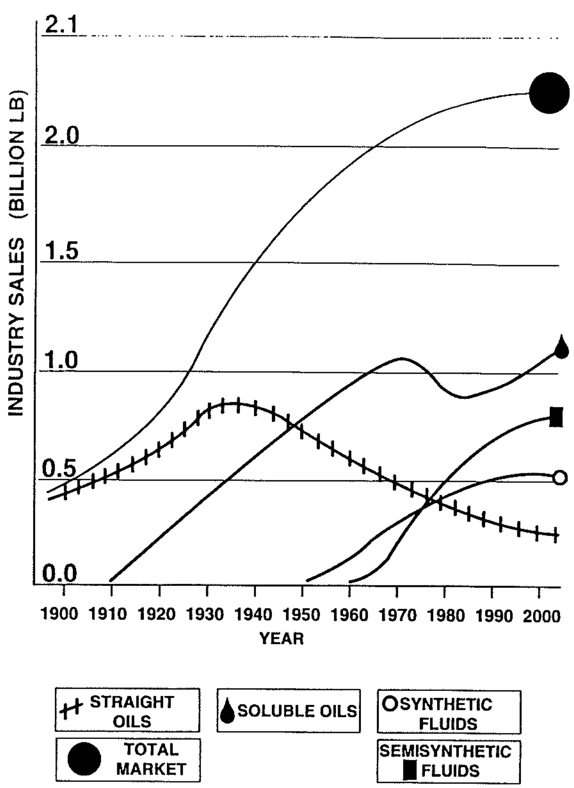


Figure 1 Evolutionary product life cycle.

stability and resistance to microbiological degradation. However, soluble oils, while indeed more susceptible to bacteria growth, provide better lubricity and easier waste treatability than synthetic fluids. These trade-offs encouraged the development of semisynthetic fluids. These water-based fluids contain some oil-based additives emulsified into water to form a tight microemulsion system. These semisynthetic fluids are an attempt to reap the benefits of oil-soluble technology while retaining the good microbial control and long tank life of synthetic fluids.

In the 1980s, synthetic and semisynthetic fluids were growing in a mature market, displacing oil-based technology. However, in the early 1990s, oil prices dropped, placing oil technology at the forefront in pricing. With increasing waste treatment costs, easier to waste-treat soluble oils gained market share over synthetics. Additionally, hazard regulations on ethanolamines commonly used in synthetic

fluids for corrosion control further encouraged the use of soluble oils. Therefore, mature straight and soluble oil technology has held its 65% market share.

The chemistry of metalworking fluids is as diverse as a library of cookbooks. Each formulating chemist will develop his own fluid formula to meet the performance criteria of the metalworking operation. But like lasagna, each "recipe" will have common ingredients or raw materials: noodles, cheese, meat, sauce, etc. That is why fluids are at times called "black box chemical blends." No user is fully aware of the exact composition of the fluid used, but the user knows whether it meets certain performance criteria (tastes good). There are many additive blends that will function as metalworking fluids and there is no assurance of the "perfect" fluid for an operation. Misapplication of that perfect fluid could render it unacceptable.

This review of the chemistry of metalworking fluids will identify the building blocks of metalworking fluids, the reasons for utilizing them, and the key parameters for additive selection.

II. FUNCTIONS OF FLUIDS

A metalworking fluid's principal functions are to aid the cutting, grinding, or forming of metal and to provide good finish and workpiece quality while extending the life of the machine tools. The fluids cool and lubricate the metal/tool interface while flushing the fines or chips of metal from the piece. The fluid should also provide adequate temporary indoor rust protection for the workpiece prior to further processing or assembly.

III. ADDITIVE TYPES

The chemical additives used to formulate metalworking fluids serve various functions. These include emulsification, corrosion inhibition, lubrication, microbial control, pH buffering, coupling, defoaming, dispersing and wetting.

Most of the additives used are organic chemicals that are anionic or nonionic in charge. Most are liquids, used for ease of blending by the compounder. Some of the basic chemical types utilized are fatty acids, fatty alkanolamides, esters, sulfonates, soaps, ethoxylated surfactants, chlorinated paraffins, sulfurized fats and oils, glycol esters, ethanolamines, polyalkylene glycols, sulfated oils, fatty oils, and various biocide/fungicide chemical entities.

The functional additives used in metalworking fluids each contribute to the total composition. The effect of the addition of an additive is tested by the chemist to ensure that optimal properties of a fluid are maintained. In general, a fluid should be stable, low foaming, and waste treatable. Many of the properties of additives are mutually exclusive. Typically, if a fluid has excellent biological and hard-water stability, it may be difficult to waste treat. Or if it provides excellent lubricity, it may be difficult to clean. The following reviews the typical properties of additives and the significance to the formulator and user.

A. Stability

The fluid concentrate must be stable without clouding or separating for a minimum of six months storage. The fluid may be tested in cold and hot atmospheres to assess the effect of shipment or storage in winter and summer climates. Some chemists check for gelling, freezing, or "skinning" of the fluid, which may signify handling problems.

B. Oxidative Stability

Some consider the oxidative stability of the additives important. Aerating and heating the coolant can accelerate any destructive oxidation of the chemical additive.

C. Emulsion Stability

In soluble oils, emulsion stability is the most critical property. The emulsifier system must be balanced based on its alkalinity, acidity, and HLB (hydrophilic/lipophilic balance) to ensure a white emulsion with no cream or oil forming at the surface of the fluid.

D. Hard-Water Stability

All fluid types are tested for hard-water stability because of the progressive increase in hard-water salts in the used fluid. As the fluid evaporates, only deionized water is removed, leaving behind water salts like calcium and magnesium. Carry-out of the fluid on the parts also depletes the fluid volume. As more water and fluid concentrate is added, more salts are accumulating in the tank. Calcium and magnesium cations build up in the fluid. Therefore, in soluble oils, the sodium sulfonate emulsifier is changed to calcium sulfonate, an additive that is not an emulsifier. This destabilization of the emulsion causes oil separation and loss of fluid concentration. In synthetic fluids, hard-water stability problems are visible as soap scum formation on the surface of the fluid. Typically, anionic additives may have hard-water stability problems, whereas nonionic-type additives are stable to hard-water salts.

E. Mixability of Fluid Concentrate

The ease of dilution of the fluid concentrate is important from a practical perspective. The oil must "bloom" into the water without gelling to ensure fast and complete mixing. Many times fluid concentrate is not premixed and is added at a

point in the tank where there is little agitation. Without good mixability, the fluid concentrate could sink, thereby not contributing to the fluid concentration intended. High soap components can cause mixability problems.

F. Foam

Because of constant agitation, spraying, and recirculation of metalworking fluids, foam can easily form in the tank. Besides being a nuisance, foam interferes with the lubricity and cooling functions of the fluid. Air does not lubricate, so air entrained in the fluid renders a fluid ineffective. Foam also interferes with the worker's view of the workpiece, affecting machining accuracy and measurements. Many emulsifiers and lubricity additives may serve their function very well in a stagnant system but may be marginally useful if they foam excessively.

G. Residue/Cleanability

The fluid should not leave a sticky or hard-to-clean residue on the parts or equipment. Some boron-based corrosion inhibitors can leave a sticky residue. Chlorinated paraffins and pigmented lubricant additives can be difficult to remove in cleaning operations.

H. Corrosion Inhibition

Fluids are tested for their corrosion-inhibiting properties. Since water is the diluent for the majority of fluids, corrosion inhibition is critical. Some additives are film forming (amine carboxylate), some are more like vapor phase inhibitors (monoethanolamine borates), while others actually form a matrix with the metal surface to provide protection (azoles).

I. Lubricity

Additives tested for lubricity can be combined to obtain various types of lubricity, depending on the fluid requirments.

Boundary lubricants like lard oil, overbased sulfonates, esters, soaps, and sulfated oils provide a boundary between the workpiece and tool. This slipperiness is ideal for all systems, especially when machining aluminum. Soft metals need boundary lubricants to allow metal removal with good tolerance by inhibiting the tool from welding onto the aluminum workpiece.

Extreme-pressure additives like sulfur, chlorine, and phosphorus actually form metal complexes with the metal surface at elevated temperatures. Chlorinated additives are the most effective with typically 40–70% chlorine in the product compared to sulfurized additives with 10–15% sulfur, or phosphate esters with 5–15% phosphorus. Each has its problems. Chlorinated additives in general are under scrutiny because of their hazardous nature. Sulfurized materials can stain

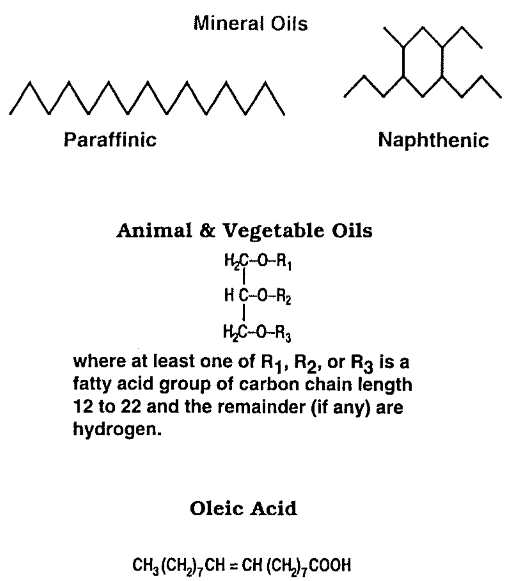


Figure 2 Oils and fats.

metals and can quickly cause rancidity. Phosphate esters, the least effective of the three as a lubricant, can cause fungus and mold growth because phosphorus is a good nutrient.

Hydrodynamic lubricity additives provide a variation on boundary lubricity through a high viscosity in the fluid. Typically, this term is used when describing straight oils with viscosity improver added, although some synthetic fluids are formulated with high-viscosity polymer additives that give the fluid a slippery, thick appearance. These elastic polymers may drop in viscosity under shear and heat, but if they are true rheological additives they will regain their viscosity when cooled.

J. Chemical Structures

The chemical nature of most metalworking fluid additives is organic. Figures 2–6 show the chemical structures of some of these additives. Emulsifiers, corrosion inhibitors, and lubricant additives are all of importance in formulating metalworking fluids, as described in Secs. IV–VIII.

IV. STRAIGHT OILS

A straight oil is a petroleum or vegetable oil that is used without dilution with water. It can be alone or oil compounded with various polar and/or chemically active

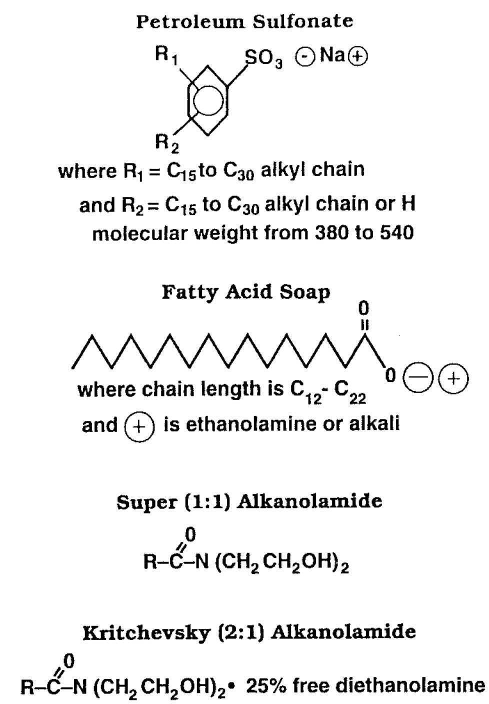


Figure 3 Emulsifiers. (From Ref. 5.)

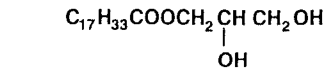
additives. Light solvents, neutral oils, and heavy bright and refined stocks are among the petroleum oils used.

Paraffinic oils offer better oxidative stability and less smoke during cutting than naphthenic oils. However, most compounded oils contain naphthenic oils because the lubricant additives are more soluble and compatible in naphthenic oils [1].

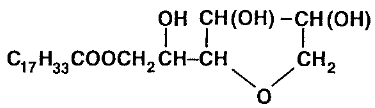
For environmentally favorable requirements, vegetable oils are the oils of choice. Although considerably more expensive than petroleum oils, they are easily biodegraded for disposal. It follows then that they are more prone to biological deterioration than petroleum oils. Nondrying oils like rapeseed, castor, and coconut oils are best. Rapeseed oil, being the lowest in saturated fatty composition, is the best in lubricity because of its long C_{22} carbon fatty chains. It burns clean and is smoke-free, which is a great advantage over petroleum oils which are frequent fire and smoke hazards.

Straight oils provide hydrodynamic lubrication. When compounded with lubricant additives, they are useful for severe cutting operations, for machining difficult metals, and for ensuring optimal grinding wheel life.

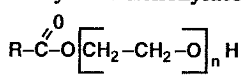
Glycerol Monooleate



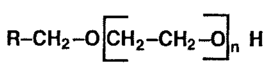
Sorbitan Monooleate



Fatty Acid Ethoxylate



Fatty Alcohol Ethoxylate



Alkyl Phenol Ethoxylate

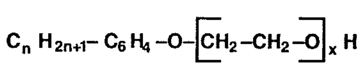


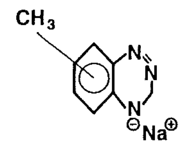
Figure 3 *(continued)*

A. Compounded Oils, Mineral Oils, and Polar Additives

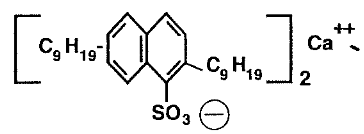
One of the basic compounded straight oils is a naphthenic oil with 10–40% boundary lubricants added. These may include animal oils like lard oil or tallow, or vegetable oils like palm oil, rapeseed oil, or coconut oil [2] Oil-soluble esters of these oils are beneficial because they reduce the inherent biodegradation of fatty oils. Examples are methyl lardate and pentaerythritol esters. *Blown oils*, oxygen-polymerized vegetable and animal oils, increase the affinity of the additive for the metal surface, thereby providing added slip between the tool and work-piece.

These polar additives increase the wetting ability and penetrating properties of the oil and provide a slippery boundary lubricant film. The keys to choosing these additives are oxidation resistance, oil solubility, and gumming properties. Petroleum oil fortified with these polar lubricant additives are used in machining nonferrous metals where staining by other additive systems are problematic. The polar additives provide a rust-inhibiting barrier film from the atmosphere thereby

Tolyltriazole Salt



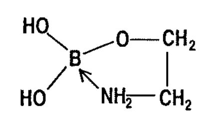
Calcium Sulfonate



Triethanolamine

$(HO\,CH_2CH_2)_3N$

Monoethanolamine Borate (7)



Amine Dicarboxylate

where acid chain length is C_9 - C_{12} and ⊕ is $NH_2(CH_2CH_2OH)_2$

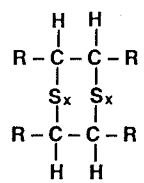
Figure 4 Corrosion inhibitors.

Chlorinated Compound

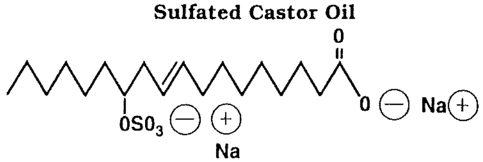
$C_xH_yCl_z$

where X is about 9 to 20 and the weight percent of the chlorine is 20 to 70.

Sulfurized Fatty Oils, Acids or Esters



Sulfated Castor Oil



Polyethylene Glycol Esters

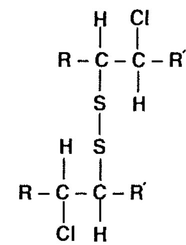
$R-\overset{O}{\overset{\|}{C}}-O-(CH_2-CH_2-O)_n-H$

Propylene Oxide Ethylene Oxide Block Polymer

$HO-(C_2H_4O)_x-(-C_3H_6-O)_y-(C_2H_4O)_z-H$

Figure 5 Lubricants.

Sulfochlorinated Fatty Oils & Esters



Phosphate Esters

Where R = ethoxylated alcohol or phenol

Dibasic Acid Ester

$R\,O_2\,C(CH_2)_x\,CO_2\,R$

Molybdenum Disulfide

MoS_2

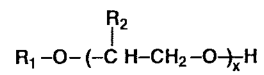
Figure 5 *(continued)*

providing excellent indoor rust protection. These fortified oils are primarily used for light duty cutting operations.

B. Chemically Active Lubricant Additives

For more difficult machining operations, extreme-pressure additives like sulfurized, chlorinated, or phosphated additives are added to the mineral oil. These

Glycol Ethers



where R_1 = butyl, etc. and $R_2 = CH_3$ or H

Propylene Glycol

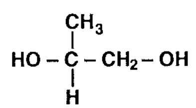


Figure 6 Couplers.

additives are surface reactive and form metallic films on the tool surface, thereby acting much like a solid lubricant at the metal/tool interface.

These additives are used alone or in combination with one another and paired with polar additives to give a lubricating oil with a wide range of effectiveness at various temperatures and pressures. An oil that contains lard oil, chlorinated paraffins, and sulfurized lard oil can bridge the lubrication needs as follows: At low temperatures and pressures, the lard oil provides good boundary lubrication until temperatures reach 570–750°F. Then the chlorinated paraffin takes over, forming an iron chloride film. Then as temperatures climb to approximately 1300°F, the sulfurized fat takes over, forming the metallic sulfide lubricant film. [3]

The chlorinated additives could be chlorinated waxes, paraffin, olefin, or esters. Chlorinated additives are nonstaining but they can be corrosive, since small levels of HCl can be released. Therefore, inhibitors like epoxidized vegetable oils are often used to inhibit corrosion on the workpiece.

The sulfurized additives are either active or inactive. A sulfurized mineral oil is an active additive in that there is free unbound sulfur that easily reacts as the EP lubricant. However, this free sulfur can stain yellow nonferrous metals. Sulfurized fats like lard oil have a stronger chemical bond and can be less likely to stain metals. Typically, a straight oil that contains sulfurized oils is dark in color and has a pungent odor. There are, however, other sulfurized additives like TNPS (trinonylpolysulfide) that is light yellow in color and ideal for water- and amine-free metalworking fluids. The simplest sulfurized mineral oil formulation would contain approximately 1% sulfur and a fluid for difficult tapping or threading operations would contain approximately 5% sulfur.

There are sulfochlorinated additives where both S and Cl are reacted onto one molecule. These are good for machining low carbon steel and nickel–chrome alloys.

Phosphate esters provide both boundary lubricity from the ester component and phosphorus extreme-pressure lubricity at low temperatures. The effects are less dramatic than with sulfur and chlorine. Phosphate esters must be oil soluble and can be used "as is" in their free acid form, or can be neutralized with an alkaline material. Neutralized phosphate esters are nonstaining and noncorrosive and can provide rust protection properties to the oil blend.

Solid lubricants are used to a limited extent in nonrecirculating systems. Molybdenum disulfide (MoS_2) and graphite are dispersed or suspended into the oil. These additives form metallic sulfide films and flat lubricant structures that provide excellent lubricity for very difficult machining operations.

C. Straight Oil Formulations

Oil formulation	% by wt.
Naphthenic 100 s mineral oil	90
Lard oil	2
Chlorinated paraffin	6
Sulfurized lard oil	2
	100

Straight cutting oils are used in difficult machining and forming operations. They are ideal in recirculating systems with a lot of downtime and where rancidity of the water dilutable fluid is a problem. Straight oils are very stable to degradation, provide good rust protection, and with regular removal of metal chips, are the most trouble-free metalworking fluids from a service aspect. Their limitations are higher cost, smoke and fire hazards, operator health problems, and limited tool life through inadequate cooling.

In drawing and forming operations, oils of high viscosity are valuable. The thicker, more viscous oils provide a tougher hydrodynamic lubricant barrier film. In chip removal operations, however, high-viscosity oils will not clear the chips very well and will act as an insulator, thereby further reducing the cooling properties on the tooling. The viscosity of a finished cutting oil should be low enough to clear the chips and not insulate the heat from the operation but high enough to control oil misting, a common health concern associated with the use of straight metalworking oils.

V. SOLUBLE OILS

With the changeover to carbide tooling and increased machine speeds, water-diluted metalworking fluids were developed. Soluble oils or emulsifiable oils are the largest type of fluid used in metalworking. The product concentrate, an oil fortified with emulsifiers and specialty additives, is diluted at the user's site with water to

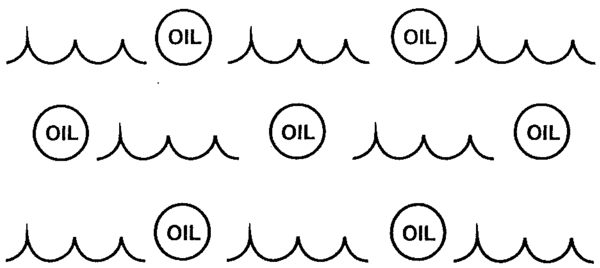


Figure 7 Oil-in-water emulsion.

form oil-in-water emulsions. Here the oil is dispersed in a continuous phase of water.

Dilutions for general machining and grinding are 1–20% in water, with 5% being the most common diluton level. Drawing compounds are diluted with less water—typically 20–50%. At rich 50% dilutions, an invert emulsion is often purposely formed with the oil as the continuous phase. This thickened lubricant has superb lubricating properties and clinging potential on the metal to avoid run-off prior to the draw.

A. Oil

The major component of soluble oils is either a naphthenic or paraffinic oil with viscosities of 100 SUS (Saybolt universal seconds) at 100°F, sometimes termed a 100/100 oil. Higher-viscosity oils can be used with greater difficulty in emulsification, but with possibly better lubricity. Naphthenic oils have been predominantly used because of their historically lower cost and ease of emulsification. Today, naphthenic oils are hydrotreated or solvent-refined to remove potential carcinogens known as polynuclear aromatics.

B. Emulsifiers

The next major class of additives in a soluble oil is the emulsifiers. These chemicals suspend oil droplets in the water to make a milky to translucent solution in water. The size of the emulsion particle determines the appearance. Normal milky emulsions have particle sizes approximately 0.002 to 0.00008 in. in diameter (2.0 to 50 μm), whereas microlike emulsions with a "pearlescent" look have emulsion particle sizes of approximately 0.000004 to 0.00008 in. (0.1 to 2.0 μm)[1]. Some compounders relate the effectiveness of the two types of emulsions to comparing basketballs to small ball bearings. One can visualize more ball bearings entering a tight metal/tooling interface for lubrication than basketballs. Others agree that

biostability can be enhanced with a microemulsion. Advantages of a standard milky emulsion are large oil droplet size for forming operations, ease of waste treatability, and lower foam than with microemulsions.

The predominant emulsifier is sodium sulfonate, which is used with fatty acid soaps, esters, and coupling agents to provide a white emulsion with no oil or cream separating out after mixing with water. Nonionic emulsifiers like nonylphenol ethoxylates, PEG esters, and alkanolamides are also used when hard-water stability or microemulsion systems are desired. Many basic soluble oils are complete with this combination of oil and emulsifier system.

C. Value Additives

Many specialty compounders include other additives to add further value to the product. Since the fluid will be diluted with water, the possibility of rust forming is introduced. Normal rust control is usually satisfactory, but this depends on the emulsifier. Some added rust inhibitors used include calcium sulfonate, alkanolamides, and blown waxes. To impart biostability along with rust inhibition, boron containing water-soluble inhibitors are coupled into the formulation.

The pH of the diluted fluid should be 8.8–9.2 to ensure rust protection, metal safety, and rancidity control. This pH should be buffered so the pH is maintained upon recirculation of the fluid. This is more attainable with amines as alkaline sources rather than caustic soda or potash.

To further control rancidity of the fluid from bacteria growth, biocides are often added to the oil. Further tankside additions will be necessary to prolong bacteria control.

The lubricity of a soluble oil comes from the oil emulsion. Because the viscosity of water-dilutable fluids is almost equal to that of water, the film strength or hydrodynamic lubrication potential is negated compared to straight oils. Lubricant additives are commonly added for medium to heavy duty operations. Boundary lubricants like lard oil, esters, amides, soaps, and rapeseed oil are used just as they were in straight oils. Likewise, chlorinated, sulfurized, and phosphorus-based extreme-pressure additives discussed earlier are popular value lubricant additives.

Defoamers are sometimes added if the product foams excessively due to the emulsifier system's properties. Both silicone and nonsilicone defoamers are used, silicone being the most effective at low doses. However, many plants forbid the use of silicone where plating, painting, and finishing surfaces will be affected because of "fish eyes" forming in the painted surface.

The advantages of soluble oils over straight oils include lower cost, since they are diluted with water; heat reduction; and the ability to run at higher machining speeds. Soluble oils are also cleaner, cooler, and more beneficial to the health of the workers because oil mists are no longer inhaled.

The advantages of straight oils over soluble oils include no rancidity, good wettability of the metal surface, good rust protection, and no destabilization problems from emulsions oiling out from hard-water buildup and bacterial attack.

The following is a typical formulation showing the proportions of the additives in a soluble oil product:

Function	Component	% by wt.
Oil	100/100 naphthenic hydrotreated oil	68
Emulsifier	Sulfonate emulsifier oil base	17
EP lubricant	Chlorinated olefin	5
Boundary lubricant	Synthetic ester	5
Rust inhibitor	Alkanolamide	3
Biocide	Biocide	2
		100

VI. SEMISYNTHETIC FLUIDS

A. Oil/Water Base

Semisynthetic fluids are similar to soluble oils in that they are emulsions and similar to synthetic fluids in that they are water-based fluids. The product concentrate usually appears to be a clear solution of additives. However, there is usually 5–20% mineral oil emulsified into the water to form a microemulsion. The emulsion particle size is 0.000004 to 0.0000004 in. (0.1 to 0.01 μm) in diameter [1]. This is small enough to transmit almost all incidental light.

B. Emulsifiers

The emulsifiers used to achieve this microemulsion combine the oil and water to form a clear blend. Alkanolamides are the most commonly used emulsifiers along with sulfonate bases, soaps, or esters as coemulsifiers. A good waste-treatable fluid would contain an amide and sulfonate base or soap package. A hard-water stable product would use a nonionic-type emulsifier along with the amide.

C. Value Additives

Couplers like fatty acids and glycol ethers may be required to regulate the clarity and viscosity of the fluid. Both oil- and water-soluble rust inhibitors are used, keeping in mind that oil-soluble additives must also be emulsified. Alkanolamines like triethanolamine are added to help buffer the pH to a good alkaline level for rust protection.

Lubricant additives can also be either oil or water soluble. Boundary lubricants and extreme-pressure additives like S, Cl, and P can fortify a semisynthetic fluid for more difficult machining operations. Water-soluble chlorinated fatty acid soaps or esters are an example of this type of additive that need not be emulsified into the microemulsion.

Many compounders also add a biocide/fungicide package to protect the product from microbial growth. Because an excess of emulsifiers is required (typically two parts emulsifiers to one part oil), a defoamer may be required. However, selection of defoamers for semisynthetics can be difficult because if the defoamer can be coupled or emulsified into the microemulsion, it will no longer defoam the fluid. If it separates in the drum of product concentrate, it is effective only if totally removed with product concentrate.

Because of the abundance of emulsifiers, the semisynthetic fluids will also emulsify tramp oil. To some users this is a plus, because they have no means of tramp oil removal and their system stays cleaner with this fluid. After time, the once translucent fluid will appear milky, much like a soluble oil. Many feel they are creating an in situ soluble oil. Others believe this acceptance of foreign oil deteriorates the quality of the fluid. Should a formulator want to make a semisynthetic that rejects tramp oil, the formulator should carefully emulsify the oil with alkanolamide. The alkanolamide must be a 2:1 amide with no fatty acid present in order to neutralize the excess mole of diethanolamine, which forms a soap.

D. Semisynthetic Formulation

Function	Component	% by wt.
Emulsifier	Sulfonate base	5
Emulsifier	Alkanolamide	15
Oil	100/100 naphthenic oil	15
Corrosion inhibitor	Amine borate	6
Coupler	Butyl carbitol	1.5
Biocide/fungicide	Triazine/pyridiethione	2
Diluent	Water	55.5
		100

The chemical additives must be mixed together first, then the water should be slowly added to obtain a clear microemulsion. The product should be quality controlled before adding the water. All adjustments should be made at this point to ensure a stable and clear product. Instability will result in a separated product that cannot be reconstituted without removal of the water.

Many users like the "semi" nature of these fluids because of the advantages of both soluble oils and synthetics without many of their individual disadvantages. The advantages of semisynthetic fluids are rapid heat dissipation, cleanliness of the system, resistance to rancidity, and bioresistance. The bioresistance is due to the small emulsion particle size and small amount of oil in the fluid for anaerobic bacteria to feed on. Rust protection and lubricity are better than in a synthetic fluid because the oil and oil-soluble additives provide a barrier film that protects from corrosion and adds lubricity. The disadvantage is foam in grinding operations, acceptance of tramp oil, and less lubricity than soluble oils.

VII. SYNTHETIC FLUIDS

Synthetic metalworking fluids are water-based products containing no mineral oil. The particle size of a synthetic fluid is typically 0.000000125 in. (0.003 μm) in diameter [1].

A. Water Base

The water in the products provides excellent cooling properties, but no lubricity. Water also causes corrosion on metal surfaces. Synthetic fluids are formulated with multiple rust inhibitors and lubricant additives to reproduce the machinability properties of oil-based products.

B. Corrosion Inhibitors

Synthetic fluids usually contain an ethanolamine for general corrosion inhibition and pH buffering capability. Synthetic corrosion inhibitors are amine borates commonly termed borate esters and amine carboxylate derivatives. These low-foaming additives are replacements for amine nitrites, which were discontinued from use due to potential carcinogenicity. Nonferrous inhibitors include benzotriazole, tolyltriazole, and mercaptobenzothiazole. An amine-free inorganic inhibitor is sodium molybdate. Basic amine–fatty acid soaps and alkanolamide also provide excellent rust protection for synthetic systems. They are also good lubricants.

C. Lubricant and Other Value Additives

Other synthetic lubricants include polyalkylene glycols and esters, both of which are low-foaming lubricants with good hard-water stability. Because of their nonionic water solubility, however, they are difficult to waste treat, which results in high COD (chemical oxygen demand) contents. Boundary and extreme-pressure lubricants must be water soluble. Boundary lubricants include soaps, amides, esters, glycols, and sulfated vegetable oils. Chlorinated and sulfurized fatty acid soaps and esters and neutralized phosphate esters provide extreme-pressure lubricity.

A fungicide is added to protect the synthetic fluid from yeast, fungus, and molds that are prevalent in these fluids. Bacteria are nearly nonexistent due to the high pH and oil-free nature of the synthetic system. Defoamers, wetting agents, and dyes are auxiliary additives found in many synthetic fluids. The wetting agents, or surfactants, reduce the surface tension of the fluid thereby promoting good coverage of the metals for lubrication.

D. Synthetic Formulation

Function	Component	% by wt.
Diluent	Water	70
Rust inhibitor	Amine carboxylate	10
pH buffer and inhibitor	Triethanolamine	5
EP lubricant	Phosphate ester	4
Boundary lubricant	PEG ester	5
Boundary lubricant	Sulfated castor oil	4
Fungicide	Pyridinethione	2
		100

Much new product development is centered around synthetic products in order to produce additive systems that provide optimal lubricity and rust protection in an easily disposed fluid. One such concept is the marriage of semisynthetic technology with synthetic chemistry. By using multiple emulsifiers to couple synthetic water-insoluble lubricants into water, a waste-treatable system is created with petroleum oil absent from the formula.

Synthetic fluids have found widespread use in multiple machining, grinding, and forming operations. They are the products of choice where clean fluids with long tank life and modest lubrication is needed.

VIII. BARRIER FILM LUBRICANTS

A. Drawing, Stamping, and Forming Compounds

In stamping, drawing, cold forming, and extrusions, barrier film-type lubricants are used as the metalworking compound.

The emulsion products used in cutting operations are often formulated differently for drawing operations. The emulsifiers used have a lower HLB value (are more oil soluble), enabling them to emulsify high levels of lubricity additives like chlorinated paraffin. In addition, a thickened emulsion can be formed with amides and esters to give the fluid a higher viscosity enabling it to cling to the metal part during the drawing operation. Blown vegetable oils and lard oils are often used as boundary lubricants because these high-viscosity oils chemically adhere to the metal surface, providing optimal boundary lubrication. Methyl lardate is added to ensure total coverage of the metal prior to the draw. Biocides are not typically used in once-through stamping and drawing applications because bacterial colonies do not grow out of control without recirculation of the fluid.

Honey oils are used in very difficult high-stress draws of heavy gauge metals. These are essentially chlorinated paraffin with surfactant added in order to aid in the subsequent cleaning of parts.

Vanishing oils are an evaporative-type lubricant used to stamp or draw where parts will not be washed. These are typically mineral spirits with a flash point of approximately 140°F with lubricant additives including lard oil, methyl lardate, chlorinated paraffin, or chlorinated solvents. After the draw the mineral spirits evaporate leaving a dry "invisible" residue.

Before chlorinated paraffins became widely used, pigmented pastes were popular drawing lubricants. They are still used in difficult operations or where the use of chlorinated lubricants is not preferred. These are calcium carbonate/fatty acid/oil-based pastes. They may also contain mica or graphite for added lubricity. They are difficult to clean and may contain a surfactant to aid in its removal [4].

B. Wire Draw Lubricants

Solid calcium stearate and other metal stearate soaps are used in wire drawing and cold heading or forming operations. Hydrated lime is mixed with tallow, hydrogenated tallow, fatty acids, or stearic acid to form flake soaps. Borax, elemental sulfur, MoS_2, and talc are added to supplement the lubricity properties.

Dispersions of MoS_2 and graphite in mineral oil are used in cold- and warm-forming operations. After zinc phosphating a metal part, sodium stearate is applied, thereby forming a zinc stearate film on the blanks. MoS_2 will then adhere to the stearate film providing an excellent solid-film lubricant up to 750°F.

C. Prelubes

Prelubes are rust preventatives applied to coil steel that also contain a drawing lubricant package so parts can be formed without cleaning and applying the drawing compound. Polymers and dry-film lubricant packages are used without any extreme-pressure additives that would be released causing staining under the extreme weight of a coil of steel.

With thickened emulsions, solid lubricant dispersions, and pastes, product stability and dispersion properties are important, as are ease of cleaning and high levels of lubricity.

Typical wire draw lubricant formulation	% by wt.
Aluminum stearate	10
Calcium stearate	20
Hydrated lime	66
MoS_2	4
	100

IX. WASTE MINIMIZATION [6]

The waste disposal of metalworking fluids is an issue affecting the choice of metalworking fluid additives. There are three criteria that can be used in assessing the waste minimization paremeters. They are waste treatability, hard-water stability, and biostability.

The rising cost of waste disposal and environmental concerns drive the need for waste-treatable additives. Additives that are stable to bacteriological degradation and hard-water salts will promote the longer tank life of a fluid, thereby requiring less frequent disposal.

A. Waste Treatability

In general, anionic additives—those with a negative charge—are the easiest to waste treat because acidification or reaction with cationic coagulants makes removal chemically possible. Nonionic additives—additives with no charge—are difficult to treat because chemical treatment methods are ineffective.

The relative water solubility of the additive also affects its relative waste treatability. The more oil soluble an additive, the more likely it will be removed from the waste stream. For example, a soluble oil that contains oil, an emulsifier base, and a chlorinated paraffin will be easy to treat as long as the emulsifier is anionic. The oil and chlorinated paraffin, having no water solubility, will be removed with the partly water-soluble emulsifier. This phenomena explains why soluble oils are easier to treat than semisynthetic fluids, which are easier to treat than synthetic fluids.

B. Hard-Water Stability

Many additives will react with the calcium and magnesium salts in the water used to dilute a fluid. These calcium complexes are not usually soluble in water, so they

TABLE 1 Waste Treatability of Additives

	Easy	Moderate	Difficult
Emulsifiers	Sulfonates Soaps Sorbitan esters Glyceryl monooleate Alkanolamides Octylphenolethoxylate (HLB 10.4)	Sulfonate base	Nonylphenolethoxylate (HLB 13.4)
Corrosion inhibitors	Calcium sulfonates Amine borates	Triethanolamine	Amine dicarboxylate
Lubricants	Amphoteric	Sulfated oils Phosphate esters	Polyalkylene glycols PEG 600 esters Block polymers Imidazolines

TABLE 2 Hard-Water Stability

	Clear	Stable haze	Precipitate or scum
Emulsifiers	Nonylphenolethoxylate (HLB 13.4)	Octylphenolethoxylate (HLB 10.4) Alkanolamides	Sulfonate Soaps Sulfonate base Soaps
Corrosion inhibitors	Amine dicarboxylates Amines Amine borates		
Lubricants	Block polymers Polyalkylene glycols Phosphate esters PEG 600 esters	Sulfated castor oil Amphoteric salt	

separate from the fluid, thus destabilizing and diluting the effectiveness of the fluid. It can be seen in soluble oils as an "oiling out" or creaming of the emulsion. It shows up as a scum or froth in synthetic fluids. By formulating metalworking fluids with additives that are not destabilized by these salts, tank life can be extended, thereby lessening the frequency of fluids disposal. The additives that are easiest to waste treat are usually the most sensitive to hard-water salts.

C. Biostability

The third criterion for determining which additives contribute to waste minimization is the bioresistance of the additives. This is the ability of an additive to slow the growth of microorganisms in the fluid. The additive essentially does not act as a food source for bacteria or mold or it may interfere with other food sources.

A study was completed that evaluated the biostability of key water-soluble metalworking fluid additives. The test used recirculating aquariums of each additive that were periodically innoculated with bacteria, yeast, and molds from typical fluids. Microbial growth was monitored to determine which additives were biosupportive, biostable (neither supportive nor resistant), or bioresistent, see Table 3.

Bioresistant chemical additives are those that contain boron, are cyclic or saturated, and are branched chained fatty acids or amine-based compounds. These include amine borates, rosin fatty acids, ethoxylated phenols, neodecanoic acid, and monoethanolamine.

Biosupportive or biodegradable chemical additives are typically fatty acids, natural fats and oils, anionics, straight-chained additives, or phosphorus-containing additives. These include soaps, amine carboxylates, sulfonate bases, lard oil, and phosphate esters.

TABLE 3 Biostability of Metalworking Additives

	Bioresistant	Biostable	Biosupportive
Emulsifiers		2:1 Tall oil amide Natural sodium sulfonate Nonylphenolethoxylate (HLB 13.4)	Alkali fatty acid soap Octylphenolethoxylate (HLB 10.4) 2:1 Fatty amide Sulfonate base
Corrosion inhibitors	Amino methyl propanol Amine borate	Triethanolamine	Amine dicarboxylate
Lubricants		600 PEG ester Polyalkylene glycol Block polymers	Sulfated castor oil Amphoteric

Bioresistant additives are difficult to waste treat, and conversely, additives that are biosupportive or biodegradable are relatively easy to waste treat. These mutually exclusive parameters make it difficult to have the best of both worlds. By combining the waste treatability, hard-water stability, and bioresistance of metalworking fluid additives, a matrix is formed (Fig. 8) that directs a formulating chemist to the best choices for a system.

For overall waste minimization the following semisynthetic bioresistant fluid formulation guide applies:

Corrosion inhibitors	Amino methyl propanol Monoethanolamine borate ester
Coemulsifiers	2:1 DEA rosin fatty acid amide Sodium sulfonate
Coupler	Branched diacid
Oil	Napthenic oil
Microbiological aids	Biocide/fungicide
Diluent	Water

X. CONCLUSION

The needs of the consumer, e.g., lubricity, tank life, or water disposability, are paramount in fluids development. For this reason, there are many variations of fluid types within any metalworking fluid compounder's product line. Custom formulations are the nature of the metalworking fluids industry.

Regulatory reporting requirements have opened the doors to metalworking fluid formulations. Once proprietary blends are now identified on safety data sheets and drum labels. New instrumental methods of chemical analysis have unveiled

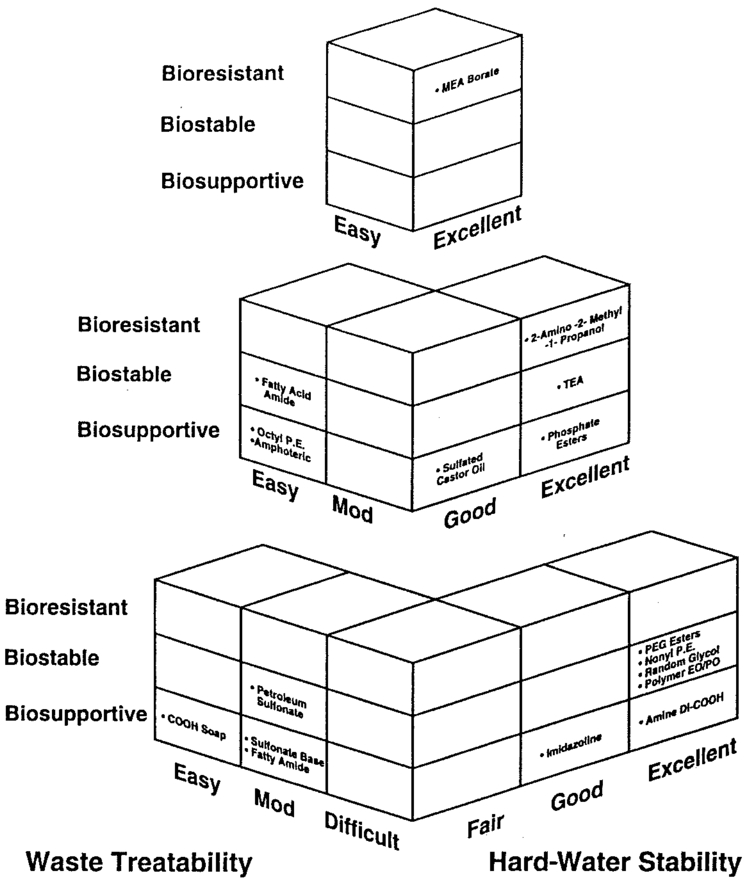


Figure 8 Waste minimization in three dimensions.

what was once closely held, confidential technology. This has placed even more emphasis on the right choice of fluid for an application.

Having developed some formulations designed for a specific task, the next chapter describes laboratory test methods for evaluating the performance and acceptability of the fluid.

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