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Understanding and controlling water dilutable metal removal fluid failure

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Introduction

Outside of the machining environment, metal removal fluids can last almost indefinitely. However, as soon as these fluids are introduced into the machining environment they begin to fail, and in some cases very rapidly. These fluids fail to such an extent that they can cause premature tool wear, damage to the tool and workpiece, and physical irritation to workers in the machining area. When these conditions occur, either all or in part, the fluids are discarded. This paper will address why metal removal fluids fail and identify methods that the end user can employ to slow down the rate of failure, increase tool life, and have a positive impact on worker safety.

Failure mechanisms

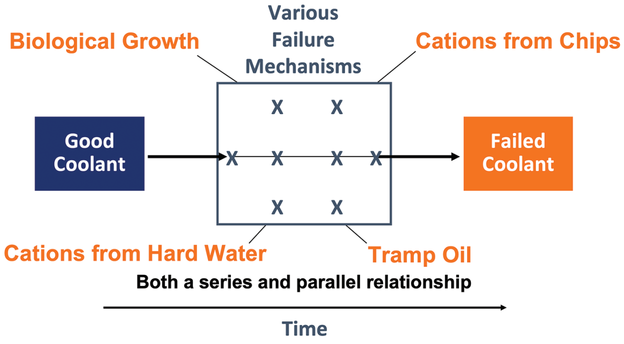

Figure 1: *Basic Failure Model – Water Diluted Metal Removal Fluids.*

Five key failure mechanisms negatively act on water-dilutable metal removal fluids (MRF). No fluid is immune to these five failure mechanisms. They are:

Category 1 MRF Failure Mechanisms:

1. Attack by positively charged contaminants.
2. Effects of negatively charged contaminants.
3. Effects of extraneous oils (tramp oils).
4. Loss of pH.
5. Effects from microorganisms (bacteria and fungus).

These five failure mechanisms are to be expected in every metal-cutting plant. However, 13 additional failure mechanisms can also be present in the metal-cutting environment. There are:

Category 2 MRF Failure Mechanisms:

1. High shear forces leading to cavitation.
2. High temperatures greater than 160°F.
3. Oxidative reactions.
4. Galvanic reactions.
5. Evaporation of alkaline components - amine loss.
6. Evaporation of light oil fractions.
7. Leaching of zinc and copper from piping systems.
8. Hydrolytic stability of bio-based esters.
9. Selective additive stripping - defoamers, oil-like components.

10. Poor cold-water mixing.
11. Freeze/thaw stability.
12. Poor initial mixing.
13. Poor grounding / stray direct currents / storage tank.

Any one of these Category 1 or 2 identified failure mechanisms can severely impact or even destroy the fluid stability and/or performance. When this happens, production rates decline, tool wear increases, residues build on machine surfaces, corrosion cells develop, foul odours increase, and worker health and safety may decline.

This paper will only address the five basic failure mechanisms and a control plan for each mechanism. Rarely will only one failure mechanism be present. It is more likely that three failure mechanisms will be present at any one time. The control plan must be implemented before the failure mechanism occurs. Once a metal removal fluid has failed, it is unlikely that it can be returned to an acceptable condition with sump-side additives. Refer to Figure 1.

Failure mechanisms and control plans

1a. Attack by positively charged contaminants: cut or ground metal surfaces

Properly formulated metal removal fluids are a careful balance of interactive chemistries. If one of the key components is neutralised or removed, the fluid will deteriorate. Most modern fluids have common negatively charged (anionic) chemistries. These chemistries are common in emulsifiable oil, semi-synthetic, and true solution synthetic fluids. These negatively charged chemistries can be from soaps, fatty acids, and wetting agents.

When metal is cut, the exposed surface has a positive (cationic) charge. Iron has two or three positive charges, aluminium has three positive charges, magnesium has two positive charges and copper has two positive charges. The freshly cut surface of the metal is highly active and reacts with the anionic chemistries in the metal removal fluid. This reaction of the cation metal surface and the anion chemistry forms an insoluble precipitate that binds to the metal chips, the metal part, or the machine surface. If the fluid is filtered, then this precipitate is removed from the metal removal fluid and it continues the failure process. Imagine links in a chain. Metal removal fluids are a balanced mixture of chemicals consisting of up to 25 raw materials. If one or two of these chemicals is partially or completely removed, then the chemical "chain" weakens or separates (i.e. fails).

It is important to note that this is a metal surface area reaction. Therefore, the more particles that are generated in the chip-making process, the more positive charges are generated because of the increased surface area. This reaction can be observed in the manufacturing environment. Single-point turning operations have a lesser effect than fine grinding or polishing operations, which have a more severe effect on fluid stability. Certain metals are more reactive than others. Grinding cast iron (a reactive metal) will generate very small particles with 2 or 3 positive charges. Single-point turning of ANSI 316 stainless steel will have a lesser effect per pound or kilogram of metal removed because less surface area is exposed in the chip-making process, and stainless steel is less reactive.

Refer to Figures 2A and 2B to understand how metal ions react with emulsions.

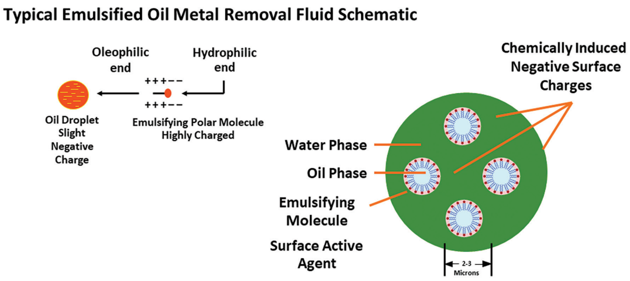

Figure 2a: *Failure Mechanism #1 - Cation Attack.*

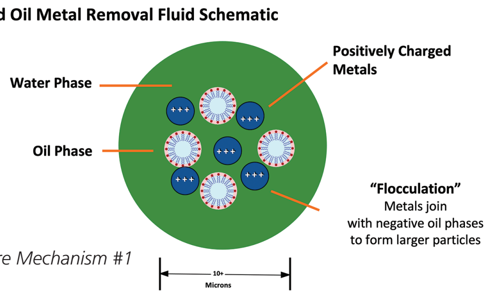

Figure 2b: *Failure Mechanism #1 - Cation Attack.*

Control plan for metals being machined:

Remove the reactive chips from the fluid as soon as possible, typically within 48 hours of the chip generation. Cations will continue to be released from chips as long as they are in contact with the fluid. Use full-flow, not side-stream filtration during the metal cutting process. When choosing your filtration media, start at 30 micron. For emulsions, do not go below 10 micron, or there is a possibility of stripping out desirable components of the metal removal fluid. Defoamers will be removed first.

Use polyester filter media instead of polypropylene. Polyester media does not have an affinity to adsorb oil, therefore it will not remove the oil phase of the fluid. If the fluid is saturated with tramp oil, polypropylene media can be used, but only for a short time or until the tramp oil is at a manageable level.

1b. Attack by positively charged contaminants: water hardness

Water harness typically consists of calcium and/or magnesium ions, and a limited amount of iron ions. The same failure effect described in 1a above is the same failure effect of water hardness releasing cations of calcium and magnesium. The failure reaction of hard water cations from water occurs in a matter of a few minutes. Since water in the manufacturing metal removal area evaporates preferentially, the cation load from the water increases over time. Metal removal systems generate a significant amount of heat (such as in a grinding operation), and evaporate the water phase rapidly, leading to an increased rate of fluid failure.

Between the cations released from the metal cut or the water supplied for dilution, the effect can be devastating on the fluid stability as well as the metal removal process.

Table 1 depicts how various cations interact in hard water, the metal removal process, and in wastewater treatment to split emulsions.

Table 1 – Common Cations

Cation	Symbol and Charge	Hard Water	Metal Removal Process	Wastewater Treatment
Zinc	Zn^{++}		X	
Calcium	Ca^{++}	X		X
Magnesium	Mg^{++}	X	X	X
Iron Ferrous	Fe^{++}		X	X
Iron Ferric	Fe^{+++}		X	X
Aluminium	Al^{+++}		X	X
Titanium	Ti^{++++}		X	

2. Effects of negatively charged contaminants

There are 5 primary anions of concern: chlorides, sulfates, phosphates, nitrites/nitrates, and carbonates.

Note that as anions build in the fluid, the fluid itself does not fail directly. It is how the fluid performs in the metal removal system that fails, either by corrosion or increased bacteria and fungus growth. Table 2 is a summary of the effect of these anions.

Table 2: Common Anions

Enemy #1	**Chloride**	**Cl**	**= Corrosion starts at 100 mg/L**
	Sulfate	SO_4	= Major Food Source
	Phosphate	PO_4	= Major Food Source
	Nitrate, Nitrite	NO_3, NO_2	= Food Source
	Carbonate	CO_3	= Food Source

Control plan for water-related issues:

Purify the water by either reverse osmosis (RO) or de-ionisation (DI). Although these two methods are dissimilar in how they purify water, the final result on the fluid is essentially the same. The target level for water purity is a total dissolved solids (TDS) concentration below 20 mg/L. By default, a low TDS will result in low calcium, magnesium, and anion levels. High TDS, above 5,500 microsiemens (µS) can result in fluid instability. In figures 2A and 2B, the water phase is considered inert and non-conductive. When the water phase becomes highly conductive with high TDS, then the charges on the emulsion droplet are less effective.

Caution

A water softener that regenerates with sodium chloride can reduce hardness by substituting calcium and magnesium ions for sodium ions but will not reduce the anions. A poorly adjusted softener can increase the chloride levels if the backwash cycle of the softener is not set properly.

Water that is used as replenishment processed by RO or DI can lead to foaming since calcium and magnesium ions can act as a defoamer. Tool life may decline since calcium soaps offer a level of boundary lubrication. Metal soaps such as iron and aluminium can also aid in boundary lubrication.

3. Effects of extraneous oils (tramp oils).

Simply stated, tramp oil is not just "oil" from one oil source. Tramp oils can be hydraulic, way, gear, and spindle oils. Hydraulic oils can contain anti-wear components such as zinc dialkyldithiophosphate (ZDDP), dispersants, demulsifiers, viscosity index improvers, and emulsifiers. Gear oil can contain sulphur compounds which are ideal food for microorganisms. The oil in various tramp oils can be paraffin-based whereas the base oil in the metal removal fluid can be naphthenic-based.

There are at least three tramp oil failure mechanisms:

a. Sharing of the emulsifier and upsetting the hydrophilic, lipophilic balance (HLB).

b. Reactivity of the ZDDP molecule. Recall that ZDDP has zinc (Zn^{++}), sulphur, and phosphorus.

c. Dispersants and demulsifiers in the hydraulic oil also upset the HLB.

Figure 3 demonstrates various reactants involving tramp oil.

Tramp oil is not just "oil"

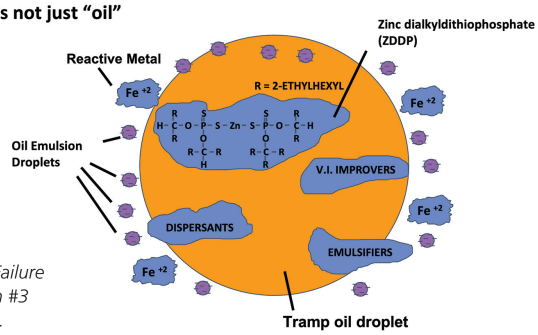

Figure 3: *Failure Mechanism #3 - Tramp Oil.*

Control plan for tramp oil:

Fix the leaks. This is the most effective plan, but it is not simple. Leaks can be ubiquitous and usually require stopping production to access the leaking components.

Use a lower additive level of hydraulic oil (if that is the source). Anti-wear and rust and oxidation-rated hydraulic oils are typically present in premium hydraulic oils. Rust and oxidation-rated hydraulic oil may be sufficient for lower-pressure hydraulic systems (less than 40 BAR).

Remove the tramp oil within 48 hours of their entrance into the fluid. This will require some type of continuous tramp oil separators such as decanting tanks or a centrifuge. Once the tramp oil is thoroughly combined into the metal removal fluid, removing the tramp oil by centrifuging will remove a portion of the metal removal fluid since the two fluids are homogeneous.

Caution

There have been some advocates that support the practice of intentionally emulsifying the tramp oil into the metal removal fluid. This is not an acceptable control plan since sulphur, phosphorus, and tackifiers can be present in the tramp oils. Machine lubricants are typically paraffin-based oils and may not be comparable with the naphthenic oils used in the base metal removal fluid. Gear oils, for example, are very high viscosity versus a lower viscosity oil in the base metal removal fluid.

4. Loss of pH.

The emulsifier packages in most emulsifiable oils and semisynthetic are designed to operate at pH ranges between 9.0 and 9.5. For non-ferrous metals, the pH would best not exceed 9.2 to avoid staining the base metal. Over time in very dry conditions, the amine packages in the metal removal fluid can selectively evaporate causing a drop in pH. Bacteria growing in and on surfaces of the machine tool and fluid sump can release acids that also lower the pH. Some steel rolling mills coat their products with "slushing oils" that may have a weak acid present that also lowers the pH.

Small pH drops from 9.3 to 8.9 may be acceptable and will not cause significant fluid damage. However, if the pH drops below 8.0, irreversible damage to the emulsifier package may occur, which will be impossible to restore.

Control plan for pH:

Discuss the acceptable ranges of pH with the manufacturer. Their typical ranges may be between 9.0 and 9.3. The use of primary and tertiary alkanolamines (MEA, TEA) may be added sump side. Less aggressive amines such as Monoisopropanolamine (MIPA), and amino-methyl propanol (AMP) may be added if there is a risk of ammonia release from the fluid.

Caution

Avoid using inorganic bases such as sodium or potassium hydroxides. These reactive bases have minimal buffering and can result in overshooting the high range of pH. (9.3). Excessively high fluid pH can be irritating to the worker, or worse, can cause severe chemical burns, as can be seen in Figure 4.

pH Ranges For Metal Removal Fluid Management

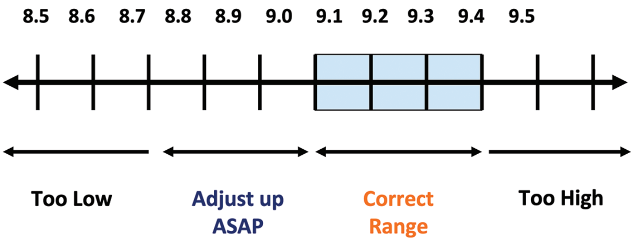

Figure 4: *Failure Mechanism #4 - Lack of pH Control.*

In all cases, add the pH-correcting fluid in small doses to prevent overshooting. Always use a calibrated (2 point, 7 & 10) pH meter and not pH paper. pH paper is difficult to read in the narrow ranges of 9.0 to 9.3, and the reactive pH surfaces of the paper lose sensitivity over time. This is especially true in high humidity conditions.

5. Effects from microorganisms (bacteria and fungus).

Bacteria and fungi can have an extremely detrimental impact on the useful life of a metal removal fluid.

Bacteria can grow rapidly, produce acids that lower pH, cause corrosion, and produce foul odors. Some types of bacteria can cause health problems such as hypersensitivity pneumonitis (HP). Bacteria can grow in the fluid and consume certain additives. They can grow on machine surfaces in the form of biofilms. They can enter metal removal systems from the water source, residues on parts, and airborne contaminants.

Fungi typically (but not exclusively) grow on the machine tool and support surfaces such as filters and associated piping. They can produce foul odors such as "sweaty socks". They can grow in lengths of more than one meter and break away, clogging filters and piping systems. They are dimensionally "thick" (centimeters or more) and are difficult to kill with fungicides.

Control plan for bacteria and fungus:

The best approach would entail the use of biostable/

bio-resistant metal removal fluids along with "dip slides" that can measure bacteria on one side and fungus on the other side. Also, be prepared to have an effective antimicrobial pesticide (i.e. biocide) dosing plan, in case it is needed.

Caution:

A biostable/bio-resistant fluid will be less likely to grow bacteria and/or fungus, however, these fluids typically require a minimum concentration to be effective. It is best to work with the fluid supplier before adding biocides. Other areas that can improve fluid life are controlling "dead spots" where fluids can stagnate and grow bacteria and/or fungus. As stated earlier, an excessive influx of tramp oil can overwhelm the best metal removal fluids. Therefore tramp oil ingress should be minimised as best as practical. Incoming water, even though safe to drink is not necessarily sterile and can also be a significant source of bacteria. Treating water by RO can minimise bacteria influx for potable water sources. Do not use rainwater or air conditioning condensate for water makeup into these fluids since these types of water sources can be highly contaminated with bacteria, fungus, and algae.

Additional steps to minimise fluid failure

Control your concentration as close as possible to the maximum level as recommended by your fluid supplier. At a minimum, check your concentration every day and make adjustments.

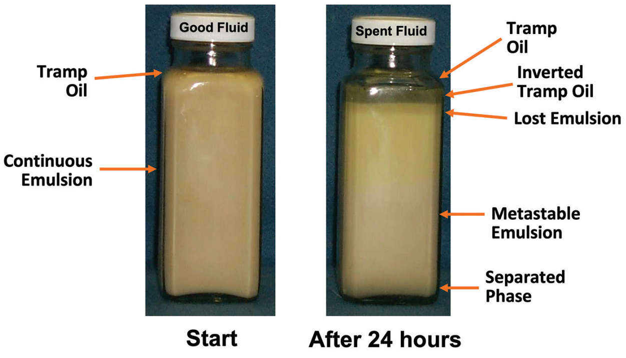

Figure 5: *Basic Demonstration of Metal Removal Fluid Stability.*

Determine fluid stability by holding a sample of the metal removal fluid in a clear glass jar for 24 hours. Take pictures before and after and compare results. If a fluid is stable, there will be minimal if any separation (see Figure 5).

In summary

Metal removal fluids will undergo some level of failure during their service life. The rate of failure can be lessened to some extent. No metal removal fluid will last indefinitely. Poor control of the metal removal fluid will cost the end user money. Over-extending the life of a metal removal fluid past the failure point, can cost the end user money through the decline of machine productivity and loss of tool life.

Control Plan Summary

1. Filter fluids well - Start at 30 micron.
2. Use good water - Low hardness and low chlorides.
3. Remove tramp oil - Continuously remove or change the tramp oil type and fix leaks.
4. Control pH - Additives are required over time.
5. Use antimicrobial pesticides (biocides) properly.
6. Measure stability - Jar test.
7. Measure and control concentration regularly – There are many fluid measurement options. At a minimum, use a hand held refractometer.

John Burke *is a consultant to Quaker Houghton specialising in fluid recycling and industrial wastewater treatment processes. He received his engineering degree in 1971. He has over 50 years of experience in the metalworking industry and 21 of those years with Quaker Houghton. He has 11 U.S. patents and over 50 international patents. He is the author of two chapters in the Third Edition of the book Metalworking Fluids. John has been an instructor for the STLE Metalworking Fluid Education Course for the past 26 years. He is a Certified Metalworking Fluid Specialist. Furthermore, he is an associate editor for the STLE Journal Tribology Transactions. He received the P. M. Ku Award from STLE in 2006 and has been a Fellow in STLE since 2011. In 2015 he received the John A. Bellanti Award for dedicated service from ILMA. John received an award from then President George Bush at the White House in 1991 for advances in waste minimisation.*

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