Emerging Technologies in Metal Working Fluids and Compatibility with Refrigeration Systems

Richard Butler
rbutler@chemtool.com

Mike Foster
mikefoster@lubrizol.com

Neil Turner
CPI Fluid Engineering, purdueherrickconf16@gmail.com

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Richard Butler[1]*, Neil Turner[2], Nicholas Bujouves[3]

[1]Chemtool, Inc., R&D Laboratory,
Rockton, Illinois, U.S.A.
(rbutler@chemtool.com)

[2]CPI Fluid Engineering, R&D Laboratory,
Midland, Michigan, U.S.A.
(netu@cpifluideng.com)

[3]CPI Fluid Engineering, R&D Laboratory,
Midland, Michigan, U.S.A.
(nibj@cpifluideng.com)

* Corresponding Author

ABSTRACT

Metal working fluids (MWF) are basically two types, metal removal (chip making) and metal forming (chip-less). MWF are used in all aspects of production fabrication of refrigeration systems. Metal removal applications typically include turning followed by finish lapping of crankshafts and piston connecting rods, also milling and finish grinding of screw compressor vanes. Metal forming applications include deep drawing of compressor housings, wire drawing, tube forming and stamping of electric motor laminations. MWF are not always completely removed before final assembly. The MWF residuals may get mixed into the refrigerant and compressor lubricant affecting system life and efficiency. To date, very little compatibility testing of residual MWF in refrigeration lubes and refrigerants has been investigated.

Unlike most lube oils, MWF are typically water-based and traditionally make very high usage of extreme pressure (EP) additives. EP additives help remove metal during the cutting process and actually increase wear. EP containing MWF interfere with compressor lube oil performance. EP are additives are known to be somewhat acidic and corrosive.

Due to environmental persistence concerns, the EPA will restrict the use of chlorinated alkanes as EP additives. Chlorinated alkanes will be phased out over the next few years and replacements are needed. It has been proved that preformed emulsions are capable of replacing traditional EP additives in MWF. Preformed emulsions allow non-traditional base “oils” to be used in MWF. These non-traditional base oils are generally very high in viscosity and viscosity index. Some of these base stocks exhibit very high film strengths under high pressures encountered in metal removal operations. These high VI and high film strength synthetic base stocks can replace corrosive EP additives without loss of machining or drawing (stamping) performance. Residual films remaining after machining are non-reactive and oil like, providing corrosion protection of in process metal parts prior to assembly. Additionally, high viscosity synthetic base stocks provide low pour points, lower volatility and less vapor interaction within a refrigeration system. Better compatibility with mostly non-polar water insoluble refrigeration lubricants are a benefit.

In the future, new refrigerants are likely to be more reactive to reduce environmental persistence.
Interactions and effects of various classes MWF with traditional compressor lubes and refrigerants are examined and reported.

1. INTRODUCTION

Manufacturing refrigeration compressors system assemblies requires a wide range of machining fluids, temporary corrosion preventatives and parts cleaning fluids. It is not common for all of the varied machining processes to be done by the same manufacturing plant in the same location. Each part utilizes separate machining skills and techniques that require special expertise. For example, an electric motor stator requires copper wire drawing, blanking insulated glass coated steel rotor laminations to hold the copper magnet wire, and rod drawing or turning of the steel motor shaft. Because all three of these operations are usually performed by different plants in separate locations by specialized companies; temporary in process corrosion preventatives are required to keep the unassembled components free of corrosion and scale. Before final assembly most parts need to be washed to remove excess machining fluid, temporary corrosion preventatives, metal fines and dirt. This paper focuses on the primary machining processes with associated process fluids and their interaction with polyol ester (POE) refrigeration lubes in common R134a systems.

Previous extensive investigations commissioned by ASHRAE (Rohatgi 2003). was limited to individual lubricant components and substances. We are looking at fully formulated metal working fluids, corrosion preventatives and parts cleaners. The difference is crucial; a free acid component un-neutralized by a free base should have dramatically different oxidation and staining behavior compared to a neutralized corrosion preventative salt or amide.

Metal working fluids have three main functions:
1) Lubricate the tool work piece interface to provide longer tool life and better surface finish on the part
2) Cool the tool work piece interface
3) Provide in-process corrosion protection

Metalworking fluids are not all oil based. In fact, only ten to fifteen percent of all metal removal or metal forming lubricants are oil based. Water dilute able MWF have several advantages over oils. Water is low cost and has a higher specific heat and higher thermo-conductivity than oil. Higher machine speeds and feeds require water based MWF for sufficient performance. Water however also brings some disadvantages. It is not compatible with oil or POE based compressor lubes. It can be corrosive and promotes microbial growth that degrade the MWF. Frequently, mineral oils are emulsified in water based metal working fluids to provide a desired oil film for in process corrosion protection. A common dilution range for water based MWF is five to fifteen percent. Before final assembly into a finished compressor the residual corrosion protecting oil may or may not be removed in parts washer. For these reasons all tested water dilute able fluids were run at two concentrations:
A) 5% to simulate unwashed parts
B) 0.5% to simulated washed parts with light residual corrosion protection film

Even washed parts must still have some light aqueous film to prevent flash rusting of the unprotected machined surfaces. Absolutely clean un-painted metal surfaces never occur with ferrous based cast iron and steels. This paper explores the interaction of POE refrigeration lubes with largely water based metal working (and polar incompatible) fluid residual films. Aluminum and copper based alloys also have specialized corrosion preventives incorporated into the water based MWF and water based parts cleaners. The nonferrous inhibitors are more efficient and present at much lower concentrations within MWF than ferrous inhibitors. Finally, extreme pressure (EP) additives are always highly polar and mostly corrosive to all alloys.

2. BACKGROUND

2.1 Metal Working Chemistries

Common chemistries to all metalworking fluids include:
I. Lubricant base stocks

   a. Mineral oils
   b. Synthetic oils such as poly alpha olefins (PAO) and polyisobutylenes (PIB)
   c. Synthetic polyalkylene glycols (PAG)
   d. Solvents and mineral seal oil

II. Friction modifiers
   a. Natural oils such as soybean oil
   b. Natural oil derived synthetic methyl esters
   c. Fully synthetic esters based upon polyhydric alcohols (POE)
   d. Waxes

III. Extreme pressure (EP) agents
   a. Chlorinated alkanes
   b. Poly sulfurized esters and olefins
   c. Mono and di esters of phosphoric acid

IV. Corrosion inhibitors (RP)
   a. Low odor low volatility bases such as triethanolamine
   b. Diacids such as sebacic acid
   c. Amides

V. Emulsifiers and surfactants
   a. Alcohol ethoxylates
   b. Fatty acid soaps
   c. Wetting agents and rinse aids

VI. Anti-microbial agents (biocides)
   a. Bactericides
   b. Fungicides

2.2 Metal Working Product Types

Table 1: MWF composition details

Metal Removal and Forming Fluids	Details	Type ID
Soluble oils are roughly 70-80% mineral oil and 20-30% emulsifiers	EP additives may or may not be present. They form milky looking emulsions.	I, L, J, N
Synthetic fluids are generally composed of PAG and EP along with large amounts of RP and biocides.	They do not contain any mineral oils. They are not emulsions	F, H
Semi synthetics are combinations of soluble oils and synthetic fluids coupled together with amides.	They form translucent micro-emulsions.	B, D
Preformed emulsions are separate class of semi synthetics utilizing a high viscosity and high viscosity index synthetic lubricant base stocks.	Upon dilution they appear to look like soluble oils.	C, G
Straight oils are non-water dilute able oils with fairly high levels of EP agents and friction modifiers.	Because they do contain any water, biocides and RP additives are not needed.	A
Corrosion Preventatives		
Solvent wax suspensions give good indoor long term protection.	Leaves oily or waxy film.	A
Synthetic water based solutions provide only short term indoor protection.	They do not contain any mineral oils. They are not emulsions	M
Parts Cleaning and Washer Fluids		
Spray *cleaners* use high pressure nozzles to remove dirt and oil residues.	Too much foam can be a problem	E, K
Soak washers use mild agitation to remove dirt and oil residues.	Foam is usually desired	E

Both types of cleaners contain significant amounts of corrosion inhibitors.

3. EXPERIMENTAL

3.1 Experimental Scope

Following the fluid classification and type ID above, the following fluids were tested. They are labeled A- N. Each is relevant to specific machining, corrosion prevention and cleaning operations found in refrigeration compressor manufacturing.

Table 2: MWF operations details

Fluid Type ID	**Description**	**Operation Suitability**
A	Solvent/wax RP oil	In process rust protection
B	High oil semi-synthetic MWF	Difficult machining
C	Preformed emulsion general purpose MWF	Difficult machining
D	Low oil semi-synthetic MWF	Light machining
E	Parts cleaner - soak or spray	Machined parts cleaner -soak
F	Synthetic general purpose MWF - no boron	Difficult machining
G	Preformed emulsion general purpose MWF	Difficult machining
H	Synthetic general purpose MWF - high boron	Light machining
I	Soluble oil MWF - no chlorine	Light machining
J	Deep draw forming - no chlorine	Difficult stamping
K	Parts cleaner - spray	Machined parts cleaner -spray
L	Soluble oil MWF - with chlorine	Difficult machining
M	Light duty synthetic water based RP	In process rust protection
N	Deep draw forming - with chlorine	Difficult stamping

Figure 1: Compressor

Figure 2: Electric Motor

3.2 Experimental Method

An accelerated aging test was used to simulate long term interactions of metalworking fluids with the ISO 32 POE lubricant in R134a compressor system.

Steel Rod and Fluid Preparation:
A continuous length of black annealed steel wire was sanded thoroughly with 120 grit Aluminum Oxide sandpaper. The wire was wiped clean with Kim wipes wetted with a small amount of acetone until no more debris was visible on the wipe. The wire was cut into rods about one inch long. Gloves were worn the while working with the metal, and changed out between sanding, wiping, and handling.

Fourteen fluids were evaluated, labeled 'A' through 'N'. Twenty-eight beakers in total were prepared and labeled according to each sample type (see Table 1). The straight oil 'A' was used at 100% concentration. Samples 'B' through 'N' were prepared in both 0.5wt% and 5.0wt% concentrations in DI water. A control was also prepared, which was only exposed to air. Three rods were submerged into each fluid preparation for ten minutes, swirled momentarily once each during that time, and were then removed with forceps. All samples were placed onto a labeled Pigmat and allowed dry in the open atmosphere overnight. The preparation and testing was performed in two separate studies – the first being Control, 'A', and 'B1'/'B2' through 'H1'/'H2'. The second series included 'I1'/'I2' through 'N1'/'N2'.

Table 3: Sample tube composition details at 0.5%

Sample Name	Fluid ID	Fluid	DI water
Control	-	0.0%	0.0%
A	A	100.0%	0.0%
B1	B	0.5%	99.5%
C1	C	0.5%	99.5%
D1	D	0.5%	99.5%
E1	E	0.5%	99.5%
F1	F	0.5%	99.5%
G1	G	0.5%	99.5%
H1	H	0.5%	99.5%
I1	I	0.5%	99.5%
J1	J	0.5%	99.5%
K1	K	0.5%	99.5%
L1	L	0.5%	99.5%
M1	M	0.5%	99.5%
N1	N	0.5%	99.5%

Table 4: Sample tube composition details at 5.0%

Sample Name	Fluid ID	Fluid	DI water
B2	B	5.0%	95.0%
C2	C	5.0%	95.0%
D2	D	5.0%	95.0%
E2	E	5.0%	95.0%
F2	F	5.0%	95.0%
G2	G	5.0%	95.0%
H2	H	5.0%	95.0%
I2	I	5.0%	95.0%
J2	J	5.0%	95.0%
K2	K	5.0%	95.0%
L2	L	5.0%	95.0%
M2	M	5.0%	95.0%
N2	N	5.0%	95.0%

Sealed Tube Preparation:
The following day, the ISO 32 POE lubricant was aspirated with nitrogen to under 10ppm water. The rods were then loaded into pre-weighed glass tubes and weighed again. Each tube was loaded with polyol ester (POE) lubricant and weighed. A photo of the fresh oil and rods was captured at this time.

A segment of each tube was stretched into a narrow neck using an oxy-propane torch. The stretched glass tubes were secured into a manifold and evacuated of atmosphere using a vacuum pump. The bottom of the tubes were submerged in a beaker of hot water while on the manifold in order to thin the lubricant and promote diffusion of dissolved gasses out of the oil. Once the bubbling of exiting gasses slowed or ceased, the tubes were then charged with a calculated pressure to each achieve around 20wt% R134a refrigerant and sealed into ampules using the torch (Rohatgi et al 2012).

Testing – Iron Content and Acid Number:
The tubes were placed in a sand bath in an oven at 175°C (347°F) for a duration of fourteen days. After the aging period lapsed, the sand baths were removed from the oven allowed to cool to room temperature. Photos were taken of the aged lubricant and catalysts in the ampules at this time. The tubes were then submerged in Dewar's containing liquid nitrogen, the glass scored, broken, and the lubricant from each triplicate was harvested together into separate pre-weighed vacuum flasks. The catalyst rods were removed and inspected more closely. Rods were placed on Pigmats and photos were captured at this time. Each sample of collected lubricant was de-gassed under vacuum on a hot-plate with a stir bar and slight heating. Free iron data was collected for the unaged lubricant and all of the aged lubricants via inductively coupled plasma – optical emission spectroscopy (ICP-OES). Acid Number (AN) measurements were then run on three blanks, the unaged lubricant, and aged samples.

Three blanks containing only 100mL AN indicator solvent were titrated to the endpoint. The weight of the indicator added to each blank flask was recorded. The volume of '0.1N KOH in Methanol' required to titrate each indicator mass was recorded and Averaged. That Average is subtracted from the endpoint volumes of each oil sample titration, and listed in the data as the "Corrected AN" - expressed in mg KOH/g Oil and defined by the equation:

$$Corrected\ Acid\ Number = \frac{((A * B) - (C * D))}{E} = \frac{mg\ KOH}{g\ OIL} \quad (1)$$

A = mL '0.1N KOH in Methanol' solution used in titration

B = 5.61mg KOH/1000mL constant (adjusted molar mass of KOH for '0.1N KOH in Methanol' solution)
C = g Indicator used in titration
D = calculated average mg '0.1N KOH in Methanol' used to neutralize Indicator blanks
E = g Oil used in titration

4. RESULTS AND DISCUSSION

After 14 days at 175C the following accelerated aging data was obtained and is graphically summarized below.

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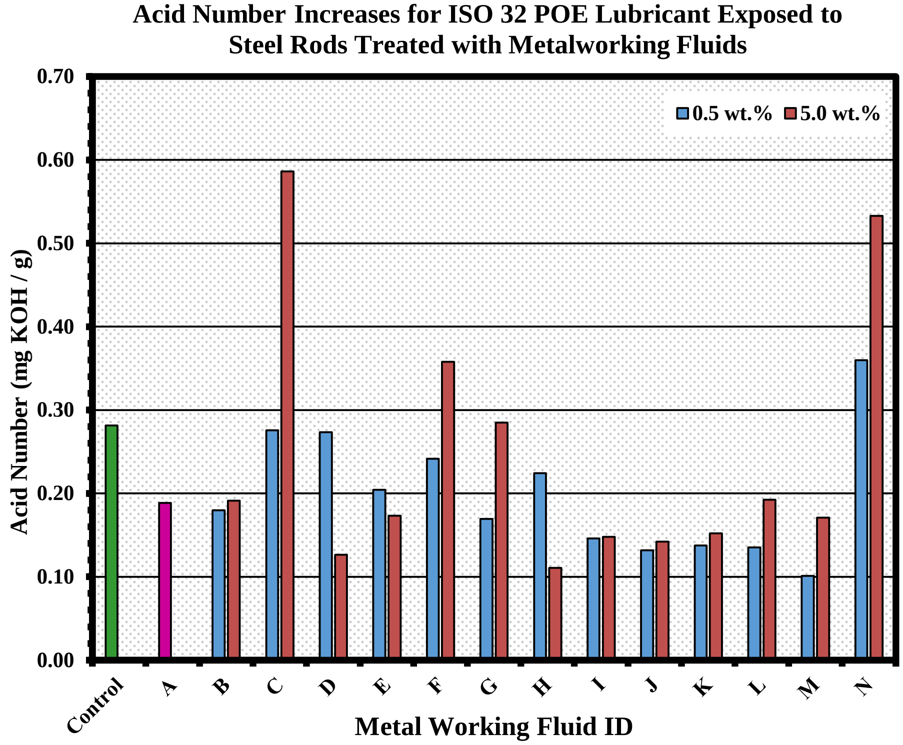


Figure 3: Acid Number Results

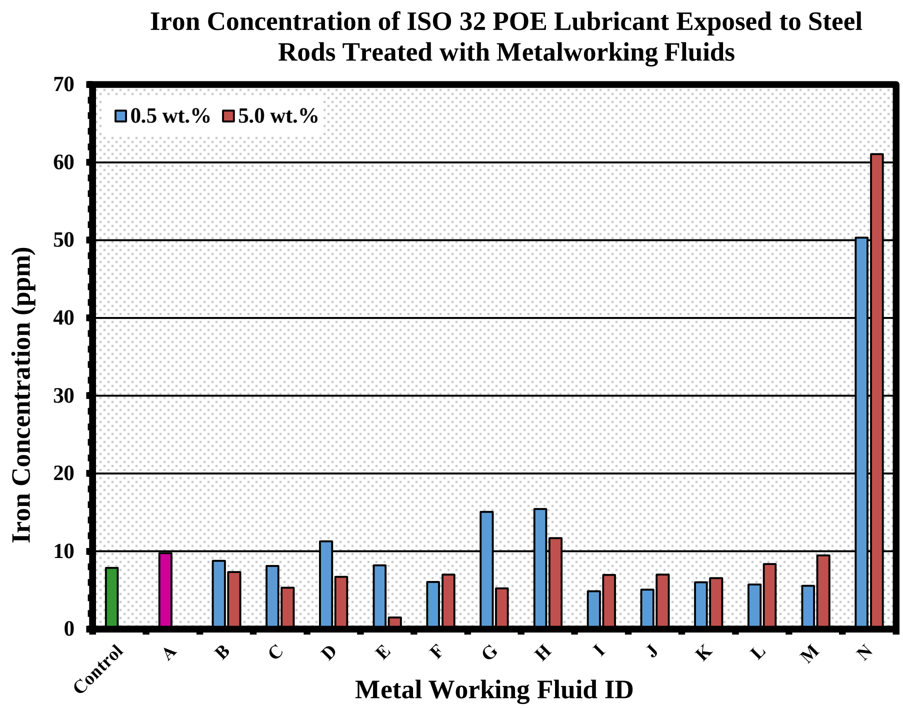
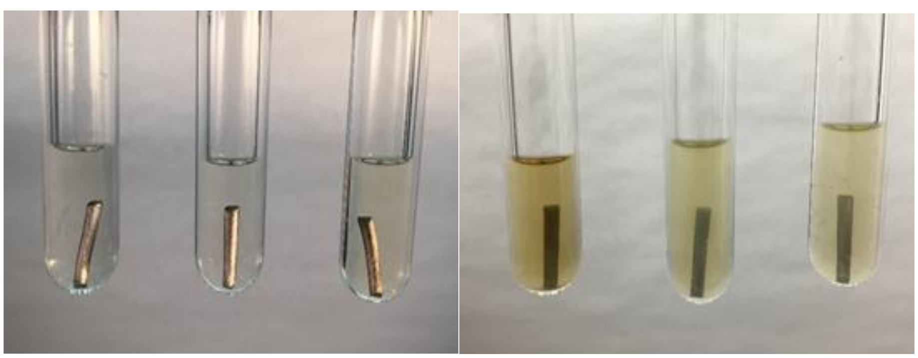


Figure 4: ICP-OES data summary



Aged Oil Appearance – Control   Aged Oil Appearance – N2

Figure 5: Final test tube appearance

5. CONCLUSIONS

Only MWF at five percent concentration with a corrected acid number less than the clean control blank 0.298 mg KOH/g are considered acceptable. Similarly, only MWF with an iron content less than clean control blank value of 7.85 ppm are considered acceptable.

- The most incompatible fluid was the deep draw forming soluble oil with high levels of chlorinated alkanes labeled as N (Rohatgi et al. 2013). Upon prolonged heating chlorinated alkanes form acid by-products causing iron corrosion and are miscible in the POE / R134a mixture. See photograph of test tubes for N2. In contrast, a similar soluble fluid without any chlorinated alkanes also able to draw deep compressor housings is labeled

J. Fluid J is acceptable both for low AN increase and low iron corrosion. This effect is repeated with lighter duty soluble for general chip removal machining. Refer to fluids I and L.

- Most fluids at 5% simulating residuals of unwashed parts had higher AN increases than fluids at 0.5% representing cleaned parts before final assembly.

- Only some fluids at 5% simulating residuals of unwashed parts had higher free iron increases than fluids at 0.5% representing cleaned parts before final assembly. It does appear that unwashed parts with residual MWF do have generally lower levels of corrosion with the exception of fluid N.

- MWF containing chlorinated alkanes should be generally avoided. Functional alternates for chlorinated alkanes exist as exhibited by fluid J.

- Boron content in the form of a corrosion inhibiting alkanol amine borates does not have any clear cut effect. Compare fluids F and H.

- Washing parts before assembly is not always beneficial for corrosion prevention but does generally reduce AN increases and corrosion.

- MWF should be screened for refrigeration lube compatibility before selection. MWF with higher levels of reactive EP additives are more prone to both acid number and free iron increases. Refer to fluids C, F, L and N.

ID	Description	Operation	Low AN Increase	Ferrous Corrosion Protection	Overall Rating
A	Solvent/wax RP oil	In process rust protection	√	X	X
B	High oil semi-synthetic MWF	Difficult machining	√	√	√
C	Preformed emulsion general purpose MWF	Difficult machining	X	√	X
D	Low oil semi-synthetic MWF	Light machining	√	√	√
E	Parts cleaner- soak or spray	Machined parts cleaner -soak	√	√	√
F	Synthetic general purpose MWF - no boron	Difficult machining	X	√	X
G	Preformed emulsion general purpose MWF	Difficult machining	√	√	√
H	Synthetic general purpose MWF - high boron	Light machining	√	X	X
I	Soluble oil MWF -no chlorine	Light machining	√	√	√
J	Deep draw forming - no chlorine	Difficult stamping	√	√	√
K	Parts cleaner- spray	Machined parts cleaner - spray	√	√	√
L	Soluble oil MWF -with chlorine	Difficult machining	√	X	X
M	Light duty synthetic water based RP	In process rust protection	√	X	X
N	Deep draw forming - with chlorine	Difficult stamping	X	X	X

Table 5: MWF Suitability with POE and R134a

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Rohatgi, N. D., (2003). *Effects of Systems Materials Towards the Breakdown of POE Lubricants and HFC Refrigerants 1158-RP*. Atlanta, Georgia, USA: American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

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