



Synergex™ neutralizing amine additives as key components of water soluble metalworking fluid rust inhibitors.

With the exit of Corfree® M1 from the marketplace, it is imperative that the amine portion of metalworking fluid rust inhibitors be adjusted to provide maximum contribution to rust protection. Synergex neutralizing amine additives¹ have anti-rust properties superior to those of commodity ethanolamines such as monoethanolamine(MEA) & triethanolamine(TEA), and they will tolerate higher carboxylate contents (with less water) when used in a water soluble metalworking fluid rust inhibitor concentrate. One such formula has been used with self emulsifying esters (SEE's), reverse block polymers and tramp oil rejecting emulsifiers in semi-synthetic metalworking fluid concentrates.

The formula for that rust inhibitor concentrate is given in table 1:

Component	Description	Weight %	Base val.	Weight equivalent	Base eq total
Water	Water	20.0000%		119.75	
Synergex	Amine	25.0000%	479	149.6	269.35
MIPA*	Amine	20.0000%	748		
			Acid val.		Acid eq total
Corfree® M1	Acid	35.0000%	509	178.15	178.150
					Base/acid ratio
Total		100.0000%			1.5

* Monoisopropanolamine

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Note that when the acid and base values are taken into consideration, the base to acid ratio is 1.5 to 1. This ratio will be maintained throughout the study. There is an unusually high level of di-acid content in this rust inhibitor, and yet it remains a liquid at room temperature. There is no need to store this product in a "hot box" prior to blending it into a metalworking fluid.

Sebacic acid, a readily available potential substitute for Corfree® M1, was used in this study. However, there are other diacids which can be considered, including dodecanedioic acid (DDDA). Note that DDDA is the majority component of Corfree® M1, and DDDA is commercially available (and forecasted to be available for the foreseeable future).² Several diacids and mixtures of diacids, neutralized with varied amines, were studied for their corrosion inhibition properties (see table 2). Five inhibitor packages were formulated @ 15% (w/w) concentrations into sample synthetic light cutting & grinding fluids, along with 15% concentration of TEA and 10% polyalkylene glycol 660, with a balance of water (~60%). The formulated sample fluids were then diluted to 3% and were used to wet cast iron chips placed on filter paper within aluminum pans. The fluid was removed, and the wet chips were evaporated to dryness overnight. Visual results of overnight corrosion are displayed in figure 1. Note that visual inspection of iron chips from various diacids neutralized with the Synergex-MIPA combination show no corrosion, whereas the chips exposed to TEA/MEA neutralized Corfree® M1 fluid display significant rust.

¹ <http://www.eastman.com/Brands/Synergex/Pages/Overview.aspx>

² <http://www.grandviewresearch.com/industry-analysis/dodecanedioic-acid-ddda-industry>

The extent of cast iron chip rust is shown in figure 1:



The formulas for the rust inhibitors are given in table 2:

	#1	#2	#3 ³	#4	#5
Description	Emerox® 1195 Synergex™	C10 & C12 Synergex	Corfree® M1 Synergex	Aqualox® 232H	Corfree® M1 MEA TEA
Water	20.00	20.00	20.00	% not known	18.00
Emerox® 1195	35.00				
DDDA		24.00			
Sebacic acid		11.00			
Corfree® M1			35.00	% not known	35.00
Synergex	25.00	25.00	25.00		
MIPA	20.00	20.00	20.00		
TEA 99				% not known	27.50
MEA				% not known	19.50

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Because only formula #5 showed rust, we conclude that Synergex/MIPA is a better amine combination than TEA/MEA for preventing rust.

At 15% by weight in the coolant concentrate, the amount TEA at 6% dilution of the metalworking fluid is 9,000 ppm. The contribution of MIPA and Synergex from 15% of the rust inhibitor is 2722 ppm, sufficient for long life activity. The rust testing was done at 3% just to stress the fluid otherwise there would be no rust at all with the fresh dilutions. Because these formulas represent synthetic metalworking fluids, there was no oil in any of the finished fluid formulas. Using Synergex and MIPA to make up the rust inhibitor instead of the more common use of TEA & MEA, allows for not only a more rust resistant formula but also one that has long life properties.

³ Formula 3 is the same as the rust inhibitor with Synergex/MIPA/Corfree® M1 from table 1 on page 1

Semi-synthetic metalworking fluid testing

The semi-synthetic work was done with a formula that contains 20% oil, 13% sulfonate/non-ionic emulsifier, 19% amine/fatty acid soap and 38% water in the concentrate. The water soluble rust inhibitor made up 6% of the formula, and the amine portion of the soap was evenly divided between primary amine (DGA) and tertiary amine (TEA LF) at 5% each. At an end use dilution of 6%, there was 3000 ppm each of primary amine, tertiary amine and about 1800 ppm from the amines in the water soluble rust inhibitor. The pH of the 6% dilution was 8.75 (formula #6), which was generally low for a long-life fluid, so we substituted MDEA for TEA LF and MIPA for DGA in the coolant formula. This resulted in a pH of about 9.20 for the 6% dilution (formula #7).

The remaining formulas for the water soluble rust inhibitors are given in table 3:

	#6 & #7	#8	#9	#10	#11	#12
Rust inhibitor ID	Aqualox® 232H	Corfree® M1 Synergex™	Sebacic acid Synergex T	Sebacic acid ⁴ Synergex T Plus	Sebacic acid DMAPF ⁵	Sebacic acid Synergex
Water	% not known	20.00	20.00	20.00	20.00	20.00
Sebacic acid			30.00	30.00	30.00	30.00
Corfree® M1	% not known	35.00				
Synergex		25.00				20.00
MIPA		20.00	20.00	25.00	25.00	20.00
Synergex T			30.00			
Synergex T Plus				25.00		5.00
DMAPF ⁵					20.00	
MEA	% not known				5.00	
TEA	% not known					

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A total of seven semi-synthetic formulas were tested. Two formulas using Aqualox® 232H, formula #6 where DGA & TEA are the neutralizing amines and the remaining formulas where MDEA & MIPA neutralize the fatty acid in the semi-synthetic metalworking fluid. After four challenges the pH of all seven solutions is 9.0 and above except the original formula with DGA & TEA. The results of the cast iron chip testing are pictured in figure 2. As expected, formula #6 with DGA & TEA LF showed rust at 3% concentration after four challenges. All but one of the remaining six formulas, in which MDEA and MIPA were substituted for DGA & TEA, did not show any rust at 3% concentration after four challenges. Only formula 9 which uses Synergex T in the rust inhibitor portion of the formula showed a little rust. Synergex T is the most water soluble of the Synergex neutralizing amine additives.

⁴ There is no Synergex LA (lipophilic amine) in this study because it is too oil soluble to form a water soluble soap with the usual acids and diacids typically used in these water soluble rust inhibitors.

⁵ DMAPF is a developmental project. It is the formamide of DMAPA (dimethylaminopropylamine).

Figure 2



Because the semi-synthetic formula contains both biocide and fungicide as well as long life amines, it was not expected that any appreciable microbial growth would take place over the course of an eight-week challenge study. The challenges were designed to stress the rust inhibiting properties of these fluids. More importantly, through four challenges, the odor of these solutions has remained bland and has not taken on any "rotten egg" smell, even though the challenge solution is black and has that very strong odor. When the metalworking solutions are first challenged, they turn grey, but within two days they turn back to a tan color without any odor. The combination of sebacic acid and Synergex™ neutralizing amine additives is more than adequate for rust inhibition in these types of metalworking fluids.

Lastly, it should also be pointed out that long-life metalworking fluids are designed to be used at a specific concentration in order to get the full effect of the synergy between alkyl amino alcohols such as Synergex neutralizing amine additives and anti-microbial additives such as biocides and fungicides. The rust test being run at 3% is one half of the operating concentration of 6%, and yet there is enough rust inhibition even after four challenges. These challenges were specifically designed to demonstrate deterioration of the rust protection of the metalworking fluid mainly through a decrease in pH of the test fluid. The resulting information demonstrates that sebacic acid can substitute for Corfree® M1 in a semi- synthetic metalworking fluid by upgrading the amine portion of the water soluble rust inhibitor over the usual MEA/TEA combination.

The combination of Synergex neutralizing amine additives and MIPA give better rust protection than the combination of MEA & TEA in a water soluble rust inhibitor.

The use of Amietol® M-12 (MDEA) and MIPA with fatty acids like TOFA has a longer lasting pH boost than TEA LF & DGA.

Sebacic acid and Synergex amine additives are an excellent alternative to Corfree® M1.

To learn more about Synergex, visit
www.SynergexAmine.com

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