Optimizing Metalworking Fluid Performance

with Primary and Tertiary Amines

Michael D. Gernon, Guy Verdino & Robert Ash at STLE 2017

TAM-4936 | 6/17

Today's discussion

A) Acid/Base content: an important parameter to know before the reformulation efforts start
B) Determination of acid/base quantity
C) Determination of acid/base strength
D) Amines as bases
E) The formulator's spreadsheet: include the acid/base ratio
F) What is the best amine?
G) Many properties to consider; Pow is an important one
H) Conclusions

Acid/Base content, quantity & strength

Acid value & base value measurements

A procedure that converts the quantity of acid or base present to a common standard of mg KOH needed to neutralize (for acids) or mg of “virtual” KOH available (for bases) per gram of material.

Note that acid and base values accurately tabulate the amount of acid or base present but not the strength. Bases weaker than KOH are treated on an equivalent for equivalent basis the same as KOH, and all acids titratable by KOH are treated the same.

$$\text{Acid Value} = \frac{\text{mg KOH needed}}{\text{g of material}}$$

$$\text{Base Value} = \frac{\text{mg KOH supplied}}{\text{g of material}}$$

Acid values

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Use a direct titration of a massed amount of material by KOH(aq) to an appropriate (usually alkaline) endpoint.

<u>Guy Verdino’s Titration Method:</u>

Weigh about 1.0 g of the substance into a 250-mL flask. Add 50 mL of a mixture of equal volumes of ethanol and ether, both of which have been neutralized with potassium hydroxide. Add about 1 mL of phenolphthalein/ethanol indicator and heat, if necessary, until the substance has completely dissolved. Cool and titrate with potassium hydroxide (≈ 0.1 N), constantly shaking the contents of the flask until a pink color persists for 15 seconds. Note the number of mL required (V)

Calculate the acid value from the following formula:

$$\text{Acid Value} = \frac{V\ \cancel{\text{ml titrant}} \times N\ \dfrac{\cancel{\text{mequiv KOH}}}{\cancel{\text{ml titrant}}} \times \dfrac{56.1\ \text{mg KOH}}{\cancel{\text{mequiv KOH}}}}{G\ \text{grams of acidic material}}$$

One convenient thing about Acid Values and Base Values is that they allow for a quick determination of the mass of a given basic material needed to neutralize a given mass of an acidic material.

$$\text{Mass Acidic Material} = \frac{\text{Mass Basic Material x Base Value}}{\text{Acid Value}} \qquad \text{Mass Basic Material} = \frac{\text{Mass Acidic Material x Acid Value}}{\text{Base Value}}$$

$$\text{Acid Value} = A = \frac{(56.1) \times (VN)}{G} \quad \frac{\text{mg KOH needed to Titrate}}{\text{gram of amine}}$$

(VN) = mequiv. base used = mequiv. of acid present.

$$VN \ \cancel{\text{milliequiv. acid}} \times \frac{1 \text{ equiv. acid}}{1000 \ \cancel{\text{milliequiv. acid}}} = \frac{VN}{1000} \text{ equiv. of amine}$$

$$\text{Acid Apparent Equivalent Weight} = EW = \frac{1000 \times G}{VN} = \frac{56.1 \times 1000}{A} = \frac{56,100}{A}$$

$$EW = \frac{56,100}{A} \qquad A = \frac{56,100}{EW}$$

For an Acid Value, the apparent EW is only valid if a pure sample is tested. If the material is in solution, then G must be multiplied by the mass fraction concentration of the acid to get an accurate EW.

Acid Value picks up both protons from dicarboxylic acids without differentiation

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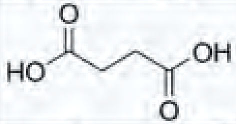
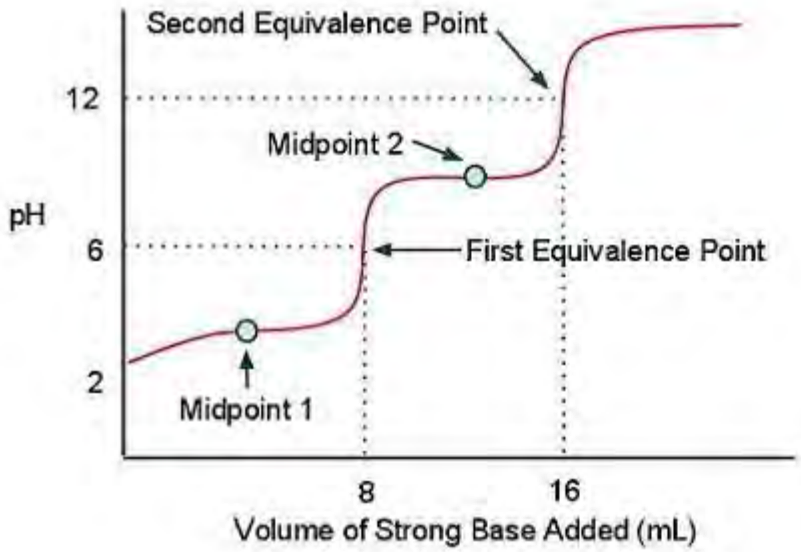
n	Common name	Systematic IUPAC name	Structure	pK_a1	pK_a2	PubChem
0	Oxalic acid	ethanedioic acid		1.27	4.27	971
1	Malonic acid	propanedioic acid		2.85	5.05	867
2	Succinic acid	butanedioic acid		4.21	5.41	1110
3	Glutaric acid	pentanedioic acid		4.34	5.41	743
4	Adipic acid	hexanedioic acid		4.41	5.41	196
5	Pimelic acid	heptanedioic acid		4.50	5.43	385
6	Suberic acid	octanedioic acid		4.526	5.498	10457
7	Azelaic acid	nonanedioic acid		4.550	5.498	2266
8	Sebacic acid	decanedioic acid				5192
10		dodecanedioic acid				12736
11	Brassylic acid	tridecanedioic acid				10458
12	Thapsic acid	hexadecanedioic acid				10459

versus Potentiometric Titration



Titration Curve of a Weak Diprotic Acid

Source: Wikipedia

Representative procedure for base value determination

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Source: SurfaTech Brochure

<u>SurfaTech Analytical Methodology Table of Contents</u>

ANALYTICAL METHOD

M-003 -- Base Value

Scope:

This method is applicable to all products which require a phenolphthalein endpoint such as hydroxyl value correction and assaying KOH and NaOH.

Summary:

The sample is dissolved in neutralized 3A alcohol and titrated to a phenolphthalein endpoint using a dilute solution of hydrochloric acid. The results are reported internally as "Strong" base value.

Apparatus:

1. Erlenmeyer flasks, 250 mL.
2. Burette, 10 mL class A.
3. Analytical balance, capable of determining weights to three decimal place accuracy.
4. Steam bath or hot plate.
5. Stir plate.
6. Stir bars.

Reagents:

1. Hydrochloric acid (HCl), 0.1N in 3A (Standardized using LTC-0030).
2. Hydrochloric acid (HCl), 0.5N in 3A (Standardized using LTC-0030).
3. 3A alcohol absolute, 95:5:5 ethanol/methanol/IPA, reagent grade (neutralized to first phenolphthalein endpoint).
4. Phenolphthalein indicator solution, 1.0% in ethanol.

Procedure:

1. Using Table I as a guide, weigh an appropriate amount of sample into a tared Erlenmeyer flask. Record the weight.

2. Add about 75 mL of neutralized 3A alcohol and a few drops of phenolphthalein indicator solution. Place a stir bar in the flask and mix thoroughly to dissolve sample, using heat if necessary. Allow the sample solution to cool to room temperature before titrating.

3. Titrate with the appropriate HCl solution (See Table I) until the pink color disappears from the sample solution. Record the volume of titrant used to reach this endpoint. Using Equation 1 in the Calculations section of this method, determine the amine value. Report this value to one decimal place.

Calculations:

$$\text{Base Value} = \frac{(\text{mL of titrant})(\text{N of titrant})(56.1)}{(\text{sample wt.})}$$

Endpoint determines strength of bases counted as KOH

Sample Weight Needed to Obtain a Titration Volume Under 7 mL

Expected Base Value	Wt. of Sample (+10%), g	Titrating Solution
0 to 1	20	0.1 N HCl
1 to 4	10	0.1 N HCl
4 to 15	2.5	0.1 N HCl
15 to 75	0.5	0.1 N HCl
75 to 375	0.5	0.5 N HCl
375 to 1875	0.1	0.5 N HCl

Amines as Bases

Amine value: a unique sort of base value

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$$\text{Amine Value (amine number)} = \text{Base Value} = \frac{\text{mg KOH}}{\text{g amine}} = \frac{\text{mg KOH}}{\text{1000 mg amine}} = A$$

Where mg KOH is the mass of KOH necessary to titrate the amount of acid required to titrate one gram of the amine.

Volume Acid Titrant in ml = V   Normality of Acid Titrant = N   Grams of Amine = G

KOH: GMW = GEW = 56.1 grams/mole = 56.1 grams/equivalent

$$A = \frac{V\,(\cancel{\text{ml titrant}}) \times N \dfrac{\cancel{(\text{mequiv acid})}}{\cancel{(\text{ml titrant})}} \times \dfrac{1\ \cancel{\text{mequiv KOH}}}{1\ \cancel{\text{mequiv Acid}}} \times \dfrac{56.1\ \text{mg KOH}}{\cancel{\text{mequiv KOH}}}}{\text{G (grams of amine)}}$$

$$\text{Amine Value} = \text{Amine Number} = A = \frac{(56.1) \times (VN)}{G} \quad \frac{\text{mg KOH}}{\text{gram of amine}}$$

$$\text{Amine Value} = \text{Amine Number} = A = \frac{(56.1)\times(VN)}{G}\ \frac{\text{mg KOH}}{\text{gram of amine}}$$

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(VN) = mequiv. H^+ consumed = mequiv. of amine base OH^- equivalents.

$$VN\ \sout{\text{milliequiv. amine}} \times \frac{1\ \text{equiv. amine}}{1000\ \sout{\text{milliequiv. amine}}} = \frac{VN}{1000}\ \text{equiv. of amine}$$

$$\textbf{Amine Equivalent Weight} = EW = \frac{1000 \times G}{VN} = \frac{56.1 \times 1000}{A} = \frac{56,100}{A}$$

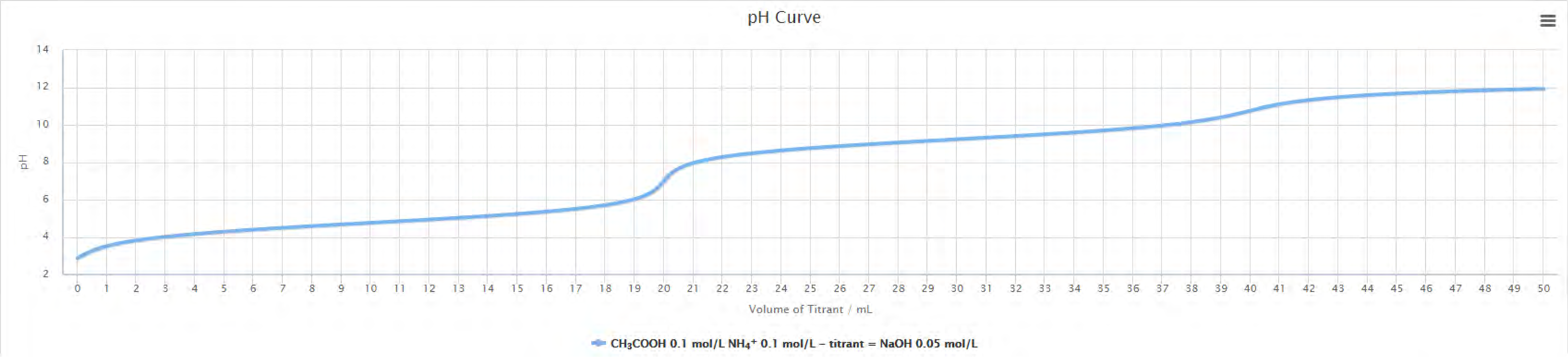
$$EW = \frac{56,100}{A} \qquad A = \frac{56,100}{EW}$$

Assuming a pure amine is used. If the original amine sample is a solution, then G must be multiplied by the mass fraction of amine in the solution to get an accurate EW. The amine solution solvent must also be "blanked".

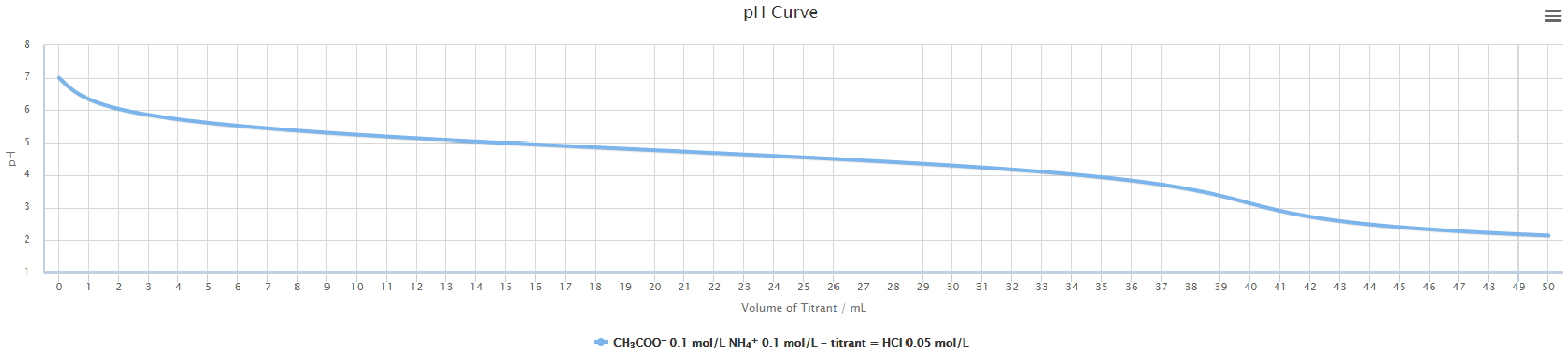
Note that an "Amine Value" implies a purified amine sample whereas a "Base Value" or "Acid Value" can apply to any type of mixture with some net excess base.

Various ways to determine the base/amine value

One can add an excess of acetic acid (helps to decarbonate the amine) and back titrate with base.



Titrate an acetic acid neutralized base with an acid stronger than acetic acid



From Wikipedia; test method TBN ASTM D2896: A sample is typically dissolved in a pre-mixed solvent of chlorobenzene and acetic acid and titrated with standardized solution of perchloric acid in glacial acetic acid for fresh oil samples. The end point is detected using a glass electrode.

Amines	Amine (Base) Value (mg KOH/gram amine)	Apparent Equivalent Weight
MEA	920	61
MIPA	748	75
Morpoline	645	87
AMP 95	591	95
Triazine Biocide	578	97
DEA	534	105
Synergex	479	117
MDEA	471	119
45% KOH	450	125
DMAPF	432	130
DIPA	422	133
Corrguard EXT	387	145
TEA 99	377	149
DIPA 85	367	153
Synergex T	348	161
TEA LF	327	171
Synergex LA	324	173
DCHA	309	181
TIPA	294	191
Synergex T Plus	259	217
Toly Triazole 50%	195	288

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$$EW = \frac{56{,}100}{A} \qquad A = \frac{56{,}100}{EW}$$

Acid values

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Example	Acid Value	Apparent Equivalent Weight
Boric Acid	905	62
Eastman™ 1,4-CHDA-HP	652	86
Sebacic acid	555	101
Octenyl succinic anhydride	534	105
Corfree M1	510	110
Octenyl succinic acid	492	114
Isononanoic acid	355	158
Undecylenic acid	305	184
TOFA 28	191	293
Dover EM 706	155	362
Mayfree 133	155	362
Mayfree NCL2	125	449
Maylube 830	72	779
Maylube S003	20	2805
Doverlube NCEP	10	5610
Klorfree 100	5	11220

$B(OH)_3 + KOH \rightarrow KB(OH)_4$

diprotic acid

diprotic acid

hydrolyzed to diacid; not pure

diprotic acid

$$EW = \frac{56{,}100}{A}$$

$$A = \frac{56{,}100}{EW}$$

The formulator’s spreasheet

Light duty full synthetic formula I

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Original formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	65.80			
Secondary amine A	Amine	8.75	479	41.91	
DCHA	Amine	4.50	309	13.91	60.32
45% KOH	Amine	1.00	450	4.50	
			Acid value		**Acid eq. total**
Boric acid	Acid	3.50	905	31.68	
C6 to 12 Diacid blend	Acid	4.25	509	21.63	59.41
Isononanoic acid	Acid	1.50	355	5.33	
Acid phosphate	Acidic	0.50	155	0.78	
PAG	Nonionic	8.00			
Anti-microbial	Biocide	2.00			
Anti-foam	Anti-foam	0.20			
					B/A ratio
Total		100.00%			1.02

Modified formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	68.95			
MDEA	Amine	5.00	471	23.55	
DBAE	Amine	3.00	324	9.72	60.81
MEA	Amine	3.00	918	27.54	
			Acid value		**Acid eq. total**
Boric acid	Acid	3.50	905	31.68	
Sebacic acid	Acid	3.30	555	18.32	59.82
Isononanoic acid	Acid	2.55	355	9.05	
Acid phosphate	Acidic	0.50	155	0.78	
PAG	Nonionic	8.00			
Anti-microbial	Biocide	2.00			
Anti-foam	Anti-foam	0.20			
					B/A ratio
Total		100.00%			1.02

(blue)	Bases
(yellow)	Acids

Revised light duty full synthetic formula I

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Original formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	52.20			
TEA 99 LFG	Amine	17.50	327	57.23	
MEA	Amine	9.00	918	82.62	147.95
45% KOH	Amine	1.80	450	8.10	
			Acid value		**Acid eq. total**
Boric acid	Acid	7.00	905	63.35	
Corfree M1	Acid	8.50	509	43.27	118.82
Isononanoic acid	Acid	3.00	355	10.65	
Dover EM 706	Acidic	1.00	155	1.55	
					B/A ratio
Total		100.00%			1.25

Modified formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	56.30			
Amietol M12	Amine	8.00	471	37.68	
Synergex LA	Amine	6.00	324	19.44	148.92
MEA	Amine	10.00	918	91.80	
			Acid value		**Acid eq. total**
Boric acid	Acid	7.00	905	63.35	
Sebacic acid	Acid	6.60	555	36.63	119.64
Isononanoic Acid	Acid	5.10	355	18.11	
Dover EM 706	Acidic	1.00	155	1.55	
					B/A ratio
Total		100.00%			1.25

(blue)	Bases
(yellow)	Acids

Heavy duty full synthetic formula

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Original formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	62.75			
TEA 99	Amine	5.00	327	16.35	
MEA	Amine	5.00	918	45.90	74.30
Triazine Biocide	Amine	2.00	578	11.56	
Toly-Triazole 50%	Basic	0.25	195	0.49	
			Acid value		**Acid eq. total**
Corfree M1	Acid	5.00	509	25.45	33.20
Mayfree 133	Acidic	5.00	155	7.75	
220 cSt PAG		15.00			
					B/A Ratio
Total		100.00%			2.24
Modified formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	61.50			
Synergex LA	Amine	5.00	324	16.20	
MEA	Amine	5.00	918	45.90	73.81
MIPA	Amine	1.50	748	11.22	
Toly-Triazole 50%	Basic	0.25	195	0.49	
			Acid value		**Acid eq. total**
Octyl succinic anhydride	Acidic	4.75	534	25.37	33.12
Mayfree 133	Acidic	5.00	155	7.75	
220 cSt PAG		15.00			
BIT 20		2.00			
					B/A ratio
Total		100.00%			2.23

(blue)	Bases
(yellow)	Acids

Revised heavy duty full synthetic formula

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Original formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	62.75			
TEA 99	Amine	5.00	327	16.35	
MEA	Amine	5.00	918	45.90	74.30
Triazine biocide	Aminic	2.00	578	11.56	
Toly-triazole 50%	Basic	0.25	195	0.48	
			Acid value		**Acid eq. total**
Corfree M1	Acid	5.00	509	25.45	33.20
Mayfree 133	Acidic	5.00	155	7.75	
220 cSt PAG		15.00			
					B/A ratio
Total		100.00%			2.29
Modified formula					
Component	**Description**	**%BW**	**Base value**	**Weight equivalent**	**Base eq. total**
Water	Water	61.65			
Synergex T	Amine	5.00	348	17.40	
MEA	Amine	5.00	918	45.90	75.01
MIPA	Base.	1.50	748	11.22	
Toly-triazole 50%	Basic	0.25	195	0.48	
			Acid value		**Acid eq. total**
Sebacic acid	Acidic	4.60	555	25.53	33.28
Mayfree 133	Acidic	5.00	155	7.75	
220 cSt PAG		15.00			
Bit 20		2.00			
					B/A ratio
Total		100.00%			2.25

(blue)	Bases
(yellow)	Acids

What is the best amine?

Amine choice is a formulator’s decision

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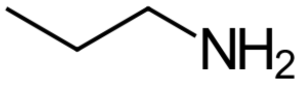
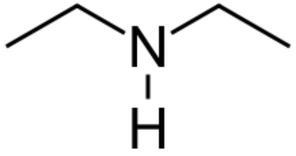
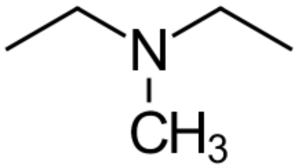
Examples of Amines



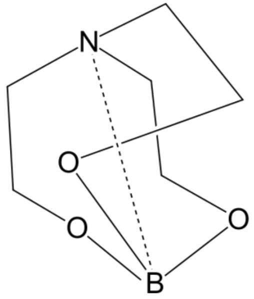
Primary
1°



Secondary
2°

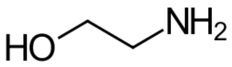


Tertiary
1°

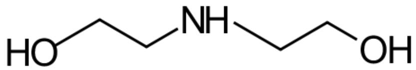


Boratrane
TEA + Boric Acid

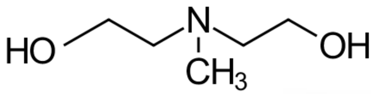
A) Hydrophobic versus hydrophilic
B) Volatile (odorous) versus non-VOC
C) Alkanolamine versus alkylamine
D) Functional (e.g., corrosion Inhibitor) versus pH adjustment



Monoethanolamine



Diethanolamine



N-Methyldiethanolamine

Properties to consider

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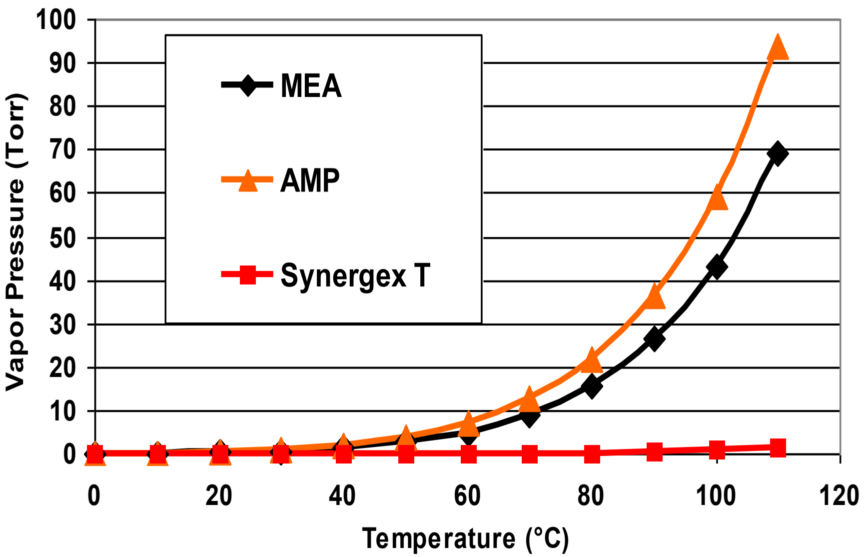
What properties of an amine are ideal?

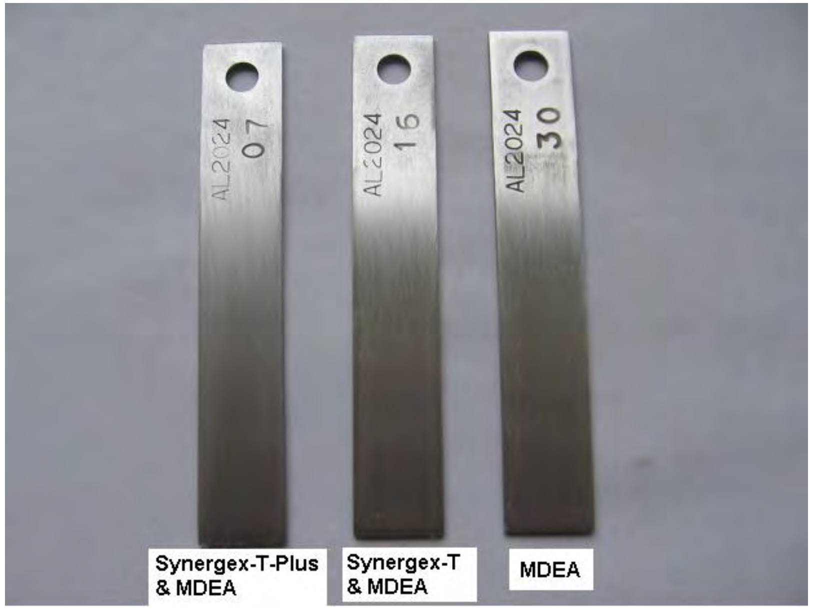


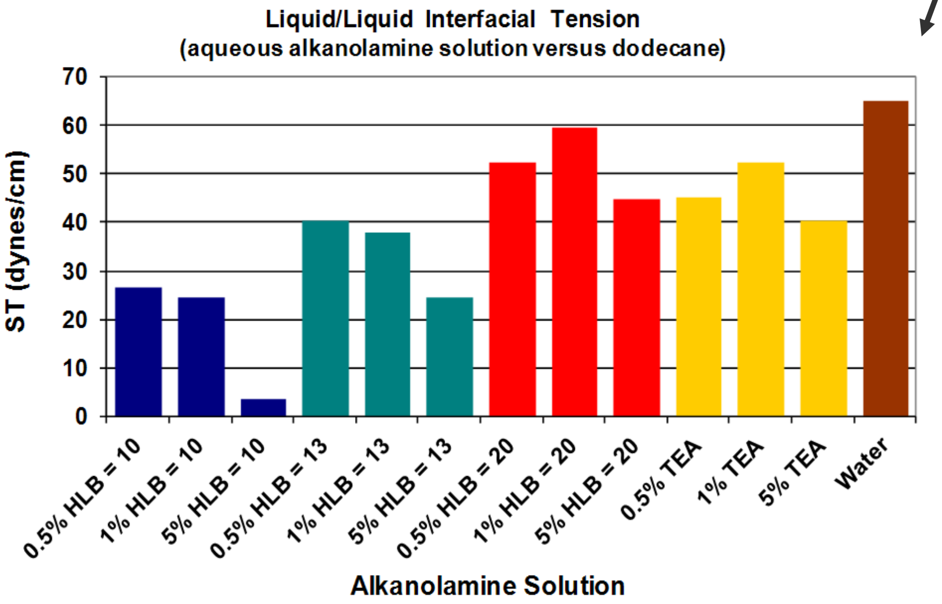
Odor/Volatility

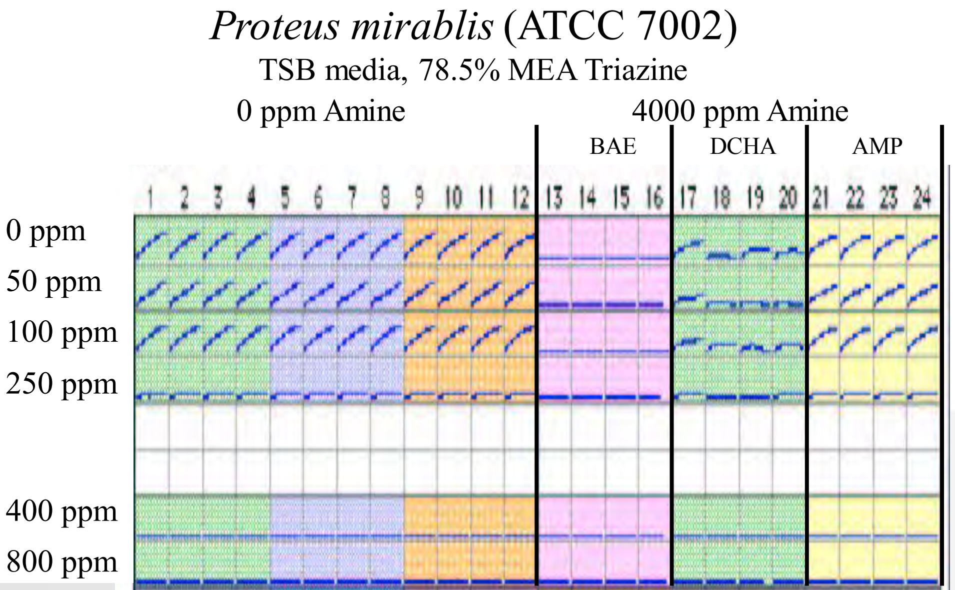
Staining

Emulsion Stability

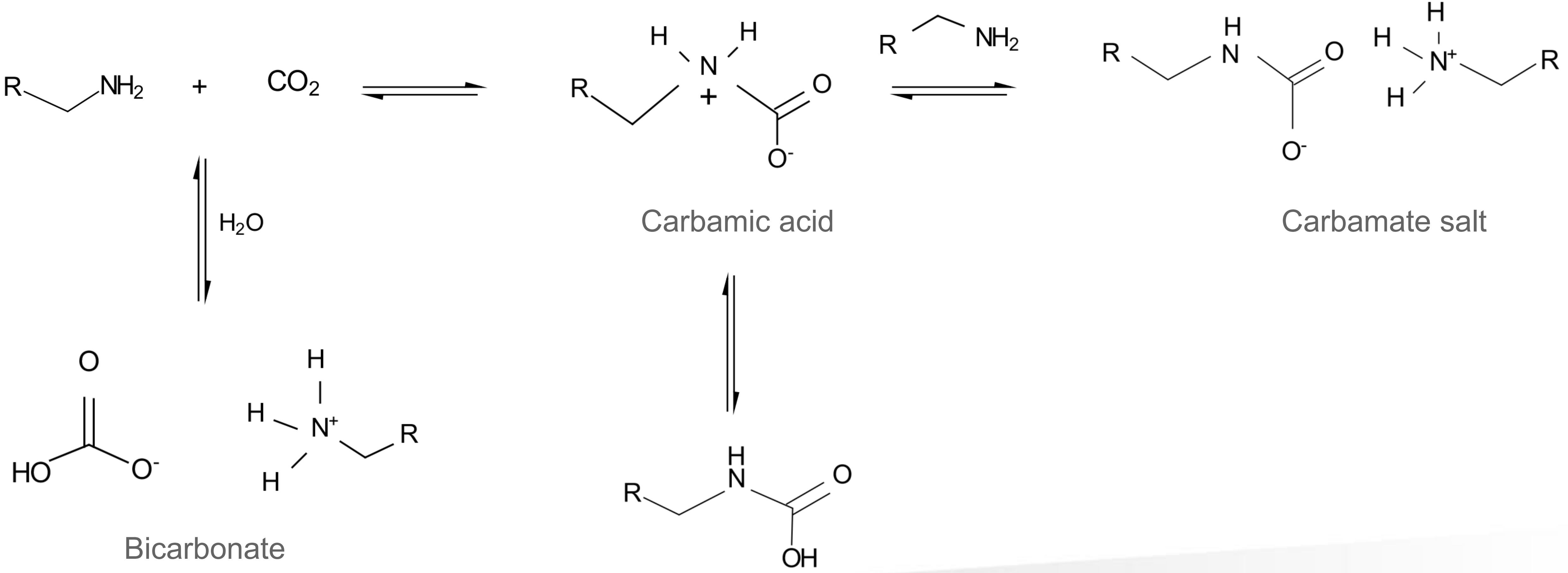
Biostability







How does the chemistry of primary/secondary/tertiary amines differ?



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Technical Data Sheet

Di-N-Butylaminoethanol
CAS No. 102-81-8

Chemical Synonym

Di-N-Butylaminoethanol; 2-(dibutylamino)ethanol; Dibutylethanolamine; DBAE; DNBAE

Application/Uses

- Inks

Product Description

Di-n-butylaminoethanol (DBAE) is available as a colorless liquid with an ammoniacal odor.

DBAE, an oil soluble alkanolamine, is useful in fuel additives and as a neutralizing agent in thermally cured coatings.

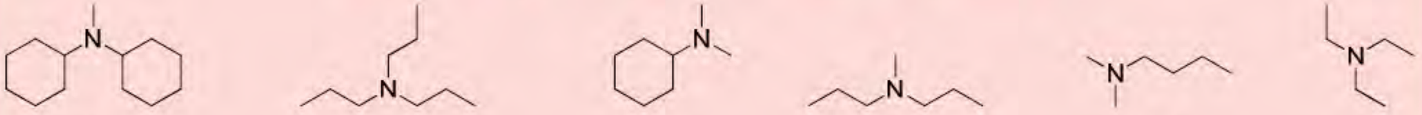
Typical Properties

Property	Typical Value, Units
Molecular Formula	$(C_4H_9)_2$-N-C_2H_4-OH
Molecular Weight	173.3 g/mol
Autoignition Temperature	165°C
Boiling Point	227.3°C
Coefficient of cubical expansion	0.00082/°C
Density @ 20°C	0.8601 g/cm^3
Dissociation constant, pKa	10.26
Flash Point Closed Cup	96°C
Freezing Point	-75°C
Octanol-water partition coefficient, log Pow @ 20°C	1.86
Solubility @ 20°C	
DBAE in water	0.4% (slightly soluble)
Water in DBAE	6.8%
Vapor Density	6.0 g/cm^3
Vapor Pressure @ 20°C	<0.05 hPa
Viscosity @ 20°C	7.48 mPa·s

Switchable-Hydrophilicity Solvents for Product Isolation and Catalyst Recycling in Organocatalysis

Julia Großeheilmann,[a] Jesse R. Vanderveen,[b] Philip G. Jessop[b] and Udo Kragl[a]

$$NR_3 + CO_2 + H_2O \leftrightarrows [NR_3H^+][HCO_3^-]$$



1a	1b	1c	1d	1e	1f
3.79	2.83	1.99	1.95	1.51	1.26

Figure 1. The amines used in this study. The number in plain font is the predicted log K_{OW} whereas the number in bold font is the compound number.

log(P_{OW}) for switchable amine solvents is
1.8 < Ideal log P_{OW} < 2.0

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Image 1

test formula

Coolant formula	%
100-second naphthenic oil	55.00
Soap sulfonate emulsifier	15.00
Alkanolamide emulsifier	15.00
Tall oil fatty acid	2.00
10 HLB nonionic surfactant	3.00
MIPA	5.00
AAA	5.00
Total	100.00

By diluting the fluids to 6%, both the MIPA and AAA are used at 3000 ppm for an amine total of 6000 ppm. Triethanolamine 99 was compared to Amietol™ M12, and DCHA was compared to Synergex, Synergex LA, and Synergex T.

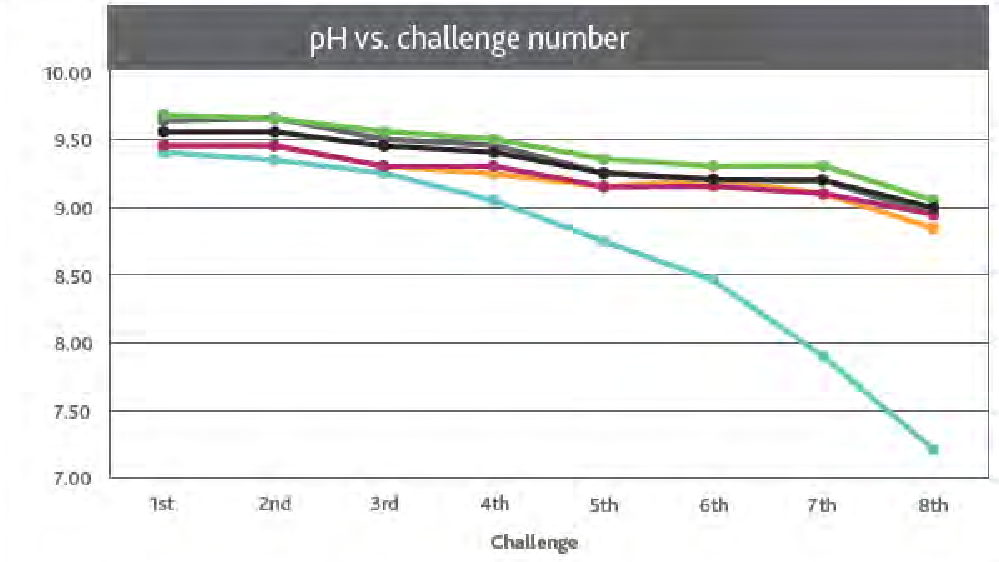
Image 1 shows results of cast iron chip tests on fluids halfway through testing (4th challenge). Fluids across the top row are at 6% concentration. Fluids in the middle row are at 4%. Fluids across the bottom row are at 2%. This is where most of the rust appears on those fluids with triethanolamine 99 and DCHA.

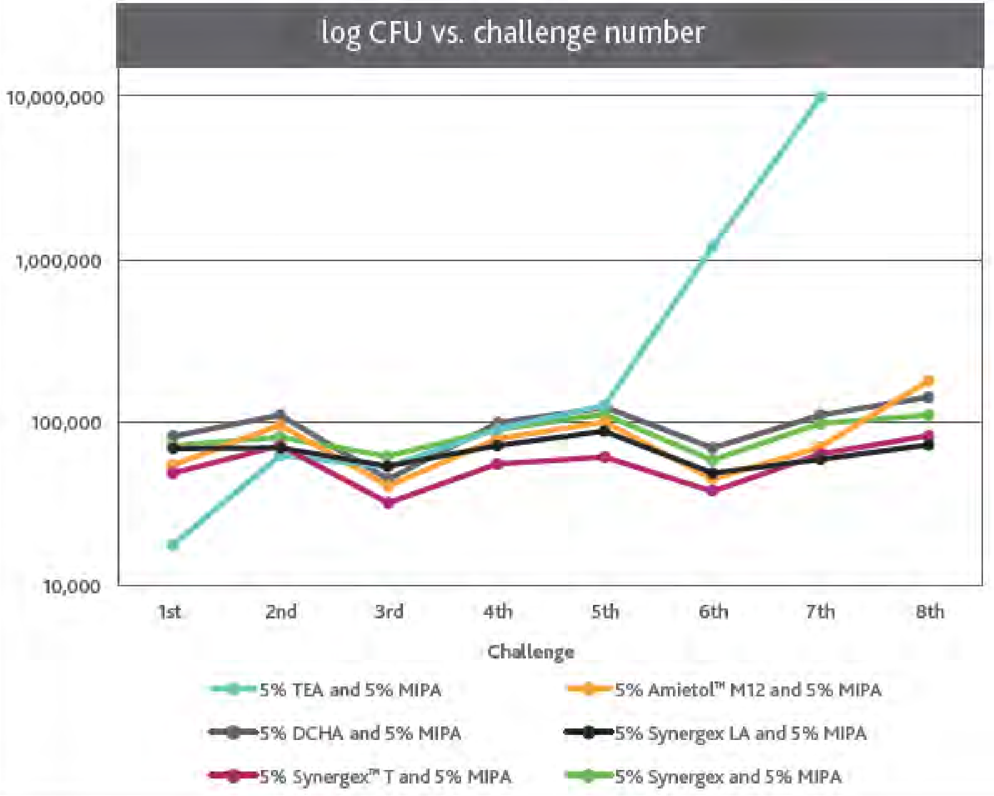
Table 1	
Coolant formula	%
100-second naphthenic oil	55.00
Soap sulfonate emulsifier	15.00
Alkanolamide emulsifier	15.00
Tall oil fatty acid	2.00
10 HLB nonionic surfactant	3.00
MIPA	5.00
AAA	5.00
Total	100.00

By diluting the fluids to 6%, both the MIPA and AAA are used at 3000 ppm for an amine total of 6000 ppm. Triethanolamine 99 was compared to Amietol™ M12, and DCHA was compared to Synergex, Synergex LA, and Synergex T.

Synergex/MIPA was the best. **TEA/MIPA was the worst**.

Measuring biological activity using the HMB IV Bacteria Tester from Biotech International, all microbial populations are reported as CFU/mL regardless of whether they are bacteria or mold; **despite lower pH readings, Synergex T & Synergex LA ran much lower CFU counts than DCHA.**





EASTMAN

Synergex LA and stability

Conclusions

I) Use of B/A ratio is a convenient shortcut in formulation
II) Selection of the right amine(s) is an important first step
III) Tertiary amines have unique chemistry that allows O/W partition
IV) Optimized formulas will last longer and work better

Thank you