Synergex™ multifunctional amine additives for metalworking fluids

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Eastman Chemical Company

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- Fortune 500 specialty materials company with 2017 revenue of ~$9.5B
- Global manufacturer and marketer of advanced materials and specialty additives
- Four business segments
- Global team of ~14,500
- Serving customers in >100 countries

A global industry **leader**

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Today’s discussion

A) Use of amines in metalworking fluids

B) Benefits of alkanolamines

C) Synergex

D) Synergex T

E) Synergex LA

F) Conclusion

Use of amines in metalworking fluids

- **Amines are soluble bases that are:**
  - Less corrosive than an inorganic base
  - Compatible with O/W and W/O emulsions

Amines are *necessary* to adjust the pH of functional fluids.

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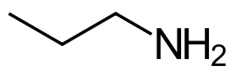
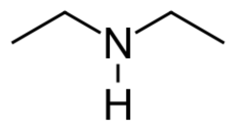
Benefits of alkanolamines

Amine choice is a *formulator's decision.*

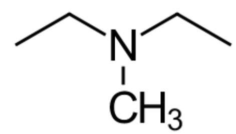
Examples of amines



Primary
1°

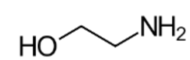


Secondary
2°

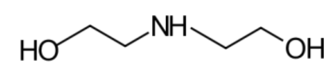


Tertiary
3°

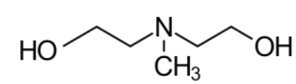
A) Hydrophobic versus hydrophilic
B) Volatile (odorous) versus non-VOC
C) Alkanolamine versus alkylamine
D) Multifunctional (e.g., corrosion inhibitor) versus pH only



Monoethanolamine



Diethanolamine



N-Methyldiethanolamine

What are the ideal properties of an amine?

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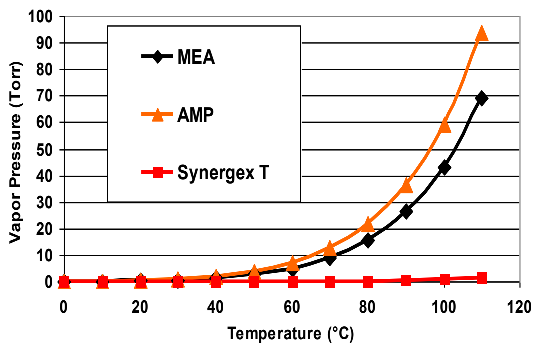
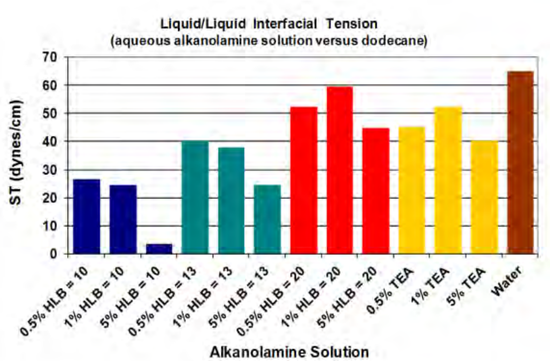
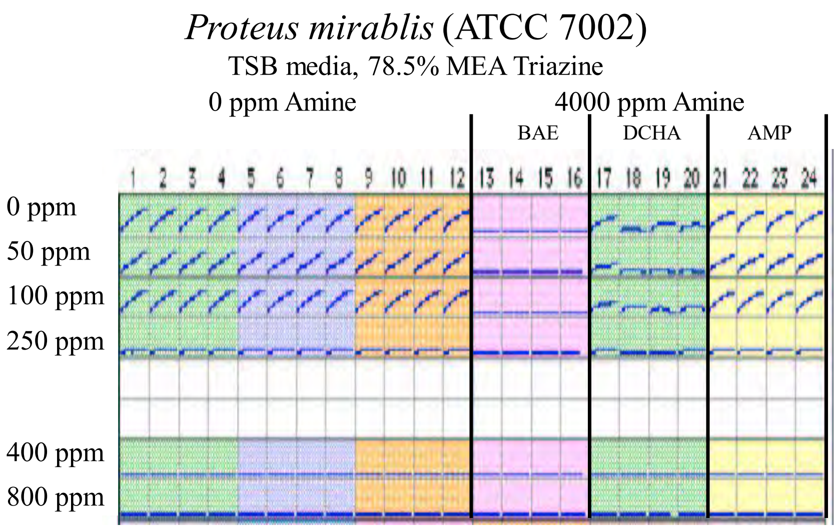
Low odor/volatility



Emulsion stability



Biostability

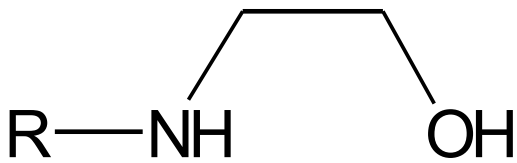


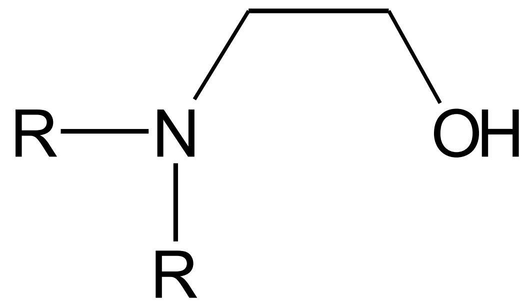
Low staining

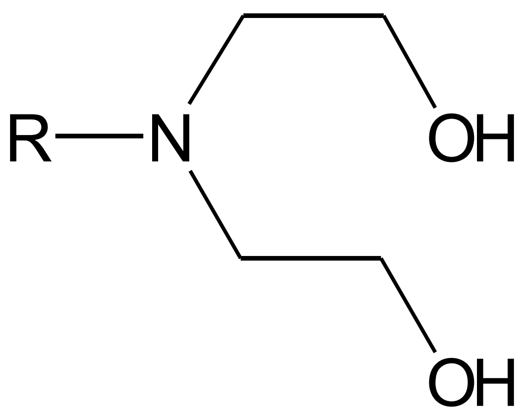
Alkanolamines provide good base strength and capacity at a reasonable cost with low VOC contribution and low odor.

The Synergex product line

N-alkyl alkanolamines (AAAs)







R = C1 - C8

The Synergex product line

- Synergex—excellent supplementary biostability, low volatility and odor, good corrosion inhibition, colloid stabilization
- Synergex T—good supplementary biostability, tertiary amine, very low volatility and odor, colloid stabilization
- Synergex LA—capable DCHA replacement that pairs well with lower-MW primary alkanolamines such as MEA and MIPA

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Amine	MW	EW	pKa	mg KOH/g	HLB	BP
Synergex T	161.24	161.24	8.9	347	12	285°C (normal)
Synergex	117.19	117.19	9.7	478	10	200°C (normal)
Synergex LA	173.30	173.30	10.3	324	6	230°C (normal)
MDEA	119.16	119.16	8.8	471	17	247°C (normal)

MW = molecular weight (g/mole)
EW = equivalent weight (g per equivalent of amine)
pKa = negative log of the equilibrium constant for dissociation of the protonated amine (water, RT)
mg KOH/g = mass of KOH with same number of moles as 1 gram of the amine
HLB = calculated floor function of {60/MW} x 20 for monoethoxylate and {104/MW} x 20 for diethoxylate
BP = boiling point; normal designates a pressure of 1 atmosphere

Synergex and biostability

Fluid user and formulator—Working together to optimize biostability

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Emulsion fluid

100 SUS oil	72 g/kg
60% sulfonated oil	72 g/kg
DEA fatty acid amide	72 g/kg
Tall oil fatty acid	72 g/kg
BASF 17R4	24 g/kg
Triethanolamine (85%)	100 g/kg
Alkanolamine	**40 g/kg**
Water	Balance

→ Add biocide.

→ Keep fluid clean.

→ Optimize formula.

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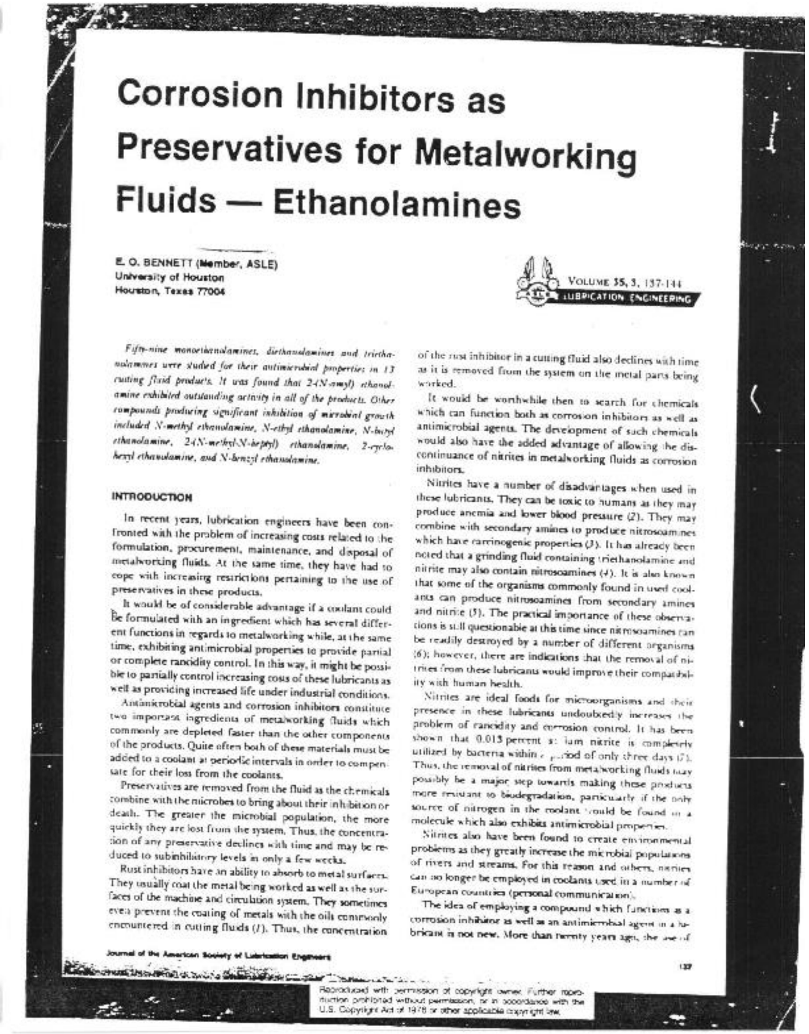

Corrosion Inhibitors as Preservatives for Metalworking Fluids — Ethanolamines

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Fifty-nine monoethanolamines, diethanolamines and triethanolamines were studied for their antimicrobial properties in 13 cutting fluid products. It was found that 2-(N-amyl) ethanolamine exhibited outstanding activity in all of the products. Other compounds producing significant inhibition of microbial growth included N-methyl ethanolamine, N-ethyl ethanolamine, N-butyl ethanolamine, 2-(N-methyl-N-heptyl) ethanolamine, 2-cyclohexyl ethanolamine, and N-benzyl ethanolamine.

INTRODUCTION

In recent years, lubrication engineers have been confronted with the problem of increasing costs related to the formulation, procurement, maintenance, and disposal of metalworking fluids. At the same time, they have had to cope with increasing restrictions pertaining to the use of preservatives in these products.

It would be of considerable advantage if a coolant could be formulated with an ingredient which has several different functions in regards to metalworking while, at the same time, exhibiting antimicrobial properties to provide partial or complete rancidity control. In this way, it might be possible to partially control increasing costs of these lubricants as well as providing increased life under industrial conditions.

Antimicrobial agents and corrosion inhibitors constitute two important ingredients of metalworking fluids which commonly are depleted faster than the other components of the products. Quite often both of these materials must be added to a coolant at periodic intervals in order to compensate for their loss from the coolants.

Preservatives are removed from the fluid as the chemicals combine with the microbes to bring about their inhibition or death. The greater the microbial population, the more quickly they are lost from the system. Thus, the concentration of any preservative declines with time and may be reduced to subinhibitory levels in only a few weeks.

Rust inhibitors have an ability to absorb to metal surfaces. They usually coat the metal being worked as well as the surfaces of the machine and circulation system. They sometimes even prevent the coating of metals with the oils commonly encountered in cutting fluids (*1*). Thus, the concentration of the rust inhibitor in a cutting fluid also declines with time as it is removed from the system on the metal parts being worked.

It would be worthwhile then to search for chemicals which can function both as corrosion inhibitors as well as antimicrobial agents. The development of such chemicals would also have the added advantage of allowing the discontinuance of nitrites in metalworking fluids as corrosion inhibitors.

Nitrites have a number of disadvantages when used in these lubricants. They can be toxic to humans as they may produce anemia and lower blood pressure (*2*). They may combine with secondary amines to produce nitrosoamines which have carcinogenic properties (*3*). It has already been noted that a grinding fluid containing triethanolamine and nitrite may also contain nitrosoamines (*4*). It is also known that some of the organisms commonly found in used coolants can produce nitrosoamines from secondary amines and nitrite (*5*). The practical importance of these observations is still questionable at this time since nitrosoamines can be readily destroyed by a number of different organisms (*6*); however, there are indications that the removal of nitrites from these lubricants would improve their compatibility with human health.

Nitrites are ideal foods for microorganisms and their presence in these lubricants undoubtedly increases the problem of rancidity and corrosion control. It has been shown that 0.015 percent sodium nitrite is completely utilized by bacteria within a period of only three days (*7*). Thus, the removal of nitrites from metalworking fluids may possibly be a major step towards making these products more resistant to biodegradation, particularly if the only source of nitrogen in the coolant could be found in a molecule which also exhibits antimicrobial properties.

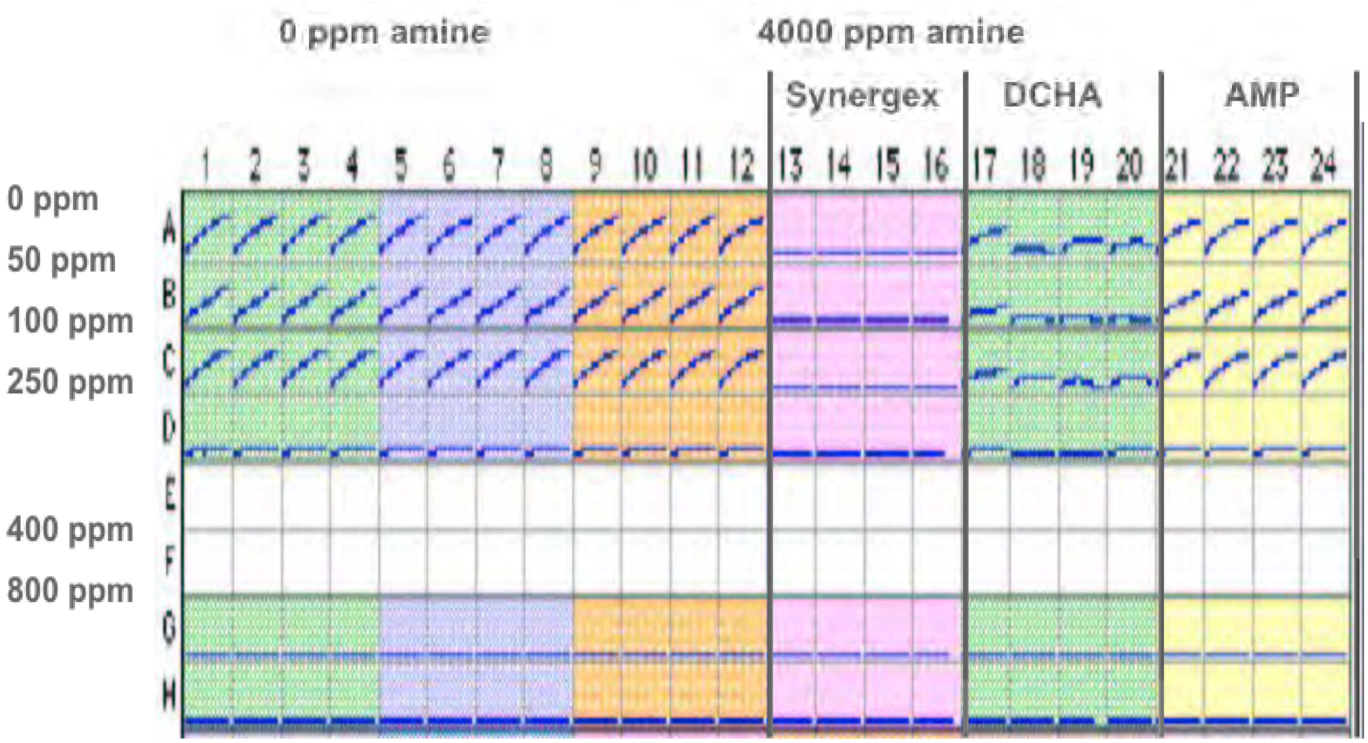
Nitrites also have been found to create environmental problems as they greatly increase the microbial populations of rivers and streams. For this reason and others, nitrites can no longer be employed in coolants used in a number of European countries (personal communication).

The idea of employing a compound which functions as a corrosion inhibitor as well as an antimicrobial agent in a lubricant is not new. More than twenty years ago, the use of

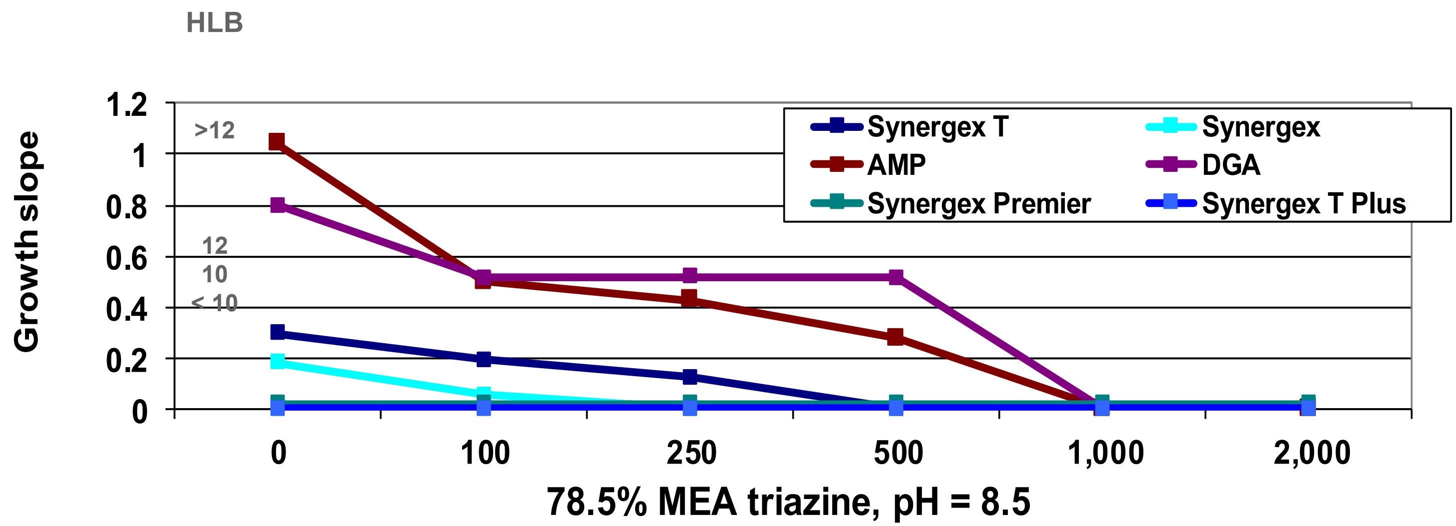
- Using amines as multifunctional additives in metalworking fluids – not a new concept
- In 1979 journal article, E.O. Bennett affirmed **Synergex™** as “producing significant inhibition of microbial growth”

Proteus mirabilis (ATCC 7002)

TSB media, 78.5% MEA triazine



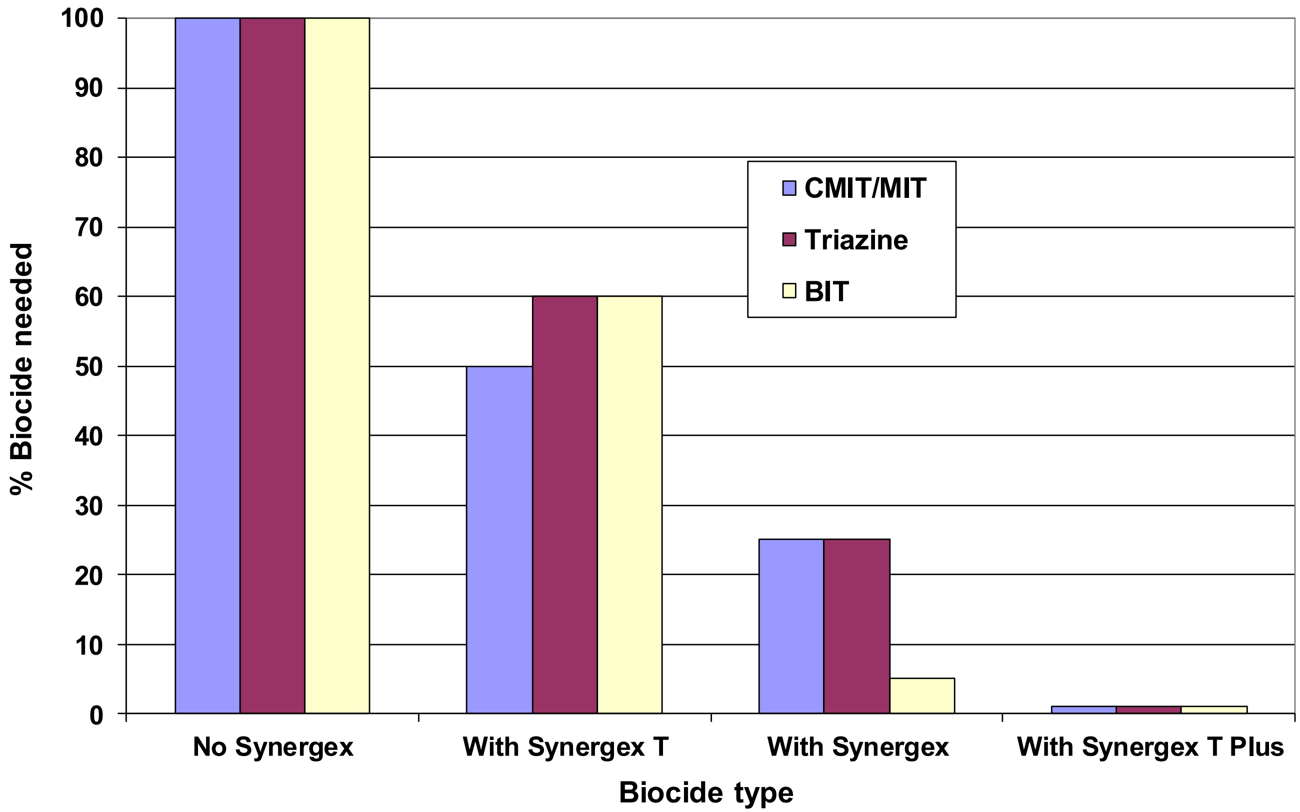
4,000 ppm amine, *Psuedomonas aeruginosa*, TSB growth slope in millOD/min, 48-hour run



Observations

- Synergex T can be used as part of a biostable, low-VOC metalworking fluid.
- Fluids based on the Synergex *N*-alkyl alkanolamines do not stain aluminum (AL 2024 pieces dipped in the fluids shown; MDEA for reference).

Biocide reductions possible with Synergex products



Synergex and emulsion stability

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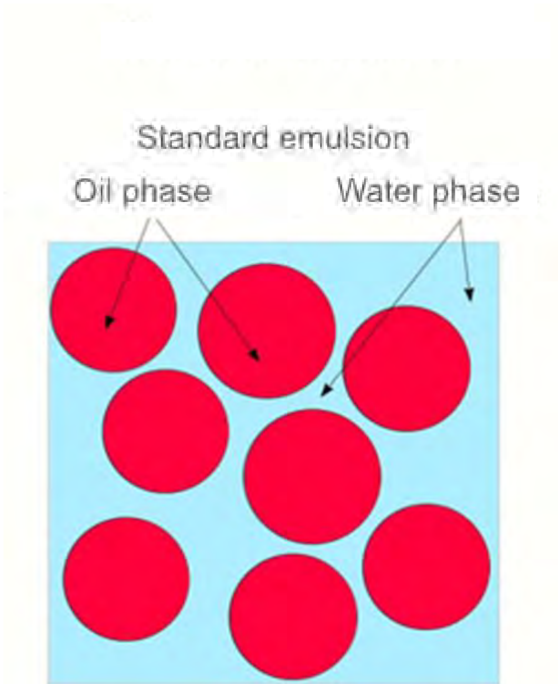
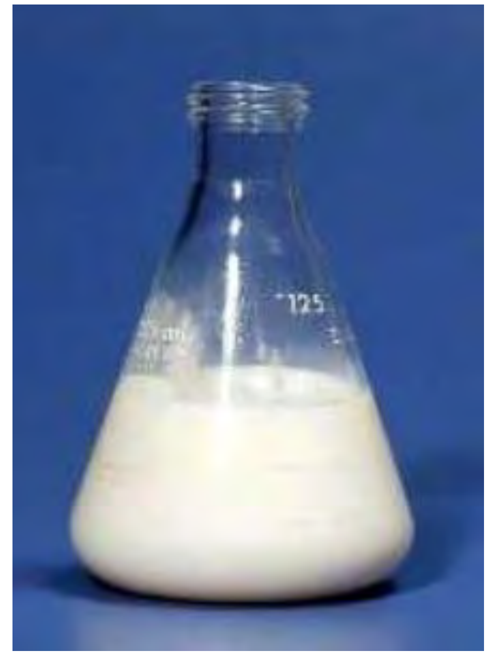
Emulsion basics

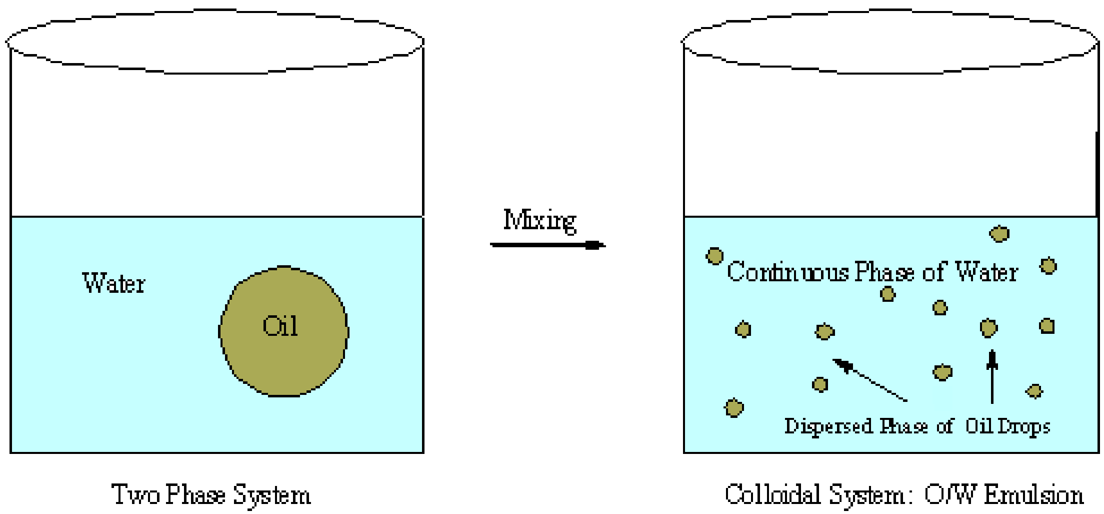




Phase		Dispersed phase		
		Gas	**Liquid**	**Solid**
Continous phase	**Gas**	None (miscible)	Aerosol (mist)	Solid aerosol (smoke, dust)
	Liquid	Foam	Emulsion (O/W, W/O)	Solid (dispersion)
	Solid	Solid foam	Gel	Solid sol

Why is liquid/liquid interfacial tension important?

Emulsions are destabilized by a large increase in oil/water surface area

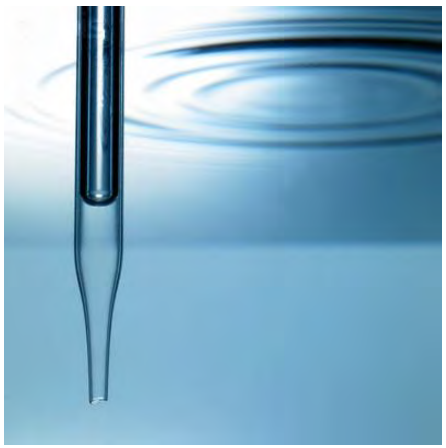


Energy difference between O/W emulsion and two separate oil and water phases

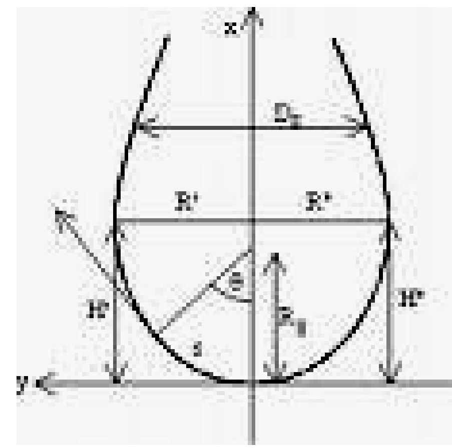
$$\Delta E = (\gamma_{water/oil})\Delta A_{water/oil} - T\Delta S_{mixing}$$

Contact angle vs. drop weight

Capillary contact angle (new method)



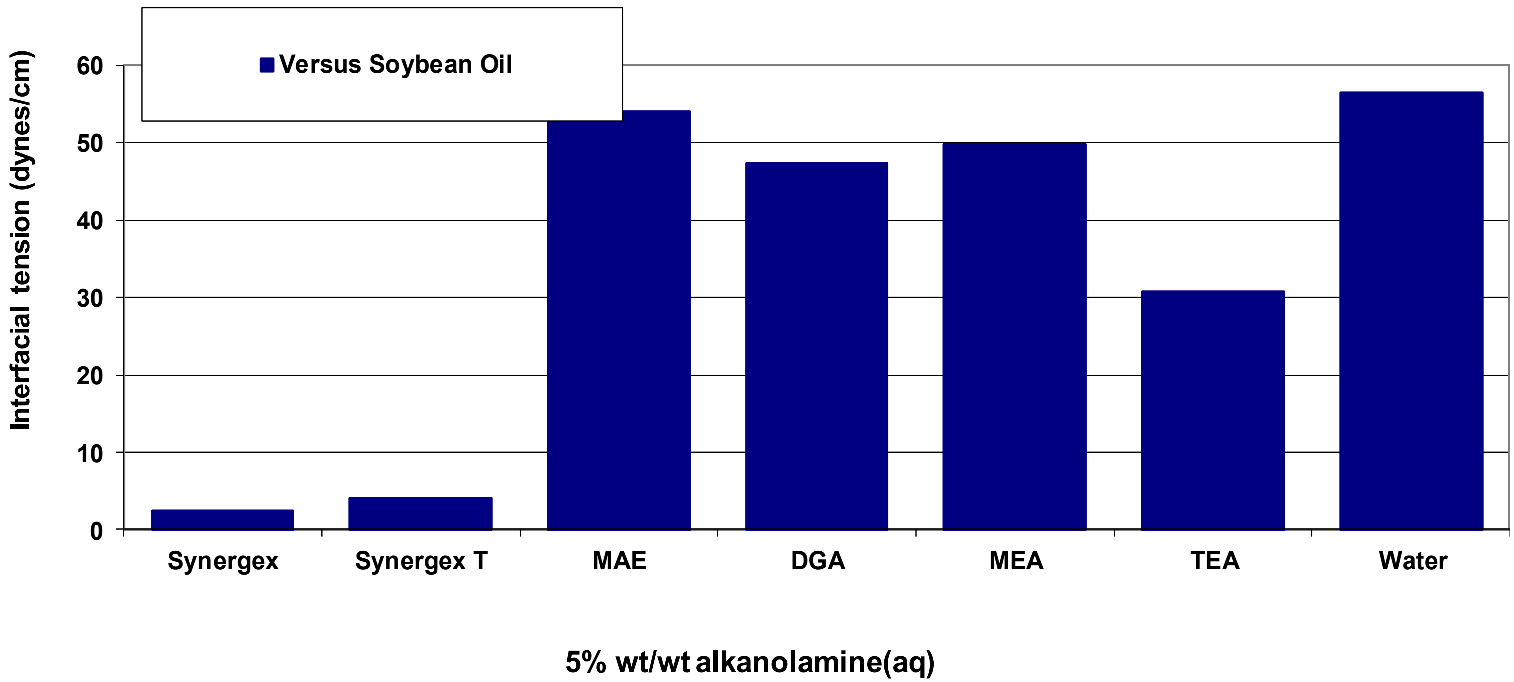
Drop shape analysis



Tate's law:

$2\pi r\gamma$ = drop volume x $\Delta\rho$ = drop weight

Liquid/liquid interfacial tension in dynes/cm



Air/solution and air/oil interfacial tensions by bubble pressure (dynes/cm)

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[ ]	SYNERGEX	SYNERGEX T	AMP	DGA	MAE	MEA	TEA
0.1%	59.8	60.1	70.4	72.1	70.7	72.3	70.2
0.5%	52.8	54.8	68.8	70.9	69.7	72.3	70.1
5%	37.9	41.0	60.6	68.0	64.6	70.6	66.6
50%	29.8	33.4	41.3	55.6	46.0	60.7	54.8

Oil	Surface tension (dynes/cm)
Soybean oil	54.8
Methyl oleate	34.6
Dodecane	39.3

Representative liquid/liquid interfacial tension calculations

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Oil/aqueous interfacial tensions (γ) in dynes/cm

Solution	Oil	θ Aq	θ Oil	θ Aq/oil	$f(\theta)$	$g(\theta)$	$h(\theta)$	γ Air/aq	γ Air/oil	γ Oil/aq
Water	SB	29	53	43	0.295	0.167	0.217	72.8	54.8	56.5
0.5% SYN	SB	35	53	57	0.260	0.167	0.148	59.8	54.8	43.2
0.5% MAE	SB	39	53	54	0.238	0.167	0.162	70.7	54.8	47.4
1% SYN	MeOle	36	47	44	0.255	0.197	0.212	52.8	34.6	31.3
1% AMP	MeOle	40	47	56	0.233	0.197	0.153	68.8	34.6	60.4

SB = soybean oil, MeOle = methyl oleate, SYN = Synergex,
MAE = methylaminoethanol, AMP = 2a-amino-2-methyl-1-propanol

Why do alkanolamines behave differently?

$$\text{HLB} = \frac{20\ (\text{hydrophilic molecular weight})}{(\text{total molecular weight})}$$

Floor Function:

Hexane:	HLB = 00
Synergex:	HLB = 10
Synergex T:	HLB = 12
AMP	HLB = 13
Methylaminoethanol:	HLB = 15
Monoethanolamine:	HLB = 20

Why is HLB important?

- The hydrophile/lipophile balance (HLB)
  - Low HLB is good for corrosion inhibition and biocide synergy, but too low an HLB leads to low water solubility.
  - High HLB is good for water solubility, but too high an HLB leads to poor secondary performance and poor coupling.

Mid-range HLB leads to the optimal balance of solubility and performance.

Synergex LA—Newest addition to the line

Synergex LA

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As the newest addition to our Synergex product line, Synergex LA serves as an excellent hydrophobic alkanolamine for hydrophobic/hydrophilic amine combinations. **Excellent biostability and easy incorporation into O/W emulsions.**

Formulating with the Synergex amines

Amine	NBP	% VOC	HLB	Typical use level	Mycobacterial inhibition	Oil/water partition	pKa
Synergex	200 °C	99	mid-range	4% - 6%	moderate	water	19
Syergex	285 °C	< 8	hydophilic	2% - 10%	none	water	9
Synergex LA	230 °C	99	hydrophobic	4% - 8%	none	oil	10

Optimal replacement for DCHA; wise choice for formulators looking for alternatives

NBP = normal boiling point
% VOC per ASTM-D1868
NK = not known
Biostability assessment via integrated MTA (microtiter assay) experiments
Mycobacterial inhibition
Typical use level designates the typically optimal amount to use in a concentration, which in turn will be diluted to = 5% in the working fluid.

Summary

- Selection of the best amine(s) is the critical first step in formulation.
- Synergex™ alkanolamines are the optimal choice for metalworking fluids, providing biostability and enhanced emulsion stability.
- By optimizing your formula, you're ensuring formulation longevity and enhanced product performance.

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- To learn more about Synergex, visit www.SynergexAmine.com.
- To place an order in North America or for more information, contact Caroline Johnson: Car.Johnson@eastman.com or one of our distributors:

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Thank you!