HUNTSMAN

Enriching lives through innovation

Aminology in Tribology

October 11, 2019 Houston STLE

Anabel Rubio, Sr. Scientist
Huntsman Performance Products

Topics of Discussion

HUNTSMAN
Enriching lives through innovation

- **Overview of Huntsman Corporation**
- **Amines for Tribology**
  - Introduction
  - Trends
- **Amine Basics**
- **Applications**
  - Fuels and Lubricants
  - Metalworking
- **EH&S and Regulatory**

Huntsman Corporation

We are a global manufacturer and marketer of differentiated chemical products that improve the quality of life for people around the world.

- Approx. 10,000 Associates
- 140 Locations Worldwide
- USD 9.4 bil. in Revenue
- Listed on NYSE Feb. 2005

Huntsman Businesses

Polyurethanes	Performance Products	Advanced Materials	Textile Effects
MDI Polyols PO/MTBE TPU PU Systems	Amines Surfactants Maleic Anhydride Upstream Intermediates	Composites Adhesives Resins	Dyes Chemicals Inks ——— Apparel Home & Institutional Technical Textiles




HUNTSMAN

Enriching lives through innovation

Amines in Tribology

Tribology is the study of science and engineering of interacting surfaces in relative motion which includes the study and application of friction, lubrication and wear.

HUNTSMAN
Enriching lives through innovation

- **Typical Additives in Lubricants**
  - Antioxidants
  - Extreme Pressure/ Antiwear Additives
  - Detergents
  - Dispersants
  - Viscosity Index Improvers
  - Friction modifiers/ Boundary Lubricants
  - Corrosion Inhibitors
  - Metal Deactivators
  - Pour Point Depressants
  - Foam Inhibitors
  - Demulsifers

Global Fuels and Lubricants Development

HUNTSMAN
Enriching lives through innovation

Market Trends Impacting Amines

- **Market Trends for Fuels**
  - Higher fuel efficiency standards
  - Tighter fuel emission standards
  - Move towards direct injection engines and turbocharging to improve fuel economy
- **Market Trends for Metalworking**
  - Cleaner labeling
    - **Green Additives**
  - Multi-metal metalworking formulations
  - Move to semi-synthetic and synthetic formulations
  - Longer fluid life

- **Market Trends for Lubricants**
  - Reduction in ash limits
  - Long drain intervals

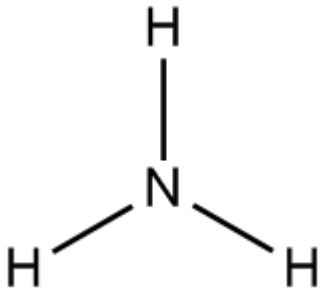
HUNTSMAN

Enriching lives through innovation

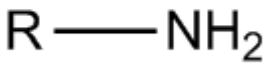
Amine Basics

Amine Basics

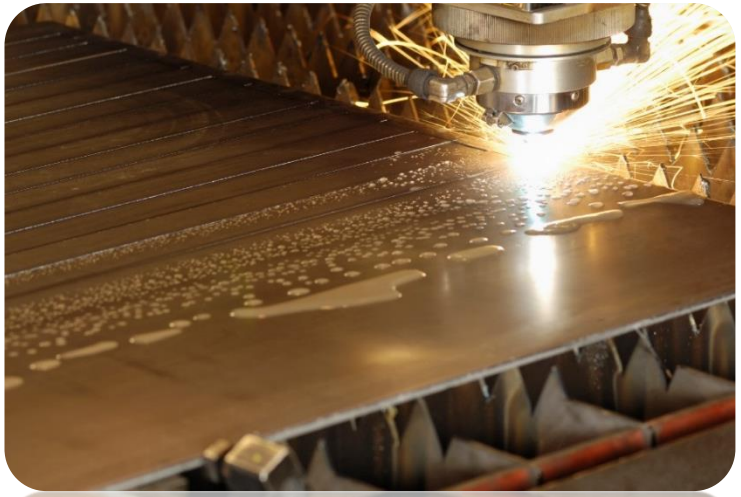
Types of Amines

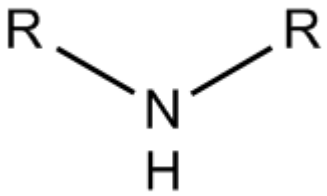


Ammonia

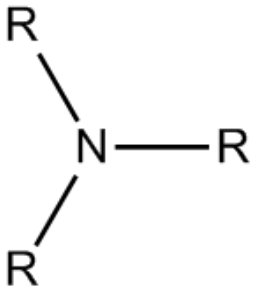


1°Amine





2°Amine

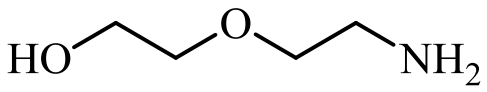


3°Amine

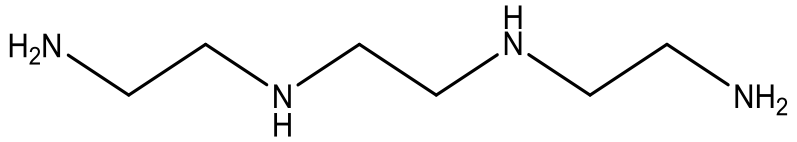
Amine Basics

Examples

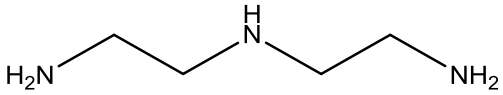
HUNTSMAN
Enriching lives through innovation



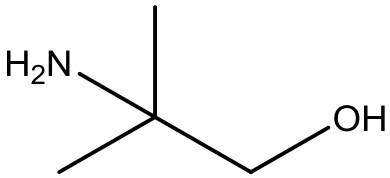
DGA™ Etheramine



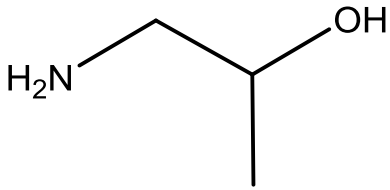
TETA



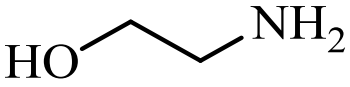
DETA



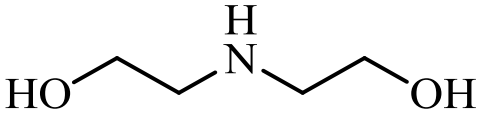
AMP



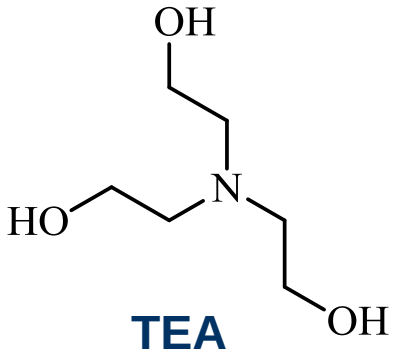
MIPA



MEA



DEA

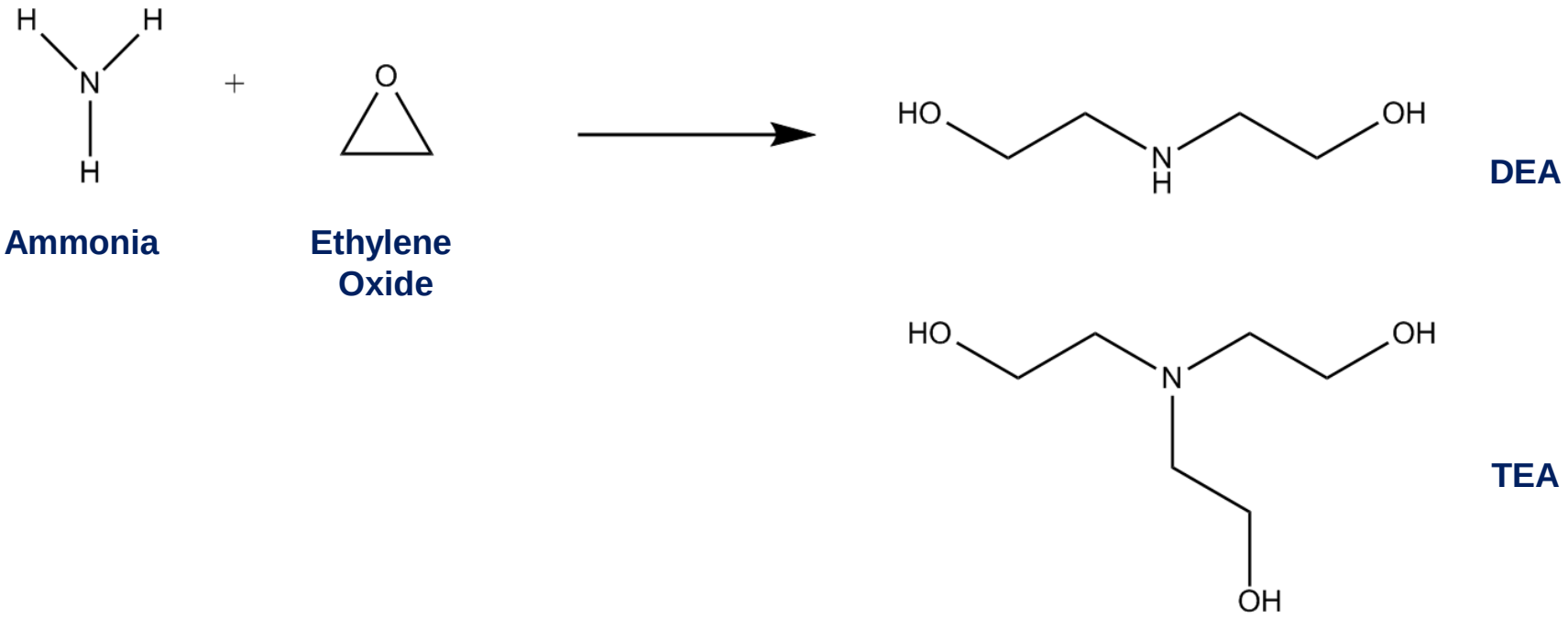


TEA

Amine Basics

Ethanolamine Synthesis

HUNTSMAN
Enriching lives through innovation



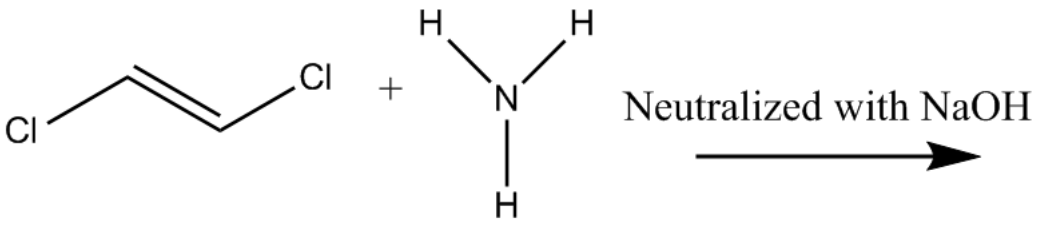
Ammonia

Ethylene Oxide

Amine Basics

Ethyleneamine Synthesis

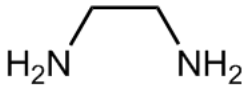
HUNTSMAN
Enriching lives through innovation



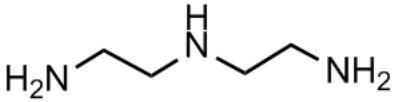
Ethylene Dichloride

Ammonia

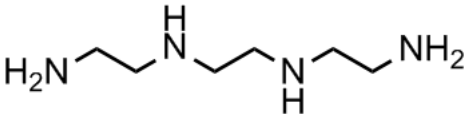
NaCl



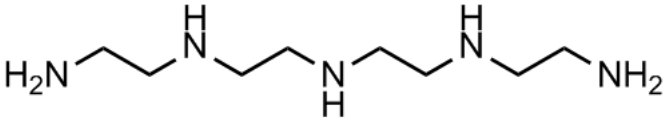
EDA



DETA



TETA



TEPA

HUNTSMAN

Enriching lives through innovation

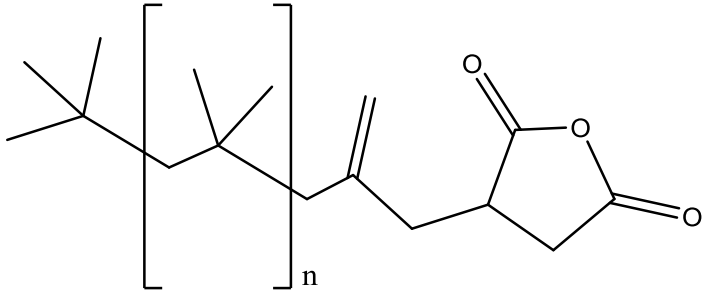
Applications

Ethyleneamines and Polyetheramines

Use in Lubricants

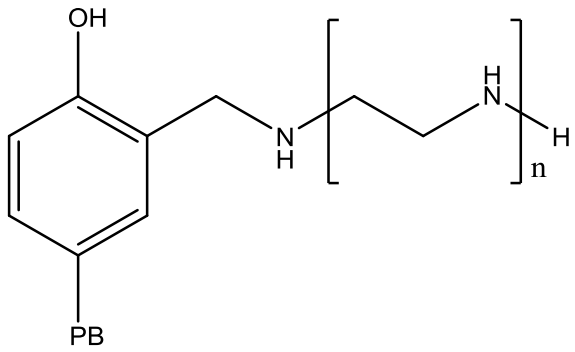
HUNTSMAN
Enriching lives through innovation

- **Polyetheramines** are products used in fuels. For this application, they are usually comprised of an alcohol that is alkoxylated to a degree and aminated. These molecules are balanced to be compatible with the fuel and clean up/ keep clean the combustion chamber



- **Ethyleneamines** and **Polyetheramines** can be reacted with PIBSA to create an ashless dispersant for motor oils

  Typical dispersant molecules are composed of a polar head (in this case the head is an N group) and a hydrocarbon tail (polybutylene)



- **Ethyleneamines** and some **polyetheramines** may be used to create a Mannich base

Amines in Metalworking

HUNTSMAN
Enriching lives through innovation

- **Process of working with metals to create individual parts, assemblies, or large-scale structures. This includes a wide range of objects, processes and tools**

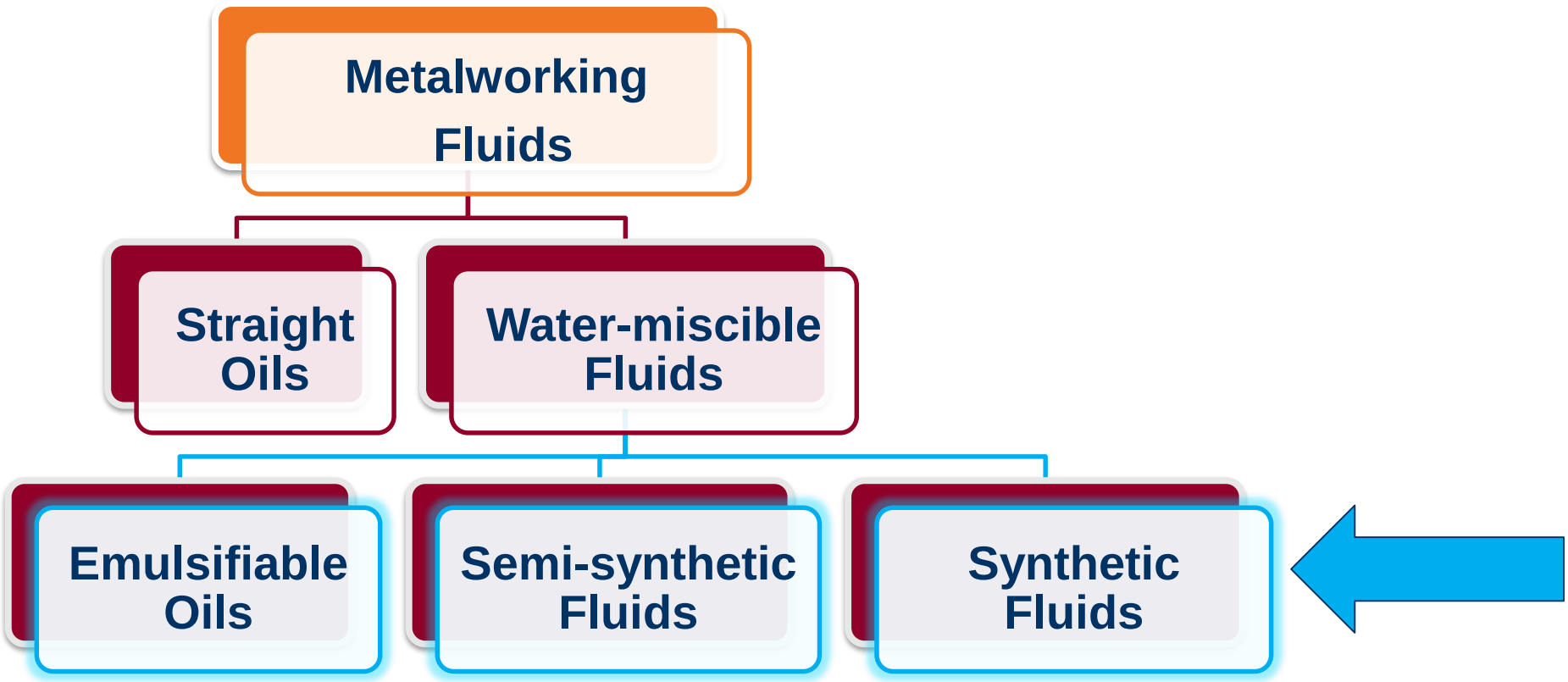
- **Four main processes exist**

Removal	Forming	Treating	Protecting
Process for which a cutting action is the primary machining technique	Process that involve changing the shape and contour without cutting	Process like cleaning or annealing in order to prepare material for the next Process step	Process to preserve metal surfaces from corrosion. This for short or longer term
			

Amines in Metalworking

Fluid types

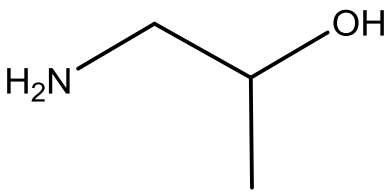
HUNTSMAN
Enriching lives through innovation



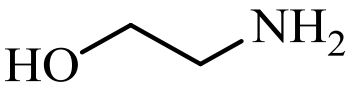
Amines in Metalworking

HUNTSMAN
Enriching lives through innovation

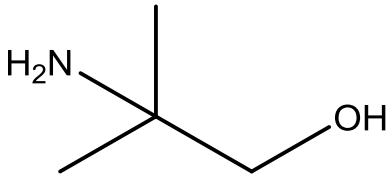
- **In water-miscible metalworking formulations, amines help to**
  - Maintain dilution pH
    - aids in corrosion protection
    - helps control microbial control
      - higher pH is known to help extend fluid life
- **Provide pH reserve alkalinity**
  - Neutralize acidic components in formulation to form amine carboxylates
  - Neutralize acidic components that form from oxidation



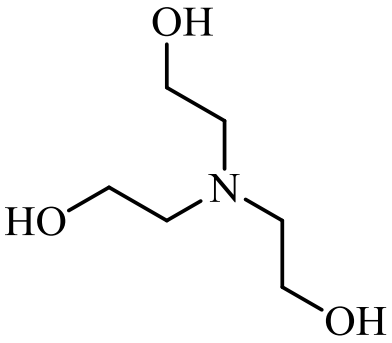
MIPA



MEA



AMP



TEA

Amines in Metalworking

Comparison of Physical Properties

HUNTSMAN
Enriching lives through innovation

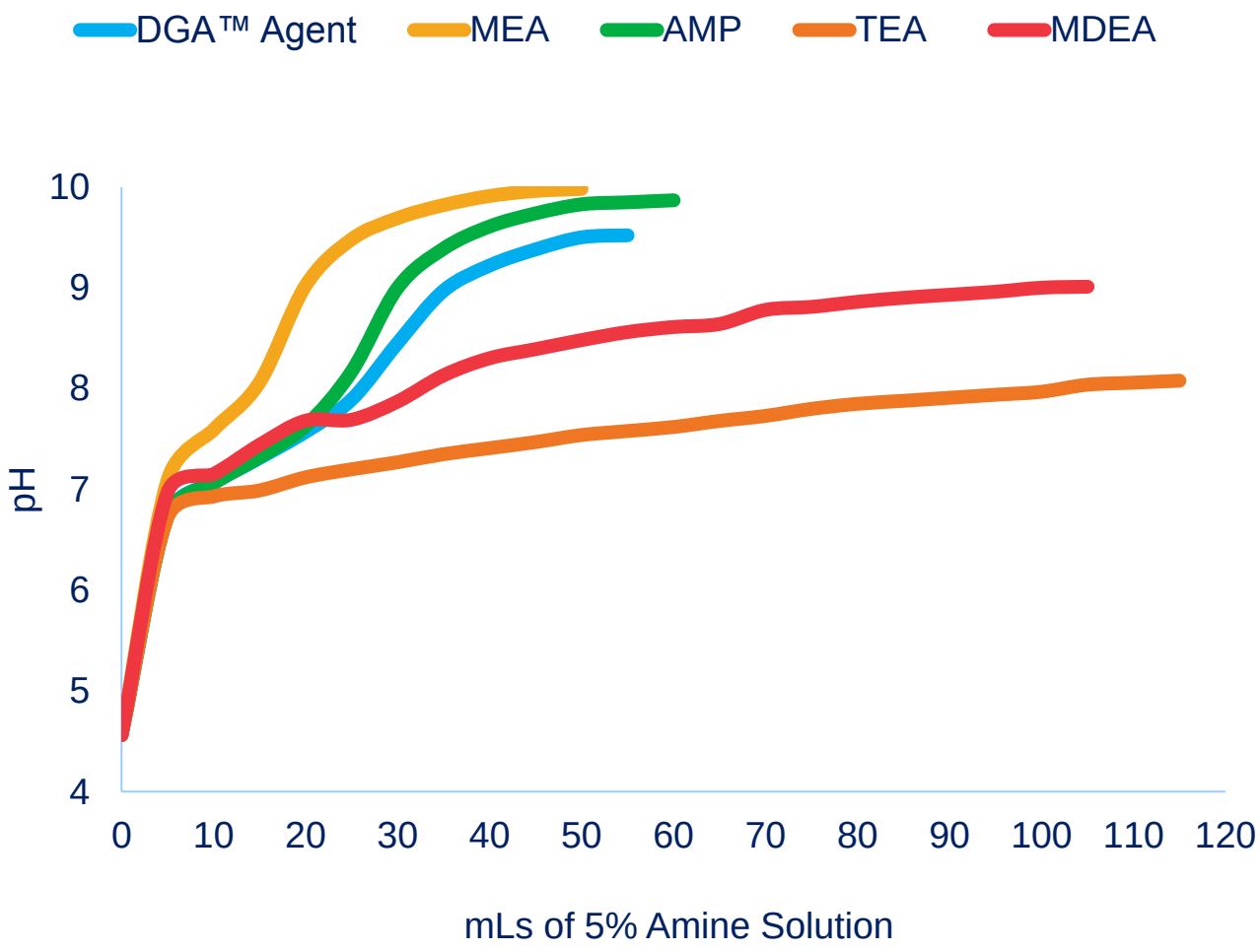
Amine	Molecular Weight	Flash Point ° C	5% pH	pKa
Monoethanolamine (MEA)	61	95	11.87	10.03
Monoisopropanolamine (MIPA)	75	71	11.40	9.40
2-Amino-2-methyl propanol (AMP)	94	78	11.46	9.82
DGA™ Agent	105	128	10.68	9.45
Diethanolamine (DEA)	105	149	10.34	8.88
Triethanolamine (TEA)	149	202	9.64	7.76
Methyldiethanolamine (MDEA)	119	141	10.7	8.76

The higher the pKa the stronger the amine

Amines in Metalworking

Titration of 5% Decanoic Acid solution with Different Amines

HUNTSMAN
Enriching lives through innovation



- MWF can be between 8.5-10.5 pH depending on alloy being used and application
- Primary amines important to attain desired pH
- Tertiary amines important for pH buffering

Amines in Metalworking

Other considerations

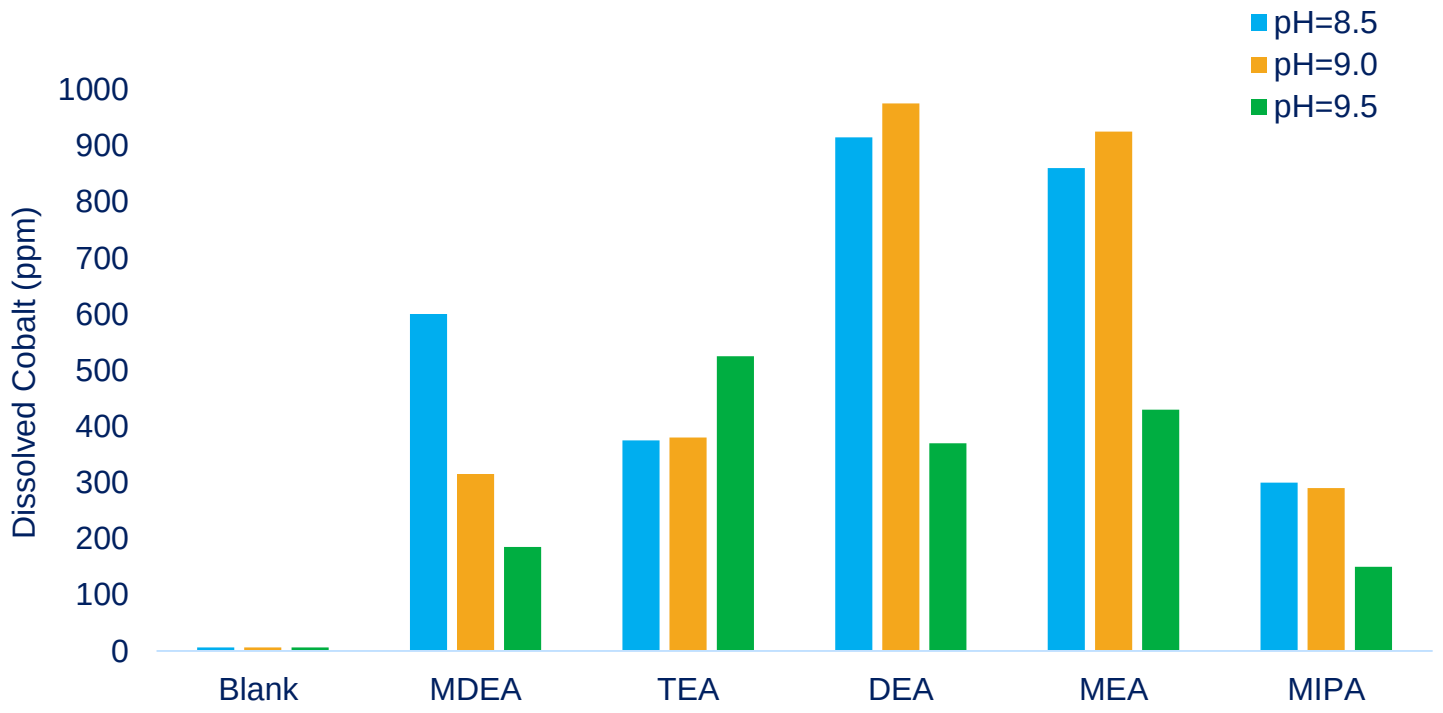
- Odor
- Cobalt Leaching
- Aluminum Staining
- Corrosion inhibition

Amines in Metalworking

Cobalt Leaching

HUNTSMAN
Enriching lives through innovation

- Cobalt leaching is affected by pH
  - In general lower pH shows higher leaching
- Amine selection is important as certain amines leach cobalt more than others



Amines in Metalworking

Aluminum Staining

HUNTSMAN
Enriching lives through innovation

DGA™ Agent	AMP	TEA
		
MDEA	**DEA**	**Blank**
		

2.5 weight % amine
aqueous
Al 6061
24 hours
pH = 8.8

Amines in Metalworking

Aluminum Staining

HUNTSMAN
Enriching lives through innovation

DGA™ Agent	AMP	TEA
		
MDEA	**DEA**	**Blank**
		

2.5 weight % amine
aqueous
Al 6061
24 hours
pH = 8.0

Amines in Metalworking

Aluminum Staining

HUNTSMAN
Enriching lives through innovation

DGA™ Agent	AMP	TEA	Blank
			

MDEA	DEA	MEA
		

2.5 weight % amine-isononanoic acid salt aqueous
Al 6061
24 hours
pH = 8.8

Amines in Metalworking

Aluminum Corrosion

HUNTSMAN
Enriching lives through innovation

2.5% Amine Aq. Soln.	Dissolved Aluminum			
	Al 7075	Al 6061	Al 2024	Al 390
DGA™ Agent	5	5.5	7.6	9
AMP	9	7.9	12	11.5
DEA	7.9	9.3	10	11
TEA	**155**	**195**	**235**	**215**
MDEA	7.2	4.8	8.6	9

2.5% Amine Salt Soln. (0.1 mole of amine/0.083 mole of acid)	Dissolved Aluminum			
	Al 7075	Al 6061	Al 2024	Al 390
DGA™ Agent	3.1	3.8	2.8	1.3
AMP	4.7	5.5	3.6	4.5
DEA	2.5	3.8	1.2	2.7
TEA	**40**	**39**	**34**	**32**
MDEA	1.6	2.2	1.4	1.8

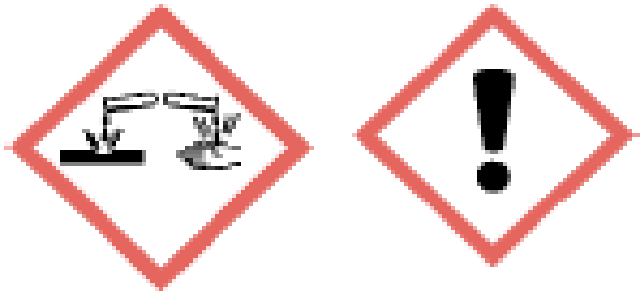
pH of solutions = 8.8

Amines in Metalworking

Environmental, Health, and Safety

HUNTSMAN
Enriching lives through innovation

- **Desire minimal labeling and skin compatibility**
  - Amines tend to be corrosive and an irritant
  - DEA includes health hazard label for target organ toxicity, repeated exposures
- **Reduced misting and volatility**
  - Lower vapor pressure preferred for amines



	MEA	DEA	TEA	DGA™ Agent	AMP	MDEA
Exposure limit	6 mg/m^3 OSHA PEL	15 mg/m^3 TWA ACGIH	5 mg/m^3 TWA ACGIH	None	None	None

Amines in Metalworking

Regulatory

HUNTSMAN
Enriching lives through innovation

- **Registration on chemical inventories**
- **TEA and MDEA listed on Chemical Weapons Convention List**
- **Nitrosamine formation in MWF**
  - EPA cautioned on the use of certain amines in combination with nitrites
    - **DEA and TEA**
- **Reduced biocide use**
  - EPA under FIFRA has lowered the concentration use of formaldehyde based biocides

HUNTSMAN

Enriching lives through innovation

Thank you

HUNTSMAN

Enriching lives through innovation

Huntsman Corporation warrants only that its products meet the sales specifications stated in Huntsman's current Technical Bulletin for the product. Typical properties, where stated, are to be considered as representative of current production and should not be treated as specifications. While all the information presented in this document is believed to be reliable and to represent the best available data on these products, HUNTSMAN MAKES NO WARRANTY OR GUARANTEE OF ANY KIND, EXPRESS OR IMPLIED, INCLUDING BUT NOT LIMITED TO ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, NON-INFRINGEMENT OF ANY INTELLECTUAL PROPERTY RIGHT OF ANY THIRD PARTY, OR WARRANTIES AS TO QUALITY OR CORRESPENDENCE WITH PRIOR DESCRIPTION OR SAMPLE, AND ANY USER OF PRODUCTS DESCRIBED HEREIN SHOULD CONDUCT A SUFFICIENT INVESTIGATION TO ESTABLISH THE SUITABILITY OF ANY PRODUCT FOR ITS INTENDED USE AND ASSUMES ALL RISK AND LIABILITY WHATSOEVER RESULTING FROM THE USE OF SUCH PRODUCT, WHETHER USED SINGLY OR IN COMBINATION WITH OTHER SUBSTANCES. Product(s) described in this publication may be hazardous and/or toxic and require special precautions in handling.

For all product(s) described herein, the user should obtain from Huntsman detailed information on hazards and/or toxicity, together with proper shipping, handling, and storage procedures, and should comply with all applicable safety and environmental standards. The behavior, hazards and/or toxicity of the product(s) referred to in this publication in manufacturing processes and their suitability in any given end-use environment are dependent upon various conditions such as chemical compatibility, temperature, and other variables, which may not be known to Huntsman. It is the sole responsibility of the user of such product(s) to evaluate the manufacturing circumstances and the final product(s) under actual end-use requirements and to adequately advise and warn future purchasers and users thereof. All information contained herein is provided "as is" without any warranties, express or implied, and under no circumstances shall the author or Huntsman be liable for any damages of any nature whatsoever resulting from the use or reliance upon such information. Nothing contain in this publication should be construed as a license under any intellectual property right of any entity, or as a suggestion, recommendation, or authorization to take any action that would infringe any patent. The term "Huntsman" is used herein for convenience only, and refers to Huntsman Corporation, its direct and indirect affiliates, and their employees, officers, and directors.
The information contained in this publication is provided for informational purposes only. While efforts have been made to verify the completeness and accuracy of the information contained in this publication, it is provided AS IS, without any warranty of any kind, express, or implied.

Main Offices US: Huntsman Corporation /10003 Woodloch Forest Drive/ The Woodlands, TX 77380/ (281) 719-6000

Technical Service US: 8600 Gosling Road / The Woodlands, Texas 77381 / 281-719-7780

Main Offices Europe: Huntsman Belgium BVBA / Everslaan 45 / B-3078 Everberg, Belgium / 32-2 -758-9211
Technical Service Europe: Technical Services Representative / Everberg Office / 32-2-758-9392

Main Office Asia Pacific:
Huntsman Performance Products
No. 455 Wenjing Road, Minhang Economic & Technological Development Zone, Shanghai 200245, P. R. China
Tel : +86-21-3357-6588

Technical Service Asia Pacific:
Huntsman Chemistry R&D Center (Shanghai) Co.,Ltd
No. 479 Wenjing Road, Minhang Economic & Technological Development Zone, Shanghai 200245, P. R. China
Tel : +86 21 3357 2888w

www.huntsman.com

References

HUNTSMAN
Enriching lives through innovation

- Phadke,Milind.(January 2014). Global Lubricant Additives: Market Analysis and Opportunities 3rd Edition. Retrieved from Kline & Company, Inc.
- Childers, J.C., “The Chemistry of Metalworking Fluids” in Byers, J.P., editor “ Metalworking Fluids”, Second Edition, CRC Press, 1994, pp 167-171
- Huntsman Corporation. (2007). “Ethyleneamines: A Global Profile of Products and Services”.:Author
- Huntsman Corporation. (1999). “Ethanolamines”.:Author
- Huntsman Corporation. (2003, September). “Amine Selection for Metalworking Applications”. CMF Plus 59 (9), 24-26.