“Amines 101” for Metalworking Fluids

Houston Section STLE
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Dow Consumer & Industrial Solutions
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Technical Services & Development
Overview

• Application areas

• Neutralizers vs. pH adjusters vs. pH buffers

• Typical acids (good & bad)

• Neutralizer characteristics & choices

• pH adjuster characteristics & choices

• pH buffer characteristics & choices

• Secondary benefits

• Health, safety & regulatory factors
Primary Application Areas

• Water-dilutable metalworking fluids
  – Metal removal (drilling, tapping, grinding, etc.)
  – Metal forming (drawing, rolling, stamping, etc.)
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Neutralizers vs. pH Adjusters vs. pH Buffers

• Neutralizers
  – Typically used in initial formulation (concentrate) to form salts of acid-functional components (organic & inorganic acids)

• pH Adjusters
  – Commonly added to virgin fluids to form stable concentrate/dilution & adjust alkaline pH
  – Sometimes added “tank-side” in MWF systems to restore starting pH of fluid
Neutralizers vs. pH Adjusters vs. pH Buffers

• **pH Buffers**
  – Added to concentrates to neutralize “bad acids” formed during use of fluid and to prevent pH drop (i.e. provide reserve alkalinity)
  – Sometimes added tank-side to renew buffering capacity of fluid
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Typical Acids

• Functional acids (good)
  – Organic acids such as oleic, tall oil, nonanoic, decanedioic and many others provide: corrosion control, emulsification, lubrication
  – Inorganics such as boric acid & phosphate esters impart: corrosion control, biostatic effects, lubrication

• Acid contaminants (bad)
  – By-products of microbial growth (short-chain organic acids)
  – Carbonic acid from dissolved carbon dioxide
  – Oxidative degradation products (mostly organic acids)
  – External contaminants (acid-based cleaners, etc.)
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The Ideal Neutralizer

- Low Molecular Wt.
  - Less is needed to neutralize a given amount of acid

- High Base Strength (pKa)
  - pKa is the pH where ½ the base is neutralized
    - At higher pHs less is neutralized, at lower pHs more is
  - Reaction of highest pKa neutralizer dominates

- Favorable Salt Characteristics
  - A “salt” is the neutralization product of an acid & base (ionic bond)
  - Neutralizers can influence the performance of the corresponding salts
    - Corrosion control
    - Emulsification
    - Solubility
    - Microbial resistance
    - Lubrication
## Typical Neutralizers

<table>
<thead>
<tr>
<th>Neutralizer</th>
<th>Molecular Wt.</th>
<th>pKa</th>
<th>Other Relevant Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Hydroxide</td>
<td>40</td>
<td>13.8</td>
<td><strong>Most efficient overall</strong>, lower performing salts (vs. amines), handling hazards</td>
</tr>
<tr>
<td>Potassium Hydroxide</td>
<td>56</td>
<td>13.5</td>
<td>Lower performing salts (vs. amines), handling hazards</td>
</tr>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>61</td>
<td>9.5</td>
<td><strong>Most efficient amine</strong>, microbially degradable (forms ammonia), leaches cobalt, aggressive on Al alloys</td>
</tr>
<tr>
<td>Monoisopropanolamine (MIPA)</td>
<td>75</td>
<td>9.6</td>
<td>Slightly better microbial resistance (doesn’t release ammonia), leaches cobalt</td>
</tr>
<tr>
<td>Aminomethylpropanol (AMP)</td>
<td>89</td>
<td>9.7</td>
<td>Good microbial resistance (doesn’t release ammonia), leaches less cobalt</td>
</tr>
<tr>
<td>Diglycolamine (DGA)</td>
<td>105</td>
<td>10.0</td>
<td>Microbiologically degraded (fungi), leaches less cobalt</td>
</tr>
<tr>
<td>Butylethanolamine (BEA)</td>
<td>117</td>
<td>10.0</td>
<td>Enhances biocide performance, secondary amine</td>
</tr>
<tr>
<td>Diisopropanolamine (DIPA)</td>
<td>133</td>
<td>9.0</td>
<td>Some microbial resistance, secondary amine</td>
</tr>
<tr>
<td>Octanolamine (OA)</td>
<td>145</td>
<td>9.8</td>
<td>Significantly enhances biocide performance, maintains good ferrous corrosion control</td>
</tr>
<tr>
<td>Triethanolamine (TEA)</td>
<td>149</td>
<td>7.8</td>
<td><strong>Least efficient</strong>, microbially degradable (forms ammonia), leaches cobalt</td>
</tr>
</tbody>
</table>
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The Ideal pH Adjuster

- High pKa
  - High base strength equals efficient pH development

- Minimally reactive with atmospheric CO₂
## Typical pH Adjusters

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<thead>
<tr>
<th>pH Adjuster</th>
<th>pKa</th>
<th>Molecular Wt.</th>
<th>Other Relevant Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>13.8</td>
<td>40</td>
<td><strong>Most efficient overall</strong>, highly reactive with atmospheric CO₂</td>
</tr>
<tr>
<td>KOH</td>
<td>13.5</td>
<td>56</td>
<td>Highly reactive with CO₂</td>
</tr>
<tr>
<td>DGA</td>
<td>10.0</td>
<td>105</td>
<td><strong>Most efficient amine (tied)</strong>, moderately reactive with CO₂</td>
</tr>
<tr>
<td>BEA</td>
<td>10.0</td>
<td>117</td>
<td><strong>Most efficient amine (tied)</strong>, not tested for CO₂ reactivity</td>
</tr>
<tr>
<td>OA</td>
<td>9.8</td>
<td>145</td>
<td>Not tested for CO₂ reactivity</td>
</tr>
<tr>
<td>AMP</td>
<td>9.7</td>
<td>89</td>
<td>Less reactivity with CO₂</td>
</tr>
<tr>
<td>MIPA</td>
<td>9.6</td>
<td>75</td>
<td>Moderately reactive with CO₂</td>
</tr>
<tr>
<td>MEA</td>
<td>9.5</td>
<td>61</td>
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</tr>
<tr>
<td>DIPA</td>
<td>9.0</td>
<td>133</td>
<td>Not tested for CO₂ reactivity</td>
</tr>
<tr>
<td>TEA</td>
<td>7.8</td>
<td>149</td>
<td><strong>Least efficient</strong>, not tested for CO₂ reactivity</td>
</tr>
</tbody>
</table>
pH Adjuster: Base Strength Impact

• KOH & NaOH
  – Strong bases

• Amines
  – Moderate to weak bases
NaOH or KOH Titration Curve

Steep Inflection: high pKa = efficient pH development
Amine Titration Curves

**Figure 5**

Comparison of various metalworking amines used to neutralize INVISTA™ CORFREE® M1

- **DGA**: Steep inflection; moderate pKa = efficient pH development
- **TEA**: Flat inflection; low pKa = inefficient pH development
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The Ideal pH Buffer

- Flat pH response in desired pH range
  - Flat titration curve

- Low molecular weight

- Low reactivity with CO₂

- Good microbial resistance
## Typical pH Buffers

<table>
<thead>
<tr>
<th>pH Buffer</th>
<th>Low pKa = flatness in MWF pH range 8.5-9.5</th>
<th>Molecular Wt.</th>
<th>Other Relevant Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>7.8</td>
<td>149</td>
<td>Flatest titration curve = best buffer, highest molecular wt., highly degraded by microorganisms</td>
</tr>
<tr>
<td>DIPA</td>
<td>9.0</td>
<td>133</td>
<td>Some microbial resistance, not tested for CO₂ reactivity</td>
</tr>
<tr>
<td>MEA</td>
<td>9.5</td>
<td>61</td>
<td>Readily degraded by microorganisms, reactive with CO₂</td>
</tr>
<tr>
<td>MIPA</td>
<td>9.6</td>
<td>75</td>
<td>Some microbial resistance, reactive with CO₂</td>
</tr>
<tr>
<td>AMP</td>
<td>9.7</td>
<td>89</td>
<td>Good microbial resistance, less reactive with CO₂</td>
</tr>
<tr>
<td>OA</td>
<td>9.8</td>
<td>145</td>
<td>Excellent enhancement of biocide performance, not tested for CO₂ reactivity</td>
</tr>
<tr>
<td>DGA</td>
<td>10.0</td>
<td>105</td>
<td>Microbially degraded (fungi), reactive with CO₂</td>
</tr>
<tr>
<td>BEA</td>
<td>10.0</td>
<td>117</td>
<td>Very good microbial resistance, not tested for CO₂ reactivity</td>
</tr>
<tr>
<td>KOH</td>
<td>13.5</td>
<td>56</td>
<td>Steepest titration curve = worst buffer, highly reactive with CO₂</td>
</tr>
<tr>
<td>NaOH</td>
<td>13.8</td>
<td>40</td>
<td>Steepest titration curve = worst buffer, highly reactive with CO₂</td>
</tr>
</tbody>
</table>
NaOH & KOH = High pKa = Poor Buffers

NaOH/KOH buffering range

Desired MWF buffering range: pH 8.5-9.5
Amines = Low/Med. pKa = Better Buffers

Figure 5

Comparison of various metalworking amines used to neutralize INVISTA™ CORFREE® M1

DGA: Poor buffering in desired pH range

BHEMA & TEA: Flatness in desired pH range = excellent buffering

Desired MWF buffering range
Reactivity with Atmospheric CO$_2$

% of Initial Amine Lost to Carbonate Formation

(Recirculated amine solution in open aquarium – 2 weeks at 38°C)

- MEA: 29.5%
- MIPA: 31.9%
- DGA: 37.2%
- AMP: 21.1%

Less reactivity = better pH stability (next slide)
Lower CO$_2$ Reactivity = Better pH Stability

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>MIPA</th>
<th>DGA</th>
<th>AMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.19</td>
<td>11.23</td>
<td>11.16</td>
<td>11.27</td>
</tr>
<tr>
<td>pH 8</td>
<td>9.73</td>
<td>9.55</td>
<td>9.56</td>
<td>10.15</td>
</tr>
</tbody>
</table>
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Secondary Benefits

• Some amines significantly enhance the performance of registered biocides
  – Better control of bacteria & fungi
  – Better pH stability even with lower reserve alkalinity
  – Better maintenance of iron/steel corrosion control
  – Less aggressive on aluminum alloys

• Example
  – Partial replacement of TEA with much lower levels of OA
# Synthetic MWF Formulation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>MEA/TEA</th>
<th>OA/MEA/TEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicarboxylic Acid</td>
<td>3%</td>
<td>3%</td>
</tr>
<tr>
<td>Inversely Soluble Ester</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Phosphate Ester</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>OA</td>
<td>--</td>
<td>4</td>
</tr>
<tr>
<td>TEA</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>MEA</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Triazine</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Deionized Water</td>
<td>64</td>
<td>71</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td><strong>Total Alkalinity</strong></td>
<td><strong>83</strong></td>
<td><strong>60</strong></td>
</tr>
<tr>
<td>(moles amine/100 lbs fluid)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Bacterial Control*

* Weekly inoculation 10E6 CFU/mL bacteria, 10E4 CFU/mL fungi
Fungal Control*

* Weekly inoculation 10E6 CFU/mL bacteria, 10E4 CFU/mL fungi
pH Control

- Steep pH drop due to microbial growth
- Rapid pH rise; likely due to ammonia generation (microbial degradation of MEA & TEA)
- Better pH stability due to better microbiological control

Graph showing pH changes over microbial aging (weeks) with two lines: MEA/TEA and OA/MEA/TEA.
Faster loss of corrosion control due to microbiological growth.
Secondary Benefits: Conclusions

- Good microbial control is critical

- Controlling microbes prevents formation of “bad acids”; a high level of reserve alkalinity isn’t needed

- TEA is an ideal pH buffer for MWFs but is susceptible to biological attack; buffering ability is rapidly lost

- Ammonia generation due to biodegradation of ethanolamines can fool operators into thinking pH is under control
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Health, Safety & Regulatory Factors

• Strong bases are hazardous to handle (KOH, NaOH)

• Secondary amines (DEA, DIPA, BEA) are regulated in Germany (TRGS 611) due to possible formation of nitrosamines

• Ammonia formed by biodegradation of certain amines can result in sudden release during tank-side pH adjustment

• Some amines (TEA, others) can leach high levels of cobalt during carbide tool production; possible adverse health effects if leaching inhibitors (tolyltriazole, etc.) aren’t present
Questions?

Thank You!