Silver Electrodeposition from Sodium and Ammonium Thiosulfate Solutions

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Silver Recovery from Photographic Fixer

- Revenue generating
- Environmental compliance
- Removing silver accomplishes two things:
  - that which is lost to the effluent is controlled and minimized
  - fixer solution can be recycled and reused
Photographic Fixer

- Removes silver halide from the photographic emulsion
- Conventionally done by thiosulfate
- Some components regulated by municipalities
  - silver
  - ammonium (and other) salts
- Plating from ammonium and sodium thiosulfate solutions necessary
Silver Electrodeposition

• Successfully done for many years

• Majority of information remains empirical

• Solutions evolve to better environmental positions, silver electrodeposition has changed
Film Processor with Desilvering System

Electrochemical Cell
Silver Removal from Photographic Emulsion

In the Photographic Emulsion, silver halide reacts with thiosulfate:

\[ \text{Ag}^+ + 2\text{S}_2\text{O}_3^{-2} \rightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{-3} \]
Silver Recovery in Photographic Systems

At the Cathode silver is plated:

\[ [\text{Ag(S}_2\text{O}_3\text{)}_2]^{-3} + \text{e}^- \rightarrow \text{Ag}^0 + 2\text{S}_2\text{O}_3^{-2} \]

At the Anode sulfite is reduced to sulfate:

\[ \text{SO}_3^{-2} + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{SO}_4^{-2} + 2\text{e}^- \]
Experimental Setup

• Rotating Stainless Steel disk cathode
  – 1 cm in diameter
  – incased in Teflon bar 2.5 cm in diameter

• rectangular graphite anode
Effect of Rotation Rate on the Limiting Current for 0.092 M AgBr + 1.0 M (NH₄)₂S₂O₃ Solution
Limiting Current vs. Square Root of Angular Velocity for 0.092 M AgBr + 1.0 M (NH₄)₂S₂O₃
Effect of Rotation Rate on the Limiting Current for 1.0 M Na$_2$S$_2$O$_3$ + 0.092 M AgBr
Limiting Current vs Square Root of Angular Velocity for 0.092 M AgBr + 1.0 M Na$_2$S$_2$O$_3$
Limiting Current vs Square Root of Angular Velocity

- 0.092 M AgBr + 1.0 M (NH₄)₂S₂O₃
- 0.092 M AgBr + 1.0 M Na₂S₂O₃

I/Area (mA/cm²) vs Square Root of Angular Velocity (rad/sec)₁⁄²
Levich Equation

\[ i_L = 0.62 \, n \, F \, D^{2/3} \, \nu^{-1/6} \, C^0 \, \omega^{1/2} \]

where:

- \( i_L \) = limiting current density
- \( n = 1 \) (for silver)
- \( F \) = Faraday’s Constant
- \( \nu \) = kinematic viscosity
- \( D \) = diffusion coefficient
- \( \omega \) = angular velocity of rotating disk
### Walden Product for Sodium and Ammonium Thiosulfate Systems

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>VISCOSITY (g/cm-s)</th>
<th>DIFFUSION COEFFICIENT (cm²/s)</th>
<th>WALDEN PRODUCT (cm⁴/s²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M (NH₄)₂S₂O₃ + 0.092 M AgBr</td>
<td>0.0130</td>
<td>4.51 x 10⁻⁶</td>
<td>5.86 x 10⁻⁸</td>
</tr>
<tr>
<td>1 M Na₂S₂O₃ + 0.092 M AgBr</td>
<td>0.0147</td>
<td>3.73 x 10⁻⁶</td>
<td>5.48 x 10⁻⁸</td>
</tr>
</tbody>
</table>
Current Density vs Potential Curves for \( \text{Na}_2\text{S}_2\text{O}_3 \) and \( (\text{NH}_4)_2\text{S}_2\text{O}_3 \) Solutions with and without AgBr up to -2 V vs SCE

Graph showing the current density vs potential for different solutions:

- 1M \( \text{(NH}_4)_2\text{S}_2\text{O}_3 \) + 0.053M AgBr
- 1M \( \text{Na}_2\text{S}_2\text{O}_3 \) + 0.053M AgBr
- 1M \( \text{(NH}_4)_2\text{S}_2\text{O}_3 \)
- 1M \( \text{Na}_2\text{S}_2\text{O}_3 \)
Current Density vs Potential Curves for Na$_2$S$_2$O$_3$ and (NH$_4$)$_2$S$_2$O$_3$ Solutions with and without AgBr up to -2 V vs SCE
Standard Potential for Cathodic Reactions

\[ \text{Ag(S}_2\text{O}_3\text{)}_2^{3-} + e^- \rightarrow \text{Ag}^0 + 2\text{S}_2\text{O}_3^{2-} \]

\[ E_{\text{Ag/Ag(S}_2\text{O}_3\text{)}_2^{3-}}^0 = 0.0164 \text{ V} \]

\[ \text{S}_2\text{O}_3^{2-} + 8\text{H}^+ + 8e^- \rightarrow 2\text{HS}^- + 3\text{H}_2\text{O} \]

\[ E_{\text{HS}^-/\text{S}_2\text{O}_3^{2-}}^0 = 0.221 \text{ V} \]
Comparison of Ammonium and Sodium Thiosulfate Systems

- Limiting Currents for \((\text{NH}_4)_2\text{S}_2\text{O}_3\) system consistently higher than that for \(\text{Na}_2\text{S}_2\text{O}_3\) system
- Diffusion Coefficient for \((\text{NH}_4)_2\text{S}_2\text{O}_3\) system greater than that for \(\text{Na}_2\text{S}_2\text{O}_3\) system
- Beginning of a second reaction at -825 mV in the \((\text{NH}_4)_2\text{S}_2\text{O}_3\) system
- The reduction of thiosulfate is displaced by -400 mV by replacing \((\text{NH}_4)_2\text{S}_2\text{O}_3\) by \(\text{Na}_2\text{S}_2\text{O}_3\)
Future Work

• Ammonium versus Sodium Thiosulfate
  – Advance understanding
  – Evaluate the environmental impact
  – Effect on industrial silver recovery
• Electrochemistry of sulfur/oxygen compounds
• Electrochemical side reactions that effect the photographic emulsion
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