Purification of phosphoric acid from the waste acids in LCD manufacturing process

2006. 4. 21

Daeil Development Co., Ltd

Research Institute of Industrial Science & Technology
Contents

1. Research Background
2. Process of Treatment
3. Experiment and Results
4. Summary
Present State of Industrial Waste Acid

742,000 tons/year (in 2002 standard)

25.8% of total industrial waste discharged
(The source of resource recycling white book)

<table>
<thead>
<tr>
<th>Waste acid</th>
<th>Discharged amount</th>
<th>Semiconductor etchant</th>
<th>MLB etchant</th>
<th>MLB plating</th>
<th>MLCC manufacture</th>
<th>LCD etchant</th>
<th>PCB etchant</th>
<th>AI pickling</th>
<th>STS pickling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field of IT</td>
<td>181,000 tons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical Industrial</td>
<td>13,000 tons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal Industrial</td>
<td>184,000 tons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Units: tons/year)
The Situation of LCD Manufacturing

Recent progress in production of LCD manufacturing

Discharge industrial waste solution by manufacturers

The source of Korea Electronics Technology Institute

Present discharged amount: above 5000 tons/month in 2005

Environment & Energy Research Center
The Recovery of Phosphoric Acid

**Waste acid**
- Phosphoric acid 60%
- Nitric acid 6%,
- acetic acid 6%
- Metal ions

**Vacuum evaporation**
- 85% phosphoric acid

**Solvent extraction**
- 40% phosphoric acid
- removal of Mo

**Separation of acid**
- acetic acid
- Nitric acid

**Vacuum evaporation**
- High-purity phosphoric acid
- metal ions less than 1 ppm

**Ion exchange**
- metal ions less than 1 ppm

**Vacuum evaporation**
- 85% phosphoric acid
The Removal of Nitric Acid and Acetic acid by vacuum Evaporation

Separation of nitric acid and acetic acid by controlling the degree of vacuum and temperature
The recovery of phosphoric Acid From the Waste Acid in LCD Manufacturing

- **Test range**: under degree of vacuum -670~760 mmHg, 100~160 °C at temperature
- **Commercial range**: under degree of vacuum -750 mmHg, 130 °C at temperature

<table>
<thead>
<tr>
<th>Degree of vacuum</th>
<th>Concentration of phosphoric acid</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>-700 mmHg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comp.</td>
<td>Temp.(°C)</td>
<td>Concentration (g/kg)</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>HNO₃</td>
<td>H₂PO₄</td>
</tr>
<tr>
<td>100</td>
<td>11.62</td>
<td>11.88</td>
</tr>
<tr>
<td>110</td>
<td>6.95</td>
<td>0</td>
</tr>
<tr>
<td>125</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-730 mmHg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comp.</td>
<td>Temp.(°C)</td>
<td>Concentration (g/kg)</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>HNO₃</td>
<td>H₂PO₄</td>
</tr>
<tr>
<td>100</td>
<td>8.66</td>
<td>0</td>
</tr>
<tr>
<td>110</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>125</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

- **Removal of nitric and acetic acid above 110 °C.**
**The Process of Solvent Extraction**

*For the Removal of nitric acid and acetic acid*

The composition of 40wt% diluted phosphoric acid

<table>
<thead>
<tr>
<th>composition</th>
<th>acetic acid</th>
<th>nitric acid</th>
<th>phosphoric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration (g/L)</td>
<td>77.5</td>
<td>58.9</td>
<td>537.7</td>
</tr>
</tbody>
</table>

**Diagram Description:**
- **Waste solution** goes through dilution to enter the extraction process.
- **Extraction** yields 44% recovered phosphoric acid.
- **Strippering** results in the neutralization of the stripped solution with 50% NaOH.
- DI water is used as a solvent in the extraction and strippering processes.
- Steam is used in the vacuum evaporation of industrial phosphoric acid (85%).
- Regenerated solvent is obtained from the strippering process.

*Environment & Energy Research Center*
1. Stages: 6 stage extraction, 6 stages stripping
2. Concentration: diluted waste acid
   \[ H_3PO_4 : 40\text{wt\%} \]
3. A/O ratio: 1/3
4. Conc. of Solvent: 50vol\%(TOP/kerosine)

1. Extraction stages
   - Removal of nitric acid: 5 stages
   - Removal of acetic acid: 6 stages
2. Recovery of \( H_3PO_4 \): above 95%
3. Regenerated Solvent: 6 stage stripping
   (uniform concentration of recovered acid)
The extraction of nitric acid and acetic acid is more effective in Pilot scale testing.

- **Stages:** 6 stage extraction, 6 stages stripping
- **Concentration:** diluted waste acid
  - \( \text{H}_3\text{PO}_4 : 40\text{wt}\% \)
- **A/O ratio:** 1/3
- **Conc. of Solvent:** 50vol% (TOP/kerosine)

The recovery of \( \text{H}_3\text{PO}_4 \) and regeneration of solvent is similar to the result of Bench scale testing.
### The removal of metal ions by diffusion dialysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Waste acid</th>
<th>Recovered acid</th>
<th>Dialysate</th>
<th>Removal of metal ions (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3PO_4$ (g/kg)</td>
<td>226.34</td>
<td>87.78</td>
<td>156.95</td>
<td>-</td>
<td>Recovery of $H_3PO_4$ 38.78%</td>
</tr>
<tr>
<td>Al (mg/kg)</td>
<td>74.99</td>
<td>1.93</td>
<td>87.3</td>
<td>97.35</td>
<td></td>
</tr>
<tr>
<td>Mo (mg/kg)</td>
<td>70.64</td>
<td>26.20</td>
<td>17.62</td>
<td>75.06</td>
<td></td>
</tr>
</tbody>
</table>

- Preliminary runs of ion exchange process
- Reduction of the capacity for ion exchange, adjusting concentration of phosphoric acid, 21%
- Removal of impurities (%) : Al 97.3%, Mo 75.0%
The removal of metal ions by ion exchange

Pre-Regeneration
- Cation exchange resin
  \[ RSO_3Na + HCl \rightarrow RSO_3H + Na^+ \]
- Anion exchange resin
  \[ RNCl + NaOH \rightarrow RNOH + Na^+ + Cl^- \]

Treatment
- LCD waste acid
  \[ H^+ \rightarrow Al^{3+}, OH^- \rightarrow MoRn^{M^-} \]

Recovery of phosphoric acid

Regeneration
- Cation exchange resin (HCl)
  \[ Al^{3+} \rightarrow H^+ \]
- Anion exchange resin (NaOH)
  \[ MoRn^{M^-} \rightarrow OH^- \]

Expulsion (H_2O, Air)

Rinse (H_2O) PSA remove

Rinse (H_2O)
**Test Conditions**

- **Crude phosphoric acid:**
  - RIST manufacture $\text{H}_3\text{PO}_4$ (Al contains)
- **$\text{H}_3\text{PO}_4$ Concentration:** 21.04%, 33.35%, 41.35%
- **Column:** 35mmx 200mm (glass)
- **Resin volume:** 100mL

- Removal of Al with cation exchange resin
- Removal of Al is effective as concentration of $\text{H}_3\text{PO}_4$ decreases
- Monoplus SP112 (Bayer Chemicals) Na type (porous type) is the most efficient
- 21.04% $\text{H}_3\text{PO}_4 \rightarrow 99.4\%$ removal of Al
The removal of Mo with anion exchange resin

Test conditions

- Crude phosphoric acid: RIST manufacture 22.52% H₃PO₄ (Mo contains)
- Initial Conc. of Mo: 72.56 mg/kg
- Column: 24mmx220mm
- Regeneration: 10%NaOH, S.V = 4.0
- Rinse: S.V = 10.0 (BV=20)
- Service: S.V = 2.5 (60min)

<table>
<thead>
<tr>
<th>Component</th>
<th>Mo (mg/kg)</th>
<th>Removal of Mo (%)</th>
<th>Component</th>
<th>Mo (mg/kg)</th>
<th>Removal of Mo (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4400CI</td>
<td>3.86</td>
<td>94.7</td>
<td>MP62WS</td>
<td>4.05</td>
<td>94.4</td>
</tr>
<tr>
<td>IRA 96</td>
<td>0.54</td>
<td>99.3</td>
<td>A100</td>
<td>0.99</td>
<td>98.6</td>
</tr>
<tr>
<td>A378D</td>
<td>0.16</td>
<td>99.8</td>
<td>A103S</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td>MP62</td>
<td>0.74</td>
<td>99.0</td>
<td>WA300</td>
<td>1.23</td>
<td>98.3</td>
</tr>
</tbody>
</table>

- Weakly basic anion exchange resin
Regeneration: 15% HCl, S.V=4.0, B.V=2

- The regeneration efficiency of resin is efficient with regeneration solution of 15% HCl

Evaluation of regeneration efficiency

- Concn. of Al (mg/kg) vs Service time (min.)

- Regeneration efficiency of resin is efficient with regeneration solution of 15% HCl
**Evaluation of regenerate wastewater**

- **Test conditions**
  - **Regeneration**: 15% HCl (S.V=4.0)
  - **Rinse**: water (S.V=10.0)

- **The discharged HCl and H₂O after regeneration and rinse is reusable**
- **about 88% recovery of HCl for regeneration solution**
- **about 87.6% recovery of H₂O for rinse solution**
The process of continues operation

- 4th unit continues operation (S.V= 0.8)

Recovered $H_3PO_4$ → HCl

1Column
- Service-1
  - Regeneration

2Column
- Service-2
  - Service-1

3Column
- Service-3
  - Service-2

4Column
  Regeneration
  - Service-3

Waste solution from Regeneration

Crude phosphoric acid
Summary

- The establishment of conditions for the removal of nitric acid and acetic acid from the mixed waste acid by vacuum evaporation:
  - Degree of vacuum, temperature (-700mmHg, 120 °C)

- The establishment of conditions for the removal of nitric acid and acetic acid by solvent extraction:
  - Phase ratio A/O= 1/3, nitric acid 5 stages, acetic acid 6 stages

- The removal of metal ions (impurities) by diffusion dialysis:
  - 97.3% removal of Al, 75.0% removal of Mo, organic phase; TOP

- The removal of metal ions by ion exchange technology:
  - Al: SP112 (strong cation exchange resin), 99.4% removal, 21.04% H₃PO₄
  - Mo: A103S (weakly anion exchange resin, 100% removal, 22.5% H₃PO₄

- The establishment of continuous process of recovering phosphoric acid for efficient automation of system