Exposure to DMF in a Laminate Manufacturing Facility in China

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N,N-Dimethylformamide - Properties and Use

- DMF (C₃H₇ON) is a solvent widely used in urethane resin, synthetic films, fibers and coating production.
- Polar liquid at room temperature, miscible with water
- Low vapor pressure – 3 mmHg at normal temperature
- DMF penetrates the skin very rapidly.
N,N-Dimethylformamide - Health Effect and Exposure Limit

- Well-known hepatotoxicity – cause occupational hepatitis
- IARC classified Group 2B carcinogen (possibly carcinogenic to humans)
- N-methylformamide (NMF) in urine – Biomarker for DMF exposure.
- ACGIH BEI® for DMF – 15 mg/L NMF
- ACGIH TLV® for DMF – 10 ppm 8hr TWA
Project Background

- Cases of abnormal liver function identified among workers during a pre-acquisition due diligence study.
- 9 cases among workers in Resin Mixing and Treating department were suspected to be occupationally related.
Overview of Manufacturing Processes

- Product – copper-clad laminate
- Fiber glass sheet coated with resin and then pressed on copper foil and baseboard
- Main production departments: Resin Mixing and Treating, Composing and Pressing, Quality Assurance and Inspection
Manufacturing Processes
- Resin Mixing & Treating
Manufacturing Processes
- Cutting & Composing
Manufacturing Processes
- Pressing, Cutting & Inspection
DMF, acetone and toluene are primary solvents used in resin coating.

Most resin mixing and material handling are automated and in pipelines, but some are manual operations.

Equipment cleaning between formula changes involve a lot manual operations.

Skin contact reportedly unavoidable.
Liver Function Abnormality

- ALT, AST, GGT – Blood enzymes tested
- 47 out of 209 tested with at least one enzyme at abnormal level.
  - ALT 46-518 IU/L
  - AST 37-207 IU/L
  - GGT 86-498 IU/L
- 40 male and only 7 female among abnormal.
- 114 male and 85 female among all tested.
- Doctor referred 16 employees to specialists.
## Liver Function Abnormality - Distribution

<table>
<thead>
<tr>
<th>Department</th>
<th>Abnormal</th>
<th>Total</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin Mixing and Treating</td>
<td>11</td>
<td>50</td>
<td>22%</td>
</tr>
<tr>
<td>Composing and Pressing</td>
<td>15</td>
<td>75</td>
<td>20%</td>
</tr>
<tr>
<td>Quality Inspection in Pressing</td>
<td>4</td>
<td>23</td>
<td>17%</td>
</tr>
<tr>
<td>Quality Assurance Lab</td>
<td>2</td>
<td>14</td>
<td>14%</td>
</tr>
<tr>
<td>Equipment and Utility</td>
<td>4</td>
<td>19</td>
<td>21%</td>
</tr>
<tr>
<td>Production Management</td>
<td>8</td>
<td>20</td>
<td>40%</td>
</tr>
<tr>
<td>Administrative and Other</td>
<td>3</td>
<td>8</td>
<td>38%</td>
</tr>
</tbody>
</table>
Biological Exposure Monitoring

- **1\textsuperscript{st} Biological Monitoring** – 8 in Resin Mixing and Treating, 1 in QA Lab
- **2\textsuperscript{nd} Biological Monitoring** – all 46 employees in Resin Mixing and Treating, QA Lab.
- **3\textsuperscript{rd} Biological Monitoring** – all 46 employees in Resin Mixing and Treating, QA Lab.
Biological Exposure Monitoring - Procedures and Method

- Urine samples taken during last hour of 8hr shift.
- Sample collected in plastic bottles and supervised by facility EHS management.
- Urine samples preserved and tested by same clinical laboratory in a medical university.
- Creatinine in urine sample determined
- Sample tested for NMF via GC/FID
Summary of Urine Test Results

- 1\textsuperscript{st} Sampling – 6 over 15 mg/l and three approach the ACGIH BEI
- 2\textsuperscript{nd} Sampling – 28 over 15 mg/l
- 3\textsuperscript{rd} Sampling – 34 over 15 mg/l
Summary of Urine Test Results

**Logprobability Plot and Least-Squares Best-Fit Line**

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**DESCRIPTIVE STATISTICS**

- Number of samples (n) 46
- Maximum (max) 87.83
- Minimum (min) 3.50
- Range 84.33
- Percent above OEL (%>OEL) 73.9
- Mean 31.29
- Median 26.36
- Standard deviation (s) 20.69

**TEST FOR DISTRIBUTION FIT**

- W-test of logtransformed data (LN) 0.9578
- Lognormal (a = 0.05)? Yes

**LOGNORMAL PARAMETRIC STATISTICS**

- Estimated Arithmetic Mean - MVUE 32.54
- LCL1,95% - Land's "Exact" 26.91
- UCL1,95% - Land's "Exact" 41.71
Employee Training

- Company program and procedures
- Potential health effects from DMF exposure
- Importance of avoiding skin contact
- Use of appropriate protective equipment (both respirator and skin protection)
- Specific work practices necessary to work safely with DMF
Other Assessment and Analysis

- Previous air monitoring results show negligible airborne DMF in work areas.
- PID and Drager tube testing for DMF conducted during 2nd biological monitoring.
- Highest DMF reading from Drager tube inside Treater enclosure – 10 ppm.
- Data suggest that dermal exposure is a primary cause.
Qualitative Exposure Assessment

- Analysis focused on resin mixing and treating, material handling, QA lab.
- Production process broken down into tasks and analyzed for exposure potential and to determine level of personal protection necessary.
- All employees participated in the last monitoring interviewed and their routine activities and hygiene practices understood.
DMF Exposure Control Guidelines

- Management roles and responsibilities
- Risk assessment
- Exposure assessment
- Exposure controls
- Medical surveillance
- Employee education and training
- Documentation/record keeping
- Emergency preparedness and response
Summary and What Missed

- Dermal contact with DMF is a primary exposure route at the facility.
- Work practice and personal hygiene play the most important roles in DMF exposure control.
- Biological exposure monitoring provides a true picture of real exposure.
- DMF exposure in other department was not assessed, but likely significant.
DMF Exposure in China

- Acute DMF poisoning involves multiple patients, some involve tens of workers.
- Synthetic leather industry a hard hit.
- In many cases reported worker fully recovered after medical treatment.
- Current DMF exposure limit – 20 mg/m³ TWA; 40 mg/m³ STEL
- Biological exposure index – 10 mg/l NMF
- DMF sampling and analytical standard