Improvement of the Time Sensitive Chemical Process at Los Alamos National Laboratory

EFCOG Safety Working Group
Industrial Hygiene and Safety Technical Task Group

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What are time-sensitive chemicals?

Time-sensitive chemicals are chemicals that when stored for prolonged periods can develop hazards which were not present in the original formulation.

Hazards may develop from inappropriate or improper storage, or from simply storing the chemical too long.
What are time-sensitive chemicals?

- Materials that become shock sensitive upon evaporation of a stabilizer, including azides, nitrate esters like collodion, and other energetic materials such as picric acid. These are often shipped with a stabilizer (usually water), to prevent sensitization and reduce flammability.
What are time-sensitive chemicals?

- Peroxide forming chemicals: peroxide formers and materials that can undergo hazardous polymerization such as ethyl ether and sec-butyl alcohol.
What are time-sensitive chemicals?

- Materials that generate significant additional hazards by undergoing slow chemical reactions. Examples include: unstabilized chloroform or chloroform stabilized with amylene, and metal fulminates such as Tollen’s reagent (silver nitrate, dilute sodium hydroxide, and ammonium hydroxide). Prolonged storage in containers with incompatible materials can also result in hazardous conditions. Examples include: calcium carbide stored in a glass container with a metal lid, and anhydrous hydrogen fluoride in mild steel cylinders.
What are time-sensitive chemicals?

- **Class A: Severe Peroxide Hazard:** Spontaneously decomposes and becomes explosive with exposure to air without concentration.\(^1\)
- **Class B: Concentration Hazard:** Requires external energy for spontaneous decomposition. Forms explosive peroxides when distilled, evaporated or otherwise concentrated.\(^1\)
- **Class C: Shock and Heat Sensitive:** Highly reactive and can auto-polymerize as a result of internal peroxide accumulation.\(^1\)
- **Class D: Potential Peroxide Forming Chemicals:** May form peroxides but cannot be clearly categorized in Class A, B, or C.

\(^1\) Bretherick's Handbook of Reactive Chemical Hazards
What are time-sensitive chemicals?

- Compressed Gases where a shelf life is provided by manufacturer; and moisture creates corrosion, allowing gases to react with the metal to produce hydrogen, weakening cylinder, increasing internal pressure.
- Polynitrated Aromatics
- Shock sensitive materials that degrade over time
References

- Trio of articles authored by members of the EFCOG Chemical Life Cycle Management (one of the predecessors to IH/S TTG):
  - Management of Time-Sensitive Chemicals (I): misconceptions Leading to Incidents,
  - Management of Time-Sensitive Chemicals (II): Their identification, chemistry, and management, and

- Bretherick's Handbook of Reactive Chemical Hazards.

- Numerous good practices documented on university websites.
Current LANL Requirements and Guidance

- P101-14 “Chemical Management”
  - “Containers of materials that might become hazardous (i.e., peroxidizable chemicals) during prolonged storage will be dated when first opened. At the end of 6 months after opening, the material will be evaluated or tested for continued safe use. Material that is found to be safe or that can be stabilized to be made safe will be permitted to be re-dated and retained for an additional 6-month period, or according to manufacturer’s instructions, whichever is more stringent. All other material will be safely and compliantly discarded.”

- Chemical management Tool # 8 “Minimum Requirements for Peroxidizable Chemicals.”


- Updated list of time-sensitive chemicals.
Why did LANL look to improve management of time-sensitive chemicals?

- Risk assessed as part of a Chemical Management Critical Function Evaluation.
- Various levels of worker knowledge, experience, and opinion regarding time-sensitive chemicals and associated good practices.
- Challenges with legacy chemicals.
- Departures of chemical owners resulting in orphan chemicals.
- Hazmat responses for time-sensitive chemical containers.
- Unclear requirements in chemical management policy documents.
How is LANL approaching an improved time-sensitive chemicals process?

- Tap Chemical Users Group/Chemical Hygiene Officers, and Chemist SMEs.
- Perform a causal analysis.
- Obtain concurrence on process.
- Update tools and policy documents.
The LANL Chemical Management Team Approach

- Chemical Users Group/Chemical Hygiene Officers
  - Chartered and endorsed by senior management.
  - Responsibility to review and discuss improvements to chemical safety, as well as provide recommendations for improving the process of chemical management.
  - Work with line managers to identify and implement changes.
  - Authority to request assistance and resources from any member of the Director’s Management Team.
  - Members provide suggested solutions for problems, and demonstrate the ability to work with people at all levels within and across organizations.
Time Sensitive Management Improvement Strategies and Objectives

- Continuous improvement in time-sensitive chemical management.
- Ensuring that the “solution” does not increase risk, i.e., waste, radiological.
- Implement a process that is transparent, easy to understand, easy to implement.
- Ensure a formal change control process for the list of time-sensitive chemicals.
- Assess the cost impacts of implementing, or not implementing improvements to the time-sensitive chemical management process.
- Ensure protection of workers and facilities.
- Reduce risk for LANL.
Proposed Approach for Time-Sensitive Chemical Management

Identify time-sensitive chemicals (LANL listing).

Ensure that users are trained and qualified in accordance with P101-14, *Chemical Management*.

Define proper storage time and evaluation (e.g., visual inspection, testing) based on MSDS/SDS and LANL guidance, and by talking with LANL chemical SMEs.

Inspect time-sensitive containers at least annually.

Document inspection dates and results for each ChemDB barcoded container in ChemDB.

Determine an appropriate shelf life for time-sensitive chemicals, and work with Waste Management Coordinators to dispose of time-sensitive chemicals well before the chemical can become unsafe.

Purchase of only the smallest amount of a time-sensitive chemical for immediate experimental needs. No “stockpile” of time-sensitive chemicals.
Controlling the Hazards of Time-Sensitive Chemicals

Call Emergency Management immediately if:

• The container holds a peroxide former and the peroxide test strip results are > 100 ppm.
• The container has a “mossy” look around the cap, white film or residue around the neck threads or cap of the containers, precipitate, or crystals or viscous oily layer in the liquid.
• No liquid remains in the container.
• The container holds a polynitrated aromatic and is pale in color, and/or crystals are present.
Use and Limitations of Peroxide Test Strips

• Do not use expired test strips.
• Results may not be accurate if the container is very old.
• The test strip cannot always detect polyperoxides.
• Test strips have a limited shelf life.
• The pH of the peroxide former to be tested must be between 2 and 9.
• Precipitation of peroxides out of solution or formation of polyperoxides results in a lower reading than the actual concentration of peroxides.
• Avoid sunlight and moisture.
• Store unopened packs in refrigerator.
• Store open packs in cool/dry place.
Storage of time-sensitive chemicals

- Remove original container from packaging materials, i.e., cardboard, Styrofoam, packing peanuts.
- Avoid storage in containers other than the original manufacturer’s container.
- If one or more secondary containers must be used, ensure that the container is compatible with the time-sensitive chemical, allows for proper storage of the time-sensitive chemical, and is labeled in accordance with **P101-14 Chemical Management, Attachment A, Section 1.5**.
- Store in a cool, dry, well-ventilated area, separate from incompatible materials.
- Check regularly for spills and leaks.
Testing and Stabilization for Peroxides

1. Mark container with date received and date opened, and apply a “PER” sticker or other means of identification.
2. Test for peroxides at first use and record the results on the label, in a notebook, or in ChemDB. Store the container out of direct sunlight, in an area below 30°C.

If test results are: then:

<table>
<thead>
<tr>
<th>If test results are:</th>
<th>then:</th>
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<tbody>
<tr>
<td>0-25 ppm</td>
<td>Continue testing on a six month basis, or monthly if used daily.</td>
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<tr>
<td>25-90 ppm</td>
<td>Contact a Responsible Line Manager (RLM)-approved subject matter expert (SME) to perform stabilization. Stabilization must be defined in a work document. Continue testing the container quarterly.</td>
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<tr>
<td>91-110 ppm</td>
<td>Inform the FOD, and contact an SME to perform stabilization. Stabilization must be defined in a work document. Continue testing the container quarterly.</td>
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<tr>
<td>&gt;110 ppm</td>
<td>Secure the area and call 7-6211 or 911.</td>
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</table>
## Storage Categories

The storage category indicates how long a time-sensitive may be stored.

<table>
<thead>
<tr>
<th>Description</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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</thead>
<tbody>
<tr>
<td>Exceptions to Storage Categories</td>
<td>Untested open containers: discard after three months unless exception is met.</td>
<td>Untested open containers: discard after six months unless exception is met.</td>
<td>Untested open containers: discard after one year unless exception is met.</td>
<td>Storage period per manufacturer or distributor shelf life.</td>
<td>Indefinite storage with testing unless exception is met.</td>
<td>Indefinite storage with no testing required.</td>
</tr>
<tr>
<td>1. Containers of open time-sensitive chemicals stored in inert atmospheres</td>
<td>An SME verifies that the container contents will not develop a hazardous condition.</td>
<td>An SME verifies that the container contents were packaged under an inert atmosphere by the chemical distributor or manufacturer.</td>
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<td>(e.g., a glove box) may be stored indefinitely, and do not require testing,</td>
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<td>as long as an SME verifies that the container contents will not develop a</td>
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<td>hazardous condition in an inert atmosphere.</td>
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<td>2. Containers of unopened time-sensitives may be stored indefinitely in</td>
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<td>proper storage as stated by the manufacturer, as long as:</td>
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<td>• An SME verifies that the container contents will not develop a</td>
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### Inspection Categories

The inspection category indicates the frequency of an evaluation, e.g., visual inspection, testing, or that no evaluation is required.

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<thead>
<tr>
<th>Description</th>
<th>1</th>
<th>2</th>
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<tbody>
<tr>
<td>At first use</td>
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<td>Quarterly</td>
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<td>Semi-annually</td>
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<tr>
<td>Annually</td>
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<td>Upon receipt</td>
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<tr>
<td>No inspection required</td>
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Evaluation Categories

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<tr>
<th>Evaluation Categories</th>
<th>1</th>
<th>2a</th>
<th>2b</th>
<th>3</th>
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</thead>
<tbody>
<tr>
<td>Description</td>
<td>Visual inspection</td>
<td>Testing: test strip</td>
<td>Testing: other</td>
<td>No evaluation required</td>
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</tbody>
</table>

The evaluation category indicates the type of evaluation: visual inspection, test strip (peroxide formers only), or that no evaluation is required.
Points of Discussion

- Isopropyl alcohol (2-propanol) is a time-sensitive chemical because it forms peroxides, albeit very slowly. There are differences in the safety of anhydrous isopropyl alcohol (more hazardous) vs. 60-70% Isopropyl alcohol (minimal hazard).

- Most time-sensitive chemicals are routinely made safe with the addition of stabilizers, or by being in solution. Concern only arises if stabilizers evaporate or are otherwise consumed.
Where we are headed

- Walk down all areas to verify both active chemical containers, and any legacy containers.
- Finalize the approach.
- Update ChemDB.
- Update our policy.