SAFETY BULLETIN
Time-Sensitive Chemicals

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Introduction

Recently a 20-year-old chemical bottle disintegrated and spilled its contents after being picked up by a researcher. The plastic bottle was extremely brittle and easily broke during routine handling. A check of other bottles in the same area uncovered more in a similar state. Other incidents have occurred when chemicals have been stored longer than recommended by the manufacturer. Over time, some chemicals become dangerously unstable. Adherence to SDS and manufacturer recommendations is critical. The following guidance will be useful in managing chemical inventories but should not be considered exhaustive. Always consult the SDS and do your research when planning experiments.

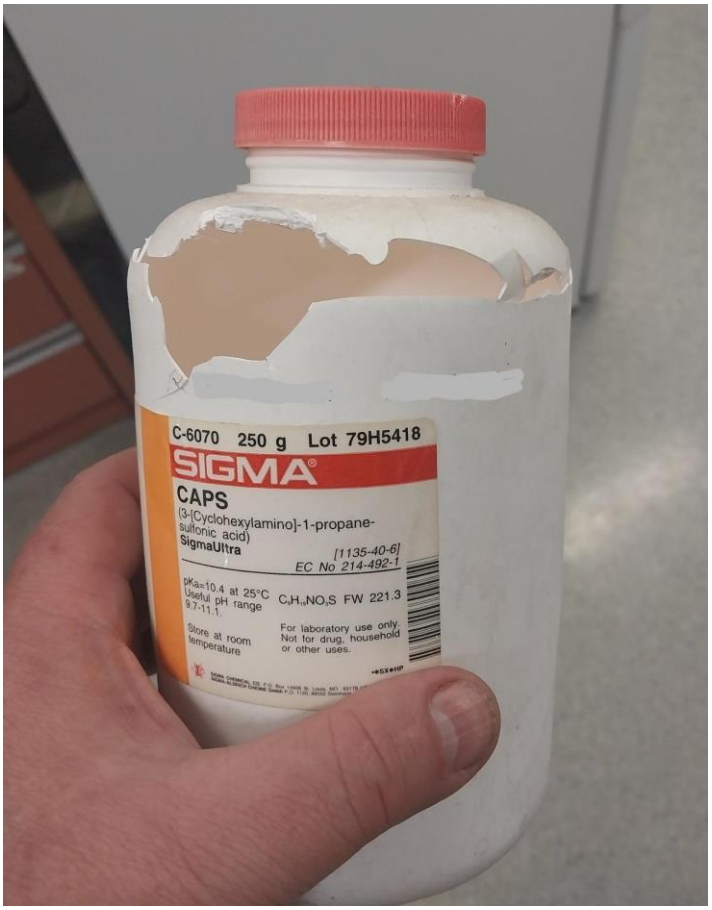
Advice and Action

Various factors can affect the condition and integrity of chemical containers. These include:

- Age – best practice is to mark bottles with a date received and date opened.
- Exposure to UV radiation (if stored near windows or other UV sources)
- Exposure to heat
- Exposure to chemical contents. Some chemicals slowly degrade their containers.

Warning signs include:

- Faded colour (note the faded red lid in the photo)
- Condition of other similar containers. If one bottle fails, others with a similar age and storage history are likely to break as well.
- Time-sensitive chemicals. Some chemicals become unstable and unsafe over time. This usually does not affect the container but may in some instances. Refer to the SDS and manufacturer recommendations. Manage these chemicals carefully and dispose of them before they become hazardous. Add these checks to your cyclic events checklist or lab tasks calendar and ensure they are completed.



Time-Sensitive Chemicals

Time-sensitive chemicals are those which become unstable or otherwise unsafe if stored too long. Some chemicals become explosive, either through the formation of explosive peroxides or if part of their moisture content is lost to evaporation. Others build up pressure over time. Some chemicals attack their containers, resulting in failures and the release of vapours or other spills.

Peroxide-Forming Solvents

Peroxide forming chemicals slowly react with atmospheric oxygen during storage. This autooxidation can lead to the formation of unstable, explosive peroxides (reactive chemicals containing weak O-O bonds). The reaction can be initiated by exposure to free radical sources including air, heat, light, or contaminants. Most of these solvents are available with inhibitors/stabilisers to slow the

peroxide formation. It's critical to adhere to the manufacturer's storage guidelines and limitations. Refer to the list of Peroxide-Forming Solvents.

Shock-Sensitive Chemicals

Some chemicals are shock sensitive and may explode if exposed to shock, friction or grinding. Some are peroxide formers and others must retain their moisture content to avoid becoming shock-sensitive and explosive. As they dry out, they transition from flammable solids or other stable chemicals to shock-sensitive explosives.

Refer to the list of Shock-Sensitive Chemicals—note this list is not exhaustive and SDS documents must be consulted.

Also refer to the list of Other Time-Sensitive Chemicals.

Chloroform

In contact with air, chloroform decomposes to form highly toxic phosgene gas.

- Always use chloroform in a fume cupboard. Chloroform vapour is a chronic health hazard, in addition to the acute phosgene hazard.
- Purchase inhibited/stabilised chloroform, especially the grade inhibited with ethanol. Amylene-inhibited chloroform may not effectively inhibit phosgene formation.
- Always store in the dark. Light drives phosgene formation.
- Do not store for excessive lengths of time:
    - Ethanol-stabilised chloroform – recommend disposal three years from purchase date.
    - Other stabilised chloroform – recommend disposal one year from purchase date.
    - Unstabilised chloroform will have a much shorter shelf life.
    - Refer to SDS and follow manufacturer's recommendations for shelf life and safe storage.

Perchloric Acid

Also listed as one of the shock-sensitive chemicals, users must be particularly careful to never use perchloric acid in standard fume cupboards. Fume cupboards with special scrubbers, designed for use with perchloric acid, must be used instead. The use of perchloric acid in standard fume cupboards will lead to the accumulation of explosive perchlorate salts in the duct work. These perchlorate salts are shock-sensitive, presenting a severe explosion hazard for future disturbance or maintenance of the fume cupboard ducts.

Pressure Building Chemicals

Methyl Ethyl Ketone Peroxide (MEKP) is shock sensitive. It also decomposes during storage in sealed containers which may result in a large pressure build-up and subsequent explosion. Shelf life is three months at 25°C.

Formic Acid (>90%) decomposes to carbon monoxide, accumulates pressure within its container and must be disposed of after 12 months due to this risk. Do not open these containers near your face.

- Purchase lower concentrations.
- Install vented caps.
- Store in a plastic bottle
- Vent containers regularly and dispose of 12 months since last venting.

Hydrogen peroxide slowly decomposes over time and liberates oxygen.

- Store upright in the original container, which will be vented for reasonably high concentrations.
- Impurities catalyze decomposition and must be excluded. Do not return unused hydrogen peroxide to the original container.
- Refrigerated storage is recommended to prolong life.
- Hydrogen peroxide above 30% concentration is extremely hazardous and should not be purchased.

Bromine

Bromine is extremely corrosive and has been known to attack the Bakelite lids used on older bottles. This has led to the accumulation of yellow bromine vapour within corrosives cabinets.

Time-Sensitive Gas Cylinders

Some gas cylinders have a shelf-life provided by the manufacturer which must be strictly followed. Storing these gases too long can

lead to violent cylinder explosions which create dangerous projectiles and release toxic gas. Refer to the list of Time-Sensitive Gas Cylinders.

References

- Purdue University – Time Sensitive Chemicals
- Queensland Dept of Education – Dangers of Prolonged Storage of Time Sensitive Chemicals
- ACS Publications – Management of Time Sensitive Chemicals: Misconceptions Leading to Incidents
- USC Environmental Health and Safety – Time Sensitive Chemicals
- USC Environmental Health and Safety – Other Time Sensitive Chemicals
- University of Tennessee, Knoxville Environmental Health and Safety – Time Sensitive Chemicals
- East Carolina University – Shock-Sensitive Chemicals