FEATURE

Management of time-sensitive chemicals (II): Their identification, chemistry and management

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INTRODUCTION

In a previous paper[1] it was shown that the practice of storing time-sensitive chemicals for extended periods is dangerous. As one reviews the literature, one observes more and more cases of time-sensitive chemicals being stored for prolonged periods. Sometimes these chemicals are also improperly stored. Questions that come up include how time-sensitive chemicals are identified, what chemistry is present with time-sensitive chemicals, and how are time-sensitive chemicals effectively managed? Without fully understanding issues such as these, one cannot effectively manage time-sensitive chemicals.

TIME-SENSITIVE CHEMICAL CLASSIFICATION

Time-sensitive chemicals are those chemicals that, when stored for prolonged periods or under improper storage conditions, can develop hazards that were not present in the original formulation. There are four general categories of time-sensitive chemicals loosely based on those unsafe properties that can develop. They are (1) peroxide formers, (2) peroxide formers that can undergo hazardous polymerization, (3) materials that become shock or friction sensitive upon the evaporation of a stabilizer, and (4) materials that generate significant additional hazards by undergoing slow chemical reactions. It should be noted that time-sensitive chemicals can be pure reagents or they can be commercial mixtures formulated as cleaners, adhesives and other products. (Note: In this paper the term "chemical" will be used to mean both pure reagents and chemical products.)

Peroxide Forming Chemicals/ Chemicals that Undergo Hazardous Polymerizations

Peroxide formation is the best known of all time-sensitive chemical classes.[2–4] In spite of being so well known, there are many aspects that are not well understood. One area that is not well understood is that of peroxide detection. There are many methods that can be used for quantitatively detecting peroxides in solution. Methods include the qualitative ferrous thiocyanate method,[5,6] iodine tests,[7] titanium sulfate method[8,9] and quantative dip strips. These tests do have limitations. While the dip strips are the fastest, least intrusive, and the most accurate,[10] limitations they suffer include difficulty detecting polyperoxides,[4] difficulty testing nonvolatile solvents, and having a limited shelf life. Other methods also have difficulty in detecting polyperoxides as well as alkylperoxides and require much more time as well as reagents and equipment.

The solvent being tested will also affect peroxide measurements. As stated before, testing nonvolatile solvents using a dip strip can be difficult. Besides this, solvents can make peroxide testing difficult in other ways. Peroxides will be more soluble in some solvents than others. If the peroxide is not very soluble, then a small amount will remain in solution and the rest will precipitate out of solution (see 1,4-dioxane, laser dye in Table 1). Precipitated peroxides can be very difficult to see in some containers (e.g., safety cans, amber glass bottles, opaque plastic bottles, etc.) or when the precipitate is very fine. These precipitates can also be at the bottom of the container, floating on the surface, around the cap on the inside, etc., which all make it difficult to see. If a precipitate is present, then a saturated solution exists and one will never observe a concentration greater that that of a saturated solution. Also, some solvents will allow polyperoxides to be generated. This form of peroxide is difficult to measure regardless of the method chosen and the measurements will always be lower than the actual concentration of peroxide present. Because of these measurement issues, one must always assume that peroxides are present in concentrations greater than that measured.

An example of how much greater a concentration of peroxide may be present over that measured comes from actual experience. We observed a container of a waste that was generated prior to 1993. This container tested positive for peroxides and the concentration was measured at 30 ppm. The product was present in two 10-liter plastic bottles and was labeled as a "cleaner" with no specified

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components. No MSDS was available for this product so the contents were largely unknown. A process was set up to neutralize the peroxides present so that the product could be sent out as waste. The process involved the addition of 5% aqueous ferrous sulfate. Upon addition of the ferrous sulfate, the temperature increased such that an ice bath was required to cool and slow the reaction. A 10% hydroquinone solution was also added to aid the reaction, but so much heat was given off that the "cleaner" solution had to be diluted with diesel fuel. During this treatment, measurable amounts of peroxides increased. A total amount of 3 kilograms ferrous sulfate was required to quench peroxides present indicating that the initial concentration of peroxides present was a minimum of 65,000 ppm. After the neutralization was complete, the volume of neutralized waste was approximately 30 gallons. This undermeasurement was not an isolated event. In another case, a 1 liter bottle was tested with a dipstick and found to have 10 ppm, but after neutralization, it was found to have had over 1% peroxide present. These undermeasurements are likely due to the formation of polyperoxides that do not react with the dipstick but are believed to react with the hydroquinone to be cleaved into the individual hydroperoxides.

To further understand peroxide formation in organic solvents, we have compiled our testing data over several years with that which has been published (Table 1). Several observations can be made by examining these data. One observation is that a mixture of water and tetrahydrofuran (THF) formed a considerable concentration of peroxide. Conventional wisdom has always held that peroxides would not be formed when water was present or that the water would help eliminate any peroxide that might be present. Finding a peroxide concentration in excess of 100 ppm in a mixture of water and THF would seem to refute this idea. Another observation that can be made is that containers do not have to be opened to have a potential peroxide problem. Unopened containers of diethyl ether and isoamyl alcohol both showed 100 ppm and more of peroxides. One would assume that these peroxides developed over time due to some leak that would allow air into the container, but that may not be a valid assumption. If air were allowed to leak into the container, then a highly volatile solvent would be allowed to leak out, but records do not indicate that any ethyl ether had evaporated from the container. Furthermore, 1-pentyne that was present in a sealed glass ampoule was found to have 10 ppm peroxide. Together, these observations suggest that the peroxide was present at the time of packaging so the assumption that product arrives from the manufacturer free of peroxide may not be valid. The argument that peroxides were formed by air trapped in the headspace of factory sealed containers does not seem to be valid since a relatively small amount of air would be present and peroxide concentrations in the unopened containers were relatively high.

The next logical question concerns what concentrations of peroxide are hazardous. Clearly, there cannot be a precise answer that applies to all solvents. It would seem obvious that the greater the concentration of peroxide, the more hazardous the situation and that concentrations exceeding the saturation point leading to the presence of crystals would be considered hazardous. (Solid peroxide structures of low molecular weight ethers are shock and friction sensitive, therefore, their presence, even in the liquid, greatly increases the hazard present.) Efforts have been made to determine which level of peroxide is considered hazardous and these estimates have ranged from 50 to 10,000 ppm, but no information was provided to support these values. Some chemical safety programs use a 100 ppm concentration as control point because this concentration can easily be measured using the dipstick and other methods without having to perform dilutions. Whatever level is chosen, it should be kept in mind that some solvents will generate polyperoxides and that relatively low peroxide measurements can hide rather large concentrations.

Evaporation Hazards

Many compounds exist that are stable when wet but become shock and friction sensitive explosives upon desiccation. These compounds are typically multi-nitro aromatics with picric acid being the most notable.[11] Picric acid when wetted with 30% water is classified by DOT as a flammable solid but, when the water content falls below 30%, it changes to a class 1.1 D explosive.[12] As one can see, the explosive nature of picric acid increases as the amount of water present decreases. When picric acid is completely dehydrated, it becomes extremely sensitive to shock or friction. Unscrewing a cap with dried crystals in the threads can be enough to cause the picric acid to explode.[13] When dried picric acid is found, bomb squads are many times called in to remove it.

Another problem with multi-nitro aromatics like picric acid is that they are able to form salts over time that can become dangerously sensitive. For example, contact with metal caps or lids can lead to the formation of metal picrates that are sensitive to friction, heat or impact.[13] Contact with cement can also lead to friction sensitive calcium salts. Extreme care must be used when old containers of multi-nitro aromatics are found where there has been a potential for the multi-nitro aromatic to come into contact with other materials such as metals or metal cations.

Development of Additional Hazards

We have chosen to provide a few examples of chemicals that develop additional hazards over time. The current usage of these chemicals is not important; the issue here is that they have a limited shelf life and these items should be disposed if they are no longer in use or if they have been in your chemical inventory for a prolonged time.

Chloroform

Chloroform can react with air to form phosgene, but this information does not seem to be well documented in recent literature despite it being commonly discussed in textbooks and safety manuals prior to 1960. In a sur-

Table 1. Peroxide Test Results

Chemical Name	CAS#	# Samples	PPM Peroxide	Age (years)	Test Method and Comments (a)	Reference
Acetal	105-57-7	2	10 to 30	6 to >10	(f)	{l}
Acetaldehyde	75-07-0	6	1 to 20	>1 (g) to 8	(f)	{34} {m}
Acetophenone	98-86-2	2	2 to 3	>1 (g)		{34}
Acrylonitrile	107-13-1	2	0	>1 (g)		{m}
Amyl acetate	628-63-7	1	0	>9	(f)	{l}
Benzaldehyde	100-52-7	1	1	(g)	(f) (b)	{l}
Benzyl alcohol	100-51-6	9	0 to 100	>1 (g) to 11		{34} {m}
1-Butanol	71-36-3	4	0 to 4	>1 (g)		{34} {l}
2-Butanol	78-92-2	11	3 to >1,000	>1 (g)	(f)	{34} {3} {l} {m}
2-Butoxyethanol	111-73-2	1	>100	>1 (g)	(f)	{l}
2-Butoxyethylacetate	112-06-2	1	3	>1 (g)	(f)	{l}
Chloromethyl methyl ether	107-30-2	1	1	>10	(f)	{l}
Collodion	Mixture	2	0 to <10	>9 to >21	(f) (b)	{l}
“Cleaner”	Mixture	2	30	>12	(f)	{l}
Crown ether and toluene	Mixture	1	1	> 8	(f)	{l}
Cumene	98-82-8	2	3 to 30	>9	(f)	{l}
Cyclohexanol	108-93-0	8	3 to 2,000	>1 (g) to 30		{3} {34} {l} {m}
Cyclohexanone	108-94-1	9	1 to 3	>1 (g)		{34}
Cyclohexene	110-83-8	5	0 to 50	>1 (g) to 30	(f)	{34} {l} {m}
2-Cyclohexen-1-ol	822-67-3	1	30	>1 (g)		{34}
Cyclohexene oxide	286-20-4	1	1	>1 (g)		{34}
Cyclopentanol	96-41-3	1	3	>1 (g)		{34}
Cyclopentanone	120-92-3	4	1 to 4	>1 (g)		{34}
Dicyclopentadiene	77-73-6	1	3	>1 (g)	(f)	{l}
5-Decyne	1942-46-7	1	10	>1 (g)	(f)	{l}
Dibenzyl ether	103-50-4	1	1	>1 (g)		{34}
2,5-Dimethyltetrahydrofuran	1003-38-9	1	10	>1 (g)	(f)	{l}
Dimethoxymethane	109-87-5	2	>100	<2 to >10	(f)	{l}
3,4-Dimthoxybenzyl alcohol	93-03-8	1	3	7	(f)	{l}
2,2-Dimethoxypropane	77-76-9	2	3 to 10	>1 (g)	(f)	{l}
1,4-Dioxane	123-91-1	18	0 to >100	>1 (g) to 24	(f)	{34} {l} {m}
1,4-Dioxane, laser dye	Mixture	9	3 to 30	>9	(f) (b)	{l}
Dipropylene glycol methyl ether	34590-94-8	1	3	30	(f)	{l}
Dipropyl ketone	123-19-3	1	1	>10	(f)	{l}
Ethylbenzene	100-41-4	2	6 to 8	>1 (g)		{34}
Ethyl ether	60-29-7	52	0 to >100	>1 (g) to 12.5	(f) (c)	{34} {l} {m}
Ethylene glycol dimethyl ether	110-71-4	9	0 to 100	0.5 to >1 (g) to 9	(f)	{l} {m}
Ethylene glycol monobutyl ether	111-76-2	7	1 to 3	>1 (g) to >9	(f) (b)	{l}
Ethyl methyl ketone	78-93-3	1	1	>1 (g)	(f)	{l}
Ethyl acetoacetate	141-97-9	1	30	>10	(f)	{l}
4-Heptanol	589-55-9	1	30	>1 (g)		{34}
3-Heptanone	541-85-5	1	2	>1 (g)		{34}
2-Hexanol	626-93-7	1	10	>1 (g)		{34}
Isoamyl alcohol	123-51-3	48	0 to >1,000	0.5 to >1 (g) to 30	(f) (c)	{l} {m}

Table 1. (Continued)

Chemical Name	CAS#	# Samples	PPM Peroxide	Age (years)	Test Method and Comments (a)	Reference
Isobutyraldehyde	78-84-2	1	2	>1 (g)	(f)	{34}
Isopentyl alcohol	123-92-2	2	100	>1 (g)	(f)	{l}
Isopropyl alcohol	67-63-0	32	0 to >100	>1 (g) to >9	(f) (b)	{l}
bis(2-Methoxyethyl) ether	111-96-6	2	1	>1 (g) to >10	(f)	{l}
Methyl acetate	79-20-9	2	0	>9	(f) (b)	{l}
3-Methyl-1-butanol	123-51-3	7	10 to 30	>1 (g)		{34}
1-Methylcyclohexene	591-49-1	1	1	>1 (g)		{34}
3-Methylcyclohexene	591-48-0	1	3	>1 (g)		{34}
4-Methylcyclohexene	591-47-9	1	1	>1 (g)		{34}
Methyl ethyl ketone	78-93-3	9	1 to >100	>1 (g) to >10	(f)	{l}
Methyl isobutyl ketone	108-10-1	10	0 to 70	1 to >1 (g) to >9	(f) (b) (i)	{34} {l} {m}
3-Methyl-3-hexanol	597-96-6	1	>20	>1 (g)		{3}
4-Methyl-2-pentanol	108-11-2	1	20 to 30	>1 (g)		{3} {34}
Methyl methacrylate	80-62-6	1	<10	>9	(f) (b)	{l}
2-Methyltetrahydrofuran	96-47-9	5	0 to 100	>1 (g) to >10	(f)	{l}
Nitrocellulose	9004-70-0	2	0	>9	(f)	{l}
1-Octanol	111-87-5	1	20	>1 (g)		{3}
2-Octanol	123-96-6	2	2 to 20	>1 (g)		{3} {34}
1-Octene	111-66-0	3	3 to 10	>1 (g)		{34}
2,4-Pentanedione	123-54-6	1	1	>1 (g)	(f)	{l}
2-Pentanol	6032-29-7	3	1 to 20	>1 (g)		{3} {34}
2-Pentanone	107-87-9	5	1 to 12	>1 (g) to >10	(f)	{34} {l}
3-Pentanone	96-22-0	2	4 to 6	>1 (g)		{34}
4-Penten-1-ol	821-09-0	1	20	>1 (g)		{34}
1-Pentene	109-67-1	5	1 to 10	>1 (g) to >10	(f) (d)	{34} {l}
Phenethyl alcohol	60-12-8	1	100	>1 (g)	(f)	{l}
1-Phenylethanol	1514-69-7	3	30	1		{34} {l}
2-Phenylethanol	60-12-8	2	10, 12	1 to >1 (g)		{34}
dl-1-Pheylethanol	1517-69-7	1	>20	>1 (g)		{3}
Petroleum ether	109-66-0	9	<10 to >100	>9	(f) (b)	{l}
1-Propanol	71-23-8	3	1 to >100	>1 (g) to 27	(f) (b)	{3}
2-Propanol	67-63-0	28	0 to 100	>1 (g) to >10	(f) (b)	{34} {l}
Propiophenone	93-58-3	1	3	>1 (g)		{34}
Styrene	100-42-5	4	3	>1 (g) to >9	(f) (j)	{l}
Tetrahydrofuran	109-99-9	86	0 to >1,000	1 to 15	(f) (b) (k)	{34} {l} {m}
Tetrahydrofuran + water	Mixture	1	>100	>1 (g)	50:50 mix	{l}
Adhesive with tetrahydrofuran	Mixture	50	<100	>9	(f)	{l}
1,2,3,4-Tetrahydronaphalene	119-64-2	4	0	>9	(f)	{1} {l}{m}
Vinyl acetate	108-05-4	1	0	3		{m}
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(a) Test strips were obtained from Aldrich Chemical Co. Tests were performed under an inert atmosphere following the manufacturer's instructions. (b) Some samples stored in an amber glass bottle. (c) One container was unopened. (d) Sealed in a glass ampoule. (e) Visible clusters of crystals present. (f) Tested with Dip Strip. (g) Most likely greater than 1 year but ultimate age unknown. (h) Visible crystals in one container. (i) The 1-year-old sample contained 70 ppm peroxide. (j) One partially polymerized, one fully polymerised. (k) One was HPLC grade, one with septum. (l) Data provided by authors. (m) Data courtesy of Larry McLouth of Lawrence Berkeley National Lab.

vey of MSDSs from eight different manufacturers only one indicated that phosgene could be formed at room temperature and six indicated that phosgene was only a by-product from thermal decomposition in a fire situation. Prudent Practices[14] indicates that chloroform will thermally decompose into phosgene while both The Merck Index[15] and Sax's[16] provide no information about the potential of phosgene formation. What is interesting is that several of these resources indicate that alcohol or alpha-amylene is added to prevent decomposition, but no mention is made as to the identity of room temperature decomposition products. It is also interesting to note that the decomposition of chloroform into phosgene has been well documented in earlier literature.[18–20]

Phosgene is a highly toxic gas that has a LC_{50} between 225 and 570 ppm/minute.[16,17] Phosgene can be formed from chloroform at room temperature and the phosgene formed is both stable and soluble in chloroform. It is indicated that sunlight, humidity or a metal catalyst is required and any metals that are required to catalyze the reaction need only be present in trace amounts.[17] Phosgene concentrations have been reported as high as 1.1% dissolved in chloroform and 15,000 ppm in the headspace above the solution.[17] Phosgene can be monitored using Dräger tubes or colorimetric assay.[1] While all published limits for phosgene are all 0.1 ppm, there are no guidelines as to what levels of phosgene in chloroform would be acceptable.

Anhydrous hydrogen fluoride and hydrogen bromide

Anhydrous hydrogen fluoride (AHF) is a gas that, when compressed to about 15 psig, condenses into a liquid. When stored in carbon steel cylinders, the AHF slowly reacts with the steel to form iron fluoride and hydrogen. Since the hydrogen cannot condense into a liquid, the pressure in the cylinder builds up as more hydrogen is generated. This can cause the cylinder to catastrophically fail.[21–23] Failure of cylinders containing AHF can result in fragmentation damage, release of flammable hydrogen and exposure to hydrogen fluoride gas that is both toxic and corrosive. Hydrogen bromide is a liquefied gas with a vapor pressure of 320 psig at 70 °F and has been reported to undergo a similar reaction that can lead to overpressurization.[24] It is interesting to note that no reference to this type of reaction could be found for hydrogen chloride.

Formation of hydrogen from AHF in steel cylinders starts within days of filling and proceeds slowly.[24] One lecture bottle of AHF that had been stored for 14 years had an estimated pressure of 2,400 psig. Cylinders that fail typically have been in storage for 14–25 years. Because of this over pressurization issue, Air Products, a manufacturer of AHF, recommends that cylinders of AHF have a maximum shelf life of two years if not in service.[24] Cylinders of AHF should be returned to the manufacturer once the two-year shelf life has been exceeded. No information could be found concerning the rate of formation of hydrogen gas in cylinders containing hydrogen bromide or of any hydrogen bromide cylinders failing from overpressurization.

Another problem that we have observed is that hydrogen bromide and hydrogen fluoride can cause corrosion of the cylinder valve on lecture bottles. This has been observed in several cases regardless of valve material or type. Attempts to open the valve to sample or empty the container have caused the valve stem to be ejected from the valve body or the cylinder contents to be released.

Liquid hydrogen cyanide

Hydrogen cyanide is a liquid that boils at 26 °C and is sold/stored in low pressure gas cylinders. If liquefied hydrogen cyanide is stored without a stabilizer present (e.g., 0.1% sulfuric acid), then exothermic polymerization can occur.[25] A product of the reaction is ammonia that helps catalyze the reaction. One result of this reaction is a crust that builds on the surface of the liquid. Even slight movement of the cylinder can cause part of the crust to break off and fall into the liquid which can lead to an accelerated reaction causing cylinder failure from the dramatic increase in cylinder pressure.[26,27] Cylinder failure can lead to fragmentation and shock damage as well as the release of a highly toxic gas.

Formic acid

Concentrated formic acid (90–100%) slowly decomposes to form carbon monoxide and water upon prolonged storage. Gas pressure from carbon monoxide formation has been reported to reach 101 psig within a year of storage which can be sufficient to rupture sealed glass containers.[28–30] Merck and other manufacturers recognized the problem some years ago, and in 1984 changed the original standard screw cap to a screw cap incorporating a pressure relief valve. The significance of the change was, however, not widely communicated. A review of 18 current MSDS provided a variety of warnings and recommendations ranging from no mention of the potential pressurization hazard to recommendations that included vent periodically, refrigerate at 4 °C, and use a pressure relief cap. The majority only hinted at the potential hazard by listing the decomposition products at elevated temperature.

Alkali metals

Slow reactions of alkali metals and their alloys with oxygen to form oxides and superoxides have been well documented.[31,32] Even when these metals are stored under mineral oil, oxygen can dissolve in the mineral oil and react. Potassium, under these circumstances, forms yellow or orange coating that can explode or catch fire upon cutting. NaK, a eutectic mixture of potassium and sodium, can undergo a similar reaction. Lithium stored under dry nitrogen can react with the nitrogen to form a nitride. Formation of the nitride is autocatalytic and can eventually lead to autoignition of the lithium.[33] Fires of alkali metals are extremely dangerous and difficult to extinguish.

IMPLICATIONS OF TIME-SENSITIVE CHEMICAL MISMANAGEMENT

The most significant implication stemming from the mismanagement of time-sensitive chemicals is liability.

This liability may be personnel safety, facility safety, environmental safety or financial. While each may have some specific hazards, the chemistry of these chemicals is well understood when first purchased and used as intended. At this point the financial and safety liabilities are generally well defined and manageable. As these chemicals age, the liability increases as a function of the degradation of the chemical.

One of the implications of mismanagement of chemicals is increased mitigation costs. An informal survey of companies that specialize in remediation of time-sensitive chemicals was conducted. Most of these companies were involved with the remediation of peroxide forming solvents. The typical protocol for remediation of peroxide formers is to set up required barriers and equipment, determine the type of material and peroxide level, select a treatment methodology, and treat the sample. Once completed the sample is inoculated with an appropriate inhibitor, sealed, and labeled with the date and certified peroxide free. The recommendation is to dispose of the material within 30 days. This 30-day period coincided with the requirements of many waste handlers who will only take materials within 30 days of their certification date.

In order to get a realistic idea of the remediation costs involved we have broken them out into three categories, travel (includes per-diem if required), treatment, and disposal. Travel and per-diem are a job-specific expense and there is no practical way to quantify them. The cost to treat hazardous chemicals varies widely with the amount of chemical and the degree of associated hazard. In our survey, commercial providers quoted costs ranging from $1,600 to $6,000 to treat a container of peroxide former. A typical cost for a 1-liter sample containing 100-ppm peroxide is $2,000. Consider the "cleaner" of unknown composition previously mentioned. After treatment the total volume increased from 20 liters to 120 liters (approximately 240 pounds). The cost of treatment was approximately $12,000. Add to that the cost of disposal which, using an average cost to the Department of Energy of $60 per-pound for hazardous waste, is approximately $14,400. Without factoring in the cost of travel, the cost of remediating the "cleaner" was $26,400.

While the costs to remediate a time-sensitive chemical such as the "cleaner" can be easily calculated, costs associated with the safety liability of having these materials around cannot be estimated. During use, distillation, storage, etc., time-sensitive chemicals may explode and damage equipment or facilities. They may trigger fire suppression systems that can damage facilities or destroy records. Worse of all, an explosion or exposure to a toxic material could injure or kill an employee.

With all these costs associated with time-sensitive chemicals, it is easy to see that it would take very few chemicals to become outdated for costs and liabilities to rise to potentially prohibitive levels. Also, if a chemical management program does not effectively manage time-sensitive chemicals, then costs and liabilities for outdated time-sensitive chemicals would continue year after year. The question that needs to be answered is how can a cost effective, time-sensitive, chemical management program be built?

ELEMENTS OF A TIME-SENSITIVE CHEMICAL MANAGEMENT PROGRAM

The essential elements of a time-sensitive chemical management program are (1) identify time-sensitive chemicals, (2) define storage conditions, (3) define "unsafe", (4) track time-sensitive chemicals, (5) define inspection periods, (6) manage expired/unsafe chemicals, (7) control acquisition of time-sensitive chemicals, and (8) management support. The specific "how to" is left to the institution as there are many methods to complete each of the elements, the methods are determined by the specific chemicals and processes employed, and the "how" should be customized to your specific purchasing and management systems.

Identification of Time-Sensitive Chemicals

The single, most important element of a time-sensitive chemical management program is to determine how time-sensitive chemicals will be defined and identified. This is not an easy task for several reasons. First, one must take into account those activities being performed with the material in question. For example, if one chooses to define secondary alcohols as being time sensitive, then one may place an unnecessary burden upon those that will use them. If the secondary alcohols are only used as a cleaning solvent where no distillation or concentration is involved, then the risk of an incident coming from the use of secondary alcohols containing small amounts of peroxide is very small. In this case, requiring workers to periodically test and then label tested containers may be a large effort that provides little or no benefit at some cost.

A second reason for the difficulty in determining which chemicals should be classified as being time-sensitive is the uncertainty involved. In looking at Table 1, one can see there is a large amount of variation among those chemicals that can develop peroxides. For example, one 24-year-old bottle of dioxane had no measurable amount of peroxide present while others that were much younger had significant amounts present. This variability can cause some to think that a measurable amount of peroxides in a container of a chemical while not being found in others is not sufficient to label that chemical as being time sensitive. A third issue is that it may not be prudent to treat dilute solutions or very small quantities as being time sensitive.

Since there is no definitive answer as to what should or should not be defined as being time sensitive, written guidance should be developed so that consistent judgements can be made. This guidance should take into account the type of work being performed, the nature of the chemical in question, storage conditions, other safety systems present, etc., and should be implemented by a qualified person designated by management. It should also be made public so that all employees are aware of what criteria are being used for the determination and the employees should be encouraged to question any determinations that do not appear to be valid.

Define Storage Conditions

Different time-sensitive chemicals have different storage needs and these needs need to be defined and published for all to see. The first reason for this is to prevent incorrect storage conditions that could result in hazardous situations. For example, many do not realize that lithium should never be stored in a nitrogen environment or that potassium stored in kerosene should still be stored in an inert gas. A second reason to define storage conditions is to define company policy concerning the storage of time-sensitive chemicals. Some organizations may chose to store ethers refrigerated to reduce evaporation, but storing ethers in the cold dramatically reduces the effectiveness of inhibitors present. Other organizations store ethers under a nitrogen blanket to prevent peroxide formation and not rely upon inhibitors to function.

Defining "Unsafe"

As chemicals are inspected, there needs to be a definition as to what constitutes "unsafe". If "unsafe" is not defined, then one cannot determine when a container fails inspection. Many feel that 100 ppm peroxide is the concentration at which a solvent becomes unsafe, but that number is based upon the maximum amount of peroxide that can be measured using a dipstick. Being that peroxides measurements have the potential to show lower concentrations than that which are really present, the value of 100 ppm may not be sufficient. One may choose to determine the level of peroxide that a waste handler will take and use that as the definition of "unsafe". At this concentration the chemical can be removed without any treatment thereby saving treatment costs. This may not be appropriate since most waste handling services surveyed indicated that they would only accept chemicals that were certified peroxide free within the last 30 days. Methods used to test time-sensitive chemicals and the definitions of "unsafe" for each chemical should be published as apart of a written chemical management program.

Tracking of Time-Sensitive Chemicals

Once a chemical is determined to be time-sensitive, then it needs to be tracked. Data elements that need to be present would include the container's contents, location, and last date inspected and/or next inspection date. These data elements can be noted on a label, in a logbook, or in a chemical tracking database. If this information is not present, then the container cannot be found and inspected at the required time. Some feel that the inspection results such as peroxide concentration should be tracked as well, while others feel that simply indicating the container passed inspection is good enough. One argument for tracking peroxide concentrations is that the rate of peroxide formation is nonlinear and increases with time.[7,34]

Define Inspection Period

Just as all chemicals are not the same, inspection periods need to be adjusted to each chemical. For example, some ethers, such as diisopropyl ether, should be inspected every few weeks while other chemicals should be inspected annually. Some chemicals may only need to be inspected before a specific use (e.g., distillation of a secondary alcohol). Environmental factors should also be included in determining the inspection frequency. Inspection periods for picric acid stored in Miami might be less frequent for picric acid stored in Las Vegas. An important part of managing time-sensitive chemicals is to determine appropriate inspection periods for each chemical in the program. Inspection periods for each chemical should be defined and published as apart of the organization's chemical management program.

Managing Expired/"Unsafe" Chemicals

Once a chemical has become unsafe due to dehydration or the formation of hazardous products, processes used to manage the material must be clearly defined in the chemical management program. Employees need to know if they are to treat the chemicals themselves (not a good idea), if they are to call the bomb squad or emergency response, etc. Without clear instructions defining how these materials are to be managed, then workers are not sure of what to do. They might try to move or neutralize the material which could lead to injury or they might just hide it away/ignore it. This increases the possibility of hazardous time-sensitive materials accumulating.

Acquisition Control

All of the above information puts a chemical user in a quandary. For example, if one procures a solvent that can form peroxides, then it may arrive with peroxides already present. If any peroxides are present, then few, if any, waste handlers will take it without being processed and certified as peroxide free. Suddenly, the can of ethyl ether that was purchased for $50 has become a several thousand dollar liability. The solution to this situation is to control the acquisition of time-sensitive chemicals. Time-sensitive chemicals are too much of a liability to hoard for "just in case" purposes. Experiments and processes should be planned appropriately so that necessary quantities can be procured. With "Just In Time" contracting, time-sensitive chemicals can be obtained within a short period. This could be used to meet the needs of chemical workers while keeping inventories of time-sensitive chemicals to a minimum. Using "Just In Time" contracting essentially causes the chemical supplier to become the storage facility for one's time-sensitive chemicals. "Just In Time" types of contracts usually consist of agreements with suppliers that provide for a firm delivery time. This time, coupled with internal delivery time, allows the worker to plan ordering lead-time in order to have the chemicals arrive just prior to commencing work. These materials are usually ordered with slight excess and any left over materials are disposed with waste to reduce the potential of aging inventories (leftover reagent) in storage.

Management Support

The last aspect to time-sensitive chemical management is management support. Management needs to understand liabilities associated with time-sensitive chemicals and support those programs necessary to support their management. Management also should develop clear roles responsibilities and authorities so that various aspects of chemical management are never in question. Management should also make sure that employees who handle, store, or use time-sensitive chemicals are trained to recognize when a time-sensitive chemical has gone "unsafe". This type of training is typically absent in most chemical safety programs and is incorporated only after an incident occurs.

CONCLUSION

As can be seen from information presented, there is a substantial amount of information concerning time-sensitive chemicals "known" that is not completely accurate or well understood. What is required is a better understanding of what time-sensitive chemicals are and how they should be managed. From the information presented, it is clear that the proper method of managing time-sensitive chemicals is not to simply make a list of these materials and require an inspection at the same frequency for each. What is required is a better understanding of the chemistry behind time-sensitive chemicals and the development of an effective management program to control them safely. Additionally, chemical waste may contain time-sensitive chemicals and, if present, require a similar level of chemical management.

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