



PREVENTION OF REACTIVE CHEMICAL EXPLOSIONS

CASE STUDY: WASTE FUEL/OXIDIZER REACTION HAZARDS

EPA is issuing this *Case Study* as part of its ongoing effort to protect human health and the environment by preventing chemical accidents. EPA is striving to learn the causes and contributing factors associated with chemical accidents and to prevent their recurrence. Major chemical accidents cannot be prevented solely through command and control regulatory requirements; understanding the fundamental root causes of accidents, widely disseminating the lessons learned, and integrating these lessons learned into safe operations are also required. EPA will publish *Case Studies* and *Alerts* to increase awareness of possible hazards. It is important that facilities, SERCs, LEPCs, emergency responders and others review this information and take appropriate steps to minimize risk. This document does not substitute for EPA's regulations, nor is it a regulation itself. It cannot impose legally binding requirements on EPA, states, or the regulated community, and may not apply to a particular situation based upon circumstances. This guidance does not represent final agency action, and may change in the future, as appropriate.

Problem: The mixing of organic fuels and oxidizers is generally recognized as inherently dangerous. Accident histories reveal many examples of fires and explosions triggered by improper mixing of these substances. The incident described here is an example of the potential consequences associated with improper mixing of organic solvents and oxidizers. This Case Study is designed to raise awareness about the hazards associated with blending waste fuels and reactive chemicals and to offer recommendations to reduce the potential for accidents.

HASKELL, OKLAHOMA (MARCH 26, 1997)

On March 26, 1997, at about 3 p.m. an explosion occurred within a fuel blending tank at Chief Supply Corporation (Chief), in Haskell, Oklahoma. One worker was killed and two others injured. The explosion and resulting fire caused extensive damage to the facility. Several smaller explosions occurred as over 1,000 drums containing waste paints, oils, thinners, inks, cleaning solvents, assorted acids, bases, metal sludge, and four 5,000-gallon tanks holding waste fuels became involved in the fire. A highway next to the site was closed; the facility and an area 1.5 miles north and one mile east of the facility in the path of a large smoke plume were evacuated. The fire was fully extinguished three days later.

FUEL BLENDING OPERATIONS

The waste fuel blending industry grew from a need to provide large quantities of fuel to cement production kilns while

providing a way to reuse flammable hazardous waste. For years, cement producers have burned flammable hazardous waste liquids, such as solvents, thereby reducing raw fuel consumption and cost. Fuel demand for cement production and availability of flammable waste has increased the amount of hazardous waste-derived fuels being blended by smaller operations.

Fuel blenders process many types of hazardous wastes, such as paints, solvents, and used oil, into fuels with sufficient heat value for use in cement kilns. The specifications for the fuel blend (e.g. BTU value and amount of impurities) are normally established by the cement kiln operator, dictated by the emissions standards set for that kiln.

By 1996, over 140 U.S. companies were blending and processing fuels derived

CHEMICAL SAFETY

CASE STUDY

from hazardous wastes for use in cement kilns. These facilities are subject to regulations under the Resource Conservation and Recovery Act (RCRA) for the treatment, storage, and disposal of hazardous waste. The RCRA regulations establish general operating practices and procedures for blending operations. For example, "the owner or operator of a facility that treats, stores or disposes ignitable or reactive waste, or mixes incompatible waste or incompatible wastes and other materials, must take precautions to prevent reactions which: (1) Generate extreme heat or pressure, fire or explosions, or violent reactions; ..." (US EPA, 40 CFR 264.17)

Although the regulations do not place extensive requirements on the types of hazardous wastes that can be blended, some states prohibit the blending of certain wastes. "Beyond these restrictions, the specifications for the hazardous wastes that are blended into fuels are primarily determined by the cement producers, whose operations must meet the regulations' standards for emissions and other requirements." (US GAO, 1996)

ACCIDENT INVESTIGATION

Because of the severity of the consequences and the opportunity for lessons learned, EPA conducted a limited accident investigation to better understand and communicate the major causal factors contributing to this event. EPA's investigation focused on the fuel blending operations and characteristics of the substances involved.

Fuel Production and Chemicals

Chief produced various fuels by blending different wastes composed primarily of spent (used) solvents and cleaners (liquid and sludge). Several months prior to this incident, Chief instituted a practice of adding "lab pack" materials, which had been left on-site by the previous owners of the facility, to the fuel blending process. "Lab packs" are containers that hold small jars, bottles or other containers of assorted laboratory chemicals destined for disposal. These lab packs contained various oxidizers including perchlorates, nitrites, and chlorates.

Compatibility tests performed by Chief's lab personnel on the lab pack oxidizers showed that mixing different oxidizer groups caused reactions, ranging from simple heat buildups to small detonations. The lab personnel were concerned about these reactions; consequently various types of oxidizers from the lab packs were separated from each other. Five-gallon buckets were

used to store the segregated oxidizers for later addition to the waste fuel blend.

Blending Process and Equipment

Chief blended wastes in two, 1,000 gallon vertical tanks called "dispensers." The disperser involved in the incident was equipped with a mixer (a blade mounted on a shaft connected to a motor on top of the tank). The blade was positioned about 1½ feet from the bottom of the tank. To avoid excessive splashing and generation of vapors and fumes, the mixer was not supposed to be started until the liquid level in the disperser fully covered the blade; the amount needed to cover the blade was 400-500 gallons (between seven to nine 55-gallon drums of liquid), or about half of the tank capacity. The disperser was open to the atmosphere; no nitrogen or other inert gas blanketing was used to suppress flammable vapors.

The disperser had two top openings: a large semi-circular "half-moon" opening with a tray for adding liquids from 55-gallon drums; and a one foot square opening used for adding lab packs. A grate was positioned across the large opening to keep any "large chunks" in the waste from falling into the tank. Typically, wastes of greater fuel value and lower contamination were added to the disperser first followed by lower grade materials to achieve a better quality fuel blend.

Oxidizers were to be added to the fuel blend only after ensuring that the disperser was 3/4 full and the mixer running, according to an unwritten procedure used by lab personnel. Chief employees stated that there was no concern for adding the oxidizers to the liquid fuels, but addition might be dangerous if the oxidizer powders were mixed together without a large quantity of liquid fuel in the disperser. The liquid fuel acted as a heat sink for the oxidizers.

The Incident

On the day of the incident, two workers were on top of the disperser pouring liquids from 55-gallon drums into the disperser. They were starting a new batch and only four drums of liquid had been added to the tank when a lab employee at the top of the tank added one bucket of chlorates, one bucket of perchlorates, and one bucket of nitrites (about 3-4 inches of dry material in each 5-gallon bucket) to the disperser. The mixer was not running at this time.

Thirty-to-sixty seconds after the oxidizers were added

and while waste from a fifth drum was being dumped into the tank, liquid suddenly erupted back out of the large tank opening, followed by an explosion and fireball. The fireball fatally engulfed the employee who was pouring the drums and started a large fire in the building. The fire spread to other flammable materials stored throughout the building.

Chemical Hazards - Oxidizers

As noted above, Chief attempted to dispose of a variety of strong oxidizers including chlorates, nitrites, and perchlorates. Strong oxidizers generally are considered to be incompatible with many organic substances because of the potential for dangerous reactions. EPA indicates that chlorates, perchlorates, and other strong oxidizers are potentially incompatible with alcohols, halogenated hydrocarbons, other reactive organic compounds and solvents, and other flammable and combustible wastes. The potential consequences of mixing such incompatible materials are fire, explosion, or violent reaction. Although "It is possible for potentially incompatible wastes to be mixed in a way that precludes a reaction . . .," none of the examples provided applies to mixing oxidizers with organic substances. EPA knows of no method of mixing oxidizers with oxidizable substances that would preclude a reaction (US EPA).

Perchlorates in particular may undergo hazardous reactions with organic substances and have been involved in a number of hazardous incidents. "Mixtures of any perchlorates with oxidizable substances are . . . highly explosive and must be treated accordingly . . . avoid friction, heating, sparks, or shock from any source, and provide suitable isolation, barricades, and protective clothing for personnel." (Schumacher, 1960)

Further, methyl, ethyl, benzyl, and propyl perchlorate are readily formed by reaction of perchloric acid with the corresponding alcohol (Schumacher, 1960 and Bretherick, 1985); ethyl perchlorate formed from ethanol and perchloric acid is "reputedly the most explosive substance known" (Bretherick 1985). In addition, the above alcohols can also react violently or explosively with perchlorates (Kirk-Othmer, 1995).

Chemical Analysis

EPA collected residue samples at various locations after the incident to determine what chemical substances may have been present and what may have triggered the explosion. **Exhibit 1** lists the substances and concentrations found in samples taken from the disperser where the accident originated. The exhibit also notes potential reactions of each substance with oxidizers and perchlorates or perchloric acid.

Most of the substances present after the explosion are flammable or combustible. The phenols and benzyl alcohol are readily oxidizable and could have participated in reactions (possibly violent) with the oxidizers added to the mixture. In addition, the phenols and the alcohol are hydroxyl compounds and potentially could have reacted with perchlorates to form perchlorate esters (which are generally very explosive), particularly if free perchloric acid was present along with the perchlorate salt or formed when the perchlorate salt was added to the solvent mixture.

Although more extreme conditions are required than for phenols and alcohols, the ketones and aromatic hydrocarbons could have been oxidized under some conditions by the oxidizers added to the mixture (e.g., other reactions could have provided enough heat to initiate oxidation; materials that might act as a catalyst could have been present). The ketones and two of the aromatic hydrocarbons (toluene and xylenes) are commonly used in printing ink solvents handled by Chief (Kirk-Othmer, 1995).

Exhibit 1: Substances Detected in Samples Collected From Top of Disperser

| Chemical | Conc. (mg/L) | Potential Reaction with Oxidizers | Potential Reaction with Perchlorates (Other than Oxidation) |
|---|--------------|--|---|
| Ketones - Solvent for rotogravure inks; limited use for flexographic inks. (Flammable) | | | |
| Acetone | 7,000 | Oxidized by strong oxidizers under vigorous conditions to carboxylic acids (not found in residues). Could be oxidation product of isopropyl alcohol. | None reported. |
| Methyl ethyl ketone | 2,700 | Oxidized by strong oxidizers under vigorous conditions to carboxylic acids (not found in residues). Could be oxidation product of alcohol. | None reported. |
| Phenols Not commonly used as solvent. Phenolic resins are used in certain types of inks. (Combustible) | | | |
| 4-Methyl phenol (p-Cresol) | 32 | Phenols readily oxidize to a variety of products | Not reported - might expect formation of perchlorate esters with perchloric acid, by analogy with alcohols. |
| Phenol | 276 | Same as above. | Same as above. |
| Aromatic Alcohol - Not commonly used as solvent in printing ink. (Combustible) | | | |
| Benzyl alcohol | 353 | Oxidized by strong oxidizers to benzoic acid. | Potentially could form benzyl perchlorate (reported to be explosive) in reaction with perchloric acid. |
| Aromatic Hydrocarbons - Some solvent use for rotogravure inks. (Flammable) | | | |
| Ethyl benzene (Not commonly used as solvent in printing ink) | 370 | Side-chain oxidation by strong oxidizers under vigorous conditions. | None reported. |
| Toluene (Solvent for rotogravure inks.) | 14,000 | Side-chain oxidation by strong oxidizers under vigorous conditions to benzoic acid, other products. | None reported. |
| Xylenes (Solvent for rotogravure inks.) | 2,400 | Side-chain oxidation by strong oxidizers under vigorous conditions. | None reported. |

Note: The analytical results presented in this Exhibit may not provide an accurate representation of the composition of the solvent before the explosion and fire for several reasons: (1) some substances, particularly those directly involved in the explosion, may have been decomposed by the explosion or heat of the fire, or may have been completely combusted; and (2) analysis, conducted by the Oklahoma Department of Environmental Quality, was not carried out for all possible substances present.

KEY FINDINGS

The immediate cause of the explosion and fire was most likely a violent reaction of oxidizers in the disperser in the presence of flammable liquid and vapor. Since only four drums had been dumped into the previously empty disperser, only about 9" of liquid would be in the bottom of the tank, or about half of the amount needed to reach the mixer. This allowed the solid oxidizers to pile up at the bottom of the tank, most likely right below the small tank opening, in direct contact with each other and with flammable solvent liquid and vapor. Although the exact chemical mechanism is not precisely known, given the chemicals present in the disperser residue (**Exhibit 1**), a violent reaction could have occurred because:

- The waste printing ink solvents typically handled by Chief could have violently reacted with the

perchlorates added to the disperser.

- The perchlorate salt could have contained free perchloric acid, or perchloric acid possibly could have formed when the salt was added to the solvent mixture. If the solvent contained even a small amount of ethanol (or other alcohols), and if even a small amount of perchloric acid was present, explosive ethyl perchlorate (or other explosive organic perchlorate esters) could have been formed.
- Waste printing ink solvents potentially could contain a variety of pigment residues that could react violently with strong oxidizers. Such a reaction could have initiated or contributed to the explosion.

Contributing Factors

Several management and operational safety factors contributed to the reaction, explosion and fire, including, but not limited to:

- Although chemical compatibility tests were conducted on the oxidizers and concern was raised about the potential for an adverse reaction, the reaction chemistry, potential for explosion and fire in the blending operation, recognition of accident history, and evaluation of hazards may not have been completely examined, understood, or documented prior to instituting the practice of adding lab pack materials to the fuel blends.
- Lab results and concerns were not communicated clearly to all other operators. No system for instituting and documenting such communications was in place at the facility.
- Although a procedure for adding the oxidizers to the waste fuel blend was established, it was not evaluated for safety or documented as a Standard Operating Procedure (SOP). The consequences of deviation from this procedure were not evaluated, communicated or understood. It is not known if any training on this procedure occurred or if the company had a management system for SOPs.
- No controls, barriers, or layers of protection, other than the unwritten procedure, were established to ensure that the mixing procedure was always followed, to minimize the consequences of human error, or to preclude or minimize the possibility of an abnormal reaction situation or its consequences when the oxidizers were added to the solvent mixture.

STEPS FOR ACCIDENT PREVENTION

Disposing of oxidizers by mixing them with organic solvents is generally recognized as inherently hazardous; common references warn against mixing oxidizers with organic or combustible materials. Perchlorates, which Chief added to the solvent mixture, are recognized as a particularly severe explosion hazard. Many past accidents have been reported involving explosions and fires that have resulted from reactions between oxidizers and organic substances. Although the analysis presented here does not identify the exact cause of the explosion and fire at Chief, the analysis shows that the potential for such an incident exists whenever strong oxidizers, such as those used at Chief, are mixed with oxidizable and combustible organic substances, like the solvent

mixture at Chief. When the oxidizer is a perchlorate, as was one of the oxidizers mixed with solvents at Chief, the danger increases.

Here are some steps that facilities should take to address the hazards of reactions between oxidizers and waste fuels. If these hazards are not well understood and addressed, oxidizers and oxidizable substances (fuels) must not be mixed because of the potential for dangerous unknown reactions. These steps are based on the findings associated with this incident and on the recognition that most chemical accidents can be successfully prevented if a management system is in place that ensures that all chemical and process hazards are well understood. Facilities should be designed, constructed, maintained, and safely operated day-after-day with those hazards under control. This approach, and these steps, applies to any facility handling any hazardous substance.

- The chemicals and reaction mechanisms associated with the substances mixed or blended must be well understood and documented. Facilities need to conduct the necessary information searches or laboratory tests to ensure that all reaction mechanisms are known and documented, especially those that may trigger fires or explosions as a result of abnormal situations or changes in chemicals mixed.
- Chemical and process hazards must be understood and addressed. Once the reaction mechanisms are well understood, facilities need to ensure that process equipment, controls, and procedures are designed, installed, and maintained to safely operate the process. A formal hazard review using techniques like 'What-If' or 'Hazop' can help identify opportunities for failure (e.g., human error, mechanical failure) and layers of protection to minimize the consequences of such failures, based on established codes and standards, industry practices, regulations (federal or state) and common sense.
- All employees need to understand the chemical and process hazards. All personnel should openly communicate information about hazards and process conditions and understand the consequences of deviations and unusual situations. Facilities should establish mechanisms for documenting and sharing such information.
- Standard Operating Procedures (SOPs) are essential to safe operations. Facilities should

establish a system to develop and maintain written SOPs and ensure that they are understood and followed at all times. The SOPs must address all phases of operation, safe limits for operation, consequences of deviation, and identification of corrective measures during emergency situations.

- Before starting a process or procedure that has been changed or modified, the chemical and process hazards must be evaluated. Abnormal or non-routine circumstances are a leading factor in chemical accidents. Facilities should make use of management of change (MOC) and pre-startup safety review techniques to ensure that modified processes or procedures will function as intended without unanticipated impacts on other operations.
- Employees must be properly trained in the processes they work on using the SOPs for that process or job tasks. Training must include potential hazards, reduction of those hazards, safety consequences if procedures are not followed, and proper emergency response to abnormal situations. Training should contain clear and concise objectives that can easily be evaluated for operator competence.

REFERENCES

Bretherick, L. *Handbook of Reactive Chemical Hazards*, Third Edition. Boston: Butterworths, 1985.

Chase, M.W., Jr., et al. *JANAF Thermochemical Tables*, Third Edition. Published by the American Chemical Society and the American Institute of Physics for the National Bureau of Standards, 1986.

Design Institute for Physical Property Data (DIPPR), American Institute of Chemical Engineers. *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*. Washington: Taylor & Francis, 1997.

Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Vol. 14. "Inks," page 483 ("Printing Inks"). New York: John Wiley & Sons, 1995.

Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Vol. 18. "Perchloric Acid and Perchlorates," page 157. New York: John Wiley & Sons, 1996.

Lewis, Richard J. *Sax's Dangerous Properties of Industrial Materials*, Ninth Edition. New York: Van

Nostrand Reinhold, 1996.

Lide, David R., ed. *CRC Handbook of Chemistry and Physics*, 75th Edition. Boca Raton: CRC Press, 1994.

National Fire Protection Association (NFPA). NFPA 49, *Hazardous Chemicals Data*, 1994 Edition and NFPA 325, *Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids*, 1994 Edition. Quincy, MA: NFPA, 1994.

Schumacher, Joseph C., ed. *Perchlorates, Their Properties, Manufacture and Uses*. American Chemical Society Monograph Series. New York: Reinhold, 1960.

US EPA; *Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities*, 40 CFR 264; Appendix V to Part 264 - *Examples of Potentially Incompatible Waste*.

US GAO; *Inspections of Facilities Treating and Using Hazardous Waste Fuels Show Some Noncompliance*, US General Accounting Office, Report to Congress, GAO/RCED-96-211, August 1996.

For More Information.....

**Contact the Emergency Planning and
Community Right-to-Know Hotline:**

**800-424-9346 or 703-412-9810
TDD 800-553-7672**

Monday-Friday, 9 AM to 6 PM (EDT)

- - - - -

Visit the **CEPPO Home Page on
the World Wide Web at:**

<http://www.epa.gov/ceppo/>