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Before the
Pipeline and Hazardous Materials Safety Administration
U.S. Department of Transportation
Washington D.C.

Petition for Rulemaking:

Packaging for Nitric Acid

Submitted by:

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Under the provisions of 49 CFR 106.95, UPS, Inc. takes this opportunity to petition for amendment to the packaging requirements for Nitric acid, UN2031 when the material is prepared for shipment via surface modes. Nitric acid is both a Corrosive Liquid and an Oxidizer. Experience shows that when allowed to contact organic packaging material, such as fiberboard, Nitric acid will ignite the packaging materials. The changes UPS proposes in this petition seek to prevent Nitric acid leaks from inner packagings that rapidly progress to fires.

Overview

In a period of just over six months, UPS has experienced four fires due to leaks involving Nitric acid. Three of these incidents occurred during loading operations, while one occurred during sorting operations.

- The first of the three loading incidents had relatively low consequences because the UPS operation was able to isolate the package within a trailer that was moved to the middle of the yard at the UPS facility.
- In the second loading incident, the package involved was added to a nearly full trailer. The fire spread through the trailer and led to over $150,000 in damages to UPS equipment and other customers' packages.
- In the third incident, which occurred in the primary sorting aisle within a UPS hub, the fire was confined to the Nitric acid package and scorched one additional package. Although the package was inside a UPS facility, the people, equipment and thousands of other packages escaped harm.
- In the fourth instance, the package was damaged during the loading of a trailer. The package fell from a roller bed of about waist height and began to fume, causing the UPS personnel to move the trailer away from the building to keep the fumes out of the facility. A UPS designated responder, wearing PPE, then removed the damaged package from the trailer and placed it (held by a "spill tray") into a 55-gallon drum. At first, the responder placed a lid on the drum, but later they removed the lid, at which point the package ignited.

These incidents are notable because UPS has not had a similar cluster of fires involving Nitric acid. Each of the packages involved in these recent incidents included glass inner packages within fiberboard outer packages.[1] In each case, one or more inner package was breached, and the resulting leakage first released fumes and then initiated a fire involving the fiberboard packaging material. Inquiries within the package testing community suggest that some recent trends in packaging design may be bringing changes to many combination packages used for hazardous materials, including Nitric acid. Among those changes are elimination of molded expanded polystyrene (EPS) inserts and replacing them with molded fiberboard trays and caps to secure inner packages within outer packagings. In other words, new package designs appear to be replacing packaging components made of EPS, which are inherently shock-absorbent, with more rigid inserts which also are capable of reacting with strong Oxidizers such as Nitric acid.

The oxidizing hazard of Nitric acid is well known, as demonstrated by the following extracts from sample laboratory safety instructions for working with Nitric acid, as well as Safety Data Sheets for concentrations not over 70%:

> Nitric Acid (**HNO3)** is a clear, colorless to slightly yellow inorganic acid. . . .The material is not combustible, however it is a strong oxidizer and care should be taken in storing it away from incompatibles . . . . Spontaneous ignition or combustion takes place when a substance reaches its ignition temperature without the application of external heat. Materials susceptible to spontaneous combustion due to contact with nitric acid include oily rags, dust accumulations, and many organic materials.[2]

> **Fire & Explosion Hazards:** Not combustible, but substance is an oxidizer and its heat of reaction with reducing agents or combustibles may cause ignition. Can react with metals to release flammable hydrogen gas. May react explosively with combustible organic or readily oxidizable materials such as: alcohols, turpentine, charcoal, organic refuse, metal powder, hydrogen sulfide, etc.[3]

> **Special Remarks on Fire Hazards:**
> Flammable in presence of cellulose or other combustible materials.[4]

> **Special Fire and Explosion Hazards**: Oxidizing material – contributes to combustion of other materials. Emits toxic fumes under fire conditions. Contact with other materials may cause fire and/or explosion.[5]

UPS believes that the packaging requirements of the HMR fail to provide adequate recognition of this hazard – especially in light of the recent packaging trends

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[1] In one case, the inner bottle had been placed within a plastic bag before being inserted into the outer fiberboard box. With the ignition of the packaging materials, however, it is evident that the plastic bag did not succeed in containing the acid.

[2] University of Pittsburgh Safety Manual. http://ccc.chem.pitt.edu/wipf/SOPs/Nitric%20Acid_SOP.pdf

[3] Safety Data Sheet for Nitric acid, 65% - 70% concentration, Ricca Chemical Company. See the following link: http://www.riccachemical.com/Technical-Support/MSDS/RABN0010

[4] Safety Data Sheet for Nitric acid, 65% concentration, ScienceLab. See the following link: http://www.sciencelab.com/msds.php?msdsId=9926241

[5] Safety Data Sheer for Nitric acid, 60% - 70% concentration, Seastar Chemicals. See the following link: http://wwwsci.seastarchemicals.com/safety/01NitricMSDSRev2010.pdf

UPS identified through its investigations of the incidents described above. Accordingly, UPS suggests enhancements to reduce the inevitable contact between any leakage of Nitric acid and packaging materials that are subject to ignition through contact with this oxidizing material. The hazards of a chemical spill are profoundly different than the hazards of an active fire, and the Oxidizer sub-risk of Nitric acid warrants special packaging efforts to contain the liquid should an inner package be breached. Experience demonstrates the need for an intermediate component that is non-reactive and fully capable of retaining the released acid. Such containment would help prevent a fire resulting from the breach of an inner package.

Packaging Requirements for Nitric Acid

In most cases, packaging requirements for surface shipments of Nitric Acid, contained in §173.158, prescribe either outer packaging that is not reactive to the oxidizing properties of the material, or combination packagings that include intermediate packaging and absorbent material that does not react with the acid:

Concentration Range	Summary of Packaging Requirements
Nitric acid ≥ 90%	• 4C1, 4C2, 4D or 4F wooden boxes with inner glass bottles individually overpacked in tight metal packagings. Glass bottles ≤ 2.5 L, cushioned with non-reactive absorbent cushioning material within the metal liners. [§173.158(d)(1)] • 1A2, 1B2, 1D, 1G, 1H2, 3H2 or 4G outer packagings with inner glass packagings of ≤ 2.5 L, cushioned with a non-reactive, absorbent material and packed within a tightly closed intermediate packaging of metal or plastic. [§173.158(d)(2)]
Nitric acid ≥ 80% without sulfuric acid or hydrochloric acid as impurities	• 1B1 aluminum drums. [§173.158(c)]
Nitric acid ≤ 70%	• Composite packagings 6PA1, 6PA2 6PB1, 6PB2, 6PC, 6PD1, 6PH1 or 6PH2. Also, PHH1 and 6HA1 with plastic inner receptacles meeting requirements of 173.24(e). [§173.158(f)(1)] • 4H1 expanded plastic boxes with inner glass packagings ≤ 2.5 L. [§173.158(f)(2)] • Combination packagings 1A2, 1B2, 1D, 1G, 1H2, 3H2, 4C1, 4C2, 4D, 4F or 4G outer packagings and plastic inner packagings ≤ 2.5 L further contained in tightly closed metal packagings. [§173.158(f)(3)]
Nitric acid in any concentration which does not contain sulfuric acid or hydrochloric acid as	• 1A1 stainless steel drum, with minimum thickness requirements and other prescribed specifications. [§173.158(b)(1)]

impurities	• 4H1 expanded plastics outer packaging with glass inner receptacle of ≤ 2.5 L and up to 4 inner receptacles. [§173.158(b)(2)]

In one instance, however, the HMR allow the shipment of Nitric acid in combination packagings with glass (i.e., fragile) inner packagings and outer packagings that can be ignited by the oxidizing characteristic of Nitric acid:

Concentration Range	Summary of Packaging Requirements
Nitric acid < 90%	• 4G, 4C1, 4C2, 4D or 4F with inside glass packagings of ≤ 2.5L. [§173.158(e)]

It is this last packaging configuration that UPS has witnessed in the incidents cited above. Such a packaging configuration places the fragile inner bottle in close contact with fiberboard that can be ignited spontaneously in contact with Nitric acid. Coupled with packaging design trends, by which the shock absorbing features of EPS packaging components are eliminated as molded fiberboard trays replace EPS components, the provisions of §173.158(e) lead to packages of Nitric acid in which fragility of the glass bottle can be a critical factor. Any leak that develops during handling can progress rapidly from the release of the liquid to a spontaneous fire with all the attendant dangers to life and property.

In view of the history experienced in just over six months during 2012, UPS submits that a durable intermediate packaging component and non-reactive absorbent materials are needed for any package containing Nitric acid that includes packaging components made of fiberboard, wood or other organic materials that will react with the material.

Proposal

The sole provision within §173.158 which allows combination packages constructed of organic materials to be shipped without intermediate packaging layers is §173.158(e). This sub-section allows such packaging for a wide range of possible concentrations, *including concentrations of just under 90 percent*. UPS submits that a simple amendment to §173.158 will reduce the likelihood that leakage from inner packages containing Nitric acid will progress rapidly to fires. Therefore UPS proposes the following amendment to §173.158(e) (new material is underlined):

> (e) Nitric acid of less than 90 percent concentration, when offered for transportation or transported by rail, highway, or water may be packaged in 4G fiberboard boxes or 4C1, 4C2, 4D or 4F wooden boxes with inside glass packagings of not over 2.5 L (0.66 gallon) capacity each. The glass inner packagings must be packed in tightly closed, non-reactive intermediate packagings, cushioned with a non-reactive absorbent material.

The proposed additional text will reduce the ability of Nitric acid released due to a breached inner package to come into immediate contact with the fiberboard or other readily combustible packaging materials, such as plywood or reconstituted wood,

authorized by this sub-section. In reducing that ability for leaking Nitric acid to contact and saturate these combustible packaging components, this change in packaging requirement would make a direct contribution to safety.

Conclusion

UPS is unaware of the reasons that caused the HMR to omit intermediate packaging components from §173.158(e). However, experience has demonstrated the ability of Nitric acid packaged in a specific configuration to make immediate contact during a spill event with readily combustible packaging components authorized by this subsection. With that contact, the oxidizing acid, in turn, may spontaneously ignite the packaging materials. The safety implications of such a series of events should be self-evident. UPS urges PHMSA to move rapidly to amend the regulations as requested here, before significant additional property damage occurs – or before a fire causes an injury or other serious consequences for people, equipment, and packages exposed to these incidents.