From: "Dr. Mannan" <mannan@tamu.edu> Texas A&M University
To: Tanya Eaton <TME@nrc.gov>
Date: Mon, Sep 20, 1999 6:57 PM
Subject: Re: Spontaneous Combustible Substances

Tanya:

Donna Startz referred your e-mail to me.

In response to your request, attached please find a electronic file containing current information on Zirconium in the Center's archives. I hope this is benficial to you.

Best Regards,

==

At 09:16 AM 9/14/1999 -0500, you wrote:
>Good morning,
>
>I came across your website that stated that a database of spontaneous
>combustible
>substances commonly found in the chemical processing industry is being
>formulated. Is that website completed yet. I am looking for information on
>zirconium which is a phyrophoric metal and mitigation procedures related to
>the
>ignition of zirconium in the dust form in for scraps of zirconium stored
>together. I
>have heard of sand or graphite as being effective mitigation methods, but
>what about
>the use of a high-expansion foam. I am looking at bulk zirconium and I
>would appreciate if you could share any
>information you have or refer me to appropriate sources.
>
>
>
>
>
>
>
>
>
>
>
>
>

471

The following information (taken from available sources) will be retrievable eventually but is excerpted for your immediate use.

Zirconium

The combustibility of zirconium increases as the average particle size decreases, but other variables, such as moisture content, also affect its ease of ignition. In massive form, zirconium can withstand extremely high temperatures without igniting, whereas clouds of dust in which the average particle size is 3 microns have ignited at room temperature. Dust clouds of larger particle size can be readily ignited if an ignition source is present, and such explosions can occur in atmospheres of carbon dioxide or nitrogen as well as in air. Zirconium dust will ignite in carbon dioxide at approximately 621C and nitrogen at approximately 788C. Tests have also indicated that layers of 3-micron-diameter dust are susceptible to spontaneous ignition. The depth of the dust layer and its moisture content are important variables for ignition. Spontaneous heating and ignition are also possibilities with scrap chips, borings, and turnings if fine dust is present. Layers of 6-micron-diameter dust have ignited when heated to 190 C. Combustion of zirconium dust in air is stimulated by the presence of limited amounts of water (5 to 10%). When very finely divided zirconium powder is completely immersed in water, it is difficult to ignite, but once ignited it burns more violently than in air.

Massive pieces of zirconium do not ignite spontaneously under ordinary conditions, but ignition will occur when an oxide-free surface is exposed to sufficiently high oxygen concentrations and pressure. The explanation for this reaction is the same as that cited for a similar titanium reaction. Zirconium fires (like fires involving titanium and hafnium) attain very high temperatures, but generate very little smoke.

Explosions have occurred while zirconium was being dissolved in a mixture of sulfuric acid and potassium acid sulfate. Zirconium has exploded during and following pickling in nitric acid, and also during treatment with carbon tetrachloride or other halogen-containing materials. Spontaneous explosions have occurred during handling of moist, very finely divided, contaminated zirconium scrap.

Storage and Handling

Special storage precautions are not required for zirconium castings because of the very high temperatures that massive pieces of the metal can withstand without igniting. Zirconium powder, on the other hand, is highly combustible; consequently, it is customarily stored and shipped in 3.78-L (1-gal) containers with at least 25% water by volume.

For specific details, refer to NFPA 482, *Standard for the Production, Processing, Handling, and Storage of Zirconium.*

Zirconium powder storerooms should be of fire-resistive construction equipped with explosion vents. Cans should be separated from each other to minimize the possibility of a fire at one can involving others and to permit checking of the cans periodically for corrosion. One plant handling zirconium has established the procedure of disposing of cans containing powder that have been on the shelf for 6 months.

Process Hazards

Handling of zirconium powder, whenever possible, should be under an inert liquid or in an inert atmosphere. If zirconium powder is handled in air, extreme care must be used because the small static charges generated may cause ignition.

To prevent dangerous heating during machining operations, a large flow of mineral oil or water-base coolant is required. In some machining operations, the cutting surface is completely immersed. Turnings should be collected frequently and stored under water in cans. Where zirconium dust is a byproduct, dust collecting equipment which discharges into a water precipitation type of collector is a necessity.

Extinguishing Zirconium Fires

Zirconium fires can be extinguished in the same way. Fires exposing massive pieces of zirconium, for example, can be extinguished with water. Limited tests conducted by Industrial Risk Insurers have indicated that the discharge of water in spray form would have no adverse effect on burning zirconium turnings. When a sprinkler opened directly above an open drum of burning zirconium scrap, there was a brief flame after which the fire continued to burn quietly in the drum. When a straight stream of water at a high rate of flow was discharged into the drum, water overflowed and the fire went out.

Where small quantities of zirconium powder or fines are burning, the fire can be ringed with a Class D extinguishing powder to prevent its spread, after which the fire can be allowed to burn out. Special powders developed for metal fires have been effective in extinguishing zirconium fires. When zirconium dust is present, the extinguishing agent should be applied so that a zirconium dust cloud will not form. If the fire is in an enclosed space, introducing argon or helium can smother it.

Zirconium Incidents

Up to May 1955, no serious fires had been encountered during storage of scrap Zirconium turnings, chips, plates, rods, etc. Such scrap had been stored (pending contemplated future recovery) in segregated open-top bins. Several days after a heavy rain, a fire of unknown origin took place in one of the bins with flames extending 100 feet into the air. Shortly afterwards, contents of other (but not necessarily adjoining) bins suddenly and intermittently flared up. Material in all bins soon became involved and 159,000 pounds of Zirconium were consumed. The heat was sufficiently intense to crack windows and ignite wood located over 150 feet away. Particles of burning Zirconium were carried over one-quarter mile through the air.

In 1951, some water-wet scrap Zirconium powder in wooden barrels was placed in outside storage pending development of scrap-recovery processes. During the next several years, a few minor spontaneous fires broke out in this material. In January 1956, the material in several deteriorated wooden barrels was wet with water and repackaged in steel drums. In May 1956, employees working in the area noted that one of the steel drums lying on its side contained a black material "similar to carbon dust." What happened is uncertain, but a spontaneous explosion occurred accompanied by streaks of red fire with black smoke extending 100 feet into the air. A pronounced concussion wave was noted and the sound of the blast was heard several miles away. Two employees were killed; one having been blown 80 feet through the air, and a third lost an arm. The drum contained Zirconium, probably in the form of a fine powder. Using extensive precautions, the remaining drums of scrap Zirconium were subsequently burned. During this operation, one of the drums exploded.

Two men died and two others were seriously injured in 1954 in a spontaneous explosion initiated during removal of the friction-top lid from a polyethylene bag-lined, 1-gallon metal can containing Zirconium powder 16 percent wet with water. A ball of flame enveloped the entire area, accompanied by a concussion wave.

A 2-pound sample of carbon-tetrachloride-moistened powdered Zirconium was placed in a glass flask, vacuum applied, and the flask very gently heated with a Bunsen burner. The Zirconium suddenly began to heat up and detonated with a blinding flash. The explosion was attributed to a small amount of water.

For more details refer to: Smith, R. B., *Pyrophoricity A Technical Mystery Under Vigorous Attack,* Nucleonics, December 1956.

General reference is DOE technical standards report 1081.

==

Dr. Sam Mannan, PE, CSP
Associate Professor and Director
Mary Kay O'Connor Process Safety Center
Chemical Engineering Department
Texas A&M University
College Station, TX 77843-3122
Phone: (409) 862-3985
Fax: (409) 458-1493
E-mail: mannan@tamu.edu
URL: http://process-safety.tamu.edu