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Guide

for

ZIRCONIUM

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The National Fire Protection Association was organized in 1896 to promote the science and improve the methods of fire protection and prevention, to obtain and circulate information on these subjects and to secure the cooperation of its members in establishing proper safeguards against loss of life and property by fire. Its membership includes two hundred national and regional societies and associations (list on outside back cover) and seventeen thousand individuals, corporations, and organizations. Anyone interested may become a member; membership information is available on request.

This pamphlet is one of a large number of publications on fire safety issued by the Association including periodicals, books, posters and other publications; a complete list is available without charge on request. All NFPA standards adopted by the Association are published in six volumes of the **National Fire Codes** which are re-issued annually and which are available on an annual subscription basis. The standards, prepared by the technical committees of the National Fire Protection Association and adopted in the annual meetings of the Association, are intended to prescribe reasonable measures for minimizing losses of life and property by fire. All interests concerned have opportunity through the Association to participate in the development of the standards and to secure impartial consideration of matters affecting them.

NFPA standards are purely advisory as far as the Association is concerned, but are widely used by law enforcing authorities in addition to their general use as guides to fire safety.

Definitions

The official NFPA definitions of shall, should and approved are:

SHALL is intended to indicate requirements.

SHOULD is intended to indicate recommendations, or that which is advised but not required.

APPROVED refers to approval by the authority having jurisdiction.

Units of measurements used here are U. S. standard. 1 U. S. gallon = 0.83 Imperial gallons = 3.785 liters.

Approved Equipment

The National Fire Protection Association does not "approve" individual items of fire protection equipment, materials or services. The standards are prepared, as far as practicable, in terms of required performance, avoiding specifications of materials, devices or methods so phrased as to preclude obtaining the desired results by other means. The suitability of devices and materials for installation under these standards is indicated by the listings of nationally recognized testing laboratories, whose findings are customarily used as a guide to approval by agencies applying these standards. Underwriters' Laboratories, Inc., Underwriters' Laboratories of Canada and the Factory Mutual Laboratories test devices and materials for use in accordance with the appropriate standards, and publish lists which are available on request.

Guide for Fire and Explosion Prevention in Plants Producing and Handling ZIRCONIUM

NFPA No. 482M — 1959

This Guide has been prepared by the NFPA Committee on Combustible Metals to provide information on the fire and explosion hazards of zirconium. The report was finally adopted by the National Fire Protection Association in June, 1959. When more information and field experience are available the Committee plans to convert this Guide to a Standard.

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Guide for Fire and Explosion Prevention in Plants Producing and Handling ZIRCONIUM

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Zirconium is usually found in nature as the mineral zircon which is zirconium silicate ($ZrSiO_4$). Isolation of the metal is difficult but can be accomplished by transformation to the oxide or chloride and reduction with calcium, sodium, or magnesium. It is prepared commercially as a dark gray powder containing 85 per cent or more of metallic zirconium, a dark gray granular material, or as massive metal with a silvery lustre.

Metallic zirconium should not be confused with zirconium oxide (zirconia), an inert, infusible material used as an abrasive, refractory, and insulator, or with the hydride, both of which are sometimes loosely called zirconium. Information on geographical locations of the mineral and descriptions of reduction processes, fabrication methods, and analytical procedures are given in Bureau of Mines bulletins and other technical publications.* Data on physical and mechanical properties of the metal are available in handbooks, metallurgical reference manuals and numerous trade publications.

Flammable Properties and Explosive Characteristics

Although zirconium in massive form can withstand very high temperatures because its melting point is approximately 1830°C., or 3326°F., a sample of minus 325 mesh zirconium powder ignited at 410°F. during Bureau of Mines laboratory tests. Other laboratory reports indicate that zirconium powder or dust ignitions have occurred at temperatures as low as 304°F. When very fine zirconium powder was dispersed in air as a cloud during the Bureau of Mines laboratory tests, ignitions occurred at room temperature without any apparent source of ignition being present. Presumably, static electricity on the dust particles, frictional heat, or pyrophoricity caused ignition of the dust cloud.

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*See Appendix for availability.

Metallic zirconium definitely possesses pyrophoric properties as evidenced by its use in certain pyrotechnic applications, the data included in reports of laboratory research, and the conclusions reached in investigations of unusual fires and explosions. In powdered form it is not only highly flammable, but under certain conditions it will ignite spontaneously with explosive force.

The pyrophoric ignition hazard inherent in the metal powder apparently depends to a large extent on the particle size of the powder. In some laboratory tests zirconium powder having an average particle size of 3 microns was found to be very pyrophoric but similar powder of 12 micron size did not ignite at red heat. Other laboratory tests have indicated that the quantity or depth of the powder in a pile may have some bearing on the tendency to heat spontaneously.

Experience has indicated that the pyrophoric characteristics noted in zirconium powder may also be present in scrap consisting of chips, turnings and borings if some fines are present. The possibility of spontaneous ignition occurring in massive zirconium is negligible.

Combustion of zirconium in air is stimulated by the presence of limited quantities of water. In one case powder containing about 16 per cent moisture is reported to have exploded spontaneously while under vacuum. The application of water in fire-fighting operations usually intensifies the burning.

Quiescent layers of zirconium powder can be ignited and will burn vigorously in atmospheres of either carbon dioxide or nitrogen.

Explosions of metallic zirconium have occurred during dissolution with a mixture of sulfuric acid and potassium acid sulfate.

The Interstate Commerce Commission* classifies zirconium as a flammable solid and has issued regulations covering transportation.

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*See Code of Federal Regulations, Title 49, Transportation, Parts 71–90. See Appendix for availability.

Uses of Zirconium

Zirconium acts as a "getter" and is used to remove hydrogen, nitrogen, oxygen, carbon monoxide, and carbon dioxide from vacuum tubes and incandescent lamps. For this purpose the metal is generally used in powdered form but pieces of ductile zirconium can be used in some instances. It is also used as a deoxidizer or scavenger in making steel as it tends to eliminate nitrogen and oxygen as well as nonmetallic impurities.

In fine powder form zirconium is used in flashlight powders and in the manufacture of photo flash bulbs. A comparatively weak battery spark is capable of igniting beads of zirconium powder paste or zirconium powder coatings on wires or terminals within the flash bulbs. The fine powder is also used in flares and fireworks and either with or as a substitute for fulminate of mercury in detonators.

Zirconium is sometimes combined with other metals to form alloys such as zirconium-nickel or zirconium-copper. Some of the alloys apparently have flammable and explosive characteristics similar to the pure metal. Alloys of zirconium with lead or uranium are reported to be particularly hazardous. In powder metallurgy where zirconium may be used alone or in combination with other metal powders some unusual fire and explosion hazards may be present.

The use of zirconium for structural purposes and in the manufacture of heavy equipment is quite limited at present. It has been used in defense equipment and some commercial applications where special corrosion resistance and stability at high temperatures are necessary.

The corrosion resistant properties of zirconium make it ideal for use in certain chemical and surgical equipment. It has been used in the construction of fans, pumps, valves and nozzles and as tank linings where corrosive gases or solutions would attack other metals or plastics.

The very small affinity of zirconium for neutrons indicates certain desirable structural uses in atomic power plants and a great amount of research is being directed toward the development of other engineering and structural uses.

Hazards of Zirconium

In the process used to convert zircon to zirconium sponge there are certain inherent fire and explosion hazards which are similar to those encountered in the production of titanium. Reduction must be conducted in dry, oxygen-free atmospheres. Helium or argon can be used to prevent ignitions within the sealed reactors or furnaces. A detailed and illustrated description of the process and equipment used in the production of zirconium sponge is given in Bureau of Mines Bulletin 561, Zirconium, Its Production and Properties.* The general recommendations of the NFPA Committee on Combustible Metals covering the production of titanium sponge as given in NFPA No. 481, Standard for Titanium* are applicable in zirconium plants.

Production of ingots is accomplished by arc melting of a consumable electrode, consisting of a cold compacted zirconium bar in an inert gas-filled, water-cooled, copper crucible. At this stage the fire and explosion hazards are mainly those associated with any molten metal but pressure produced by contaminants in molten zirconium sometimes causes excessive boiling and spattering. The necessity of operating under inert gas protection also introduces some additional hazards if failures occur in seals or temperature- and pressure-control devices. In some melting operations where contaminants are present the lower chlorides of zirconium, magnesium, and carbon may form a pyrophoric material that can be easily set off by friction or a spark. Some flash fires are reported to have occurred when small consumable electrode furnaces were opened and the copper crucible contents were first exposed to air.

As indicated in preceding paragraphs the principal fire and explosion hazards in connection with the production, handling, and processing of zirconium will be found where the metal in finely divided form is exposed to rapid oxidation, temperatures above the ignition point, or the possibility of some chemical reaction that may create unstable compounds.

Some of the following references to operating experiences in which fires and explosions have occurred will serve to illustrate the conditions that require special attention or protection.

Machining of zirconium and zirconium alloys presents some serious fire hazards. Many ignitions have occurred during cutting,

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***See Appendix for availability.**

turning, grinding and other machine shop operations. Several companies have reported that fires occurred while zirconium bars, plates, etc., were being chopped and a number of fires have occurred when hot or burning chips fell into accumulations of moist fines on or under lathes or milling machines. The most violent reactions occurred when burning chips fell into drums or deep containers partially filled with moist turnings or scrap.

Production and processing of zirconium powder presents the most serious fire and explosion hazard. It is highly flammable and pyrophoric under certain conditions. It burns with an intensely brilliant flame and may react with explosive violence in the presence of moisture or when burning accumulations of powder are disturbed.

In laboratory tests dust clouds of fine zirconium powder in air ignited at 20°C. Similar clouds in carbon dioxide ignited at 650°C. Layers of the same powder on heated surfaces ignited in air at 190°C., in carbon dioxide at 620°C., and in nitrogen at 790°C. In atmospheres consisting of air and helium it was necessary to have at least 5 per cent of oxygen present to obtain ignition of zirconium dust clouds by spark. The lower explosive limit for zirconium powder in air was found to be 0.04 ounce per cubic foot.

Very fine powder with an average particle size of 3.3 microns ignited spontaneously when blown into the air as a cloud at room temperature of 20°C. Powder having an average particle size of 17.9 microns did not ignite under similar circumstances until it had been heated to 350°C.

Numerous instances of spontaneous ignitions and explosions of zirconium powder in both open and sealed drums have been reported. One report of an investigation of a zirconium powder fire states that a ball of flame enveloped the area with a definite concussion and shock wave when the lid was removed from a one-gallon tank in which the powder had been stored for some time. Zirconium powder handling or processing operations such as washing, drying, screening, weighing, blending, etc., should be conducted with extreme care in segregated rooms or cubicles where the powder can be handled in small batches and precautions can be taken to avoid injury to personnel and extensive property damage if ignitions should occur.

Fire Prevention

The importance of good housekeeping becomes obvious wherever zirconium presents the unusual fire and explosion hazards previously mentioned. Periodic cleaning, the collection of dust at the point of production, and the prompt removal of dust and fine scrap from the premises are important steps in any fire prevention program.

No storage of combustible materials (cartons, crates, etc.), nor supplies not essential for current production should be permitted in areas where zirconium fire hazards are present.

Machining operations, especially those producing fine chips, turnings or dust, should be conducted under controlled conditions to prevent dust dispersions, excessive heating, or any unusual condition that might cause ignition of the zirconium.

Special precautions should be taken to eliminate hazards, such as spills of oil or grease, which could ignite and spread a fire to the zirconium stock.

All equipment should be maintained in safe operating condition and checked frequently to detect any hot bearings, electrical defects, or charges of static electricity that might cause ignitions of dust or oil.

Any accumulation of zirconium dust or powder on beams, ledges, walls, work benches, floors, or other surfaces constitutes a fire and explosion hazard and steps should be taken promptly to prevent or control any dust dispersions that would cause such accumulations. Dust deposits that may accidentally be produced should be cleaned up and removed promptly to a safe storage or disposal area.

Dust Collection

The pyrophoric properties of zirconium dust or powder cause some complications in the planning of dust control equipment for shops or factories where such fire hazards may be present. A choice must be made between wet and dry methods of dust collection. A limited amount of moisture stimulates the burning of zirconium powder and in some cases explosive reactions have occurred. On the other hand attempts to collect dry zirconium dust or powder by suction and air currents have indicated the hazard of dust cloud ignition by static charges formed on the dust particles, or pyrophoric heating due to rapid surface oxidation of dust deposits within the ducts.

Unless the dust can be collected dry directly at the source without creating explosive dust clouds or dangerous deposits in ducts or collection chambers, the use of water precipitation-type collectors is recommended. Suitable hoods or enclosures should be installed to trap the dust at each production operation with the shortest practicable ducts connecting the hoods to the collector. The suction unit should be installed in such a way that the dust will be converted to sludge without contact in a dry state with any high speed moving parts. Figures 1 and 2 show typical water-washed dust collectors servicing fixed and portable grinding units. Figure 3 shows diagrammatically four methods of dust precipitation used in the collectors in Figures 1 and 2.

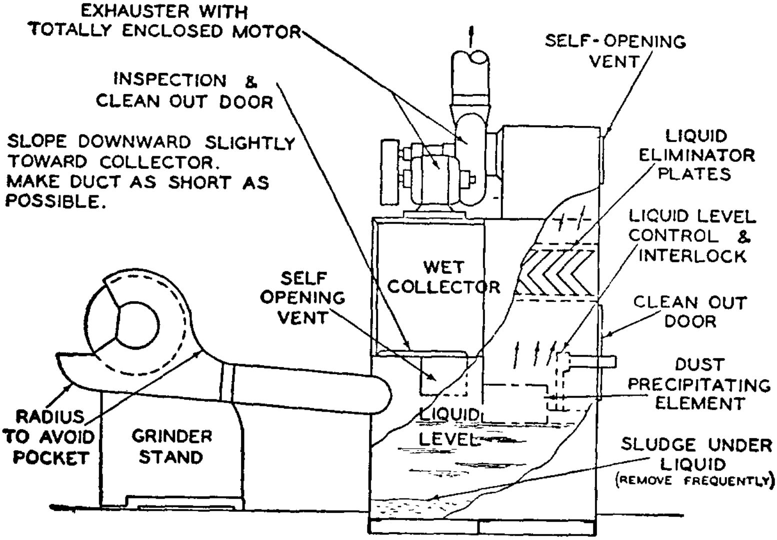

Fig. 1

Note: This drawing is schematic and intended only to indicate some of the features which should be incorporated in the design of a collector. The volume of all dust-laden air spaces should be as small as possible.

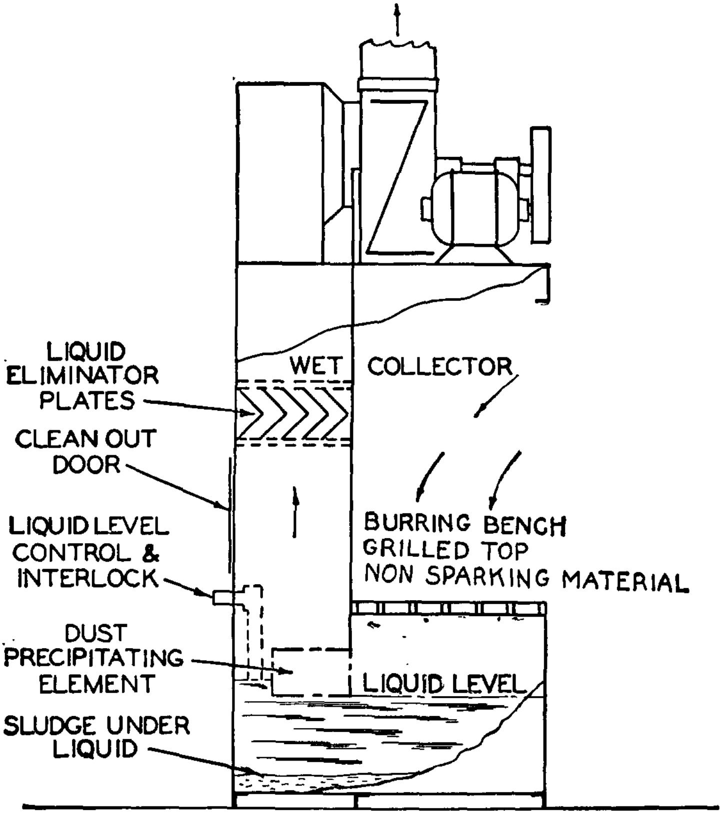

FIG. 2

Power supply to dust-producing machines should be interlocked with (1) exhaust air flow and (2) water pressure level or flow in such a way that improper functioning of the dust-collecting system will shut down the machine it serves.

Zirconium Sludge and Scrap Disposal

The hazards involved in handling or storing zirconium scrap containing a considerable amount of fines frequently outweigh any advantages to be gained by attempting to salvage such material and it is usually disposed of by burning. Prompt disposal of zirconium sludge is imperative and several methods have been proposed. Small quantities can be buried with a sufficient amount of sand or inert material to eliminate any possibility of later exposure and ignition. Where there is a continuing need for disposal of sludge and fine scrap, special incinerators or burning areas should be provided and properly protected, well-trained personnel assigned to this task.

In one disposal method that has been found satisfactory fine scrap is removed daily and stored under water in five-gallon cans. Employees wearing asbestos helmets, gloves, and other protective clothing carry the cans in a yoke between them to an

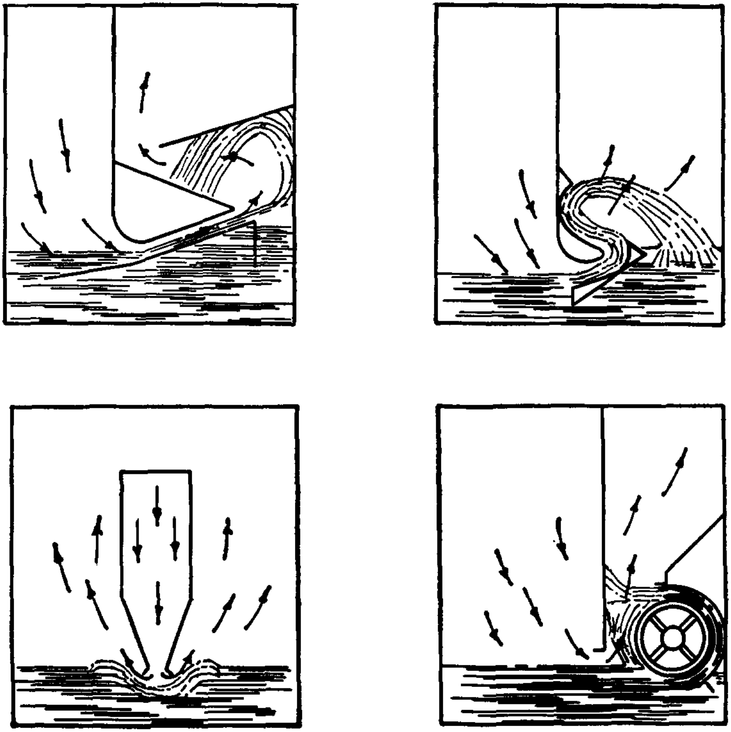

Fig. 3

open-top, bin-type, masonry incinerator in the isolated burning area. The cans suspended in the yoke are dumped into the incinerator and the charge ignited by a gasoline-soaked rag attached to a 20-foot fuse. Charges ranging from 35 to 400 pounds have been successfully disposed of in this way.

Disposal of old or waste zirconium powder packed either wet or dry in closed containers presents some additional hazards because, as previously mentioned, ignitions have occurred when attempts were made to open the cans. It is recommended that such containers be transported to the burning area in a yoke carrier by trained men wearing protective clothing, and placed on a bed of excelsior or other readily combustible material. A remotely controlled guillotine or cleaver device can be used to cut open the container and a previously placed fuse or train of combustibles can be used to ignite the powder.

Fire Protection

Prompt fire detection and alarm service are important and personnel other than trained fire fighters should be evacuated from areas where zirconium is or may become involved in a fire. Ordinary fire extinguishers are ineffective on zirconium fires and their use may intensify the fire or prove hazardous to the person using them. Any disturbance of burning zirconium powder may create an explosion.

Water can be used to cool massive pieces of zirconium exposed by a fire in ordinary combustibles but only dry powders or extinguishers approved for use on combustible metal fires are recommended where zirconium powder or fines are burning. Where a limited amount of powder or fines is burning it is suggested that the burning area be surrounded with dry sand or inert powdered material and the fire be allowed to burn itself out. A more extensive fire can be sprayed with one of the approved types of powders to form a smothering blanket. In some cases inert gases such as argon and helium will control zirconium fires if they can be used under conditions that will exclude the air. Trimethoxyboroxine has been found effective in some cases on small combustible metal fires, and other extinguishing agents are being developed and tested. Until more effective control and extinguishing agents are available the limitation of fire hazards by segregation and division of working and storage areas, and the elimination of all possible sources of ignition should be the major method of avoiding zirconium fire and explosion losses.