TITANIUM DIOXIDE

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1.0 SCOPE

This document provides recommendations for the prevention of and protection against fires and explosions in titanium dioxide facilities using sulphate or chloride manufacturing processes.

1.1 Hazards

The sulphate production process involves highly corrosive materials and the use of combustible materials for construction, ductwork, and lined equipment represent a high fire risk. Heavy-duty electrical equipment that is oil filled, such as transformers and circuit breakers, can also present a fire hazard. Large fuel-fired equipment (kilns/calciners using LPG or LNG), filters, and separators are also present at this occupancy. The loss drivers for the occupancy are fire due to combustible construction and ductwork, and explosions from process reactors.

Chloride processing is very abrasive, includes refractory-lined reactors and equipment, and involves highly corrosive materials in heated service. Titanium tetrachloride is highly corrosive with trace amounts of water. Chlorination and oxidation reactors and heat exchanger equipment are exposed to erosion and thus refractory rebuild, making equipment sparing vital. The loss drivers in this process are fire from combustible construction and equipment, explosion in the reactors or large spray dryers, and service interruption due to large oxygen and nitrogen demands to operate the process.

1.2 Changes

January 2023. Interim revision. Minor editorial changes were made.

2.0 LOSS PREVENTION RECOMMENDATIONS

2.1 Construction and Location

2.1.1 General

2.1.1.1 For areas with high corrosion risk, provide noncombustible construction materials (special alloys are available for corrosive environments) or FM Approved alternatives. For additional guidance, see Data Sheet 1-57, *Plastics in Construction*.

2.1.1.2 Install plastic ducts so they are not exposed to potential fires from equipment with oil fire hazards and/or combustible storage. For additional guidance refer to Data Sheet 7-78, *Industrial Exhaust Systems*.

2.1.2 Rubber and Plastic-Lined Equipment

2.1.2.1 Space pieces of equipment that contain combustible materials so they are not concentrated in a single area.

2.1.2.2 Label or identify rubber- and plastic-lined equipment using placards or other means if activities such as hot work (cutting and/or welding) are performed on or near the equipment.

2.1.3 Sulphate Process

2.1.3.1 Locate oil-filled transformers and/or rectifiers away from electrostatic precipitators. Provide containment capable of holding the total amount of oil.

2.1.4 Chloride Process

2.1.4.1 For facilities in which hydrogen peroxide is used, site and protect the tank for decomposition relief in accordance with Data Sheet 7-80, *Organic Peroxides and Oxidizing Materials*.

2.2 Process Hazards/Safety

2.2.1 Establish a formal process safety program, in accordance with Data Sheet 7-43, *Process Safety*. The emphasis is placed upon process knowledge (specifically for corrosion issues and process details), asset integrity, management of change, ignition source control, operators, incident investigation and emergency response.

2.3 Protection

2.3.1 General

2.3.1.1 For areas with combustible construction, ductwork, or equipment, install automatic sprinkler protection in accordance with Data Sheets 1-57, *Plastics in Construction*; 7-12, *Mining and Ore-Processing Facilities*, and 7-78, *Industrial Exhaust Systems*.

2.3.2 Indoor Fire Protection Systems

2.3.2.1 For areas in which only combustible roofs and floors are present (no plastic pipe/equipment or combustible materials), provide automatic sprinkler protection designed in accordance with Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*, using Hazard Category HC-2.

2.3.2.2 For areas with plastic equipment installed (e.g., Moore filters, rubber/plastic-lined tanks, rotating filters), regardless of the combustibility of the roof and floors provide automatic sprinkler protection designed in accordance with Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*, using Hazard Category HC-3.

For noncombustible areas with limited plastic equipment, it may be acceptable to provide local protection for the equipment as HC-3.

2.3.3 Outdoor Fire Protection

2.3.3.1 Provide directional water spray protection for important plastic equipment and ductwork located outdoors. Focus on concentrations where large ducts cross over each other or multiple vessels are positioned side-by-side. Design the system to provide a discharge pressure of 20 psi (1.4 bar) for open sprinklers or nozzles greater than or equal to 1/2 in. (13 mm), or 30 psi (2.1 bar) for smaller nozzles.

2.3.3.3 Flexible rubber compensators (couplings) on plastic ducts/equipment: Where a credible external fire exposure exists and sprinkler protection is provided in the area, install a deluge nozzle over the rubber couplings exposed. Design the nozzle(s) in accordance with Recommendation 2.3.3.1. If sprinkler protection is not provided in the area, as an alternative provide an FM Approved nonflammable insulating blanket around the rubber couplings exposed.

2.3.3.4 Provide internal sprinkler protection for the electrostatic precipitators (EPSs) in accordance with Data Sheet 7-76, *Combustible Dusts*. If the ESPs are located in a congested area with other combustible materials/equipment, also provide external sprinkler protection in accordance with Recommendation 2.3.3.1.

2.3.3.5 Provide protection for hydraulic units (e.g., filter presses) in accordance with Data Sheet 7-98, *Hydraulic Fluids*, including all the following:

A. Automatic sprinkler protection

B. Interlocks to automatically shut down the unit in the event of a fire

C. FM Approved industrial fluid

2.3.3.6 Provide sprinkler protection for the filter presses and rotary filters as follow:

A. Filter presses: within the enclosure on both sides of the filters and on top.

B. Rotary filters: within the plastic hoods and on top of the hoods.

2.4 Equipment and Processes

2.4.1 General

2.4.1.1 Protect all burners (including tail-gas burners), reactor pre-heaters, and dryers with a burner management system (BMS).

2.4.1.2 Install automatic shutoff systems for hydraulic units. Interlock sprinkler systems, or other fire detection systems, to automatically shut down the pump of the hydraulic units once actuated.

2.4.1.3 Interlock to shut down the fans and blowers in case of an actuation of the sprinkler system in ducts or equipment.

2.4.2 Sulphate Process

2.4.2.1 Provide safety controls and alarms in the reduction area where the iron scrap is added to the digestors to detect and alarm hydrogen concentration below the LEL. Interlock the iron scrap addition line to shut if 50% of the hydrogen LEL is detected.

2.4.2.2 Provide combustion safety controls for the rotating calciner in accordance with Data Sheet 6-17, *Rotary Kilns and Dryers*.

2.4.3 Chloride Process

2.4.3.1 Provide safety controls and interlocks to protect from overpressure scenarios in the chlorinator reactor. These can include stopping of raw material feeds, temperature monitoring, flue gas, etc.

2.4.3.2 Equip chlorinator reactors and off-gas piping with suitable pressure-relief systems protected for corrosive atmospheres.

2.4.3.3 For heat exchangers, provide **all** of the following:

A. Titanium tetrachloride of higher pressure than water cooling

B. Detection of hydrochloric acid in the water stream

C. Emergency operating procedures to react to acid in the cooling water system

2.5 Operation and Maintenance

2.5.1 General

2.5.1.1 Establish an asset integrity monitoring program in accordance with Data Sheet 9-0, *Asset Integrity*.

2.5.2 Chloride Process

2.5.2.1 Establish both preventive and predictive refractory monitoring programs for equipment in heated service. Consider refractory temperature profiles of the reactors based on time of service and expected life of the refractory. Include infrared detection of hot spots as heated chlorine and titanium tetrachloride can result in accelerated corrosion.

2.5.2.2 Procure suitable sparing for predicted wear items such as high alloy heat exchangers and oxidation preheater coils.

2.5.2.3 Establish standard and emergency operating procedures for chlorinator upsets such as loss of pressure, bed slips, incomplete reaction, loss of temperature, etc. Nitrogen can be used for bed suspension and inerting during startup, shutdown, or feed stoppage.

3.0 SUPPORT FOR RECOMMENDATIONS

3.1 Loss History

Figure 1 provides a summary of all losses between 1970 and 2018.

The most frequent causes of loss in this type of industry have been fire and natural hazards. One of the largest losses was centered primarily around ignition in the electrostatic precipitators (ESPs), with further involvement of plastic ductwork and combustible construction materials.

A fire that started on a rubber tube liner and spread to a rubber belt conveyor and other equipment caused severe damage to a 3-story building, filter presses, and other contents in the building.

Another large loss involved a fire in a 10-kV electrical substation that caused a temporary power outage and damage.

3.2 Process Overview

Titanium dioxide has a wide range of uses among several industries. Some of its properties, such as refractive index, good resistance to high temperatures (melting point 3400°F [1857°C]), resistance to UV radiation, etc., make this a very versatile material suited for uses mainly in the coating, plastic, paper, and cosmetic industry. Some other uses can be found in the food industry, semiconductors, and medicine.

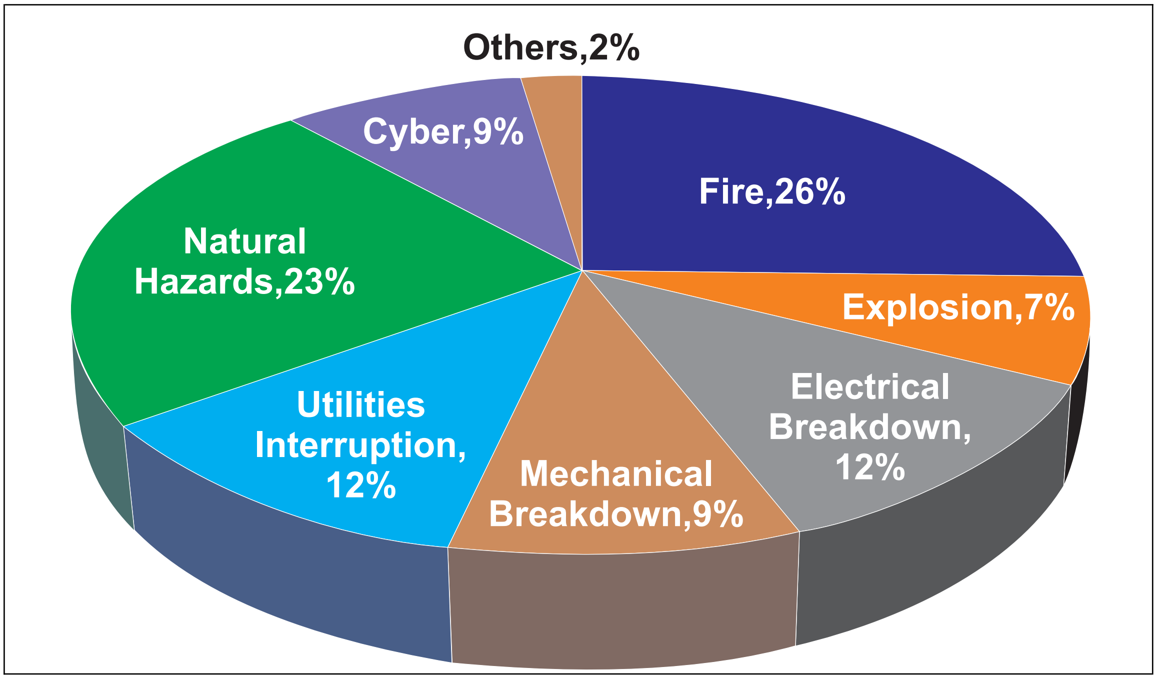

Fig. 1. Losses by cause (based on frequency), 1970-2018

Titanium dioxide can be manufactured using two main processes: sulphate or chloride.

3.2.1 Sulphate Process

The sulphate process involves the extraction of titanium dioxide from two principal ores, ilmenite (45%-60% TiO_2) and rutile (95% TiO_2), ilmenite being the most commonly used ore. Ilmenite is a black sand or rock with the theoretical chemical formula $FeTiO_3$. Mineral rutile is naturally occurring titanium dioxide. It can vary in color from brown to reddish black and its major impurities are compounds of iron.

The sulphate process extraction is run as a batch, and can be divided into the following main stages:

- Ore decomposition
- Hydrolysis
- Calcination
- Milling and conditioning

Figure 2 illustrates the sulphate process for the production of the titanium dioxide pigment.

3.2.2 Chloride Process

In the chloride process, finely ground ores react with gaseous chlorine in the presence of a source of carbon (usually coke) to produce titanium tetrachloride ($TiCl_4$) commonly known as “tickle.” This high temperature reaction is commonly done in large diameter fluidized-bed reactors. The chlorinator reactor will have a special alloy liner along with vessel refractory and refractory lined outlet piping. External reactor shell will have water cooling.

Recovered chlorine from the oxidation process is usually recycled back to the chlorination process. Chlorinator can operate independent of the oxidation process by using fresh chlorine. Nitrogen is used for both purging and keeping the fluid bed from collapsing.

Figure 3 illustrates the chloride process for the production of the titanium dioxide pigment.

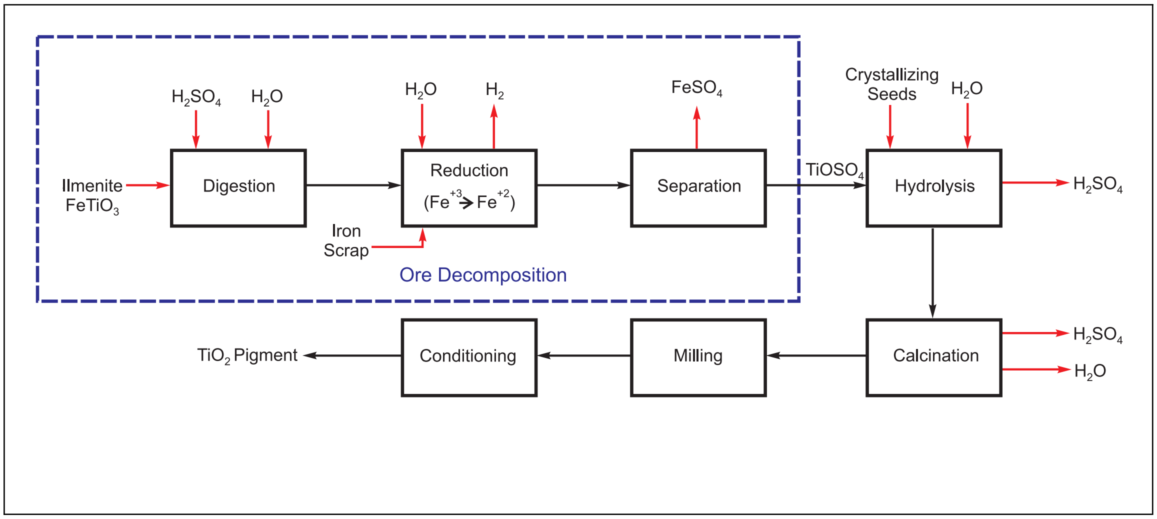

Fig. 2. Flowchart of sulphate process

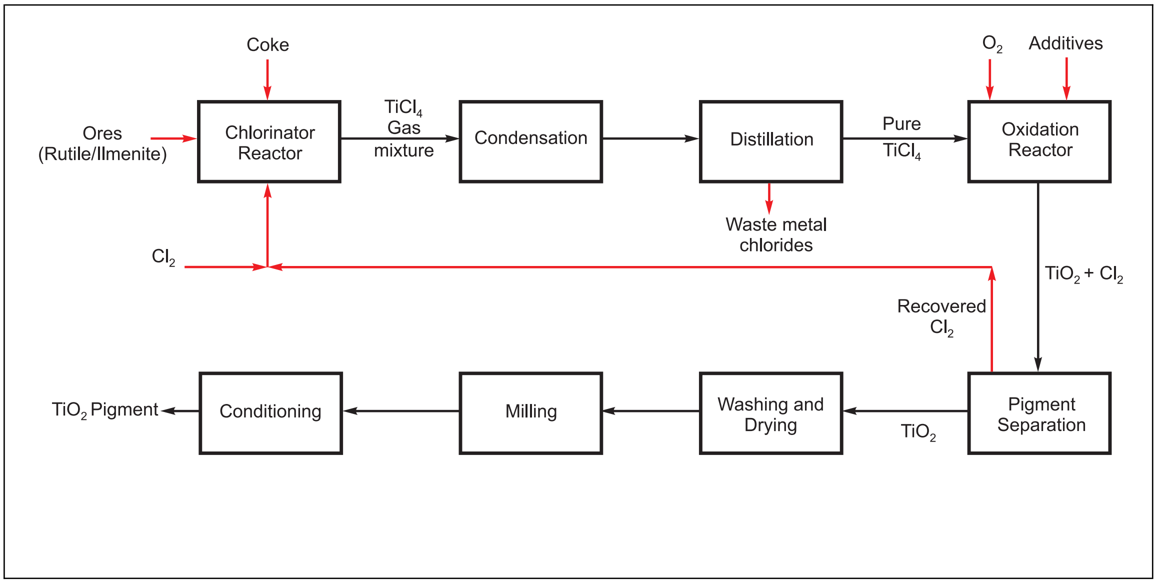

Fig. 3. Flowchart of chloride process

4.0 REFERENCES

4.1 FM

Data Sheet 1-57, *Plastics in Construction*
Data Sheet 2-0, *Installation Guidelines for Automatic Sprinklers*
Data Sheet 3-26, *Fire Protection for Nonstorage Occupancies*
Data Sheet 6-17, *Rotary Kilns and Dryers*
Data Sheet 7-12, *Mining and Ore Processing Facilities*
Data Sheet 7-43, *Process Safety*
Data Sheet 7-76, *Combustible Dusts*
Data Sheet 7-78, *Industrial Exhaust Systems*
Data Sheet 7-80, *Organic Peroxides and Oxidizing Materials*
Data Sheet 7-98, *Hydraulic Fluids*
Data Sheet 9-0, *Asset Integrity*

APPENDIX A GLOSSARY OF TERMS

See also Data Sheet 7-111.

Extremely corrosive environment: Highly acidic process environments such as those found in flue gas desulphurization systems, metal acid pickling ducts, chemical industry exhaust systems, metallurgical gas cleaning, and acid plants. The corrosive environments encountered are typically sulfuric, hydrochloric, nitric, or hydrofluoric acids, and can also include a mixture of these acids.

APPENDIX B DOCUMENT REVISION HISTORY

The purpose of this appendix is to capture the changes that were made to this document each time it was published. Please note that section numbers refer specifically to those in the version published on the date shown (i.e., the section numbers are not always the same from version to version).

January 2023. Interim revision. Minor editorial changes were made.

October 2020. Interim revision. Minor editorial changes were made.

July 2019. This is the first publication of this document.