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SAFETY & LOSS PREVENTION BULLETIN prepared by ORGANIC PEROXIDE PRODUCERS SAFETY DIVISION

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The Storage and Handling of Organic Peroxides in the Reinforced Unsaturated Polyester Fabricating Plant

INTRODUCTION

Reinforced thermosetting resins are a major segment of the plastics industry. The large number of operators and fabricators in this industry require significant safety training resources. In addition, there has been an intensified emphasis on ecology, health, and safety, accompanied by ever tighter legislation, so that even veterans in the industry will profit from the information contained in this bulletin.

In their function as free radical initiators (curing agent's often misnamed catalysts) organic peroxides are essential components in the manufacture of reinforced plastics. Small amounts, mixed with resin and decomposed by means of heat or promoters, produce active fragments (free radicals) which initiate resin polymerization. The resin polymerization occurs in combination with the various reinforcing materials (such as glass cloth) to produce thermosetting products having the required properties.

Organic peroxides are prone to thermal or contamination induced decomposition. Failure to observe these procedures can lead to poor product performance and quality and, in some instances, extremely hazardous conditions. Various peroxide formulations or products differ from each other in the hazard potential of their decomposition and, hence, in their handling requirements. Only the kinds commonly used in Fiberglass Reinforced Plastics (FRP) manufacture will be covered.

EXPLOSION AND FIRE HAZARDS Thermal (Fire and Heat)

High temperature, including from accidental fire exposure, is an important factor in decomposing organic peroxides used in the FRP industry. Although a few require refrigeration, most organic peroxides used in reinforced unsaturated polyester fabricating plants are stable at room temperature and will decompose quietly when exposed to a gradual increase in temperature. However, after reaching or exceeding the self-accelerating decomposition temperature (SADT), the internal plus the external heating accelerates the decomposition, which can result in a fire, or a mild, vigorous or violent decomposition. The length of time involved or the type of decomposition is dependent on the particular organic peroxide formulation. These same peroxides, even those that decompose mildly, may decompose violently or even explode when subjected to a rapid and excessive increase in temperature. This latter behavior is termed "thermal shock".

In general, organic peroxides that are supplied as diluted solutions or paste formulations burn at slower rates and are less sensitive to thermal and mechanical shock. Nevertheless, all forms of heat, such as steam pipes, sun light, radiators, open flames, sparks, etc., should be kept away from all peroxides. Never exceed the manufacturer's recommended storage temperature for extended periods of time.

Mechanical (Grinding and Friction)

Some pure, dry, solid peroxides, such as Dibenzoyl Peroxide, can decompose violently if subjected to "mechanical shock" such as grinding, friction, etc. The violence of the decomposition is dependent upon the quantity of material involved and the degree of confinement. The sensitivity to mechanical shock may be increased by a moderate elevation in temperature.

Contamination Hazards

The stability of organic peroxides is greatly reduced by contamination with materials such as strong acids or bases, sulfur compounds, amines, accelerators (promoters) or reducing agents of any type. For example, contamination of MEK peroxide with cobalt promoters can produce explosive mixtures, as can contamination of Dibenzoyl Peroxide with amine promoters. Contamination of organic peroxides with easily oxidized metals (such as copper, brass, or mild steel), metal oxides, resin sanding dust, dirt, etc. can also produce a violent decomposition. In addition, combustible materials, such as sawdust, sweeping compound, etc. in prolonged contact with organic peroxides may spontaneously ignite.

Health Hazards

As with most chemicals found in the reinforced polyester fabricating plant, caution must be taken to avoid contacting the skin or eyes with organic peroxides, and to guard against ingestion and the breathing of vapors or mist. To avoid harmful effects from skin contact, the contacted area should be immediately washed with soap and water. In the event of contact with the eyes, immediately flush with copious amounts of water and contact a physician. Some organic peroxides such as hydroperoxides and MEKP are very strong irritants and may cause blindness if not treated immediately (wash eyes thoroughly first then get medical treatment). In the event of accidental ingestion, administer milk or water and immediately consult a physician regarding lavage; where inhalation has occurred consult a physician.

Precautionary Recommendations

The recommendations for the storage and handling of organic peroxides have been prepared to reduce the possibility of fire and explosion through the use of these materials. The hazard evaluation of each particular peroxide formulation should be based on information furnished by the manufacturer and your fire insurance carriers, and the authority having jurisdiction, usually the fire department representative.

It has been necessary to generalize in these recommendations for organic peroxides because of the wide variety of formulations and related hazards. Whenever possible, the less hazardous peroxides, diluted pastes and liquids, should be used in place of the more hazardous concentrated peroxides.

Storage

Comply with Federal, State and Local requirements. Consult NFPA 400 for organic peroxide storage guidelines**.** Primary storage of organic peroxides should be separated from manufacturing areas, such as by a specially protected room or a separate storage facility (see NFPA 400). Opened containers should not be returned to primary storage. A separate case or room should be provided. Further storage safeguards can be attained through separation by distance or prescribed fire protection. The quantity of organic peroxides in the processing area should be limited to the minimum daily processing requirements. Adequately trained personnel and planned emergency procedures are essential for a safe operation.

1. The local insurance inspection bureau and fire authorities should be consulted on all plans concerning the location and construction of organic peroxide storage facilities or buildings. The storage facilities should be so located that the organic peroxides are in the least vulnerable position to fire exposure. Vent panels or other mechanisms for relieving pressure of decomposition should be incorporated into the building design.
2. Reinforced polyester plastics fabricators handling organic peroxides, depending on the quantity stored, should provide either a storage room separated by a fire-resistant wall or a detached storage building. All storage areas should have an automatic fire control sprinkler system. If not adequately protected by a fast-acting, deluge or automatic sprinkler system, the storage building or facility should be located an adequate distance from (a) flammable liquid storage, (b) combustible material in the open and (c) any other building or highway.
3. Large quantity storage in highly populated areas should be avoided. The quantity of organic peroxide in storage should be held to the minimum that operating conditions and safety considerations permit.
4. The storage building or facility should be constructed in accordance with the recommendations of NFPA 400 guidelines and your insurance authorities.
5. Electrical installations should be compliant with NFPA 400, chapter 14.
6. Storage buildings should not, as a rule, be heated, but if heating is required, the recommendations of NFPA 400 should be followed. It may be necessary, however, to cool some buildings or facilities in hot weather to prevent decomposition of the peroxides.
7. Organic peroxides should be stored away from all sources of heat and ignition such as open flames, electrical devices and heating equipment. Care should be taken to prevent the exposure of these materials to prolonged storage in the direct rays of the sun. Truck motors should be turned off during a loading or unloading operation.
8. Containers of organic peroxides should be stacked in such a way that water from the sprinkler system will reach and wet them in case of fire. (See Fire Protection.) Provisions should be made to contain the fire water runoff in a catch basin or equivalent.
9. Organic peroxides should be stored in the same containers used by the manufacturers for shipping the material.
10. Various organic peroxides should be separated from each other in the storage building or facility to prevent accidental misuse of materials. No other materials should be stored in the organic peroxide storage building or facility.
11. Organic peroxides should not be stored in a refrigerator that also contains food or water.

Handling

1. Organic peroxides should be brought into the manufacturing area in the original shipping containers. Opened containers should not be returned to primary storage. Material that has not been used should not be returned to the original container. Containers of organic peroxides should be securely closed to prevent contamination when not in use. Opened containers of Dibenzoyl Peroxide containing water as a phlegmatizer such as hydrous Dibenzoyl Peroxide or many pastes and slurries must be promptly closed to prevent drying of the material which will result in a large increase in hazard, including risk of explosion.
2. No secondary or loose storage of organic peroxides should be permitted in the manufacturing area. The material brought into this area should be limited to the requirements for immediate use. Organic peroxides should be removed from the manufacturing area and placed in the weighing and dispensing room each day at the close of business.
3. Areas where organic peroxides are handled should be well ventilated and protected by an automatic fire protection sprinkler system. Appropriate protective clothing, such as rubber gloves, safety glasses, goggles or face shields should always be worn to avoid bodily contact from inadvertent splashing or spills.
4. When organic peroxides are poured into mixing or dispensing containers, care should be taken to provide clean and properly designed equipment. Copper, brass, mild steel or lead equipment is dangerous in contact with organic peroxides. Zinc and galvanized equipment can also cause accelerated decomposition of organic peroxides. The use of compatible type equipment with each organic peroxide is essential. (Consult the manufacturer or supplier of organic peroxides for recommended materials to be used.)

5. Where it is necessary to slurry, mix, or dissolve organic peroxide in very small quantities of monomer (such as styrene) prior to incorporating the material into the resin mix, the peroxide should be added to the monomer and used promptly. These "small quantity" mixtures are polymerizable and they may develop considerable heat. This could be sufficient to boil the solvent monomer and cause it to ignite. Make sure no accelerators are added. Make sure that the emergency relief system design considers the reactive risk of the mixture which may include extremely rapid temperature increase due to the polymerization.
6. Dilution of organic peroxides by users is not recommended. Notwithstanding the recommended practices, it is known that some composite producers do dilute MEK peroxide. In this instance, the following instructions should be followed: Be sure to consult with the peroxide manufacturer for compatible solvents. Use only high purity solvents. Never use contaminated solvents. Never use acetone. Never use reclaimed solvents unless they have been specifically tested by the organic peroxide manufacturer. The use of an incompatible or contaminated solvent may cause a violent decomposition of the organic peroxide.
7. The fire hazard of an organic peroxide can be drastically changed by the diluent employed. The fire hazard can be increased by using a low flash point solvent, such as ethyl acetate, or decreased by using a high flash point plasticizer such as dimethyl phthalate.
8. Organic peroxides should not be used in pressurized vessels or confined unless adequate provisions have been made to relieve the sudden pressure that may develop if the peroxide is decomposed by heat or contamination. Organic peroxide may be released during venting and provisions should be made for the protection of personnel and the possibility of fire.
9. Mechanical processing, e.g. "Spray Up" equipment, should be given special consideration. Keep this equipment very clean and scrupulously avoid contaminating the organic peroxide when filling the dispensing containers. Protect dispensing containers from fire and all sources of heat. Pressurized dispensing containers should comply with item 8. Strictly observe dilution instructions (item 6). When testing, spray organic peroxide solutions into a container of water. Do not spray into the air, on resin overspray, etc. *Wear protective eye equipment* at all times.
10. Organic peroxides should never be mixed directly with any accelerators or promoters, as violent decomposition or explosion may result. The accelerator should be thoroughly dispersed in the resin mixture before adding the peroxide catalyst.
11. Organic peroxides should be kept away from all sources of ignition, such as open flames, electrical devices and heating equipment.
12. All processing equipment should be properly grounded and inter-bonded. Non-sparking tools should be used for weighing the peroxides.
13. Solid organic peroxides should not be subjected to any frictional or grinding operation.
14. Organic peroxides should not be added to materials at temperatures exceeding safe tolerances for the particular peroxide.
15. "No smoking" regulations should be strictly enforced in the organic peroxide storage and processing area. No matches, open lights or flame should be permitted in this area.

Supervision and Maintenance

1. The vast majority of fires or accidents involving organic peroxides are due to poor housekeeping, maintenance or supervision. Good housekeeping and maintenance of the plant facilities and equipment are essential in all organic peroxide storage and processing areas. A program should be established to accomplish these objectives.
2. The handling of organic peroxides in the storage and manufacturing areas should be assigned to qualified and trained personnel who are fully aware of the hazardous character of the materials. Special care should be employed to prevent rough handling or dropping of containers. Instructions and warning placards should be posted in the storage building and manufacturing area.
3. Organic Peroxides that have been spilled should be absorbed with an inert moist material. Immediately, using non-sparking equipment, transfer into double polyethylene bag or polyethylene drum, then wet thoroughly with water. Isolate the contaminated absorbent due to the possibility of spontaneous combustion. Dispose of as required by local, state and federal regulations. If packaging material becomes contaminated with an organic peroxide, place in a polyethylene bag and wet with water. Store out of the sun.
4. The performance of maintenance and repair work in the organic peroxide storage or processing area should require a "work permit" from supervisory personnel. The organic peroxides should be removed or adequately safeguarded while this work is being done.
5. The building grounds should be kept free of combustible materials, such as trash, dry weeds and grass.

Fire Protection

1. Plant personnel should be thoroughly trained in the emergency procedures required for fires, explosions or accidental spills. Cooperative liaison should be established between the plant officials and the local fire authorities for emergency planning and the exchange of information of mutual interest. If a fire occurs in the organic peroxide storage area, the automatic extinguishing system should be allowed to take over and all personnel should leave. Do not approach the fire or attempt to use fire extinguishers. An explosion is a possibility.
2. Should a fire occur in the vicinity of the organic peroxide storage area, maintain a cooling water spray over the outside of the containers to guard against overheating.
3. Fires in the manufacturing area should be extinguished with the usual fire fighting equipment. If an organic peroxide should be involved, water (fog or spray preferred) should be applied from a safe distance; in any event, peroxide containers in the fire area should be wet down as a precautionary measure.
4. Fire drills and inspections should be conducted regularly. Plant personnel should be trained in the use of fire fighting equipment.

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