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Organic peroxide's safe handling and use

1. Introduction

Chemically organic peroxides are meta-stable compounds for there is oxygen –oxygen Linkage in the molecular structure. Under conditions of heating or activation, this oxygen-oxygen Bond cleaves to form active free radicals, and these radicals can initiate polymerization or curing Easy. Organic peroxides are used in plastics industry as curing agents for thermoset resins,initiator For free radical polymerization and cross-linking agents for elastomers and polyethylene. They are dangerous for their high reactivity, so we must treat or handle them correctly. The category of organic peroxides list as flows.

A. DIACYL PEROXIDES

Dry benzyl peroxide and pure MEK peroxide are shock and friction sensitive. Except for benzyl peroxide all commercial diacyl peroxides are formulated to be non-shock or non-friction sensitive and are very safe if handled and stored properly. Examples include the wetted and paste forms of benzoyl peroxide.

B. PEROXYESTERS

Peroxyesters are quite stable at their recommended storage temperatures. Some peroxyester can freeze. Allowing them to warm at a temperature not above the maximum required can thaw frozen materials.

C. PEOXYDICARBONATES

Peroxydicarbonates are thermally unstable compounds. At their recommended storage temperatures however they are quite safe. At higher than these temperatures, decomposition will occur, in some cases rather violently.

D. DIALKYL PEROXIDES

Among the commercially available dialkyl peroxides. Di-t-Butyl peroxides have a low flash point and its vapors are highly flammable. All other dialkyl peroxides have relatively high flash points, but once ignited, will burn vigorously and are difficult to extinguish.

E. KETONE PEROXIDES

This kind of peroxides is subject to decomposition through chemical action and is particularly sensitive to metallic salts. They are widely used as room temperature catalysts for curing polyester resins, which contain accelerators such as cobalt naphthenate and cobalt/tertiary amine combinations. Direct mixtures of the peroxides and the accelerator may decompose with violence and every effort should be made to eliminate any possibility of direct contact because of the wide range of contaminants which can interact with ketone peroxides, good housekeeping practices should be strictly maintained.

F. PEROXYKETALS

Peroxyketals are extremely sensitive to acid contamination, which cause rapid decomposition releasing flammable vapors, which may self, ignite.

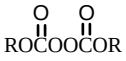
G. HYDROPEROXIDES

Commercial formulations of Hydro peroxides as supplied by Lanzhou Auxiliary Agent Plant are not shock sensitive. Pure-t-butyl hydro peroxides and 2.5-dihydroperoxy-2.5-dimethyl hexane are considered too shock sensitive for commercial handling.

II. Source of Hazards

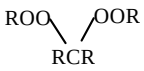
A wide variety of organic peroxides are offered commercially to meet the sophisticated needs of polymer manufactures. Among them the product representing of the classes are listed in table I. (Note: MEK or ketone peroxides are a mixture of peroxides and hydroperoxides).

Peroxyesters **peroxydecarbonates** **dialkyl peroxides**



t-butyl perbenzoate di-2-ethylhexyl peroxy- di-t-butyl peroxide
Dicarbonate 2,5-dimethyl-2,5-bis (t-butyl-peroxy)hexane
t-butyl peroxypivalate di-sec-butyl peroxy-
t-butyl peroctoate dicarbonate dicumyl peroxide
t-butyl peroxy-
neodecanoate

diacyl peroxides **hydroperoxides** **peroxyketals**



benzoyl peroxide t-butyl hydroperoxide 1,1-di(t-butyl peroxy)3,3,5-trimethylcyclohexane
lauroyl peroxide cumene hydroperoxide 1,1-di(t-butyl peroxy) cyclohexane

The major causes of peroxide decomposition (source of hazard) are heat, fire, friction, shock and contamination. Examples of the common source of these include:

Heat— Sunlight, loss of refrigeration, radiators or heating elements, hot reaction vessels.
Fire—any open flame.
Friction— mixing, pumping, grinding, traffic over spillage.
Shock— Dropping, impact during transportation.
Contamination—Metal salts, amines, acids, bases.

III. Safety Tests

The major safety characteristics to determine the relative hazard of organic peroxide include: shock sensitive, the amount of energy released during a decomposition and flash point. The ease of burning.sensitivety to rate of heat rise, thermal stability, self-accelerated decomposition temperature and ignition or auto ignition characteristics.

The organic peroxide producers safety division of the SPI has developed standardized tests for the determination of hazard ratings for peroxides .The following is a list and description of these established tests:

A. SADT (self accelerating decomposition temperature): This test establishes the lowest

Temperature at which peroxide, in its largest commercial package, will undergo self-accelerating decomposition. The type of decomposition and damage potential are measured, and the severity of decomposition is determined .The two parameters having the greatest effect on SADT are rate of decomposition and heat loss from the package.

B. Pressure Vessel Test—The PVI deals with heat sensitivity, measuring the rate and resultant energy release o thermal decomposition of peroxides under conditions of rapid heating and partial confinement.

C. Rapid heat Test—This determines the type of decomposition that occurs when peroxide composition is heated in a test tube.

D. Shock Sensitivity –This test measures the susceptibility of a peroxide to decompose from impact.

E. Trauzl Test—This is a measure of the total energy released by peroxide decomposition, when initiated by an explosive force.

F. Burring Test—This records the ease of, and time to ignition together with burning time and flame height that result when a specified quantity of peroxide is burned.

G. Flash Point—This is the temperature at which the product vapors ignite on contact with an open flame.

H. Thermal Stability Test—Results are determined by storing peroxide at a constant temperature for a specified time .The results of this test in terms of weight loss and assay are used as criteria for establishing storage temperature and shelf life requirements.

IV. The characteristic of organic peroxides flammability

All organic peroxides will burn vigorously and once ignited will be difficult to extinguish .The flammability of organic peroxides will bi affected by the decomposition products. Most peroxides decompose with vapors and heat. Such vapors may be flammable and could be the cause of an explosion.

Heat density

All organic peroxides are sensitive to heat .If peroxide is heated above a certain temperature; the rate of the decomposition will increase an uncontrolled manner. This reaction can become violent, releasing large volumes of hot, flammable gasses.

V. Storage

Exposure to a temperature that can lead to an accelerated decomposition may result in the generation of flammable gasses and in some cases, spontaneous ignition. Proper storage is critical to the sage handling of organic peroxides. Ventilation is important because air circulation around peroxides stored at low temperature reduces the chance of localized hot spots that can cause decomposition.

Organic peroxides inventory should be rotated to avoid shelf life problems. Usually it is good practice to use liquid initiators within six months of receipt. Freezer or refrigerated facilities should be provided for intermediate storage of controlled temperature products.

Note: It should be kept in mind that refrigerated storage facilities are used to maintain low temperature peroxides at the required storage temperature and not for cooling low temperature peroxides to the required temperature. If only a portion of material that is rumored from refrigerated storage is used, the remainder must be cooled to a temperature at,

or somewhat below the required before being placed back into the refrigerated storage facilities. Failure to follow this procedure could result in a serious decomposition in the refrigerated storage area.

All peroxides storage facilities should be designed along the following requirement.

- Located m an isolated area.
- Used only for the storage of organic peroxides.
- Should be of fireproof contraction.
- Electrical equipment should be explosion proof.
- Free of all combustible material.
- Prevent exposure to sunlight.
- Posted signs ”Flammable Storage-Keep Fire Away “ and “ No Smoking”.
- For controlled temperature peroxides emergency back up refrigeration should be installed.

  Large quantities of organic peroxides should ideally be stored in specially designed buildings of non-combustible construction. Detached buildings are the most common and proffered facilities for storage large quantities. Three basic types of buildings are used depending on the storage requirement of the peroxides and the amount that will be stored, plus local fire codes, insurance regulations and other lows, the tree of the kinds is uncontrolled Temperature storage. Refrigerated storage Facilities and Walk-In Refrigerated Storage Building, we can make a choice with our requirement.

VI. Packaging and Transport

The containers in which organic peroxides are packaged include polyethylene bottles and jars, polyethylene lined bags and fiber drums and specially coated steel drums. Polyethylene is the preferred material since it is relatively inert is flexible enough to withstand normal pressure buildup and will generally rupture during rapid decomposition.

The transport of the product do not exposure, rumination, super temperature, strike, pack with another goods. Every package must be isolate. Must not make electrostatic. The drivers should be trained to handle low temperature products. They should be familiar with the handling instruction and safety precautions necessary to insure safe shipment.

VII. First Aid

Don’t allow prolonged contact with skin Inhalation of vapors or decomposition products emitted during processing should also be avoided .In case of skin contact with plenty of water and soap .In this event of eye contact, flush eyes with water for at least fifteen minutes and immediately seek medical attention. Additionally, refer to the individual product bulletins for specific organic peroxides and the SPI Toxicological Data Bulletin for specific toxicity data.

VIII. Disposal of the waste material

Spillages of organic peroxides must be taken care of immediately. Spills can normally be handling by spreading an inert absorbent material directly on the spill, sweeping the area and placing the sweepings in polyethylene bags for disposal, wash down the spill area with surfactant and water to remove any traces of peroxides. Allow for sufficient ventilation to aid in the removal of fumes that may be present.

The disposal of organic peroxides has become a difficult problem. Environmentally there are some ways to disposal; as follows:

1. Dilutions and incineration

Due to current environmental regulations, this method is the most preferred for liquid peroxide disposal; Dilution of peroxide to no more than 1% active oxygen or no more than 10% by weight in a satisfactory solvent is recommended. Fuel oil #2 or common hydrocarbons are the most widely used solvents. Incineration can be accomplished after satisfactory mixing. Incineration has the advantage of providing rapid and complete decomposition along with the elimination of decomposition products. This method is not generally for disposal of solid peroxides.

2. Hydrolysis

This method can be used for limited quantities of material of certain peroxide types .It involves the addition of the peroxide to a 20~30%caustic solution, surfactant and a portico solvent such as methanol or isopropanol .The amount of caustic solution should be approximately 10 times the weight of the peroxide being hydrolyzed. After addition of the peroxide the solution must be stirred for a period of time to complete the hydrolysis reaction .in general, the hydrolysis method converts the active oxygen species present to water-soluble active oxygen species.

IX. Safety Precaution List

1. One of the mist important factors to observe when working with organic peroxide is the recommended storage temperature. Exposure to a temperature that can lead to an accelerated decomposition may result in the generation of flammable gasses and in some cases spontaneous ignition.
2. Proper storage is critical to the safe handling of organic peroxide; both those normally stored at ambient temperature and those require controlled temperature storage. Ventilation is important because air circulation around peroxides stored at low temperatures reduces the chance of localized hot spot that could cause decomposition.
3. Storage areas for peroxides should have explosion proof electrical equipment.
4. Organic peroxide inventories should be rotated to avoid shelf life problems .It is good practice to use liquid initiators within six months of receipt.
5. Any observable gassing or distortion of the container, should be treated very carefully. Contact the supplier immediately for assistance.
6. Only minimal quantities of peroxides should be kept in the immediate processing area.
7. Contact with oxidizers, reducing agent promoters and acids or bases should be scrupulously avoided.

8. Heat, flame, contamination, shock, friction and static electricity are potential hazards when organic peroxide is being charged to a reaction. Care should be taken to eliminative or minimize all of these.
9. Contamination can be avoided by using proper equipment and proper materials of construction. Polymeric materials that may be soluble in organic peroxide solutions should not be used as reaction vessels.
10. Foreign materials such as iron or dirt should be scrupulously avoided when charging peroxydes.
11. Static build-up can be minimized by proper grounding and by keeping free fall distance to a minimum.
12. Friction caused by pumping increases the temperature of the pumped solutions. Extra care should be exercised when peroxide solutions are being re-circulated.
13. Avoid any contamination, clean, dry plastic or glass containers should be used to cool samples. Dry ice should be available to cool samples in an emergency. Direct heat should never be applied to a sample or to a large container of peroxides
14. Dilution of pure peroxides will increase the safety characteristic.
15. Any spilled organic peroxides should be attended to immediately.
16. Where spills occur, allow for sufficient ventilation to aid in the removal of fumes that may be present.
17. In disposing of organic peroxides, extreme care should be exercised. The wetted absorbent material should be placed in a plastic bag and then incinerated, disposal procedures for specific organic peroxides are provided on product labels and in bulletins.
18. Work is continually being done on incineration and chemical reduction methods for organic peroxide disposal.
19. The procedure for disposal of empty peroxide containers must include a thorough cleaning, rinsing and wetting. These can then be sent to a landfill or incineration site. Empty containers should never be re-used.
20. Cutting torches should never be used on empty peroxide drums.

X. Note of The Data

The information contained here is the best of our knowledge accurate, but since the circumstance and conditions in which it may be use are beyond our control, we don't accept liability any loss or damage, however arising, which results directly or indirectly from the use of such information nor do we offer any warranty of immunity ageist patent in fragment.

4. Correlation chart (with Akzo products)

LANQUAN NAME	AKZO NAME	CHEMICAL NAME
LQ-BCHPC	**PERKADOX 16**	**DI(4-TERT-BUTYLCYCLOHEXYL)**
LQ-IPPC		**DIISOPROPYL PEROXYDICARBONATE**
LQ-EHPC	**TRIGONOX EHP**	**DI(2-ETHYLHEXYL)PEROXYDICARBONATE**
LQ-CEPE	**PERKADOX 24**	**DICETYL PEROXYDICARBONATE**
LQ-CEPE-90P	**LILADOX 90 P**	**DICETYL PEROXYDICARBONATE**
LQ-CEPE-33 W	**LILADOX 33 W**	**DICETYL PEROXYDICARBONATE**
LQ-MYPC	**PERKADOX 26**	**DIMYRISTYL PEROXYDICARBONATE**
LQ-TAPD	**TRIGONOX123-C75**	**TERT-AMYL PEROXYNEODECANOATE**
LQ-TBPD	**TRIGONOX 23**	**TERT-BUTYL PEROXYNEODECANOATE**
LQ-TBPV	**TRIGONOX 25**	**TERT-BUTYL PEROXYPIVALATE**
LQ-TAPV	**TRIGONOX 125**	**TERT-AMYL PEROXYPIVALATE**
LQ-TAPEH	**TRIGONOX 121**	**TERT-AMYL PEROXY-2-ETHYLHEXANOATE**
LQ-TBPEH	**TRIGONOX 21**	**TERT-BUTYL PEROXY-2-ETHYL HEXANOATE**
LQ-TBPIB	**TRIGONOX 41**	**TERT-BUTYL PEROXYISOBUTYRATE**
LQ-TBPMH	**TRIGONOX 42**	**TERT-BUTYL PEROXY-3,5,5-TRIMETHYL HEXANOATE**
LQ-TBPA	**TRIGONOX 27**	**TERT-BUTYL PEROXYACETATE**
LQ-TBPB	**TRIGONOX C**	**TERT-BUTYL PEROXYBENZOATE**
LQ-K	**TRIGONOX 36**	**DI(3,5,5-TRIMETHYL HEXANOYL) PEROXIDE**
LQ-DP	**PERKADOX SE-10**	**DIDECANOYL PEROXIDE**
LQ-LP	**LAUROX**	**DILAUROYL PEROXIDE**
LQ-BPO	**LUCIDOL**	**DIBENZOYL PEROXIDE**
LQ-BPDH	**TRIGONOX 101**	**2,5-DIMETHYL-2,5-DI(TERT-BUTYLPEROXY) HEXANE**
LQ-BPDH3	**TRIGONOX 145**	**2,5-DIMETHYL-2,5-DI(TERT-BUTYLPEROXY) HEXANE-3**
LQ-TBHP	**TRIGONOX B**	**DI-TERT-BUTYL PEROXIDE**
LQ-TBHP	**TRIGONOX A**	**TERT-BUTYL HYDROPEROXIDE**
LQ-CH335	**TRIGONOX 29**	**1,1-DI(TERT BUTYLPEROXIDE) CYCLOHEXANE**
LQ-CH	**TRIGONOX 22**	**1,1-DI (TERT BUTYLPEROXY) CYCLOHEXANE**
LQ-TAHP		**TERT AMYL HYDROPEROXIDE**
LQ-PMHP		**P-MENTHANE HYDROPEROXIDE**
LQ-MEKP		**METHYL ETHYL KETONE PEROXIDE**
LQ-TBEC	**TRIGONOX 117**	**TERT. BUTYL PEROXY -2- ETHYLHEXYL CARBONATE**
LQ-TAEC	**TRIGONOX 131**	**TERT. AMYL PEROXY-2- ETHYLHEXYL CARBONATE**
LQ-DDB	**PERKODOX 30**	**2,3 DIMETHYL-2,3 DIPHENYLBUTANE**
LQ-BIPB 96,04%	**PERKADOX 14 S/fl**	**DITERT-BUTYL ISOPROPYL BENZENE**
LQ-DCP 99%	**PERKADOX BC-FF**	**DICUMYL PEROXIDE**

*** This only is for your reference and orientation, as TRIGONOX is an official brandname.**

5. Product Survey (Usage of our products)

Product	Structural Formula	Acrylate	LDPE	PP	PVC	PS
LQ-BCHPC	Di(4-tert-butylcyclohexyl) Peroxydicarbonate	*		*	*	
LQ-IPPC	Di(2-ethylhexyl) Peroxydicarbonate		*		*	
LQ-EHPC	Di(2-ethylhexyl) Peroxydicarbonate	*	*		*	
LQ-CEPE	Dicetyl peroxydicarbonate	*			*	
LQ-MYPC	Dimyristyl peroxydicarbonate	*			*	
LQ-TAPD	Tert-amyl peroxyneodecanoate	*	*		*	
LQ-TBPD	Tert-butyl peroxyneodecanoate	*	*		*	
LQ-TBPV	Tert-butyl peroxypivalate	*	*		*	
LQ-TAPV	Tert-amyl peroxypivalate	*	*		*	
LQ-TAPEH	Tert-amyl peroxy-2-ethyl hexanoate	*	*			*
LQ-TBPEH	Tert-butyl peroxy-2-ethyl hexanoate	*	*			*
LQ-TBPIB	Tert-butyl peroxyisobutyrate	*	*			*
LQ-TBPMH	Tert-butylperoxy-3,5,5-trimethyl hexanoate	*	*			*
LQ-TBPA	Tert-butyl peroxyacetate	*	*			*
LQ-TBPB	Tert-butyl peroxybenzoate	*	*			*
LQ-K	Di(3,5,5-trimethylhexanoyl) peroxide	*	*		*	
LQ-DP	Didecanoyl peroxide	*	*		*	
LQ-LP	Dilauroyl peroxide	*	*		*	*
LQ-BPO	Dibenzoyl peroxide	*				*

Product	Structural Formula	Acrylate	LDPE	PP	PVC	PS
LQ-CH335	1,1-Di(tert-butylperoxy)-3,5,5-trimethylcyclohexa	*	*			*
LQ-CH	1,1-Di(tert-butyl peroxy)cyclohexane	*	*			*
LQ-BPDH	2,5-Dimethyl-2,5-Di(tert-butylperoxy)-hexane	*	*	*		*
LQ-BPDH3	2,5-Dimethyl-2,5-Di(tert-butylperoxy)-hexane-3	*	*			*
LQ-DTBP	Di-tert-butyl peroxide	*	*	*		*
LQ-TBHP	Tert-butyl hydroperoxide	*		*		*
LQ-TAHP	Tert-Amyl hydroperoxide	*				
LQ-PMHP	P-menthane hydroperoxide					*
LQ-MEKP	Ethyl Ketone Peroxide					*