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## **SAFETY AND HANDLING OF ORGANIC PEROXIDES:**

**A Guide Prepared by the**  
**Organic Peroxide Producers Safety Division**  
**of The Society of the Plastics Industry, Inc.**

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It is the desire of the OPPSD of the SPI that all transporters, handlers, and users of organic peroxides do so in a safe manner. This brochure has been designed and written with that goal in mind. If there is additional information pertaining to this subject that you would like to see included in future updates please contact us at <http://www.oppsd.org/>.

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## **Definitions and Notations:**

Active Oxygen (AO) (also called Available Oxygen): the amount of oxygen contained in an organic peroxide molecule that is available for forming free radicals. This is presented as the percentage by weight of one of the elemental oxygens contained in the peroxy group. One of the oxygen atoms in each peroxide group is considered “active”. The active oxygen is usually measured by titration methods but other methods can be used.

Active Oxygen (AO) Theoretical: the amount of oxygen contained in an organic peroxide molecule that is the theoretically maximum available for forming free radicals. This value is calculated from the number active oxygen based upon the chemical structure(s) of the organic peroxide(s) in the mixture.

Control Temperature (CT or T<sub>c</sub>): the temperature an organic peroxide formulation must be at or below when offered for transport. If the shipped goods exceed this temperature corrective measures must be initiated to avoid reaching the emergency temperature.

Emergency Temperature (ET or T<sub>e</sub>): the temperature at which emergency procedures shall be implemented during transportation of organic peroxide formulations.

Free Radical: atoms, molecules, or ions with unpaired electrons on an open shell configuration. Free radicals may have positive, negative, or zero charge. With some exceptions, the unpaired electrons cause radicals to be highly chemically reactive.

Half-life: Half-life is the time and temperature at which 50% of the peroxide will decompose.

HAST: Heat Accumulation Storage Test, a method of determining SADT

OPPSD: The Organic Peroxide Producers Safety Division of the SPI

Organic Peroxide: any organic chemical that contains an oxygen-oxygen (-O-O-) bond

Organic Peroxide Formulation: a technically pure organic peroxide or a mixture of an organic peroxide with one or more materials, usually diluents

RHDT: Rapid Heat Decomposition Temperature – the temperature at which a sample of an organic peroxide formulation visibly decomposes when heated rapidly

SADT: Self Accelerating Decomposition Temperature – the temperature at which an organic peroxide formulation will undergo a self-accelerating decomposition within one week in the package tested

SPI: The Society of the Plastics Industry

## INTRODUCTION:

### **OPPSD/SPI**

The Society of the Plastics Industry ([SPI](#)) was founded in 1937, and is the plastics industry trade association representing the third largest manufacturing industry in the United States. SPI's member companies represent the entire plastics industry supply chain, including processors, machinery and equipment manufacturers and raw materials suppliers.

The Organic Peroxide Producers Safety Division ([OPPSD](#)) of the SPI was formed by organic peroxide producers in 1962 in order to promote the science, safety and handling of organic peroxides. This guide is part of the OPPSD's activities toward this goal.

### **Organic Peroxide Basics**

An organic peroxide is any organic chemical that contains an oxygen-oxygen (-O-O-) bond (peroxy functional group). A very large number of compounds fit this definition and therefore organic peroxides may have a wide range of properties. This guide will only cover commercial organic peroxide formulations.

The peroxy functional group is thermally sensitive, containing a pseudo-stable energetic bond. For the organic peroxide to be useful as a free radical source this bond must be broken. When properly used, these free radicals can initiate polymerization or other desired chemical reactions. This decomposition leads to heat and by-products.

Each organic peroxide has a different rate of decomposition. Some organic peroxides must be stored and shipped under refrigerated conditions to preserve their usefulness and quality and for safety reasons. Other organic peroxides can be stored and shipped safely at or above ambient temperature. Determining the safe handling, storage and shipping temperatures is a significant part of the testing that must be done before an organic peroxide formulation is allowed to be transported or offered for sale.

### **TYPES OF ORGANIC PEROXIDES**

The simplified formula for an organic peroxide is  $R_1OOR_2$  where  $R_1$  is an organic group and  $R_2$  is the same or different organic group or hydrogen. In the case of difunctional peroxides (two peroxide bonds in the structure) the structure is simplified as shown for peroxyketals or dialkyl peroxides in the table below. In that case there may be three organic groups in the structure.



$R_1$  = organic group

$R_2$  = (same or different) group

Common types of commercially available organic peroxides and their typical ranges of 10 hour half-life temperatures are shown in the following table. Here the types are grouped by structural definition. Note

that within each type, the exact structure of the various organic groups (R1, R2, or R3) determines the thermal stability of any particular member. For some types, such as peroxydicarbonates, the nature of the organic groups has little effect on the thermal stability. For other types, like peroxyesters, the organic groups can have a dramatic effect on thermal stability. In the case of peroxyesters you will see a wide range of 10 Hour Half-life temperatures as a result. In some of the types, one or more of the organic groups must be tertiary-alkyl groups in order for the peroxides to be good free radical initiators.

<u>Common Types</u>	<u>Typical Formula</u>	<u>10 Hour Half-life Range (°C)</u>
dialkyl peroxides	$R_1-O-O-R_2$	117 – 133
hydroperoxides	$R_1-O-O-H$	133 – 172
diacyl peroxides	$R_1-\overset{\text{O}}{\parallel}{C}-O-O-\overset{\text{O}}{\parallel}{C}-R_2$	20 – 75
peroxydicarbonates	$R_1-O-\overset{\text{O}}{\parallel}{C}-O-O-\overset{\text{O}}{\parallel}{C}-O-R_2$	49 – 51
peroxyesters	$R_2-O-O-\overset{\text{O}}{\parallel}{C}-R_1$	49 – 107
ketone peroxides	$H-O-O-\left(\begin{array}{c} R_1 \\   \\ -C-O-O- \\   \\ R_2 \end{array}\right)_n-H$	N/A
peroxyketals	$R_1-O-O-\overset{R_2}{\underset{R_3}{ }{C}}-O-O-R_1$	92 – 115
alkylperoxy carbonates	$R_1-O-O-\overset{\text{O}}{\parallel}{C}-O-R_2$	90 – 100

R<sub>1</sub> and / or R<sub>2</sub> are generally alkyl groups, often tertiary-alkyl groups. If attached directly to the peroxy group, n is 1 - 3. One of the groups can be hydrogen.

### CHARACTERISTIC PROPERTIES

For the organic peroxide to be useful, the peroxy bond must be broken, usually by heating, to produce free radicals which can initiate polymerization or another desired end result. This decomposition also produces heat and by-products.

Each peroxy group is considered to contain one active oxygen atom. The concept of active oxygen content is useful for comparing the relative concentration of peroxy groups in formulations, which is related to the energy content. In general, energy content increases with active oxygen content and thus,

the higher the molecular weight of the organic groups, the lower the energy content and, usually, the lower the hazard.

The term ACTIVE OXYGEN is used to specify the amount of peroxide present in any organic peroxide formulation. One of the oxygen atoms in each peroxide group is considered “active”. The theoretical amount of active oxygen can be described by the following equation.

$$A[O]_{\text{Theoretical}} (\%) = [(16 \cdot p)/m] \cdot 100$$

p = number of peroxide groups in the molecule

m = molecular weight of the pure peroxide

Organic peroxides are often sold as formulations which include one or more phlegmatizing agents. That is, for safety sake or performance benefits the properties of an organic peroxide formulation are commonly modified by the use of additives to phlegmatize (desensitize), stabilize, or otherwise enhance the organic peroxide for commercial use. Commercial formulations occasionally consist of mixtures of organic peroxides which may or may not be phlegmatized.

Organic peroxides may be in the solid or liquid state. There are no organic peroxides in the vapor state. Occasionally liquid organic peroxides are desensitized by mixing with solid materials so that the mixture behaves as if it is a solid.

#### **THERMAL DECOMPOSITION:**

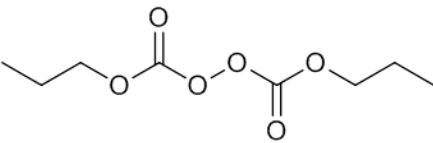
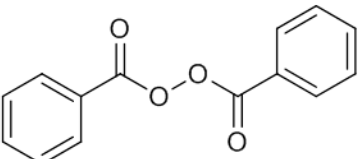
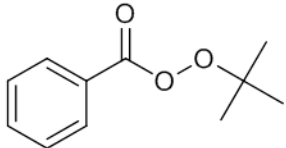
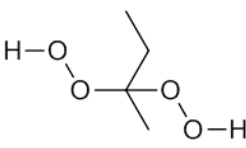
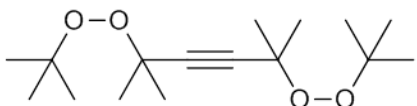
Unlike most other chemicals, the purpose of a peroxide is to decompose. In doing so it generates useful radicals that can initiate polymerization to make polymers, modify polymers by grafting or visbreaking, or crosslink polymers to create a thermoset. When used for these purposes, the peroxide is highly diluted, so the heat generated by the exothermic decomposition is safely absorbed by the surrounding medium (e.g. polymer compound or emulsion). But when a peroxide is in a more pure form, the heat evolved by its decomposition may not dissipate as quickly as it is generated which can result in increasing temperature which further intensifies the rate of exothermic decomposition. This can create a dangerous situation known as a *self-accelerating decomposition*.

A self-accelerating decomposition occurs when the rate of peroxide decomposition is sufficient to generate heat at a faster rate than it can be dissipated to the environment. Temperature is the main factor in the rate of decomposition. The lowest temperature at which a packaged organic peroxide will undergo a self accelerating decomposition within a week is defined as the self-accelerating decomposition temperature (SADT). [The SADT is an important consideration in the proper storage of organic peroxides and more detail is available in appendix I.](#)

## HALF-LIFE OF ORGANIC PEROXIDES:

The term half-life relates to the time for one half of the starting material to decompose at a given temperature. The half-life of an organic peroxide reveals its rate of decomposition at certain conditions and allows the behavior of various organic peroxides to be compared. [The half-life of organic peroxides is an important aspect and more detail is available in appendix II.](#)

Below is a chart of some commercial organic peroxides listing the respective SADT and the temperature at which the peroxides have a half-life of 10 hours.

Name	Typical Form	Structure	10 Hr Half Life (°C)	SADT (°C)
Di(n-propyl) peroxydicarbonate	Liquid with 40% diluent		50	-5
Dibenzoyl peroxide	Solid with 25% water		73	71
t-Butyl peroxybenzoate	Liquid neat		104	>60
Methyl ethyl ketone peroxide	Liquid with 60% diluent		105	63
2,5-Dimethyl-2,5-di(t-butylperoxy)-3-hexyne	Liquid with 15% diluent		131	>80

## CONTAMINATION and PROMOTED DECOMPOSITION:

In addition to thermally induced decomposition organic peroxides can be induced to decompose by contaminants such as amines, metal ions (by themselves or as a result of contact with metal surfaces), strong acids and bases, and strong reducing and oxidizing agents. Susceptibility to decomposition due to contamination or contact varies greatly among different organic peroxide types and formulations. For example, organic peroxides that are particularly susceptible are hydroperoxides (those with the -O-O-H

group). However methyl ethyl ketone peroxides (MEKP's) are also typically more susceptible to decomposition initiated by contamination. Careful thought should be put into the selection of materials of construction for all storage and handling systems that may have organic peroxides introduced to them. Selection of gaskets and materials of all sealing elastomers should also be considered for compatibility with the organic peroxide and possible solvent that might be used to introduce it into any chemical process. Although it is recommended to avoid contact with most metals and metal salts, cobalt (Co), iron (Fe) and copper (Cu) can be particularly troublesome. It is therefore conservatively recommended that all equipment and transfer lines that routinely handle organic peroxides should be fabricated of 316 stainless steel.

In some cases the use of this characteristic can be exploited through the intentional "contamination" of the organic peroxide to induce decomposition at a lower temperature than normal for a particular organic peroxide formulation. In these cases the contaminant is referred to as a "Promoter". Promoters allow organic peroxides to be used at lower temperatures than when simple thermal decomposition is the basis for decomposition. In those processes low concentrations of peroxides are used. One must be careful in handling promoters around organic peroxide formulations that have not been diluted. Severe reactions may be caused by accidental contamination of the undiluted organic peroxide formulation with the promoter.

#### **OXIDIZING PEROPERTIES:**

While most organic peroxides exhibit weak oxidizing properties toward reducing agents, contrary to widespread belief, most organic peroxide formulations are fuels, not oxidizers. Only one type of organic peroxide, peroxy acids, shows strong oxidizing properties. The oxygen-oxygen bond only rarely decomposes to give free oxygen. It should be noted that organic peroxides and strong oxidizers are not compatible.

#### **HAZARD IDENTIFICATION AND CLASSIFICATION:**

There are different hazard classification systems for organic peroxide formulations including transportation, storage and handling.

##### **Transportation:**

The transportation of organic peroxide formulations is strictly regulated. As a brief summary, the procedure for testing and classifying organic peroxide formulations for transportation that has been adopted by the United Nations International Group of Experts on the Explosion Risks of Unstable Substances ([IGUS](#)) Energetic and Oxidising Substances ([EOS](#)) workgroup is also used by the Pipeline and Hazardous Materials Safety Administration ([PHMSA](#)) of the US Department of Transportation. The testing procedures can be found in the [UN Manual of Tests and Criteria, fifth revised edition](#). Organic peroxide formulations are tested according to this procedure and classified based on test results. Organic

peroxide formulations are classified from most hazardous to least hazardous. The classifications range from Type A, considered too hazardous to transport to Type G, safe enough to be not regulated as an organic peroxide. Once tested and approved for transportation by the authorities, an entry for the organic peroxide formulation is usually added to the table of approved organic peroxide formulations. The US table can be found in The Code of Federal Regulations [49CFR173.225](#) and the UN table can be found in the UN Recommendations on the Transport of Dangerous Goods - Model Regulations (also known as the [UN Orange Book](#)). Transportation by sea or air is more restrictive than by road. Transportation by sea is regulated according to the International Maritime Dangerous Goods ([IMDG](#)) Code of the International Maritime Organization (IMO). The International Air Transport Association ([IATA](#)) regulates transportation by air.

## **STORAGE and FIRE PROTECTION:**

### **Storage:**

Storage classification systems for organic peroxide formulations are different for each country. The codes focus on the basic properties of the organic peroxides. In general the codes focus on the same characterization tests as for transportation plus the burning rate using either small-scale burning or large-scale burning test data. In Europe the PGS-8 Code is typically referenced most often for determination of storage classification.

Storage regulation in the US depends on the local Authority Having Jurisdiction (AHJ), usually the fire marshal. OPPSD was instrumental in assisting the National Fire Protection Association ([NFPA](#)) in developing a storage code for organic peroxide formulations. [NFPA 400](#) (now displacing [NFPA 432](#)) Hazardous Materials Code is the current edition covering organic peroxides. The SPI through the OPPSD remains active in the NFPA technical subcommittee responsible for maintenance and update of NFPA 400. It is a goal of the OPPSD to have all transported organic peroxide formulations listed with recommended storage classifications in NFPA 400 in the foreseeable future. Additionally the OPPSD will seek storage classifications which are consistent across geographies.

It is absolutely essential that the characteristics and the particular conditions for the safe handling of each organic peroxide formulation are read and understood. The label, product bulletin and material safety data sheet (MSDS) are typically excellent sources of reference. Consult the manufacturer, distributor or supplier for recommendations for safe use and storage. Know the NFPA 400 hazard class and the properties associated with that class. These standards define safe storage and fire fighting methods. The classification description given in NFPA 400, together with the fire hazard characteristics are described below. Classes are only for organic peroxide formulations in their original DOT shipping container. (The actual classifications are determined by transport class and small or large scale burning rate test results.)

"Class I" describes those formulations that are more severe than a Class II but do not detonate. Fire hazard characteristics: Class I formulations present a deflagration hazard through easily initiated, rapid



explosive decomposition. Class I includes some formulations that are relatively safe only under closely controlled temperatures. Either excessively high or low temperatures may increase the potential for severe explosive decomposition.

"Class II" describes those formulations that burn very rapidly and that present a severe reactivity hazard. Fire hazard characteristics: Class II formulations present an NFPA fire hazard similar to Class I flammable liquids such as acetone or toluene. The decomposition is not as rapid, violent, or complete as that produced by Class I formulations. As with Class I formulations, this class includes some formulations that are relatively safe when used under controlled temperatures or when diluted.

"Class III" describes those formulations that burn rapidly and that present a moderate reactivity hazard. Fire hazard characteristics: Class III formulations are characterized by rapid burning and high heat liberation, due to decomposition. They present a hazard similar to Class II combustible liquids such as #2 fuel oil.

"Class IV" describes those formulations that burn in the same manner as ordinary combustibles and that present a minimal reactivity hazard. Fire hazard characteristics: Class IV formulations present fire hazards that are easily controlled. Reactivity has little effect on fire intensity.

"Class V" describes those formulations that burn with less intensity than ordinary combustibles or do not sustain combustion and that present no reactivity hazard. Fire hazard characteristics: Class V formulations do not present severe fire hazards. Those that do burn do so with less intensity than ordinary combustibles.

Fire not only can originate from within the organic peroxides due to decomposition initiated by temperature or contamination, but it may spread to the organic peroxides from adjacent areas. Proper storage and use of mechanical devices can help prevent damage to surrounding areas from burning or decomposing organic peroxides. The recommendations in NFPA 400 should be followed. Keep organic peroxides well away from other combustible materials in their storage area, preferably isolating them by means of firewalls. If possible, store organic peroxides in a separate building at some distance from adjacent buildings. All areas of organic peroxide storage should be equipped with fire control systems, such as automatic sprinklers.

It is important to understand that when decomposition occurs some organic peroxide formulations release a considerable amount of gases and/or mists. Some, but not all, of these gases may be flammable. For example, carbon dioxide is a common, gaseous decomposition product for diacyl peroxides and peresters that is not flammable.

The decomposition may include small organic fragments such as methane or acetone which are flammable. When flammable gases or mists are released as part of the decomposition there is always the potential danger of a fire or vapor phase explosion. Therefore the risk of vapor phase explosion should be

kept in mind when designing storage structures. These types of materials may be released at low rates during storage and in quite high rates in the event of an upset due to failure to control storage temperature or in the event of a fire in the storage area.

It is the ease of splitting the peroxy group to give two free radicals that makes organic peroxides so useful. However, the presence of energetic free radicals during decomposition, particularly in hot gases or mists, can cause auto-ignition to occur at a lower temperature than would otherwise be normal for a similar chemical structure without the peroxy functional group. Organic peroxides do not generally release oxygen as part of the decomposition so there is little risk of enhanced burning rates due to oxygen enrichment. This is unlike the decomposition of hydrogen peroxide and solid oxidizers that can liberate oxygen.

The burning rate for an organic peroxide formulation is higher than for a similar composition without the peroxy functional group. This is the result of the energy liberated when the peroxy group decomposes, supplying heat to the burning organic peroxide in addition to the heat flux from the flame. In addition the small fragments resulting from decomposition burn rapidly. As the temperature further increases so does the rate of decomposition and heat release, further accelerating the burning rate. Some organic peroxides are formulated to absorb some of the heat of decomposition during burning, minimizing the accelerating effect.

Water is usually the agent of choice to fight fire. The effectiveness of water in the control of fires in storage and work areas varies with the individual organic peroxide formulations. It is especially useful for those formulations that are heavier than water. Water is also useful in cooling areas not yet involved in a fire. When using hoses, spray or fog is most effective. For low boiling and low-density formulations, Aqueous Film-Forming Foam (AFFF) may be more effective than water alone. In some very special cases, dry chemical formulations may be effective but may also be a problem with others. Always refer to the MSDS for the most appropriate type of fire fighting procedures for a particular organic peroxide formulation. Be aware that water can aggravate control of fires or cause decomposition of low temperature organic peroxide formulations due to the warming of the organic peroxide by the water. With low temperature organic peroxides, specialized fire control methods are required. Manual fighting of fires should be undertaken only with lower energy organic peroxides - consult NFPA 400 for additional information.

## **SAFE HANDLING RECOMMENDATIONS**

### **Receiving protocol:**

Organic peroxide formulations are packaged and shipped as per the appropriate regulating agencies. In all cases it is important that the user know the recommended storage temperature(s) of the organic peroxide formulation(s) of interest. The maximum ( $T_s \text{ max}$ ) and sometimes minimum ( $T_s \text{ min}$ ) storage

temperatures for the product(s) can always be found in the Material Safety Data Sheet (MSDS). The user should also be familiar with the control and emergency temperature (Tc & Te) and the SADT.

The Tc is derived from the SADT and is the maximum temperature at which the formulation can be safely transported. A Tc is not required if the SADT is greater than 50°C. The Te is also derived from the SADT and is the temperature at which emergency procedures must be implemented.

Prior to securing and using an organic peroxide formulation a prospective user should have knowledge of the characteristics of the organic peroxide formulation(s) of interest and have procedures in place for dealing with a possible emergency.

When product is delivered it should be immediately brought to a storage area that meets the temperature requirements and NFPA storage recommendations of the organic peroxide formulation. A refrigerated organic peroxide formulation should **never** be allowed to be left in a receiving area for any extended period of time. Along with the user it is critical that all personnel involved in the process of receiving, handling and storing the organic peroxide formulation be familiar with its properties and storage temperature requirements.

#### **Temperature Control:**

No single parameter is as important as the control of the temperature. Whether shipping, handling or storing, if the temperature is maintained well below its SADT, most hazards are avoided. For storage over a longer period of time, the manufacturer's recommended temperature for storage should be rigorously followed. It should also be noted since decomposition temperatures are time dependent, temperatures higher than the shipping temperature can be tolerated for short periods during handling and use. *To repeat, proper temperature control is important to prevent run-away decompositions, evolution of gases and mists (that may lead to vapor explosions), auto-ignition or loss of product quality.*

The maximum possible transport temperature, also known as "Control Temperature", is dependent on the SADT and is determined as follows:

Control Temperature = SADT minus 20°C if SADT ≤ 20°C

Control Temperature = SADT minus 15°C if SADT >20°C, ≤35°C

Control Temperature = SADT minus 10°C if SADT >35°C, ≤50°C

Control Temperature is not required if SADT >50°C.

The Control Temperature is the temperature up to which the organic peroxide can be safely transported for an extended period. It is also the alarm temperature. The Control Temperature is supplemented by an "Emergency Temperature" which is higher than the Control Temperature but still well below the SADT. The Control Temperature may be exceeded if maintenance is necessary or until alternative cooling (e.g. dry ice or wet ice) is available. However, if the Emergency Temperature is reached, immediate steps must

be taken to remove personnel from the area and, if possible safely, to cool down and then dispose of the organic peroxides.

Often, the recommended storage or transportation temperature is lower than the control temperature, not for safety, but to minimize the unavoidable active oxygen loss due to gradual decomposition. On the other hand, some liquid or paste organic peroxides must be stored above a certain minimum temperature as turbidity, phase separation, crystal deposits or solidification can occur. The most serious situation is if the organic peroxide is separated from the diluent due to phase separation while frozen. The recommended temperature range for storage can be found on each organic peroxide package and in the corresponding technical literature or Material Safety Data Sheet (MSDS).

#### **Contamination Control:**

Contamination can lead to rapid decomposition and all of the problems associated with lack of temperature control. Susceptibility of organic peroxides to induced decomposition from contamination varies greatly between the types of organic peroxides and the specific contaminants. Nevertheless, contamination has been a major source of accidents from run-away decompositions, particularly during handling and use. Especially sensitive are the ketone peroxides, hydroperoxides, peroxyketals, and some diacyl peroxides. The contaminants most often causing problems have been redox agents such as cobalt salts and other accelerators and promoters, as well as various metal ions and ionizing acids such as high concentrations of sulfuric acid. Strong oxidizing and reducing agents can also cause decompositions.

To avoid problems from contamination, never return unused organic peroxides to the original container. Use only scrupulously clean equipment and make certain that all materials that the organic peroxide comes in contact with are compatible, especially if equipment (such as pumps) is used for multiple services. In general, preferred materials of construction are stainless steel (316 preferred), PTFE or glass linings. Do NOT use copper, brass or iron. When a diluent is used, the selection of a diluent and its purity must be strictly controlled. Contact your supplier for recommendations. Also be cognizant of compatibility with wetted seals and o-rings in equipment that will come in contact with the organic peroxide formulation.

While it is a good practice in any situation, especially where a reactive diluent is employed, a general blending rule is to add the organic peroxide to a resin or monomer, not the reverse. Never add organic peroxides to hot diluents. Care must be taken when adding organic peroxide formulations to processes, such as extrusion, at elevated temperature. When reactive materials, such as styrene, are employed as diluents (or solvents), strictly adhere to temperature controls and venting requirements because of potential heating due to polymerization.

The effectiveness of diluents, as a phlegmatizer (or desensitizer), is due in part to the reduction in energy level by dilution or energy absorption, and may also act as a mild chain stopper since most decompositions proceed via a chain mechanism. For contamination problems from absorbents used during spills, see the section on spills.

**Confinement Control:**

Once rapid decomposition is initiated, confinement of an organic peroxide formulation may greatly accelerate the rate of its decomposition. With the higher energy classes, transition from a manageable decomposition to a higher order event can occur, which ordinary venting may not control. When it is necessary to confine high-energy organic peroxides by more than the confinement provided by the DOT shipping container, dilution of the peroxide is usually required. See diluents under "Contamination Control".

In some manufacturing operations it may be necessary or desirable to use containers, pumping systems and piping to deliver or handle the organic peroxide being used at processing areas or work stations. If the organic peroxide is not diluted and the system provides confinement beyond that of the shipping container, then the quantities must be kept to the very minimum and sufficient venting provided to prevent pressure build up.

Vent sizing for organic peroxides is a difficult task and can be accomplished by several methods including Design Institute for Emergency Relief Systems ([DIERS](#)), [United Nations](#) appendix 5, and the [OPPSD/SPI Methodology](#)". The DIERS vent sizing method is based on data obtained from small scale adiabatic calorimetry while the UN and OPPSD methods test the venting of the organic peroxide on larger scale (~10 liters).

In some cases shielding may be required. If this is not done, then the organic peroxide often must be handled as a higher hazard class material. In particular insure that it is not possible to have dead spots in lines that cannot be drained of organic peroxide after its use. This can result in decomposition in a confined space leading to the possibility of a line rupture and ensuing shrapnel.

**Quantity Control:**

Due to the potential for dangerous decompositions caused by thermal reaction, contamination, or coincident events like fire, the quantity of organic peroxide in storage must be controlled. This is one of many methods to mitigate the risk of dangerous outcomes. In addition consumers may be motivated to limit inventory to avoid regulatory coverage. For example some organic peroxides are specifically listed in national regulations like the US Process Safety Management laws.

The quantity limitations for safe storage of organic peroxides may be understood by reviewing guidelines authored by standard bodies or insurance advisory associations. For example in the United States, the authorities having jurisdiction often utilize the National Fire Protection Association (NFPA) code 400. The topic of organic peroxide storage is covered in Chapter 14. In other parts of the world guidelines like the Dutch Code may be consulted. This guideline is referred to as PGS8.

There are several reasons to control inventory. In the event of fire the potential duration of the fire is limited. The amount of fire protection water to be applied in controlling the fire is limited as well; this is

important to avoid large catch basins. The larger the inventory the more separation distance that may be required from the storage area and the more risk for explosion due to vapor phase by-product ignition.

The inventory limits for organic peroxide therefore must take into account whether or not automatic fire fighting system is applied, the separation of the storage area from other areas, the hazard classification of the formulations to be stored, and other aspects of the building design. The insurance company or corporate policy may also impose limits related to risk aversion of the parties.

#### **Quality Control:**

Assay (active oxygen content) can best be preserved by following proper storage guidelines. Always store peroxides at proper temperature. A storage temperature below the control temperature may be recommended to maximize shelf life. Store in original containers to prevent contamination and away from incompatible materials.

#### **Spill Clean Up:**

Spills can result in a host of problems. Potential hazards involved are:

1. Fire (most non-aqueous peroxide formulations contain flammable solids and/or highly combustible liquids)
2. Decomposition (due to either increased temperature or contamination)
3. Evaporation of a safety diluent (either because the diluent is volatile at ambient temperature, or because the spill involved a hot surface)
4. Increased worker exposure (peroxide formulations, especially hydroperoxides and ketone peroxides, can be strong irritants)
5. Incorrect choice of absorbent material and/or methods

Know what action is recommended for each specific formulation that is used. Cleaning up a spilled organic peroxide formulation may not present a serious problem, or considerable time may elapse before a serious problem develops. On the other hand, rapid and proper action may be required; this is normally the best procedure in order to avoid decomposition or a fire. With flammable liquids and solids the problem is immediate. Many organic peroxide formulations are difficult to ignite but burn vigorously once ignited. Depending on the peroxide and contaminant, it may take a long time for decomposition to occur, if at all. On the other hand, decomposition may occur within a short time period, so take precautions accordingly.

In many cases, dilution with a compatible inert solid absorbent followed by wetting with water is very effective. Dilution with a compatible high boiling organic liquid prior to absorption is often effective and desirable especially with the more energetic or flammable formulations. Caution: absorbents often have high surface areas which may catalyze decomposition as well as contain catalyzing impurities. Special

care must be used when water wet solids are spilled. Avoid drying out by wetting down spilled material immediately.

Use the MSDS and manufacturers technical brochures, if available, to prepare for proper action in the event of a spill. Have Personal Protective Equipment (PPE) fire fighting equipment, absorbents, diluents, clean-up tools (non-sparking), and other emergency supplies available in all areas where organic peroxides are handled or stored.

Standard precautions should be taken when handling waste from an organic peroxide spill. In addition, special precautions should be taken to prevent a subsequent decomposition due to contamination or heat. Waste after clean up should be removed from work and storage areas and isolated for further emergency treatment and prompt disposal. Do not store in tightly sealed closed containers. Permit venting of further decomposition products. The OPPSD has a [spill clean up bulletin](#) available to download.

#### **Disposal of Wastes:**

Disposal of wastes after the clean-up of an organic peroxide spill or from container leakage can present possible challenges. This material should not be reused. It is beyond the scope of this Guide to address all aspects of waste disposal due to the continual changes in the Federal and State regulations that govern waste disposal. Consult the MSDS and available manufacturers' literature for information regarding proper disposal. Workers involved in handling, dispensing and spill clean-up should be reminded of the potential hazards that some formulations may present from decomposition due to contamination or exposure to heat. The OPPSD offers the following documents that provide helpful information regarding waste disposal and spill clean-up:

- [Organic Peroxide Spill Clean Up](#)
- [Disposal of Liquid Organic Peroxides](#)
- [Disposal of Solid Organic Peroxides](#)
- [Disposal of MEKP \(Methyl Ethyl Ketone Peroxide\)](#)
- [Container Disposal](#)
- [List of Disposal Companies for Organic Peroxides](#)

## Appendix I – Self-Accelerating Decomposition Temperature (SADT) and Rapid Heat Decomposition Temperature (RHDT)

A self-accelerating decomposition occurs when the rate of peroxide decomposition is sufficient to generate heat at a faster rate than it can be dissipated to the environment. Temperature is the main factor in determining the decomposition rate, although the size of the package is also important since its dimensions will determine the ability to dissipate heat to the environment.

All peroxides contain an oxygen-oxygen bond that, on heating, can break apart homolytically to generate two radicals. As mentioned previously, this decomposition also generates heat. But the stability of the oxygen-oxygen bond is dependent on what else is present in the molecule. Some peroxides, due to their chemical make-up, are very unstable and need to be refrigerated to avoid a self-accelerating decomposition. Others, particularly those used for crosslinking purposes, are much more stable and can be stored at normal ambient temperatures without risk of self-acceleration. Due to the large variations in the stabilities of peroxides, each is tested to determine the safe maximum temperature for which the peroxide may be stored, shipped, and handled. The result of this test is the *self-accelerating decomposition temperature (SADT)*.

The SADT is the lowest temperature at which the tested package size will undergo a self accelerating decomposition within one week. The SADT is the point at which the heat evolution from the decomposition reaction and the heat removal rate from the package of interest become unbalanced. When the heat removal is too low, the temperature in the package increases and the rate of decomposition increases in an uncontrollable manner. The result is therefore dependent on the formulation and the package characteristics.

The SADT for an organic peroxide formulation is usually lower for more concentrated formulations. Dilution with a compatible, high boiling point diluent will usually increase the SADT since the peroxide is dilute and the diluent can absorb much of the heat minimizing the increase in temperature. Also, for an organic peroxide formulation, larger packages generally have a lower SADT because of the poorer heat transfer of the larger package due to lower surface area to volume ratio.

Most organic peroxides react to some extent with their decomposition products during thermal decomposition. This often increases the rate since the decomposition proceeds more rapidly as the decomposition products are generated.

The SADT measurement is made as follows:

- The package containing the peroxide is placed in oven set for test temperature
- The timer starts when product reaches 2°C below intended test temperature
- The oven is held at constant temperature for up to one week or, until a runaway event occurs.
- Test “Passes” if product does not exceed test (oven) temperature by 6°C within one week
- Test “Fails” if product exceeds test temperature by 6°C within one week



- The test is repeated in 5°C increments until a failure is reached
- Fail temperature is reported as SADT for that package and formulation
- Secondary information about the violence of the decomposition can also be recorded

As an alternative to the oven test the SADT for larger packages can be determined by substituting a Dewar flask for the package. The heat transfer of the Dewar flask can be matched to the heat transfer of a larger package size. This test is called the *Heat Accumulation Storage Test (HAST)*.

#### **Results of SELF-ACCELERATING DECOMPOSITION:**

When thermal decomposition occurs some organic peroxide formulations release a considerable amount of gases and/or mists. Some, but not all, of these gases may be flammable. For example, carbon dioxide is a common, gaseous decomposition product for diacyl peroxides and peresters that is not flammable.

The decomposition may include small organic fragments such as methane or acetone which are flammable. When flammable gases or mists are released as part of the decomposition there is always the potential danger of a fire or vapor phase explosion. Therefore the risk of vapor phase explosion should be kept in mind when designing storage structures. These types of materials may be released at low rates during storage and in quite high rates in the event of an upset due to failure to control storage temperature or in the event of a fire in the storage area.

It is the ease of splitting the peroxy group to give two free radicals that makes organic peroxides so useful. However, the presence of energetic free radicals during decomposition, particularly in hot gases or mists, can cause auto-ignition to occur at a lower temperature than would otherwise be normal for a similar chemical structure without the peroxy functional group. Organic peroxides do not generally release oxygen as part of the decomposition so there is little risk of enhanced burning rates due to oxygen enrichment. This is unlike the decomposition of hydrogen peroxide and solid oxidizers that can liberate oxygen.

#### **Rapid Heat Decomposition Temperature (RHDT)**

The *Rapid Heat Decomposition Temperature (RHDT)* is the temperature at which an organic peroxide formulation visibly decomposes when heated rapidly. The RHDT is determined by heating a one gram sample of organic peroxide formulation and a one gram sample of mineral oil in separate containers at 4°C / minute. When the organic peroxide formulation visibly decomposes the temperature of the mineral oil is reported as the RHDT.

## Appendix II – Half-life of Organic Peroxides

Half-life is the time and temperature at which 50% of the peroxide will decompose. Half-life is usually reported for dilute organic peroxide solutions in order to simulate half-life at normal use levels. The half-life time is the time at which 50% of the peroxide has decomposed at a specified temperature. The half-life temperature is the temperature at which 50% of the peroxide has decomposed at a specified time. Organic peroxide half-life temperature is usually reported for 1 hour and 10 hour periods. This is useful for application considerations but is of limited use for safety assessment.

### General Background on Half-life of Organic Peroxides

Due to the instability of the O-O bond(s) found in all peroxy compounds they decompose into free radicals under the influence of heat. As the temperature increases vibrational energy increases until eventually it exceeds the O-O bond strength and the molecules start to split into two (or more) free radicals. The rate of this decomposition reaction is described by the term "half-life". This characteristic value, which is mostly temperature-dependent, is one of the most important factors for selecting a suitable initiator to provide reactive benefits.

In general the term half-life relates to the time for one half of the starting material to decompose at a given temperature. Conversely one can specify the time for one half of the material to decompose and the associated temperature can be determined.

This concept is similar to the decomposition of radioactive materials, since it is described by the same mathematical equations, but it has nothing to do with decomposition of radioactive materials.

### THEORETICAL CONSIDERATIONS

The rate of decomposition of a peroxide compound at a certain temperature largely determines its suitability for a specific useful application. To make a polymerization reaction economical the rate of free radical generation must be reasonable, so it is important to understand the parameters that might influence the half-life of compounds under consideration.

The half-life of a peroxide reveals its rate of decomposition at a certain temperature and allows the behavior of various peroxide compounds to be compared. The half-life indicates the time when half of the quantity of peroxide originally present has decomposed. The amount of the peroxide compound remaining after successive half-life periods, compared to the starting amount, may be understood by looking at the power function.

The portion of the organic peroxide consumed after a given number of half-life periods is given by the following equation:

$$\frac{C_n}{C_i} = 1 - \left(\frac{1}{2}\right)^n$$

where,  $c_n$  is the concentration after  $n$  half-life periods

$c_i$  is the concentration at the start of the reaction

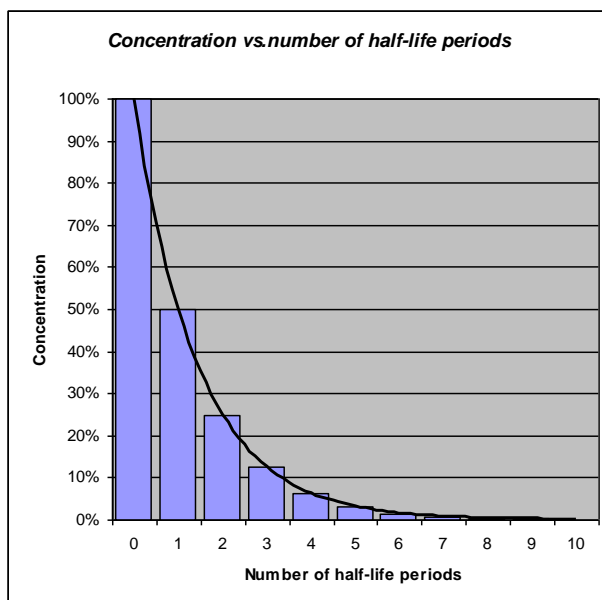
$n$  is the number of half-life periods

The concentration, relative to the starting point and percent of the starting material decomposed after  $n$  half-life periods can be seen in the following table:

<b>Time</b> <i>in half-life units</i>	<b>Concentration</b> <i>in relation to starting point</i>	<b>Amount Decomposed</b> <i>in relation to starting point</i>
0	100%	0%
1	50%	50%
2	25%	75%
3	12.5%	87.5%
4	6.3%	93.8%
5	3.1%	96.9%
6	1.6%	98.4%
7	0.8%	99.2%
8	0.4%	99.6%
9	0.2%	99.8%
10	0.1%	99.9%

It is easy to see that after three half-life periods the organic peroxide will be significantly decomposed and after ten periods it will be essentially totally consumed.

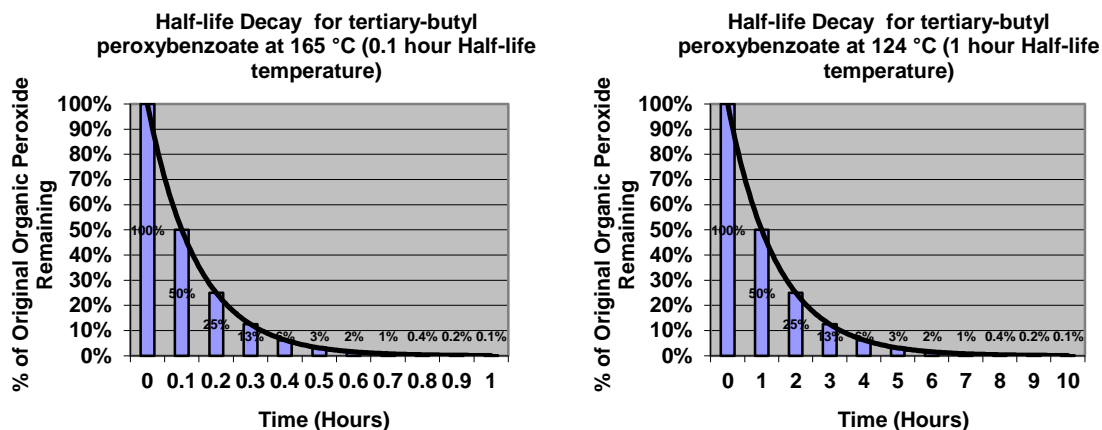
In graphical format the characteristic decline in concentration is shown in this image:



Faster decomposition rates due to increased temperature mean a shorter time is required for half of the starting organic peroxide to decompose. The thermal stability of organic peroxides is frequently characterized by giving the temperatures at which the half-life of the material is 10 hours, 1 hour, and 1 minute. One can talk about half-life time or half-life temperature where the other principle parameter has been clarified. To clarify one can consider the example of tertiary-butyl peroxybenzoate which has the following characteristics in a specific solvent.

Compound:	tertiary-butyl peroxybenzoate
10 hour half-life:	104 °C
1 hour half-life:	124 °C
0.1 hour (6 minute half-life):	165 °C

Given these concepts it is clear that the two following plots each represent the compound's behavior:



### Mathematical Basis

The thermal decomposition of organic peroxides in the gas phase (such as experienced in polymerization of some olefins) or in an inert solvent (i.e. a solvent which does not affect the decomposition reaction) takes place according to first order kinetics. First order kinetics means that the decrease in the peroxide concentration with respect to time is proportional to the amount of residual peroxide present. Equation 1 is the starting equation to describe the behavior of first order decomposition.

Equation 1 
$$-\frac{dc}{dt} = k \times c$$

where  $c$  = concentration

$t$  = time

$k$  = a reaction constant

By separating the variables and integration, as shown in equations 2 and 3, equation 4 is obtained.

Equation 2 
$$\frac{dc}{c} = -k \times dt$$

Equation 3 
$$\int_{c_0}^{c_t} \frac{dc}{c} = -k \int_0^t dt$$

$$\ln\left(\frac{C_t}{C_0}\right) = -k \times t$$

Equation 4

The reaction time (t) is derived from equation 4, giving equation 5;

$$t = \ln\left(\frac{C_0}{C_t}\right) / k$$

Equation 5

Ultimately equation 6 is gives the half-life time where  $t_{1/2}$  is the half-life time, since  $C_t = C_0/2$ , according to the half-life definition.

$$t_{1/2} = \ln 2 / k$$

Equation 6

Equation 4 is useful for calculating the velocity constant (k) and the half-life. The concentration of peroxide at a given time ( $C_t$ ) is measured at various intervals ( $t_1, t_2, t_3$ , etc.) at a given temperature. The relative concentration ( $C_t/C_0$ ) is plotted on a common logarithmic scale against the reaction time (t) on a linear scale. In such a diagram, the individual points should give a straight line with the gradient (-k/2.3). This can be used to read off the half-life at the point ( $C_t/C_0 = 0.5$ ).

### Temperature Dependence of Half-Life

The rate of reaction and consequently the velocity constant (k) are temperature-dependent. This is expressed by equation 7, where  $k_{\max}$  represents the maximum velocity constant at the maximum rate of reaction,  $E_A$  is the energy of activation for the decomposition of the peroxide concerned, R is the general gas constant and T is the absolute temperature.

$$k = k_{\max} \times e^{-E_A / R \times T}$$

Equation 7

Replace the velocity constant in equation 6 by the corresponding Arrhenius expression to obtain equation 8. The logarithmic form is given in equation 9 or 10. This indicates the connection between the half-life ( $t_{1/2}$ ) and the temperature, T.

$$t_{1/2} = (\ln 2 / k_{\max}) \times e^{-E_A / R \times T}$$

Equation 8

$$\ln(t_{1/2}) = \ln(\ln 2 / k_{\max}) + E_A / R \times T$$

Equation 9

$$\ln(t_{1/2}) = \text{const.} + E_A / R \times T$$

Equation 10

where, k = velocity constant  
 $E_A$  = Energy of activation  
 R = general gas constant  
 T = absolute temperature

A common logarithmic plot of the half-life at various temperatures against the reciprocal of the absolute temperature ( $1/T$ ) will give a straight line with the gradient ( $E_A/2.3\cdot R$ ).

The activation energy of organic peroxides is in the region of approximately 100 to 150 (kJ/mol). When peroxides have low energy of activation they decompose at a more uniform rate over a wide temperature range. Therefore organic peroxides with low activation energy are more suitable for polymerization reactions that can be carried out in temperature stages. When peroxides have a relatively high activation energy there will be a strong increase in the rate of decomposition with small increase in temperature. This character is good when the peroxide is to be incorporated into a reaction mixture at elevated temperatures (120°-140°C) without scorch, and then act as a source of free radicals after a slight increase in temperature.

### **PEROXIDE DECOMPOSITION IN PRACTICE**

The theoretical derivation of the half-life of organic peroxides is made on the basis that they decompose via first order kinetics. This approximation only applies in ideal cases. Besides temperature and pressure other parameters influence the decomposition rate. Those parameters include peroxide concentration, the specific solvent and reactive contaminants.

Decomposition can occur when the peroxide molecules are split not only by the thermal energy causing the O-O bond to break due to vibration energy but also by the attack of free radicals originating from the peroxide or from free radicals formed from the solvent. For these reasons half-life determinations are usually carried out in relatively inert solvents, such as benzene or cumene, in concentrations of 0.1 to 0.2 molar (mol/l) where concentration is low and polarity is low.

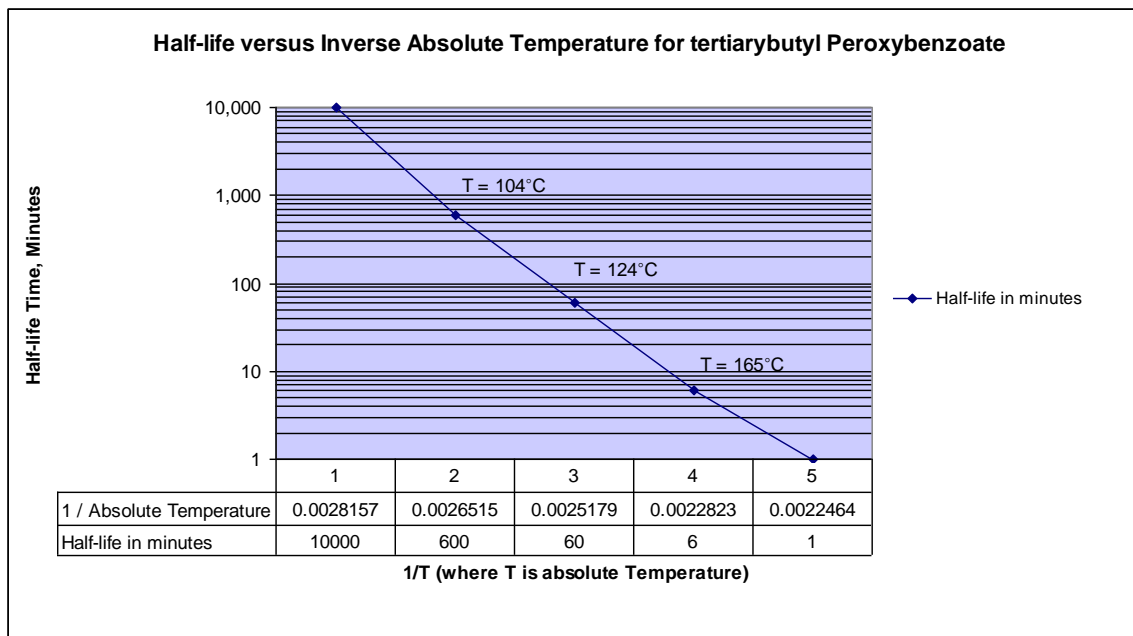
In summary, half-lives of various organic peroxides can only be regarded as fully characterized when one specifies the temperature, pressure, solvent, and the peroxide concentration.

#### **Effect of Temperature**

The half-lives of all the main commercially available organic peroxides are measured by testing done at various temperatures. They are usually tested at 0.1 molar in benzene.

The temperatures are typically selected so that half-lives are expected to be 1 to 20 hours. Determination of longer half-lives is very time consuming and the determination of shorter half-lives would not be sufficiently accurate because of rapid changes during the analysis.

The results of empirical determinations are used to develop the characteristic data for the peroxides. By use of equations above or by graphical methods the half-life is determined. When graphical methods are used the half-life at 10 hours, 1 hour, and 1 minute are extrapolated. The energy of activation  $E_A$  (kJ/mol) is also given.



Commercial producers of organic peroxides will supply plots of half-life of a wide variety of peroxides for comparison of various materials. These diagrams show that the half-life lines are nearly parallel, meaning that they have similar activation energies.

### Effect of Solvent

In trichloroethylene the primary radicals from peroxide decomposition interact with the solvent, and subsequently only unreactive secondary radicals are formed. Correspondingly longer half-lives result, particularly with diacyl peroxides and peroxydicarbonates. Peresters are less affected by induced decomposition so they show much smaller differences between solvents.

Testing with an unsaturated solvent can give an apparent increase of the half-life.

The type of solvent used, and particularly its polarity, plays an important part in the experimental determination of the half-lives. Some peroxides can be attacked and split directly by certain solvents. It is also possible for primary radicals formed during peroxide decomposition to attack some solvents to form secondary radicals which, in turn, can split undecomposed peroxide molecules.

As a result of this "induced decomposition" the half-life is considerably shorter than the pure thermal decomposition would predict.

In polar solvents such as chlorobenzene or acetophenone, the half-lives are consequently much shorter than in non-polar solvents such as isododecane or benzene.

### Effect of Peroxide Concentration

As mentioned earlier, organic peroxides should be regarded to decompose according to first order kinetics only when highly diluted. When testing with high peroxide concentration there is a greater

likelihood of induced decomposition. Primary radicals attack and split the remaining intact peroxide molecules. As a result, the rate of decomposition increases while the radical yield decreases as a result of radicals being consumed in this reaction.

The typical process conditions for peroxide initiated reactions involves low peroxide concentration and high concentration of reactive chemicals so this also implies that low concentration testing is the correct approach for use in process design considerations.

### **Effect of Pressure**

The rate of reaction and consequently the velocity constant depend on the pressure as well as the temperature. The normal explanation is that the O-O bond stretches in the transition state immediately before splitting. Higher pressures make the stretching of the bond more difficult. This is the so-called "activation volume" adjustment. Higher pressure therefore reduces the rate of decomposition compared to lower pressure. As a result the half-life time increases. Temperature has a much greater influence on the half-life than pressure, in most cases.

For example, the half-life of an organic peroxide is approximately twice as long at a pressure of 3000 bar compared to atmospheric pressure. These pressures are only used in high pressure polymerization reactions like Low Density Polyethylene. In comparison, the half-life is doubled when the temperature is reduced by approximately 5-10°C.

### **Effect of Other Reactants**

The presence of accelerators, e.g., metal salts of cobalt, iron or vanadium, and of tertiary aromatic amines or other reducing agents, such as ascorbic acid, and sulfites, changes the order of reaction and substantially reduces the energy of activation required. The use of thermally stable hydroperoxides in combination with alkali metal sulfites in low temperature (approximately 5°C) emulsion polymerization illustrates this point.

Organic peroxides in combination with accelerators are also used for curing unsaturated polyester resins at temperatures below 100°C. In these cases it is possible to measure the decrease in the peroxide concentration as a function of the reaction time and thus to determine the time at which the peroxide concentration has decreased to half the initial concentration. However, such measured values are not comparable with the half-life described and defined here, since they do not follow a simple, easy recognizable law. It is not possible to use either the first order decomposition reaction as a time function or the Arrhenius equation as a temperature function for this purpose.

### **DETERMINATION OF THE HALF-LIFE**

A dilute solution of the organic peroxide to be examined must first be prepared. Where possible, the solvent used should consist of a non-polar substance which does not promote induced decomposition. In most cases, benzene is used. The peroxide concentration is kept low, usually below 0.2 mol/l. Since the



accuracy of the analytical method is limited, an initial concentration of approximately 0.1 mol/l is generally recommended.

The peroxide solution is introduced into a number of test tubes or ampoules which are sealed and stored in a thermostatted bath at the measuring temperature until at least 75% of the original peroxide has decomposed. At specific time intervals (such as 1 hour, 2 hours, 4 hours, 6 hours, 8 hours), one sample is removed from the bath, cooled as rapidly as possible, and examined for its residual peroxide content. Chemical or physical methods can be used for this purpose. The Iodometric method of determination is generally used, although this must be adjusted to the peroxide concerned.

A graphical presentation is generally recommended, since this is the simplest method and compensates for some of the inaccuracies of the individual points of measurement. The relative concentration is plotted on a logarithmic scale against the reaction time (t) on a linear scale. By connecting the points in the graph to give a line, the half-lives can be read off from the ordinate ( $c_t/c_0=0.5$ ).

If the correlation between the temperature and the half-life is to be determined, the same determination is carried out repeatedly at 2-3 different temperatures in stages of approximately 5-15 °C. The test temperatures are chosen so that the resulting half-lives are in the region of approximately 1-20 hours. If the half-lives are shorter, the error of measurement increases, and with longer half-lives, the task of sampling becomes excessive. Consequently, only a limited temperature difference, namely maximum 20-30°C, can be determined with this limited time interval.

Most appropriately, the measured results can be represented on a graph by plotting the half-lives in hours or minutes as a function of the temperature in °C. A common logarithmic scale must be used for the half-life (ordinate) and the scale of inverse temperature for the other axis. In this way a straight line will be obtained from which the activation energy and the half-life for other temperatures not measured can be determined.

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