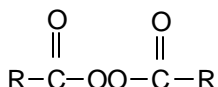


Introduction

Diacyl peroxides are free-radical initiators, which can be decomposed to useful free-radicals when heated or when activated by various promoters. They are widely used as initiators for vinyl monomer polymerizations, as curing agents for unsaturated polyester resins, and as crosslinking agents for elastomers.

These peroxides have the following general structure:



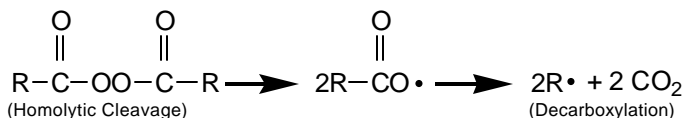
where R is an alkyl, cycloalkyl, aralkyl, aryl or heterocyclic radical. Many diacyl peroxides are described in the literature, "Organic Peroxides," J. Sanchez, T. N. Myers, Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Volume 18, John Wiley & Sons, Inc., 1996, p 230-310.

COMMERCIAL PRODUCTS

Arkema Inc. offers six commercial diacyl peroxides in seventeen formulations. Information relating to physical properties, thermal stabilities, and product packaging and handling is given in Tables 1-4. Arkema is capable of producing other formulations to satisfy customer requirements.

REACTIONS OF DIACYL PEROXIDES

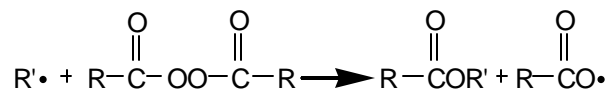
A. *Thermolysis*—Thermal decomposition of diacyl peroxides results in production of commercially useful free-radicals by means of homolytic cleavage:



In dilute solution the rate determining reaction (Homolytic Cleavage) follows first order kinetics; therefore, half-lives at various temperatures can be calculated from the kinetic data. The reactivities of various diacyl peroxides can be rated by comparing the temperature at which the half-lives are one hour and ten hours. The one hour and ten hour half-life temperatures for the commercial diacyl peroxides are

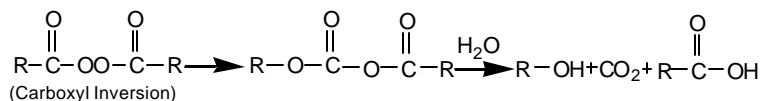
given in Table 4. Other relative temperature/half-life relationships are given in Figure 1.

B. *Induced Decomposition*—In one type of induced decomposition reaction the oxygen-oxygen bond of the diacyl peroxide is attacked by an alkyl radical. This produces an ester and an acyloxy radical:



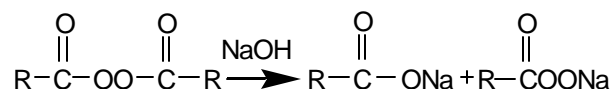
Induced decompositions are inefficient free-radical generators. No net increase in free-radicals is obtained by this type of decomposition.

C. *Heterolytic Decomposition*—Intramolecular rearrangement (e.g., Carboxyl Inversion) of certain diacyl peroxides occurs when strong acids or polar solvents are present:



This reaction, like induced decomposition, results in no net increase in free-radicals.

D. *Hydrolysis*—Diacyl peroxides react with inorganic bases (e.g., NaOH) to form the salts of acids and peroxyacids:



HALF-LIFE DATA

Half-life can be defined as the time required at a specific temperature, to affect a loss of one-half of the peroxide's active oxygen content. Because the efficiency of a free radical initiator depends heavily upon its rate of decomposition, half-life data can be a useful guide in selecting the optimum initiator for a specific application.

Several factors apply to half-life data obtained in dilute solution: (a) use only applies to thermolytic decomposition and (b) half-life can vary in different solvents due to induced decomposition if no radical scavenger is present. In the presence of monomer,

induced decomposition becomes relatively insignificant, and first order kinetics are observed in most cases.

Published half-life data are only approximations of observed polymerization kinetics, and serve as comparisons between initiators in similar systems.

Figure 1 is a composite representation showing half-life versus temperature of dilute solutions of several commercially available diacyl peroxides in common solvents. Table 4 lists these products together with values for activation energy and one and ten hour half-life temperatures.

APPLICATIONS

Diacyl peroxides are used in a broad spectrum of applications including curing of unsaturated polyester resins, crosslinking of elastomers and production of PVC, Polystyrene and Polyacrylates.

Benzoyl peroxide can be promoted to achieve room temperature polymerization of unsaturated polyester resins and acrylic monomers. Tertiary amines such as dimethyl aniline are normally employed as promoters.

HANDLING AND STORAGE

Facilities – Diacyl peroxides should be stored apart from other chemicals, ideally in an isolated location. Buildings should be well ventilated. Freezer chests or walk-in refrigerators should be used to store the less stable diacyl peroxides and shipping containers should be arranged to allow optimum air circulation.

Storage Temperatures – Diacyl peroxides are quite stable at or below their recommended storage temperatures. At higher temperatures decompositions can occur. Frozen diacyl peroxides can be thawed below their maximum storage temperatures. However, the 40% water formulation of succinic acid peroxide should not be allowed to thaw because loss of active oxygen is fairly rapid in the non-frozen state.

Shelf Life – Except for benzoyl peroxide (BPO) paste formulations, properly stored diacyl peroxides have a

shelf life of at least one year. BPO pastes have shelf lives of approximately six months when stored between 35°F and 85°F and three months between 85°F and 100°F. Reduced shelf lives are due to slight solubility of BPO in the carrier resulting in lower thermal stability.

Containers of diacyl peroxide formulations should be dated when received and used or disposed of before the shelf life period is exceeded.

As all pastes – including non-separating varieties – will separate in time, thorough mixing prior to use is stressed.

HANDLING PRECAUTIONS

Heat – If a diacyl peroxide is heated above a certain temperature, its rate of decomposition increases in an uncontrolled manner. This reaction can be violent, releasing large volumes of hot, flammable gases.

The temperature at which this occurs depends on the volume, the container, and the period of time the peroxide remains at that temperature. The Self Accelerating Decomposition Temperature (SADT) Test provides a measure of this hazard. The SADT data for each diacyl peroxide formulation in its largest shipping container are given in Table 1.

Shock and Friction – Dry forms of benzoyl peroxide (Luperox® A98) and Succinic Acid Peroxide are shock-sensitive. Commercial diacyl peroxides (except Luperox® A98) are formulated to eliminate this hazard.

Fire – Diacyl peroxides, once ignited, burn vigorously and are difficult to extinguish. If a small fire occurs, Class B extinguishers (dry chemical or foam) can be used. In case of a fire involving large quantities of diacyl peroxides, the area should be evacuated and the fire fought from a safe distance with a water spray.

Contamination – Various contaminants, particularly oxidizing and reducing agents, metal salts and amines, can cause decomposition of diacyl peroxides.

Eye and Skin Irritation – While not considered strong irritants, goggles or a face mask and gloves

should be worn when handling diacyl peroxides. In case of skin contact, wash with soap and water. For eyes, flush with water and get medical attention.

Spillage – In the event of spillage, inert absorbent material should be used to soak up liquids or to mix with solids. The absorbed peroxide should be wetted with water and disposed of immediately. When dry benzoyl peroxide or succinic acid peroxide is involved, the mixture should be wetted with water before sweeping up. The sweepings are normally disposed of by dilution, incineration, hydrolysis or private contractor.

DISPOSAL

Dilution and Incineration – Dilution and Incineration is quickly becoming the most preferred method of liquid peroxide disposal due to current environmental regulations. Dilution of peroxide to less than 10% assay– or 1% active oxygen (whichever yields the lower active oxygen concentration) in a satisfactory solvent is recommended. Fuel Oil #2 or common hydrocarbons are the most widely used. Incineration can be accomplished after satisfactory mixing with negligible heat contribution from the peroxide portion of the solution. This method is not generally accepted for disposal of solid peroxides due to solubility limitations.

Disposal Companies – Disposal companies also may present one of the most desired ways of eliminating waste organic peroxides. In most cases, dilution as described in the Dilution and Incineration section is required. Contact, however, should be made with the individual disposal company to guarantee first, acceptance of peroxides and second, their specific procedures.

Hydrolysis – Hydrolysis is another effective way of disposing of small quantities (less than 10 pounds) of benzoyl peroxide. This involves incremental addition of benzoyl peroxide to a rapidly stirred, cold 10% sodium hydroxide (caustic) solution. This reaction requires adequate agitation and temperature control between 30-40°F. (Note: *Never* add the caustic to the peroxide.) This reaction converts benzoyl peroxide to water-soluble sodium benzoate and sodium perbenzoate, which can be disposed of by normal means. In any disposal situation, when doubts or

questions exist, contact an Arkema representative, and, of course, clear all procedures before proceeding.

TOXICITY

The toxicities of diacyl peroxides have not been fully determined. Available data can be located in the booklet: “The Storage and Handling of Organic Peroxides in the Reinforced Polyester Fabricating Plant” (available on request). Prior to handling a specific diacyl peroxide, the Material Safety Data Sheet for that product should be reviewed for current and up-to-date information.

FIRST AID

Care should be exercised by all personnel handling diacyl peroxides. Avoid prolonged contact with skin and inhalation of vapors or decomposition products emitted during processing. For specific first aid recommendations consult the appropriate Arkema MSDS.

AVAILABILITY

Ambient temperature-stable diacyl peroxides are warehoused nationwide and shipped by common carrier. Controlled temperature products are stocked at Arkema facilities and shipped by a fleet of refrigerated trucks to most points in the United States and Canada, as well as to major ports and border crossings for export. Formulations of benzoyl peroxide are marketed nationwide by special distributors serving the reinforced plastics and rubber industries.

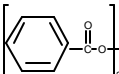
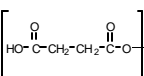
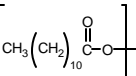
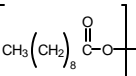
For additional information, pricing and the location of the nearest distributor, contact our Customer Service Department at:

Arkema, Inc.
2000 Market Street
Philadelphia, Pa 19103
Phone: 1.800.558.5575
Fax: 215.419.5455

FOOD AND DRUG ADMINISTRATION STATUS

For specific FDA information consult, “Organic Peroxides: Indirect Food Additives Summary”.

TABLE 1

Chemical Name, Structure, Molecular Weight	Specifications						Physical Properties						Shipping Info	
	Commercial Products	Assay % Wt.	Active Oxygen %Wt.	Form	Diluent(s)	Density g/ml Bulk Density Lbs./Ft ³	Melt/ Freezing Point °F	Viscos- ity CPS @c	Maximum Storage		S.A.D.T.			
									°F	°C	°F	°C		Pkg.
DIBENZOYL PEROXIDE  M.W. 242	Luperox A98	98.0 min	6.47 min	Granular	None	32.4 lbs/ft ³	-	-	100	38	155	68	1 lb Bag	94-36-0
	Luperox A75	73.0-77.0	4.83-5.09	Granular	Water	41.2 lbs/ft ³	-	-	100	38	159	71	50 lb Carton	94-36-0
	Luperox A70S	66-72	-	Granular	Water	52 lbs/ft ³	-	-	100	38	-	71	25 lb Carton	94-36-0
	Luperox A75FP	73.0-77.0	4.82-5.09	Fine Particle	Water	-	-	-	100	38	-	71	40 lb Carton	94-36-0
	Luperox AFR40	40.0-42.0	2.64-2.77	Pourable Paste	Proprietary	9.58 lbs/gal	<32° (F.P.)	12,800 @ 25	100	38	129	54	440 lb Drum	94-36-0
	Luperox ANS55	55.0-58.0	3.63-3.83	Paste	Proprietary	1.22 @ 77°F (25°C)	<35° (F.P.)	640,000 @ 25	100	38	129	54	40 lb Pail	94-36-0
	Luperox ANS55P	55.0-58.0	3.63-3.83	Paste	Butyl Benzyl Phthalate	1.22 @ 77°F (25°C)	<35° (F.P.)	700,000 @ 25	100	38	129	54	40 lb Pail	94-36-0
	Luperox ATC50	55.0-52.0	3.30-3.43	Paste	Tricresyl Phosphate	1.16 @ 77°F (25°C)	<-30° (F.P.)	240,000 @ 25	100	38	NE	-	40 lb Pail	94-36-0
	Luperox ACP35	35.0-37.0	2.31-2.44	Powder	Dicalcium Phosphate	41.2 lbs/ft ³	-	-	100	38	NE	-	50 lb Carton	94-36-0
SUCCINIC ACID PEROXIDE  M.W. 234	Luperox SAP** (Succinic Acid Peroxide)	54.0- 57.0	3.96- 4.85	Frozen Solid	Water	50 lbs/ft ³	257° (M.P.)	-	32	0	152	67	1lb Bag	123-23-9
DILAUROYL PEROXIDE  M.W. 399	Luperox LP (Alperox -F)	98.5 min	3.95 min	Flake	None	27.6 lbs/ft ³	129° (M.P.)	-	80	27	123	51	50 lb Lever- pak	105-74-8
DIDECANOYL PEROXIDE  M.W. 342	Luperox DEC** (Decanox - F)	98.5 min	4.60 min	Flake	None	26 lbs/ft ³	104° (M.P.)	-	60	16	109	43	50lb Carton	762-12-9

A U.S.P. grade, Luperox -70S, for use in pharmaceutical applications is also available.
* Requires refrigerated transport and storage.

(1) Self Accelerating Decomposition Temperature, A.S.T.M./U.M. method.

TABLE 2 SOLUBILITY DATA

Peroxide	Alcohols		Hydrocarbons						Chlorinated Hydrocarbons			Ester	Ketones		Ethers		Monomers			Misc.
	Methyl Alcohol	Ethyl Alcohol	Benzene	Cyclohexane	Hexane	Toluene	Xylene	Odorless Mineral Spirits	Methylene Chloride	Chlorobenzene	Trichloroethylene		Ethyl Acetate	Acetone	Methyl Ethyl Ketone	Ethyl Ether	Tetrahydrofuran	Vinyl Acetate	Methyl Methacrylate	
DIBENZOYL PEROXIDE	SL	SL	S	SL	INS	MS	MS	INS	MS	MS	MS	MS	S	S	MS	S	MS	MS	MS	INS
SUCCINIC ACID PEROXIDE	SL	MS	INS	INS	INS	INS	INS	INS	INS	INS	INS	INS	MS	SL	INS	S	INS	INS	INS	MS
DILAUROYL PEROXIDE	INS	INS	S	S	MS	S	S	SL	S	S	S	MS	MS	MS	S	S	MS	S	S	INS
DIDECANOYL PEROXIDE	SL	SL	VS	VS	S	VS	VS	S	VS	VS	VS	VS	S	S	VS	VS	S	S	VS	INS

% by weight
@ 25° C

INS = Insoluble (<1)
 SL = Slightly soluble (1-5)
 MS = Moderately soluble (5-15)

S = Soluble (15-50)
 VS = Very soluble (>50)
 CM = Completely miscible (100%)

TABLE 3 TYPICAL APPLICATIONS

Applications	Benzoyl Peroxides						
	Luperox A98	Luperox A75	Plasticizer Pastes	Luperox ACP35	Succinic Acid Peroxide	Luperox LP	Luperox DEC
Polymer Production							
Acrylic	•	•	ATC ANS-P ONLY			•	•
Styrenic		•				•	•
PVC						•	•
PVA	•	•					
Substituted Ethylene Polym.					•		
Styrenated/Acrylated Alkyls		•				•	•
Crosslinking/Curing							
Unsaturated Polyester	•	•	•	•		•	
Silicone Rubber	•						
Natural/Synthetic Rubber				•			
Miscellaneous							
Pharmaceutical	•	•		•			
Flour Bleaching							
Bleach of Oils, Fats and Waxes	•	•		•			

FIGURE 1 HALF-LIFE TEMPERATURE GRAPH (see Table 4)

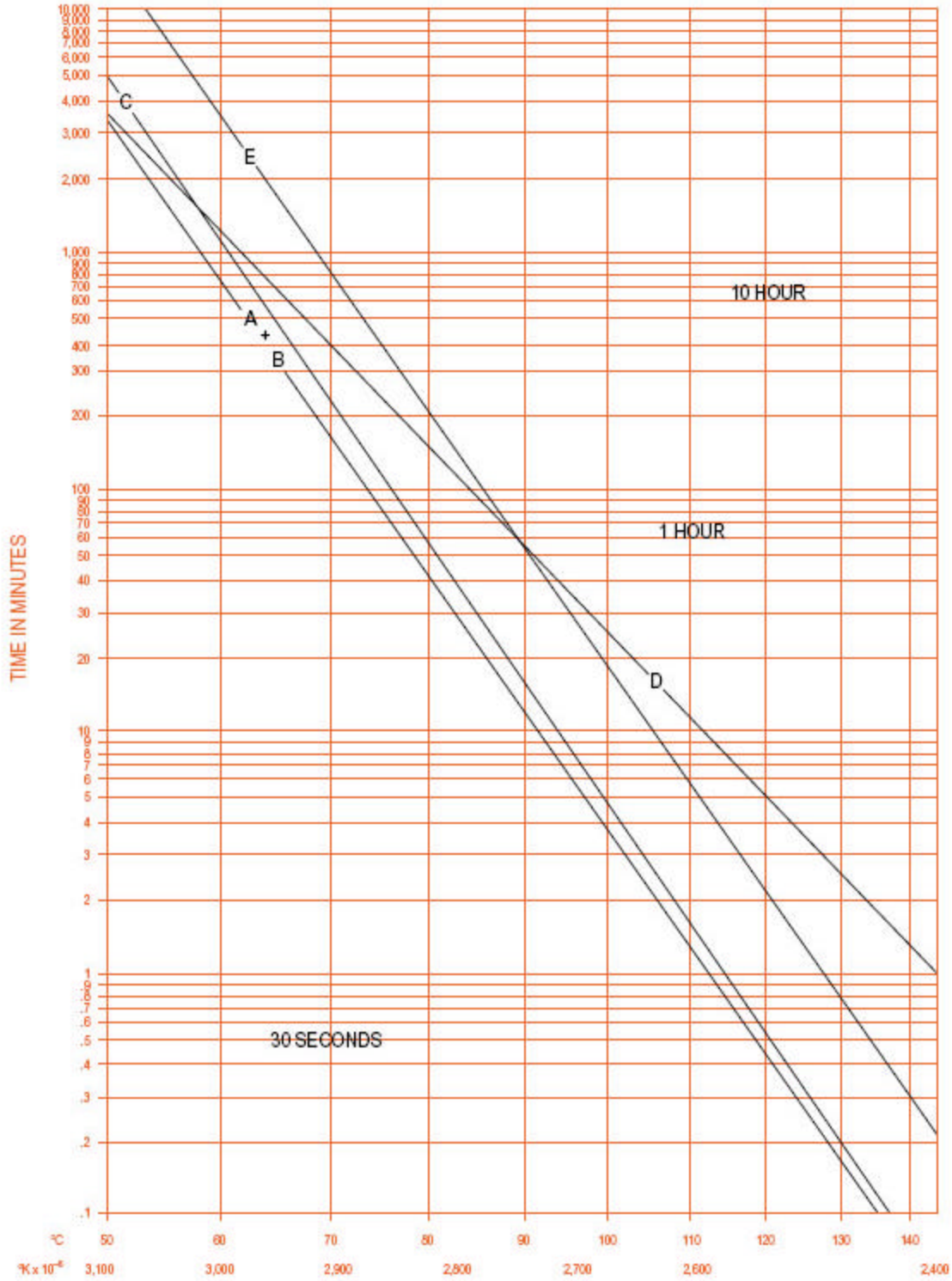


Table 4 Half Life

Product*	Solvent	Concentration	DE Act. Energy (Kcal/mole)	T _{1/2} (°C)	
				10 – hr.	1 – hr.
(A) Luperox DEC	Benzene	0.2M	30.5	61	80
(B) Luperox LP	Benzene	0.2M	30.5	62	80
(C) Luperox LP	Trichloroethylene	0.2M	31.2	62	81
(D) Luperox SAP	Acetone	0.1M	24.0	66	91
(E) Luperox A98	Benzene	0.2M	30.4	73	91

*See Figure 1

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See MSDS for Health & Safety Considerations
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