SELECTIONS OF CURING AGENTS FOR UP / VE REINS & ITS SAFETY

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ABSTRACT

For the selection of the most optimal cure system, the following items should be considered.

1. Type and characteristics of resin selected , chemical structure, speed and reactivity
2. Composition of the moulding : resin content, glass content, filler or pigment t type & content
3. Thickness and dimension of moulding : uniform thickness or large difference
4. Application technique e.g. hand lay up, spray up, RTM
5. Cure temperature and temperature of raw material
6. End use of product , this can influence requirements like transparency, color, physical properties and residual styrene content.

In this paper the most commonly used peroxides and some specialty peroxides are discussed with their cure performance in FRP application technique – hand layup, RTM, filament winding, pultrusion and moulding compounds. Non reinforced applications like button, lacquers and filled applications other then fiberglass e.g body fillers, polymer concrete, artificial marbles and sanitary ware are not illustrated in this paper.

Characteristics of good quality MEKP is highlighted as its working horse in FRP industry. Peroxides for vinyl ester resins are illustrated & basic properties of organic peroxides listed from safety perspectives.

Content

a. Curing system basic and components
b. Broad selection criteria
c. MEKP – working horse in industry and available grades
d. Impotence of good quality MEKP
e. Peroxide survey in application techniques
f. Peroxides for vinyl ester
g. Hazardous properties of organic peroxides in thermoset & basic safety

INTRODUCTION

One of the components of an unsaturated polyester resin and vinyl ester resin is the cure system, by which it meant the combination of peroxide plus possibly an accelerator, promoter and inhibitor. The role of the cure system in the processing of UP resin and the fact that many problems in the processing of resin can be overcome by the correct selection of the cure system.

In this paper role of cure system and the importance of selecting the proper cure system in processing of UP resin will be describe for major process technique. Some basic hazardous properties and safety precessions highlighted.

EXPERIMENTAL WORK

Curing System Basics

What is curing: Resin is converted from liquid to solid state. It's radical initiated polymerization between the styrene monomer and the fumaric unsaturated in the UP resin. The source of radical in most cases organic peroxide. Peroxy group (-o-o-) can decompose under influence of heat & accelerators into radicals.

To achieve controlled radical production at ambient temperature peroxide are used with accelerators.

- e.g. Ketone peroxide +cobalt (2) ethyl hexanoate / Dibenzoyl peroxide+N.N.Dimethyl aniline

To further increase reactivity of cure system promoters, inhibitors are added.

Promoters increases reactivity of accelerators.

Inhibitors – consume the first peroxy radicals formed & hence delay the cure reaction.

Combination of above four is curing system, though in minor quantity (1-4%) It influences curing process & properties of end products to large extent.

End product properties (hardness, mechanical strength, chemical resistance & thermal stability) in general directly related to residual styrene content of product i.e high residual styrene content is an indicator for an insufficient cure. (Should be 1-3%max except food product)

Curing efficiency is determined by residual styrene content – For best results of 1-2% peroxide will be 1.5-2% styrene left and lower the HDT(heat distortion temperature) of UP resin lower the styrene content. Accelerator dosage does not have any role for MEKP/Cobalt system. With post curing, styrene content can be reduced.

Basic Peroxides in Thermoset

80 different varieties are available for curing of UP Resins from below families

- Ketone Peroxides –MEKP, MIKP,AAP
- Cyclohexanone Peroxides
- Dibenzoyl Peroxides – BPO
- Peroxy Esters – TBPB, TBPEH
- Peroxy Ketals
- Hyderoperoxides – CHP
- Peroxi (di) carbonates
- Peroxide mixtures

MEKP-Methyl ethyl ketone peroxide MIKP – Methyl Isopropyl Ketone peroxide
AAP-Acetyl acetone peroxide BPO- Dibenzoyl Peroxide
TBPB – Tert butyl peroxybenzoate TBPEH – tert- butyl peroxy -2-ethylhexanoate
CHP – Cumyl hydroperoxide Di(4-tert-butylcyclohexyl)peroxydicarbonate
phr – parts per 100 parts of resin

Selection criteria are broadly based on cure temperature and process technique.

Ambient 0-40 ^{o} C : HLU, SU, RTM, Polymer concrete, Buttons, body fillers, lacquers

Elevated 40-100 ^{o}C : Continuous laminating, Centrifugal casting, Filament winding

High >100 ^{o}C : Pultrusion, Hot press molding

Ketone peroxide (Major peroxide) available in different reactivates & grades

1.High reactive MEKP –Active Oxygen (A.O) 9.9% gives very fast gelling (6 min) and can be used in corrugated sheets

2.Low reactive MEKP – AO 8.5% give slow gelling (20 min) can be used for production of large loulding, gelcoates which tend to microporosity cased by decomposition of hydrogen peroxide abd for filament wining of VE resins.

3.Medium Rective MEKP (standard MEKP) – AO 8.9-9.9% for all standatd curing applications.

4. Acetyl acetone peroxide – AAP to for fast cure & low remolding time
5. Phthalate free MEKP – in Aliphatic solvents
6. Methyl Isoproyl ketone peroxide (MIKP) for marine - For high gloss , no pinholes, no discoloration , good flow, lower shrinkage

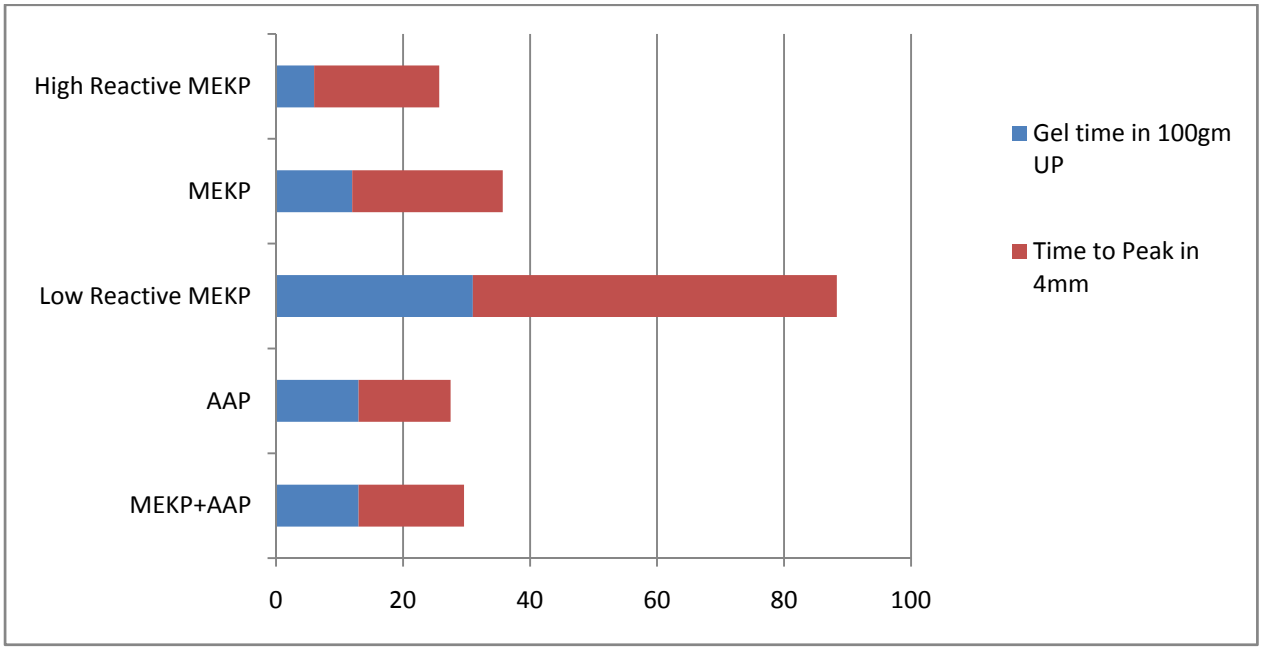
At least 1% peroxide but not more than 3% is used. Peroxides formulations have 50-65% plasticizers. Too high dosage of peroxide means too high addition of this non reactive component which has –ve influence on mechanical, thermal & chemical properties of molding. Too much accelerator can result in too fast & inefficient decomposition of peroxide which may lead to under cure of UP resin

For Ketone/cobalt cure system gel time can be adjusted by 1. Peroxide Type & Quantity 2. Cobalt quantity. For shorter gel time (RTM) promoter can be adds for long gel time (Filament winding) Inhibitor can be added.

Fast cure is obtain with AAP OR BPO however BPO gives yellow to brown discoloration and AAP green discoloration product. In fast cure system polymerization shrinkage will take place in short period of time and higher peak exotherm which results in thermal expansion followed by thermal shrinkage.

Cure experiments in a standard ortho resin at 20^{o}C with different ketone peroxides

Cure system: 2% peroxide + 0.5% Accelerator Cobalt 1%



	Peak Exotherm o C	Time in Hr to Barcol 934-1 of Rs 0-5 & 25-30
MEKP+AAP	58	0.8 / 12
AAP	44	3.4 / 15
Low Reactive MEKP	34	5 / 27
MEKP	28	9 / 32
High Reactive MEKP	67	0.5 / 1

Good quality MEKP

The reactive part of peroxide, which can form radicals is the –o-o- peroxygroup called as active oxygen part.

Active oxygen part =n*16*100/ molecular weight of peroxide, n-stands for number of active oxygen groups present in the peroxide.

The standard MEKP has three components, Hydrogen peroxide determines the gel time, MEKP-4 determines the initial cure, MEKP-3 determines the final cure.

Good quality MEKP should have

a. low water content <3% ,

b. No Alcohol & Glycol but inert solvents as phthalate, Aliphatic esters

c. Very good stability – No change in reactivity during storage

d. Consistency – No change batch to batch

Low quality MEKP gives rise to blistering and pin holing of gel coat.

Low quality MEKP generally has high water content (5-15%). To keep this water in solution alcohol or glycols are added however they do not solve in resin. When MEKP is added to resin it' leads to blistering .Alcohol & glycols are polar solvents which creates and build osmosis pressure in voids when FRP article is in water (boat, swimming pool). This solvents bubbles in UPR. This voids busts and called blistering.

Alcohol, glycol and water have negative effect on stability of MEKP, batch to batch reactivity, quality of end product. High water content reduces 'PH to 4 and product decomposition is faster which loses reactivity of peroxide.

Water in MEKP increases viscosity of gel coat and causes too much air inclusion during spraying. Too much air inclusion gives rise to pin holing. If applied by spindle, speed s reduces

which gives rise to styrene emission and less styrene is available to polymerise.. Also H2O2 partly decomposes in oxygen

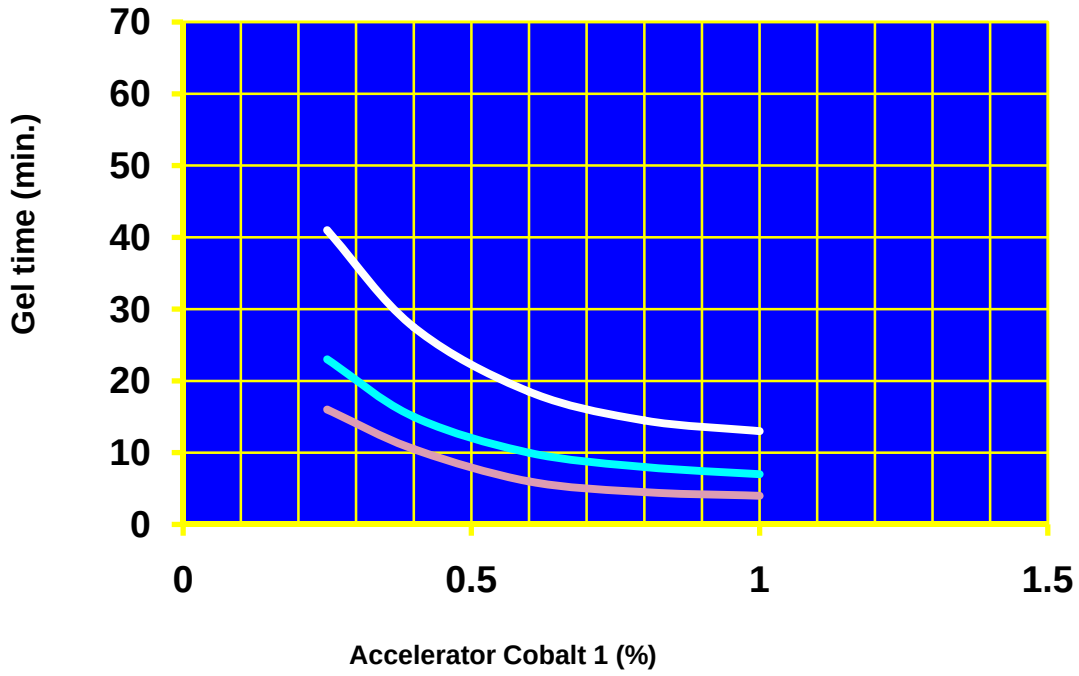
Good quality of MEKP from reputed source is very important.

Peroxide survey for some major Application techniques

A) Hand layup & Spray Up

Standard MEKP is the best choice.

Cure of 4 mm laminate at 20 degree C			
	Gel time	Time to peak	Peak Exoth
	Min	Min	Degree C
2phr APP +1phr Cobalt 1%	8	18	97
2phr MEKP +1phr Cobalt 1%	8	26	64
	Barcol	Res Styrene	
	25-30	24 h 20DC	+8hr 80DC
	h	%	%
2phr APP +1phr Cobalt 1%	<<1	0.9	0.2
2phr MEKP +1phr Cobalt 1%	1	5	0.1



The effect of MEKP and Accelerator dosage level (1%,2% & 4%) on gel time at 20 degree C

B) Resin Transfer Molding (RTM)

For ambient temperature 20-40 ^{o}C ketone peroxides +cobalt accelerators +possibly promoter+ Inhibitor to adjust gel time. For elevated temperature (60-120 ^{o}C) processes combination of a ketone peroxide & per esters like – TBPB, TBPEH

Ketone peroxide like MEKP formulations loading is 1.5-3 phr
Di benzoyl peroxide formulations is 2.5-3 phr

Amount of accelerator is less critical and therefore used to adjust gel time. It is advised not to use less than 0.5 phr of 1% cobalt accelerator.

Gel time should be chosen which is sufficiently long to fill the mould and to rinse the injection equipment and mold temperature.

AAP: - Gives comparable gel time as achieved with MEKP but with faster cure which results in a fast mould turnover.

MEKP+AAP ready mixture: specially developed for think GRP parts. This gives a lower peak exotherm then MEKP and AAP.

AAP+TBPB ready mixture: developed for RTM at elevated temperature. Product combines fast cure of AAP with optimal cure of per ester.

Cure experience of various peroxides discussed above like gel time, time to peak, peak exotherm data and required dosage can be shared upon request.

C) Filament winding :

Discontinuous filament winding:

Polymerization should start after the winding is ready adjusting of the gel time with inhibitor Standard peroxides MEKP 1-2phr, accelerator 1% 1phr and Inhibitor 0.2-0.3 phr.

Special peroxides: For VE resins: MEKP with low reactivity (Low H2o2). For faster hardening AAP, mixture of AAP+MEKP

For continuous filament winding:

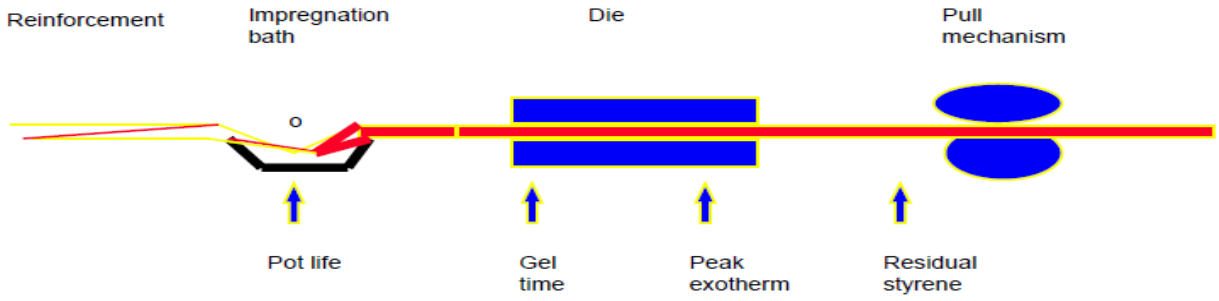
Standard peroxide is Good quality MEKP with low water content: 1-2 phr, cobalt 6% 0.1-*0.2phr

To increase speed special peroxide is used in this technology is ready mixture of AAP+TBPB In 1-2phr and speed can be increased up to 33 mtrs / hr compared to 26 mtrs /hr with standard MEKP. Also residual styrene content reduces to 0.1% compared to 2-3% with standard MEKP.

Reactivity in an standard orthophtalic resin :

Product	MEKP	AAP+TBPB (AO 3.5%) Med reactive	AAP+TBPB (AO 4.5%) High reactive
Geltime 80°C	1.05	0.6	0.5
1 mm. Layer			
8 mm. Laminate 80°C			
Time To Peak – min.			
Peak exotherm °C	10.1	7.5	6.2
Res. Styrene %	91	108	115
	2.9	0.9	<0.1

D) Pultrusion



- Important parameters are “Gel time in 1st part of die & degree of cure when profile leaves the dye. In order to have good control on process following combination of Peroxides are proven
- Kicker Peroxide - High reactive Percarbonate (Di(4-tert-butylcyclohexyl) peroxydicarbonate) with low critical temperature) to adjust the Gel time in die. Dosage up to 0.5phr
- Finishing peroxide – TBPB: to get full cure in die as cure efficiency of above Peroxide is low. Dosage 1-phr

- Quick Geglation followed by a fast cure reduces pulling force. This combination gives enhanced pulling speed and output compared to BPO/TBPB combination.

- Higher dosage of percarbonate gives faster gelation at relative low temperature in center of thick parts for uniform heat build. Decrease dosage of TBPB will slower cure speed to some extent & hence heat built up during final stage in thick parts (6 to 100mm)

Cure of 4 mm laminate at 120 ^{o}C			
High Reactive UP Resin	100	100	100
High Reactive per carbonate		0.5	
BPO Fine powder			1.5
TBPB	1.5	1	0.5
Pot life at 20 ^{o}C	35	2	52
Gel time (Min)	2.1	0.5	0.6
Time to peak (min)	4.8	2.9	2.6
Peak Exotherm (^{o}C)	174	152	160
Residual Styrene content after cure time+3min %	<0.1	0.5	0.3

E) Sheet molding & Bulk Molding compounds (SMC/BMC)

Selection criteria for the initiation system –

- Shelf life compound, flow time, minimum molding time, total molding time(surface quality 7 residual styrene) and emission of volatile form the final moulding.

Peroxides available –

Peroxide Family	Name	Act Tem ^{o}C	Loading	Remark
Peroxy esters	TBPB	80	1-1.5 phr	efficient & standard
Combination	TBPB +TBPEH	60	1.25+0.25	Faster cure system
Peroxy Ketal	DTBC	70		Long shelf life

Activation temperature where the peak exotherm is within one hour (1phr of peroxide in pure resin). The peak temperature should be 100 above bath temperature

Cure characteristics of some peroxide

Peroxide	Pot life at 30 °C	Platen gel time (sec)		MMT at 145 (Sec)
		120	140	
TBPEH	14d/10d	13	5	14
TBPB	47d/17d	85	22	60
DCP	>6m/>6m	170	30	95

Pot life in a BMC paste , blank/+5phr Iron oxide black , MMT : minimum moulding time(dimensional stable)

Hot press moulding experiments at 150 °C in BMC

Peroxide	MFT (Sec)	MMT (Sec)	Gloss	Residual Styrene%
1.5phr TBPB	19	39	77	0.01
1.25 TBPB +0.5phr TBPEH	12	27	80	0.01

MFT: Max flow time, MMT Min moulding time , Gloss and residual styrene after MMT +90sec

F) **Peroxides for Vinyl ester Resin** –

High Mechanical and chemical resistance properties and to obtain optimal properties excellent curing is needed. Std MEKP results in gassing. Use MKEP with low hydrogen peroxide content. To avoid foaming use hydrogen peroxide free peroxide or complexes cobalt accelerator.

For ambient temperature following peroxides are useful

1. MEKP with low H2o2

Best for Std V.E application and gives very good cure. Used for std applications such as laminates and concretes

2. Cumyl hydro peroxide (CHP) with promoter – Ready mixture

This is highly reactive peroxide. No strict storage condition required & this is the best peroxide if absolute no gassing is required e.g. Vinyl Ester gel-coats. It gives short gel time and fast hardening. Dosage -2phr and cobalt 6% 0.5phr

It gives low peak exotherm in thick layers. Being a low viscosity liquid, presents no difficulty in spray-up or other liquid handling equipment unlike BPO

3. CHP - For thick laminates in one run. low reactive, Low peak exotherm in thick laminates. It gives Slow cure with high temperature.

4. Dibenzoyl peroxide powder (BPO)

For application at low temperature, Application under moisture conditions In case no cobalt is allowed. Aromatic amines are used as accelerator. High residual styrene -2 to 3%.Aromatic amines become part of polymer

Std MEKP Vs Low reactive MEKP Vs CHP with Acetyl acetone promoter ready mix

Epoxy Vinyl Ester 4mm laminate			
Epoxy VE	100	100	100
MEKP	2		
MEKP with Low H2o2		2	
CHP with acetyl acetone promoter			2
Cobalt 6%	0.5	0.5	0.5
Foaming	Yes	Slightly	No
Gel time (Min) Pure resin	40	23	25
Time to peak (min)	228	105	42
Peak Exotherm (C)	27	39	39
Residual Styrene content after cure time+3min %	10	8	7

<u>Organic Peroxide Safety</u>: R - O - O - R

- Organic peroxides contain relatively weak 0 - 0 bond in their molecule.
- Due to this peroxides are thermally unstable compounds i.e. sensitive to heat and will decompose above certain temperature.
- Decomposition leads to heat production
- If this heat cannot be transferred to environment then a runaway reaction occurs and peroxide will explode violently with or without combustion after some time.
- Hence strict temperature control is required for handling and storing Organic Peroxides to prevent undesired decomposition.

Pure formulation (transport, handling, storage,…)

temperature

Peroxide ⟶ **decomposition products + HEAT**

contamination

Hazardous properties – Peroxides 5.2 class

1. **Thermal stability:**

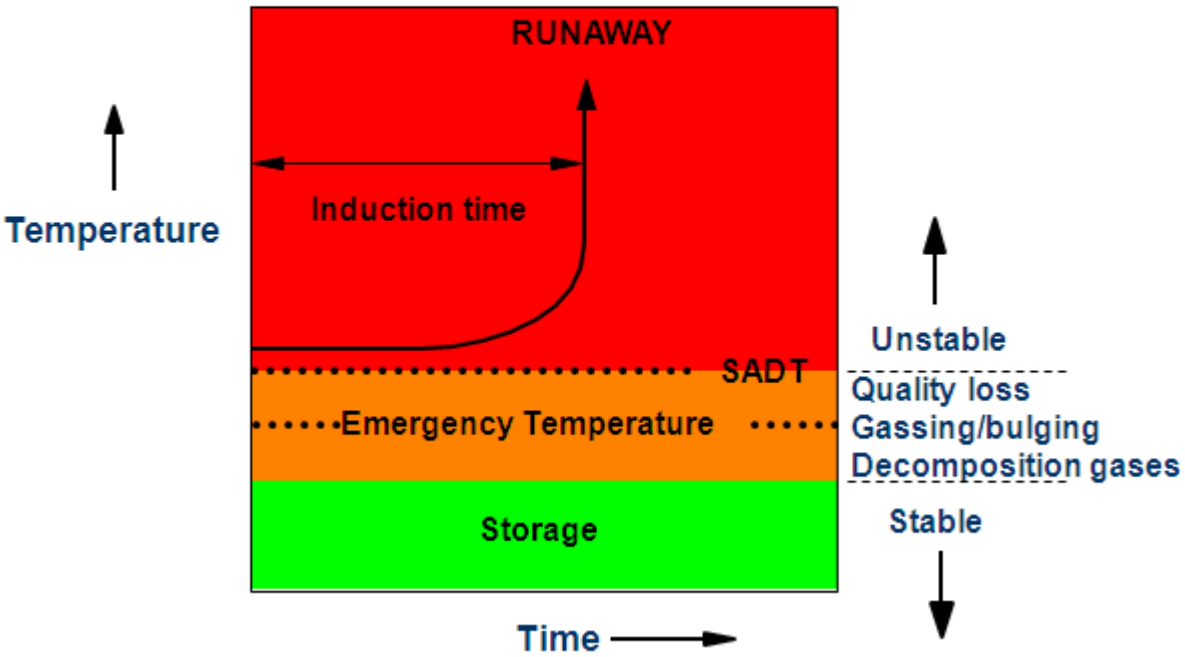
It is characterized by **SADT: Self Accelerating Decomposition Temperature**

The SADT is the lowest ambient temperature at wich self-accelerating decomposition (runaway) occurs with a product in the packaging as used for transport

Peroxides	SADT (°C)	Ts Max (°C)	Ts Min (°C)
TBPB	60	25	10
MEKP	60	25	-
CHP	75	40	-30
BPO	50	25	
AAP	60	25	-10
TBPEH	35	20	-30

Ts Max – maximum storage temperature Ts Min – minimum storage temperature

Thermal stability - Traffic light picture



2. Contamination

Contamination of peroxides with for instance metals, acid, alkalies or accelerators lowers the stability and consequently SADT of peroxides. This can possibly result in runaway reactions at ambient temperatures. Especially MEKP formulations are very sensitive for contaminations.

3. Flammability

Organic peroxides are combustible substances. The flash point of peroxides (except few) is above the SADT. Most peroxides are difficult to ignite, however once ignited they burn fiercely.

4. Mechanical Sensitivity

Generally shows low degree of mechanical sensitivity. Rough handling, Serve friction or heavy impact should always be avoided.

General Rules:

First aid in case of:

Ingestion –Do not induce omitting. Seek Medical attention

Inhalation – Move to fresh air , rest, half upright position, loosen clothing

Skin contact – Remove contaminated clothing, wash with soap and copious amount of water

Eye contact – First rinse for at least 15 min with plenty of water, Hold eyes away from the eyeball, Always seek medical attention

In case of fire – fight small fire with powder or carbon dioxide and apply water to prevent re-ignition. Alert the fire department.

In case of spillage – Liquid: absorb with inert material e.g. vermiculite and add water

Pastes **–** take up with polyethylene spatula and add water. Flush reminder with water

Solid **–** collect spilled material and collect in clean plastic bucket with loose fitting lid and add water. Remove waste to safe place arrange disposal as soon as possible. The waste should not be confined.

Storage condition: Most of peroxide in thermoset are stored in original containers tightly closed in ventilated place. Ts Max is 25 ^{o}C for most of this. Keep away from reducing agents , accelerators. Never weight out in storage rooms.

Never mix peroxides with accelerators, never heat peroxides, do not handle in rough way avoid friction and impact force. Wear safety gloves, wear safety goggles, leave product in original packing.

Please read MSDS (Material safety data sheet) of individual product and contact for more details regarding storage, handling to company representatives.

Summary

Correct selection of cure system is very important for better productivity and end product quality. Use of good quality MEKP is essential to get enough working time. Variety of MEKP grades are available depending upon reactivity.

Variety of peroxide & ready peroxide mixture available for gel time & curing speed adjustments Cure speed is expressed as the time to achieve a parsoz hardness

Peroxide are 5.2 class hazardous materials and strict control should be practiced for handling, storing it safely.

Author (Information)

Prasad Pujari – is Chemical Engineer and MBA in marketing, Total working experience is 11 years in chemical industry & working with Akzo Nobel since last 3.5 years handling sales of organic peroxides to thermoset, cross-linking rubber and polymer applications in India.

Akzo Nobel is fortune 500 MNC in specialty chemicals and coating& paints. It has wide range of organic peroxides for polymer & FRP Industry and well known for their consistent quality products and innovations.

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