Nouryon

Vinyl ester resins

Application data and cure data

Nouryon is the world's leading producer of organic peroxides for the curing of thermoset resins, coatings and specialty monomers. We're home to the best known brands in the thermoset market. Examples include Butanox®, Cadox®, Perkadox® and Trigonox®. We also have a whole range of specialty auxiliary products, such as cobalt free accelerators to meet specific production requirements.

This application guide provides an introduction to our thermoset product portfolio and can help you find a suitable curing system for your specific application. If you need more detailed information please contact your account manager or customer service representative. Sharing our thermoset experience is one of the biggest resources we offer.

Process description

Vinyl ester resins are high performance unsaturated resins chosen for their outstanding corrosion resistance and other physical properties. They can be applied through a wide array of techniques, but react differently to initiators than other unsaturated polyester systems.

General composition

- 30-100% VE or Hybrid resin
- 70- 0% Glass & filler (sand, CaCO3, ATH etc.)

Main applications

Corrosion resistant pipes, tanks, & other structural components. Used as GC liner, barrier coat, laminating resin and in other systems.

Reason for our products

- High quality
- Good aftersales and technical service
- Intensive safety research
- Worldwide distribution
- Customized application research: special formulated products for an optimal performance in this application

Cure system design

Selection of the initiator should be dependent upon the resin reactivity, filler & glass loading, part mass, cure temperatures, and part geometry. Higher resin reactivity, lower filler loadings, and thicker parts contribute to higher exotherms & faster cure, but potentially higher shrinkage.

Cadox L-50a or Butanox L-50, Methyl Ethyl Ketone Peroxides (MEKP), are the most common initiators used. Due to the different functionality of VE resins, they respond well to the type 3 dimer form of MEKP or accelerated CHP initiators. Organic peroxides with significant levels of H2O2 can cause foaming. Cadox L-50a or Butanox L-50 have low levels to avoid foaming and porosity. Trigonox 239 and Trigonox K-90 (Cumyl hydroperoxide based) are generally slower cure, but can eliminate gassing. Trigonox K-90 is more commonly used at elevated temperatures where good cure rates can be obtained.

Trigonox 239, a pre-accelerated CHP solution with no amine, can eliminate all gassing while maintaining a fast cure speed and provide the lowest porosity. Depending upon the VE resin chemistry, promotion levels may need adjustment to deliver the same processing properties and cure times. Though less common, Benzoyl peroxide accelerated with DMA or similar amines can also be used for special purposes. Typical initiator dosing rates are 1-3 phr (per hundred resin) peroxide. Below is a list of commonly used initiators used for ambient cure systems.

Table 1. Typical Initiators for ambient cure VE resins

PRODUCT NAME	CHEMICAL NAME	PHYSICAL FORM	PEROXIDE CONTENT (%)	ACTIVE OXYGEN (%)	TS, MAX. °F (°C)	SADT °F (°C)	NFPA CLASS	STANDARD PACKAGES
Cadox L-50a Butanox L-50	Methyl ethyl ketone peroxide	Solution	35	8.9	86 (30)	≥140(≥60)	II	4x8# Carton, 5 gal
Cadox L-30a	Low concentration Methyl ethyl ketone peroxide in TXIB for summer	Solution	20	5.3	86 (30)	≥140(≥60)	II	4x7# Carton
Trigonox 263	Ketone peroxide/ CHP mixture in TXIB for lower exotherm	Solution	48	9.2	86 (30)	140 (60)		4x8# Carton
Perkadox GB-50	Dibenzoyl peroxide in DCHP	Granules	50	3.3	77 (25)	131(55)	II	50# Carton
Trigonox 239	Pre-accelerated Cumyl hydroperoxide solution for fast cure & lower porosity	Solution	45	4.6	77 (25)	131(55)		4x7# Carton
Trigonox K-90	Cumyl hydroperoxide	Solution	88	9.4	104 (40)	158(70)	III	35# Hedpak, 450# Drum

** Estimated from NFPA 432 based on similar formulations

Performance in Bishphenol-A epichlorohydrin resins systems

These highly reactive resin systems can be cured with a wide variety of initiators. The following chart and exotherm graph shows the range of cure speeds and temperatures which can be obtained by choosing various initiators. Butanox LPT-IN provides the fastest cure and highest exotherm with little gassing. Cadox L-50a or Butanox L-50 is slightly slower, but can exhibit slightly more gassing. Trigonox 239 shows a similar cure rate to Cadox L-50a, but has a drastically reduced exotherm, no gassing, and provides the best final cure. Trigonox 263 typically exhibits the slowest cure rate and lowest exotherm for temperature sensitive applications such as vacuum bagging.

Table 2. 5.4 mm panels, 35% glass, 25°C

INITIATOR	GASSING	GEL TIME (MIN.)	PEAK TEMP (°C)	TIME TO PEAK (MIN.)	GEL TO PEAK (MIN.)	RESIDUAL STYRENE (%)
2.0 phr Trigonox 239	None	17.3	33.5	76.4	59.1	4.43
2.0 phr Butanox LPT-IN	Slight	23.7	46.7	61.9	38.2	5.23
2.0 phr Cadox L-50a or Butanox L-50	Slight	33.2	39.3	75.5	42.4	5.85
2.0 phr Trigonox 263	Slight	NA	29.2	96.2	NA	5.71

Table 3. Barcol development

INITIATOR	60 MIN.	75 MIN.	95 MIN.	120 MIN.	72 HRS
2.0 phr Butanox LPT-IN	0	5	15	20	45
2.0 phr Cadox L-50a or Butanox L-50	0	0	10	15	44
2.0 phr Trigonox 239	0	0	10	15	43
2.0 phr Trigonox 263	0	0	0	0	42

The exotherm traces below show the rates of reaction and exotherms. The initial spike in exotherm stems from the reaction of the hydrogen peroxide component in MEKP's with the cobalt promoter and causes the gassing seen which can be seen in MEKP's. It can be eliminated by Trigonox 239. The significantly lower exotherm of Trigonox 239 does not mean a lower degree of final cure.

Figure 1. VE8301 resin, 5.4 mm panels, 35% glass

Performance in Epoxy Novalax resins systems

Epoxy Novalax resins are much more reactive and have much faster gel times than bisphenol-A based resins. This type of resin is also very responsive to the type 3 dimer form of MEKP and responds well to both Butanox LPT-IN, L-50 varieties and Trigonox 239. Trigonox 239 was too fast in gel time in this pre-accelerated resin system to allow laboratory panel preparation at the promotion levels contained in this resin, but a comparison of 100 gram mass tests below confirms it to be the fast gel and cure speed. Some gassing still occured in this resin system with MEKP's.

Table 4. 100g cup gel test, 25°C water bath

INITIATOR	GEL TIME (MIN.)	PEAK TEMP (°C)	TIME TO PEAK (MIN.)	GEL TO PEAK (MIN.)	GASSING
2.0 phr Trigonox 239	4.7	194.0	10.1	5.4	None
1.5 phr Trigonox 239	6.0	189.2	1.9	4.9	None
2.0 phr Butanox LPT-IN	12.1	202.7	17.8	5.7	Slight
1.5 phr Butanox LPT-IN	15.2	193.1	21.9	6.7	Slight
1.5 phr Cadox L-50a or Butanox L-50	20.8	173.8	26.8	5.9	Slight
2.0 phr Trigonox 263	19.5	167.3	38.7	19.2	Slight

Panels prepared show Butanox LPT-IN to provide the fastest cure and the highest exotherm since Trigonox 239 was not included. The most commonly used L-50 varieties show a slower gel time, but fast cure and slightly higher residuals. Trigonox 263 exhibits a reduced exotherm and good final cure for temperature sensitive applications.

5.4 mm panels, 35% glass, 25°C

INITIATOR	GEL TIME (MIN.)	PEAK TEMP (°C)	TIME TO PEAK (MIN.)	GEL TO PEAK (MIN.)	RESIDUAL STYRENE (%)
1.5 phr Butanox LPT-IN	22.3	118.3	33.1	10.8	0.86
2.0 phr Trigonox 263	24.2	35.0	87.1	62.9	1.47
1.5 phr Cadox L-50a or Butanox L-50	35.0	48.9	50.1	15.1	2.28

The resin chemistry and reactivity of these resins varies more widely that ortho or iso-PE's so a thorough evaluation of initiators is recommended for each resin. Promoter and accelerator levels also vary widely adding to the need to work with resin suppliers in choosing the best resin for each application. Resin supplier's recommendations are the best starting point, but additional guidance can be obtained through your AkzoNobel representative.

Cure data

Perkadox GB-50

(also applicable for Perkadox GB-50L and Perkadox GB-50X)

Perkadox GB-50 is a free flowing, fine, granular powder containing 50% dibenzoyl peroxide for the curing of unsaturated polyester and acrylic resins at ambient and elevated temperatures. At temperatures up to 80°C, Perkadox GB-50 should be used in combination with an aromatic tertiary amine accelerator. Above 80°C the use of an accelerator is not required.

Perkadox GB-50 is easy to handle, easy to disperse and dissolves very quickly in unsaturated polyester resins and acrylic resins. When in acrylic resins a very high degree of transparency of the cured part is required the special grade Perkadox GB-50L is advised. The curing system Perkadox GB-50/amine accelerator shows a very fast cure that is hardly influenced by humidity and fillers. Even at low temperatures a relatively good cure will be obtained. A disadvantage may be the yellow colour and poor light resistance of the moulded product.

For curing at ambient temperature the following amine accelerators are available to adjust the gel time and speed of cure of the cure system based on Perkadox GB-50:

- Accelerator NL-65-100 (N,N-Dimethyl p toluidine) for short gel times
- Accelerator NL-64-100 (N,N-Diethyl aniline) for long gel times

Dosing

Depending on working conditions, the following peroxide and accelerator dosage levels are recommended:

Perkadox GB-50

2 - 5 phr *

Amine accelerator

0.05 - 0.5 phr

* (parts per hundred resin)

Cure characteristics

In a **high** reactive standard orthophthalic polyester resin the following application characteristics were determined.

GELTIME CLEAR RESIN AT 20°C (GELNORM)

UP resin	100	100	100	100	100
Perkadox GB-50	3.0	3.0	3.0	3.0	3.0
Accelerator NL-64-100	0.1	0.5			
Accelerator NL-65-100			0.0	0.1	0.4
Gel time (minutes)	160	20	20	5	1

Cure of 1 mm pure resin layer at 20°C

The speed of cure is expressed as the time to reach a Persoz hardness of respectively 30, 60 and 120 s.

Persoz	30	60	120	s
3 phr Perkadox GB-50 + 0.1 phr Accelerator NL-64-100		0.5	1	h
3 phr Perkadox GB-50 + 0.05 phr Accelerator NL-65-100	1	2.5	14	h
3 phr Perkadox GB-50 + 0.1 phr Accelerator NL-65-100			0.5	h

Cure of 4 mm laminates at 20°C

4 mm laminates have been made with 450 g/m2 glass chopped strand mat. The glass content in the laminates is 30% (w/w).

The following parameters were determined:

- Time temperature curve
- Speed of cure expressed as the time to achieve a Barcol hardness (934-1) of 0-5 and 25-30 respectively.
- Residual styrene content after 24h at 20°C and a subsequent postcure of 8h at 80°C.

	GEL TIME (min.)	TIME TO PEAK (min.)	PEAK EXOTHERM (°C)
3 phr Perkadox GB-50 + 0.5 phr Accelerator NL-64-100	21	26	140
3 phr Perkadox GB-50 + 0.05 phr Accelerator NL-65-100	28	35	64

	BARCOL		RESIDUAL STYRENE	
	0-5 (h)	25-30 (h)	24 h 20°C (%)	+8 h 80% (%)
3 phr Perkadox GB-50 + 0.5 phr Accelerator NL-64-100		<1	2.9	2.1
3 phr Perkadox GB-50 + 0.05 phr Accelerator NL-65-100	1	8.5	6.6	0.8

In a medium reactive standard orthophthalic polyester resin the following application characteristics were determined.

Geltime clear resin at 20°C (Gelnorm)

3 phr Perkadox GB-50 + 0.15 phr Dimethylaniline 15 minutes

Cure of 4 mm laminates at 20°C in Bisphenol A eopxy VE resin

4 mm laminates have been made with 450 g/m2 glass chopped strand mat. The glass content in the laminates is 30% (w/w).

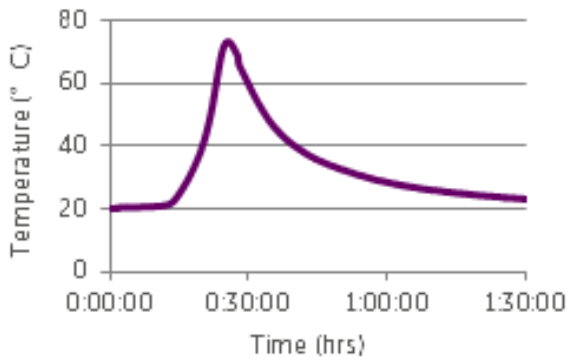
The following parameters were determined:

- Time temperature curve (SPI method)
- Speed of cure expressed as the time to achieve a Barcol hardness (934-1) of 25.
- Residual styrene content after 24h at 20°C

	GEL TIME (min.)	TIME TO PEAK (min.)	PEAK EXOTHERM (°C)
3 phr Perkadox GB-50 + 0.15 phr Dimethylaniline	16	26	74

	BARCOL	RESIDUAL STYRENE
	25 (h)	24 h, 20°C (%)
3 phr Perkadox GB-50 + 0.15 phr Dimethylaniline	1	1

Graph 1. Time temperature curve



In a high reactive Bisphenol-A epoxy vinyl ester resin the following application characteristics were determined.

Gel time clear resin at 20°C (Gelnorm)

3 phr Perkadox GB-50 + 0.15 phr Dimethylaniline 11 minutes

Clear SPI reactivity data with different types of accelerators

	GEL TIME (min.)	TIME TO PEAK (min.)	PEAK EXOTHERM (°C)
3 phr Perkadox GB-50 + 0.2 phr Accelerator NL-64-100	29	39	150
3 phr Perkadox GB-50 + 0.2 phr Accelerator NL-65-100	4	9	150

Time-temperature curve of a thin layer at 20°C (SPI-method)

	CURE TIME (MIN.)	PEAK EXOTHERM (°C)
3 phr Perkadox GB-50 + 0.15 phr Dimethylaniline	30	59

Pot life at 20°C

The pot life is determined of a mixture of Perkadox GB-50 and a non-pre-accelerated UP resin at 20°C.

21 days 3 phr Perkadox GB-50

11 days 6 phr Perkadox GB-50

Trigonox 239

Trigonox 239 is a peroxide mixture based on cumene hydroperoxide. Trigonox 239 is especially developed for the cure of vinyl ester or phenacryl resins in combination with a cobalt accelerator.

Trigonox 239 can successfully be used instead of generally applied ketone peroxides like Butanox LPT-IN with the following features:

- No 'gassing' after the peroxide is mixed in the preaccelerated vinyl ester resin. This phenomenon is very often recognized as a disadvantage of ketone peroxides in vinyl ester resins.
- The use of an amine accelerator is in general not necessary to achieve a good cure.
- A fast cure in thin coatings and laminates up to a thickness of approx. 6 mm.
- A low peak exotherm in thick laminates.

Dosing

Depending on working conditions, the following peroxide and accelerator dosage levels are recommended:

Trigonox 239

2 - 3 phr *

Accelerator NL-51PN

0.2 - 1 phr

* (parts per hundred resin)

Cure characteristics

The Cure characteristics of Trigonox 239 have been determined in comparison with the for this application area generally applied peroxide Butanox LPT-IN in the 2 commonly used vinyl ester resins:

Vinyl ester resin I = bisphenol A based type
Vinyl ester resin II = novolak based type

Gel time at 20°C

Vinyl ester resin	100	100	100	100
Trigonox 239 VR	2	2		
Butanox LPT-IN			2	2
Accelerator NL-51PN (6% cobalt)	0.5	1	0.5	0.5
N,N-Dimethyl aniline				0.1
Gel time at 20°C (min.)				
Vinyl ester resin I	28	18	32	16
Vinyl ester resin II	15	10	22	12

Long gel times of several hours, which can be necessary for filament winding operations, can easily be obtained by the extra addition of Promotor C as inhibitor.addition of Promotor C as inhibitor.

Vinyl ester resin	100	100	100	100	100	100
Trigonox 239 VR	2	2	2			
Butanox LPT-IN				2	2	2
Accelerator NL-51PN	0.5	0.5	0.5	0.5	0.5	0.5
Promotor C		0.1	0.3	0.1	0.3	
Gel time at 20°C (min.)						
Vinyl ester resin I	28	90	260	32	90	360
Vinyl ester resin II	15	120	400	22	90	390

Cure of 1 mm pure resin layer at 20°C

Cure experiments have been performed in 1 mm pure resin layers at 20°C.
The development of the hardness is expressed as the time to reach a Persoz hardness of 60 and 120 s. respectively.

Vinyl ester resin I	100	100		
Vinyl ester resin II			100	100
Trigonox 239 VR	2		2	
Butanox LPT-IN		2		2
Accelerator NL-51PN (6% Cobalt)	1	0.5	1	0.5
N,N-Dimethyl aniline		0.1		0.1
Gel time at 20°C (min.)	18	16	10	12

Time to reach a Persoz hardness of

60 s. (hours)	1.25	1.75	<<1	<<1
120 s. (hours)	1.75	2.50	<1	<1

Residual styrene contentafter a cure time at 20°C of

24 hours (%)	7.7	10.5	1.2	4.4
4 weeks (%)	4.0	6.2	0.6	2.3
4 weeks + 8 h 80°C (%)	0.1	0.1	0.1	0.1

Cure of 4 mm laminates at 20°C

4 mm laminates have been made with a 450 g/m2 chopped strand mat. The glass content in the laminates is 30% (w/w).

The following parameters were determined:

- Time-temperature curve.
- Speed of cure expressed as the time to achieve a Barcol hardness (934-1) of 0-5 and 25-30 respectively.
- Residual styrene content after 24 h at 20°C and a subsequent postcure of 8 h at 80°C.

Vinyl ester resin I	100	100		
Vinyl ester resin II			100	100
Trigonox 239 VR	2		2	
Butanox LPT-IN		2		2
Accelerator NL-51PN (6% Cobalt)	1	0.5	0.5	0.3
N,N-Dimethyl aniline		0.1		0.1

Time temperature curve

Gel time	(min.)	27	32	16	15
Time to peak	(min.)	99	88	35	21
Peak exotherm	(°C)	43	38	68	122

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0 5 (hours)	1.5	2.5	<1	<1
25-30 (hours)	5	30	<1	<1

Residual styrene content

after a cure of 24 h at 20°C (%)	7.0	8.0	1.8	1.0
plus a postcure of 8 h at 80°C (%)	0.12	0.25	0.2	0.4

Cure of 10 mm laminates at 20°C

10 mm laminates have been made with a 450 g/m2 chopped strand mat. The glass content in the laminates is 30% (w/w).

The following parameters were determined:

- Time-temperature curve.
- Speed of cure expressed as the time to achieve a Barcol hardness (934-1) of 0-5 and 25-30 respectively.
- Residual styrene content after 24 h at 20°C and subsequent postcure of 8 h at 80°C

Vinyl ester resin I	100	100		
Vinyl ester resin II			100	100
Trigonox 239 VR	2		2	
Butanox LPT-IN		2		2
Accelerator NL-51PN (6% Cobalt)	0.25	0.15	0.2	0.2
N,N-Dimethyl aniline		0.05		0.15
Gel time at 20°C (min.)	44	45	30	30

Time temperature curve

Time to peak	(min.)	243	125	59	34
Peak exotherm	(°C)	35	62	130	160

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after a cure time of 24 hours	28	24	48	48

Residual styrene content

after a cure time of 8 days at 20°C (%)	6.1	5.8	0.3	0.1
plus a postcure of 8 h at 80°C (%)	0.1	0.8	0.3	0.1

Time temperature curves

Time temperature curves have been determined at 20°C in 30 mm and
50 mm thick castings, with a diameter of 100 mm, based on a 1:1 mixture of vinyl ester resin/quartz flour.

The results can be used as an indication for the cure characteristics of thick laminates.

Vinyl ester resin I	100	100		
Vinyl ester resin II			100	100
Quartz flour	100	100	100	100
Butanox LPT-IN	2		2	
Trigonox 239 VR		2		2
Accelerator NL-51PN (6% Co)	0.2	0.5	0.2	0.2
N,N-Dimethyl aniline (DMA)		0.1		0.5
Gel time in the pure resin (min.)	30	30	28	30

30 mm thick castings
Time-temperature curve

Gel time	(min.)	21	19	17	24
Time to peak	(min.)	69	100	24	42
Peak exotherm	(°C)	113	89	144	130

50 mm thick castings
Time-temperature curve

Gel time	(min.)	14	17	17	28
Time to peak	(min.)	59	70	29	49
Peak exotherm	(°C)	136	110	150	130

- Gel time in 15 gram pure resin.
- Time-temperature curves in resin/quartz flour mixtures.

Pot life at 20°C

The pot life of a mixture peroxide/vinyl ester resin will vary considerably with the temperature, the peroxide addition level, the type of the vinyl ester resin involved and the batch size. The following indication for the pot life at 20°C in a 25 kg batch of non preaccelerated vinyl ester resin can be given.

Vinyl ester resin	100	100	100	100
Trigonox 239 VR	2	4		
Butanox LPT-IN			2	4

Pot life at 20°C (days)

Vinyl ester resin I	30	23	5	3
Vinyl ester resin II	25	17	2	1

Trigonox K-90

Trigonox K-90 may be used as an initiator for the room temperature cure of promoted unsaturated polyester and vinyl ester resins, and elevated temperature cure of non-promoted resins.

Additional end-use information is available in various application guides or directly from your Nouryon representative.

Colors

Trigonox K-90 is also available in the color red.

Contact us

For product inquiry and ordering information, please contact your Nouryon account manager or regional Nouryon sales office.

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Additional information

Product Data Sheets (PDS) and Safety Data Sheets (SDS) for our polymerization initiators are available at www.nouryon.com

Nouryon

Nouryon is a global, **specialty chemicals** leader. Markets and consumers worldwide rely on our essential solutions to manufacture everyday products, such as personal care, cleaning goods, paints and coatings, agriculture and food, pharmaceuticals, and building products. Furthermore, the dedication of more than 9,700 employees with a shared commitment to our customers, **business growth**, safety, **sustainability** and innovation has resulted in a consistently strong financial performance. We operate in over 80 countries around the world with a portfolio of industry-leading brands. Visit our **website** and follow us **@Nouryon** and on **LinkedIn**.

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