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## TECHNICAL BULLETIN

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# FORMULATING ANHYDRIDE-CURED EPOXY SYSTEMS

## Introduction

Dixie Chemical Company makes a range of alicyclic anhydrides which are highly suitable for curing epoxy resins. These anhydrides include:

- Tetrahydrophthalic anhydride (THPA)
- Hexahydrophthalic anhydride (HHPA)
- Methyltetrahydrophthalic anhydride (MTHPA)
- Methylhexahydrophthalic anhydride (MHHPA)
- Nadic® methyl anhydride (NMA)
- Formulated blends of these materials

Details about each of these are found in specific Product Technical Bulletins which are available from Dixie Chemical Company.

These anhydrides are commonly used to cure epoxy resins in many challenging applications, including fiber reinforced composites used in high performance aerospace and military applications, as well as mechanically demanding applications like filament wound bearings. They also provide excellent electrical properties for use in high voltage applications, as well as in encapsulating electronic components and circuits.

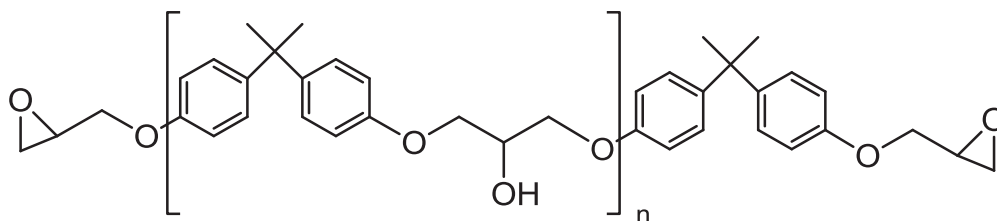
Properties of a cured epoxy resin depend on the starting epoxy resin, the curing agent, the accelerator, the ratio of curing agent to resin, the curing time and curing temperature, and the post-cure times and temperatures. No one formulation or one set of process conditions will yield a cured resin having optimum values for all properties. Therefore, it is necessary to determine the desired properties for the intended end use before choosing a formulation. In general, greater cross linking of the resin raises the heat distortion temperature (HDT), hardness, and chemical resistance, but lowers the impact resistance and flexural strength of the cured product. The following sections discuss the factors which influence performance.

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#### Epoxy Resins

Anhydrides are most commonly used to cure bisphenol A epoxy resins, with the general structure:



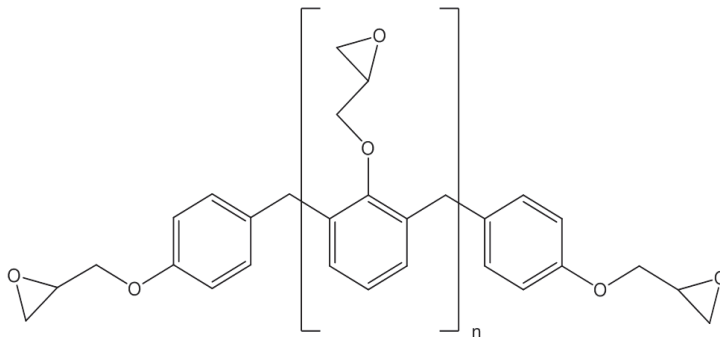
Liquid epoxy resins with “n” values generally between 0.06-0.12 and epoxy equivalent weight of about 178-192 are commonly chosen for their moderate viscosity and good processing characteristics. Typical commercial examples of such liquid epoxy resins include:

<b>Dow Chemical Company</b>	D.E.R. <sup>™</sup> 330 D.E.R. 331 D.E.R. 332	D.E.R. 383 D.E.R. 317
<b>Huntsman Advanced Materials</b>	GY-240	GY-250
<b>(Araldite<sup>®</sup>)</b>	GY-260	
<b>Kukdo</b>	YD-128	
<b>Momentive Specialty Chemicals</b>	EPON <sup>™</sup> 826	EPON 828
<b>NanYa</b>	NPEL-128	NPEL-127
<b>Reichhold (EPOTUF<sup>®</sup>)</b>	37-140	
<b>Spolchemie</b>	CHS-520	CHS-530

Anhydrides may also be used to cure higher molecular weight solid epoxy resins with higher “n” values and higher epoxy equivalent weight.

Anhydrides give excellent high temperature performance, and have been formulated with multifunctional resins such as epoxy phenol novolacs to get high levels of crosslink density and maximum performance properties at high temperature. These epoxy phenol novolacs have the generalized structure:

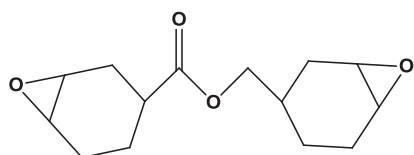
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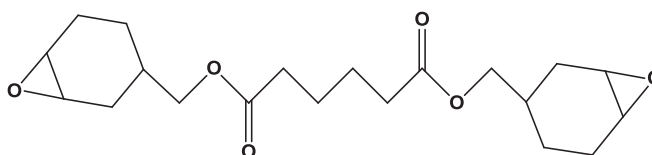
Typical commercial examples of such epoxy phenol novolac resins include:

<b>Dow Chemical Company</b>	D.E.R. <sup>TM</sup> 354 D.E.N. 439	D.E.N. <sup>TM</sup> 431 D.E.N. 439
<b>Huntsman Advanced Materials (Araldite®)</b>	EPN-1179 EPN-1183	EPN-1180 GY-289
<b>Momentive Specialty Chemicals</b>	EPON <sup>TM</sup> 154 EPON 160	EPON 162

Anhydrides give excellent electrical properties when formulated with bisphenol A epoxy resins or epoxy phenol novolacs. This performance has been extended to the cure of cycloaliphatic epoxy resins for encapsulating high performance electronic components, including light emitting diodes. Examples of these cycloaliphatic epoxies are provided below:

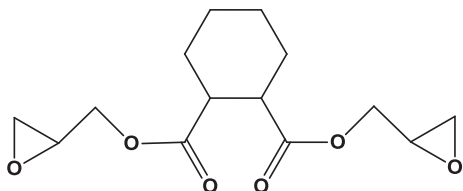


3,4-epoxycyclohexylmethyl-  
 3',4'-epoxy  
 cyclohexanecarboxylate

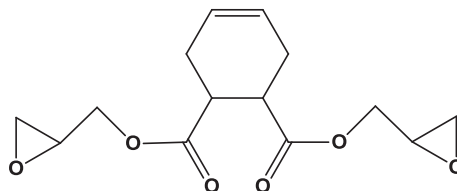


Bis(3,4-epoxycyclohexylmethyl) adipate

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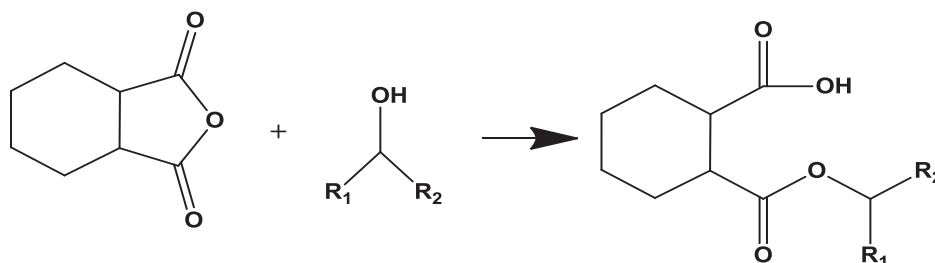
diglycidyl ester of  
hexahydrophthalic acid



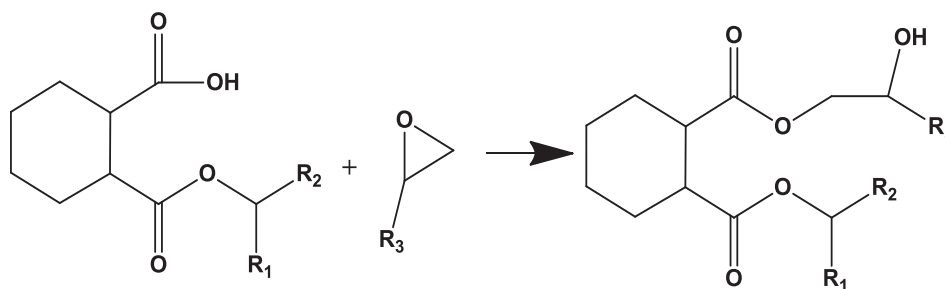
diglycidyl ester of tetrahydrophthalic acid

### Cure Chemistry

In curing an epoxy resin, an anhydride group reacts with an aliphatic hydroxyl to give an ester group and a free carboxylic acid. This is shown here using HHPA:



The free carboxyl group reacts with an epoxy group in the following way to give an  $\alpha$ -hydroxy ester:



Bisphenol A epoxy resins have low levels of aliphatic hydroxyls to initiate cure with anhydrides. Also, every time a carboxylic acid group reacts with an epoxy group, another aliphatic hydroxyl is created, and is then available to react with another anhydride group.

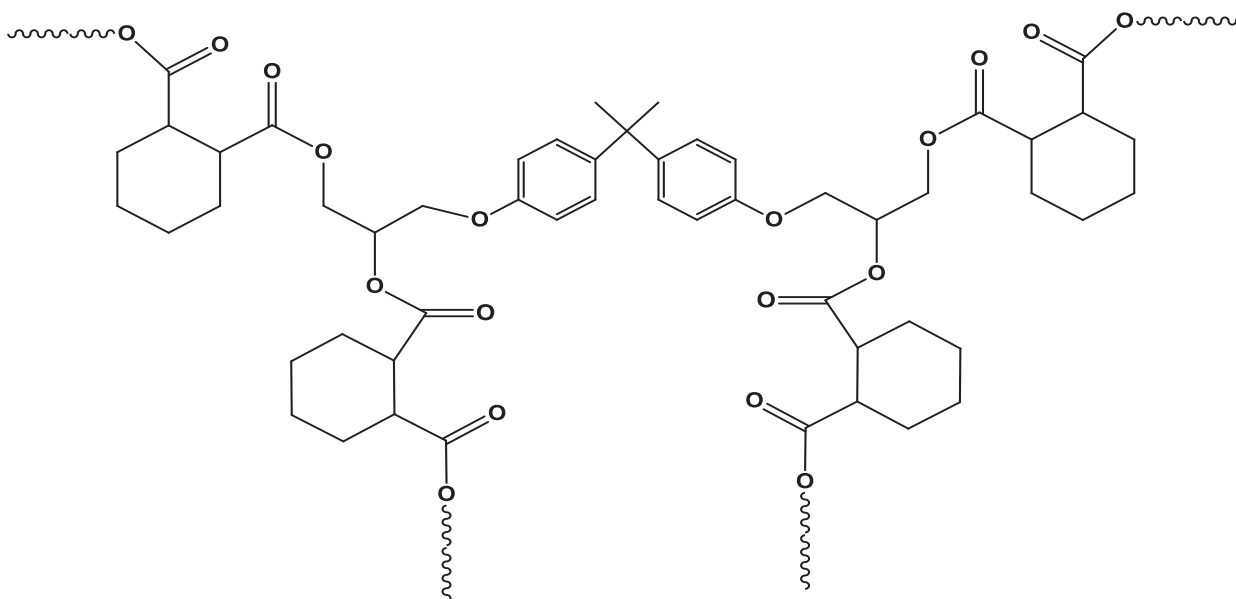
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In addition, commercial anhydrides have very low levels of residual carboxylic acid. These acid groups can react with epoxy groups to initiate cure and to create more aliphatic hydroxyl groups to cure with anhydride groups.

It can be seen that the ideal stoichiometry of the anhydride cured epoxy is one mole of anhydride per mole of epoxy.

The idealized structure for a bisphenol A epoxy resin cured with an anhydride can be represented as follows, using HHPA as the example:

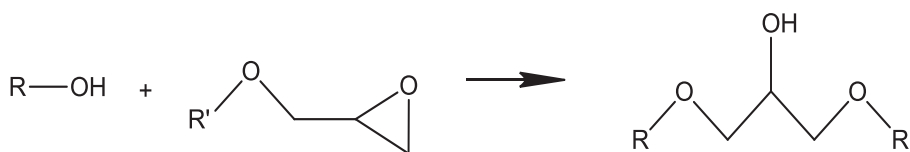


It will be noted that each epoxy molecule is connected to about four anhydride molecules and each anhydride molecules is connected to two epoxy molecules. This provides a high crosslink density which gives the excellent performance of epoxies cured with these alicyclic anhydrides.

## Side Reactions

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An important side reaction is homopolymerization of the epoxy, as shown in the following mechanism:



This reaction consumes epoxy which is otherwise needed to react with acid from the anhydride. It is acid or base catalyzed, so either free acid from the anhydride, or base accelerators can promote it. It is a significant side reaction for either under-catalyzed systems or for systems that are over-catalyzed with strong base accelerators. So when evaluating a range of accelerator levels, one typically finds an optimum accelerator level for particular physical performance properties like glass transition temperature, heat distortion temperature, tensile modulus, etc.

### Cure Accelerators

In curing an epoxy with an anhydride, cure accelerators are generally used to speed the cure process and to achieve desired performance characteristics. Various materials may be used to catalyze the reaction between anhydrides and epoxies. Tertiary amines are effective accelerators. Commonly used examples are benzyldimethylamine (BDMA), dimethylaminomethylphenol, 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30 from Dow Chemical or Ancamine K-54 from Air Products), and 1,4-diaza bicyclo[2.2.2]octane, and 1,8-diazabicyclo[5.4.0]undec-7-ene.

Liquid imidazoles are also frequently used to catalyze anhydride-epoxy reactions. Commonly used imidazoles include 2-ethyl-4-methyl imidazole, 1-methyl imidazole, 1-benzyl-2-methyl imidazole, etc.

Tertiary amines and imidazoles generally give significant amber or brown color to cured systems.

Quaternary ammonium salts, like benzyltrihexammonium chloride (BTEAC), benzyltrimethyl ammonium chloride (BTMAC), or tetrabutyl ammonium bromide (TBABr) can be used, but since they are solid salts, they must be

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dissolved in a suitable liquid like ethylene glycol or methanol so that they can be adequately mixed into a liquid anhydride. Quaternary ammonium salts have the advantage that they promote lower color cures.

Dixie Chemical Company makes a liquid blend of 60% BTEAC and 40% ethylene glycol. Named AP-6G, this liquid can be easily and conveniently dispersed in liquid epoxy-anhydride blends. AP-6G imparts good glass transition temperature (T<sub>g</sub>) and extended pot life to anhydride/epoxy formulations, and allows the production of relatively low color polymers.

Organometallic salts based on tin, zinc, or chromium can also be used. The chromium salts are generally green and give a significant green color to the epoxy-anhydride matrix. Tin and zinc salts can give relatively colorless cures.

#### **Preparing the Curing Agent/Accelerator Mixture**

The sequence of mixing can have a marked effect on the properties of the cured epoxy resin. Direct addition of an amine catalyst to the anhydride is not recommended. If the accelerator is added to the anhydride before the resin, a darker color may result. To obtain the best properties, the following procedure is recommended:

#### **Mixing method**

- a) Mix anhydride and epoxy resin.
- b) Add the accelerator.
- c) Mix until completely uniform.

#### **Anhydride Level**

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The amount of anhydride in the formulation is generally expressed in parts per hundred parts of epoxy resin (phr). To calculate the amount of anhydride required, use the following equation:

$$\text{Anhydride, phr} = (100/\text{EEW}) \times \text{AEW} \times \text{A/E}$$

Where:

EEW = epoxy equivalent weight

AEW = anhydride equivalent weight.

A/E = ratio of anhydride equivalent to epoxide equivalent. As noted above, the ideal stoichiometry is 1:1, but the optimum value for this may be in the range of 0.90-0.95 to account for side reactions such as the one discussed above which also consumes epoxy. This is best determined by experimentation, where formulations are prepared which vary from the 1:1 stoichiometry. Key performance characteristics are evaluated for each formulation to identify the optimum A/E ratio for the performance properties of interest.

### Cure Cycle

Curing an epoxy resin may be carried out in one or more stages depending on the rate of reaction and the exotherm of the mixture. Better control can be achieved by curing at a lower temperature. A slow initial cure followed by a post-cure at a higher temperature usually yields the best results. Using this approach allows the reaction to proceed more slowly and the associated exotherm to be lower. This results in better color and fewer stresses in the cured epoxy resin.

The post-cure anneals the resin thus relieving any stresses which may be present after the initial cure.

The cure cycle used has a dramatic effect on system performance. This cure cycle includes the initial time and temperature used to cure the formulation, as well as all post-cure times and temperatures used to improve performance properties. This is important because longer cure times and higher cure temperatures promote increases in crosslinking. Higher crosslinking results in higher levels of mechanical strength and chemical resistance.



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A typical cure cycle for curing liquid epoxy resins is 2 hours at 90° C, plus 4 hours at 165° C, plus up to 16 hours at 200° C.

#### **Handling Precautions**

Read and understand the relevant Material Safety Data Sheets (MSDS) for all products before use. These anhydrides are primary skin and eye irritants. Avoid contact with skin, eyes, and clothing. Use only with adequate ventilation. In case of contact, follow the procedures outlined in the MSDS. Generally, these procedures include immediately flushing the affected skin or eyes with copious amounts of water for at least 15 minutes. In the case of eye contact, get medical attention. Wash contaminated clothing before reuse.

Follow the recommendations in the MSDS for personal protective equipment when handling these materials. At a minimum, these procedures typically include protective chemical goggles, impenetrable gloves, and measures to avoid breathing chemical vapors.