CYTEC

TECHNICAL BULLETIN Specialty Additives

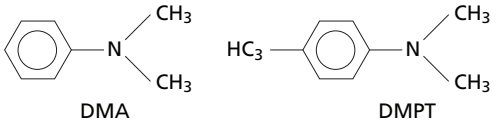
Alkyl Anilines As Accelerators/Promoters For Unsaturated Polyester Resins

Introduction

Cytec offers two alkyl aniline products that function as accelerators and promoters for unsaturated polyester resins. The products are N,N - dimethylaniline (DMA) and N,N- dimethyl-paratoluidine (DMPT). These products promote and accelerate the decomposition of organic peroxide polymerization catalyst at low or ambient temperatures. This controlled generation of these polymerization catalyst allows the curing and gelling of the polyester resin to be manipulated, leading to increased work life of the resin and a final product with optimal chemical and physical properties.

Physical And Chemical Properties

The chemical structures, nomenclature, general characteristics and properties of the alkyl aniline products are as follows:



DMA DMPT

Characteristics and Properties

Product	DMA	DMPT
Name	N,N - dimethylaniline	N,N- dimethyl-paratoluidine
Appearance	Clear pale yellow liquid	Clear yellow oily liquid
Empirical Formula	$C_8H_{11}N$	$C_9H_{13}N$
Molecular Weight	121	135
Boiling Point (°C)	192.8	211
Specific Gravity @ 25°C	0.954	0.937
Vapor Pressure (mm Hg)	1 @ 30°C	No data
Solubility	Soluble in aromatics, alcohols, acetone and insoluble in water	Soluble in aromatics, alcohols, acetone and insoluble in water
Strength (by difference)	99% minimum	99% minimum

Features And Benefits

Features	Benefits
1. Nitrogen atoms in the molecule activate peroxide catalyst at ambient or low temperatures	Induces the controlled generation of free radicals from organic peroxides initiating polymerization of the resin Reduces energy requirements
2. Facilitates controlled generation of organic peroxide free radicals	Yields acceptable resin gel times, assists in controlling workable life of resin and yields a final product with optimal properties
3. Chelating capability	Forms multiligand complexes with cobalt salts that increase shelf life stability and enhance reactivity, whilst imparting minimal color to final product
4. Liquid form	Soluble in organics, easily added to formulation
5. Low cost	Economical

Technology

A. Unsaturated Polyester Resins and Markets

Unsaturated polyester resins are extremely versatile in properties and applications. These resins can be rigid, resilient, flexible, corrosion resistant, weather resistant or flame retardant. They can also be filled, reinforced and pigmented. The unsaturated polyester resins can be used by the fabricator at ambient or elevated temperatures. Some typical applications of unsaturated polyester resins include automotive and appliance parts, boats, shower stalls, recreational vehicles, mining bolts, coatings and corrosion resistant tanks.

A commercial unsaturated polyester resin consists of an unsaturated polyester dissolved in a crosslinking monomer. The unsaturated polyester resin is the condensation product of an unsaturated dibasic acid (usually maleic anhydride) and a glycol. Common crosslinking monomers include styrene, its derivatives and methyl methacrylate. The degree of unsaturation of the polyester, the crosslinking monomer and other ingredients are all critical in determining the end properties of the resin. The formulation also must contain an inhibitor to prevent crosslinking of the resin, until it is used by the fabricator.

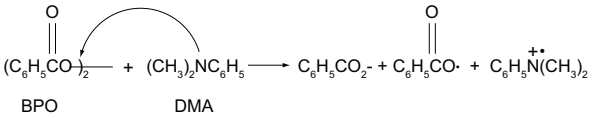
B. Role of Alkyl Amine Accelerators in the Manufacture of Unsaturated Polyester Resins

In the production of unsaturated polyester resins, the initiation of polymerization is achieved through the usage of peroxide catalysts. Control of radical generation and polymerization is critical so as to insure adequate time for working the resin and achieving optimal properties. These catalyst can be activated by heat, multivalent metal accelerators or tertiary aromatic amine promoters, all of which decompose the peroxides into free radicals.

The alkyl aniline products fall into the class of compounds known as the amine promoters and are primarily used at ambient and low temperatures to assist in the decomposition and activation of the organic peroxide catalyst. Benzoyl peroxide (BPO), methyl ethyl ketone peroxide (MEKP) and cumene hydroperoxide (CuHP) represent typical catalyst activated by the alkyl aniline products. Dependent upon the particular resin and conditions, the alkyl aniline products may be used alone or in conjunction with a cobalt napthenate or octoate accelerator.

The chemical mechanism for the amine acceleration of peroxide catalyst has been determined and can be represented as follows:

Chemical Mechanism for the Low and Ambient Temperature Amine Acceleration of Peroxide Polymerization Catalyst (DMA and Benzoyl Peroxide)



According to this mechanism, free radical initiation proceeds from both the benzoyl and amine species. The speed of cure obtained with peroxide and alkyl aniline derivatives, makes these systems ideal for two component applications at ambient or below room temperature. Additionally, in select systems, it is common practice to use the alkyl anilines in combination with cobalt napthenate and cobalt octoate accelerators. In these systems, the alkyl anilines will form multiligand complexes with the cobalt salts, which also lead to better control of the polymerization process and the production of high quality resin products.

Alkyl Aniline Applications In Unsaturated Polyesters

The alkyl aniline products are used in unsaturated polyester resins to promote and accelerate the decomposition of organic peroxide catalyst at ambient or low temperatures so as to initiate polymerization of the resin. Dependent upon the unsaturated polyester resin formulation, manufacturing conditions and desired end properties, the fabricator has a multitude of choices regarding the catalysts, accelerators and promoters.

Recommendations regarding catalysts, accelerators and promoters and their performance in select unsaturated polyesters resins are commonly available from resin manufacturers. The following examples provide some information and guidelines regarding the use and performance of the alkyl aniline promoters in combination with various catalysts and accelerators in resins.

A. Influence of DMA on Gel Times of Epoxy Vinyl Ester Resins

Table 1 demonstrates the effect of DMA on the gel times of an epoxy vinyl ester. The catalyst is BPO.

Table 1 – Effect of DMA on Gel Times of an Epoxy Vinyl Ester Resin

	Temperature		
	15°C	25°C	35°C
Gel time (minutes)	DMA	DMA	DMA
15	0.30	0.25	0.125
30	0.15	0.125	0.075
60	0.075	0.05	0.025

DMA loadings in phr. BPO catalyst loading was 2.5, 2.0 and 1.25 phr respectively at each temperature.

B. Usage of DMA to Achieve a Select Gel Time in Urethane Modified Vinyl Ester Resins

The gel times of urethane modified vinyl ester resin systems can be controlled and enhanced through the addition of DMA. Table 2 below demonstrates the effect of DMA, when used in conjunction with cobalt napthenate and MEKP (methyl ethyl ketone peroxide) in a urethane modified vinyl ester resin.

Table 2 – 35 Minute Gel Times @ Various Temperatures in a Urethane Modified Vinyl Ester Resin Through the Usage of 0.1% DMA

Temperature (°C)	DMA (%)	Cobalt Napthenate (%)	MEKP (%)
5	0.20	0.7	2.4
10	0.10	0.6	1.8
15	0.10	0.6	1.8
25	0.10	0.4	1.2
30	0.10	0.2	0.9

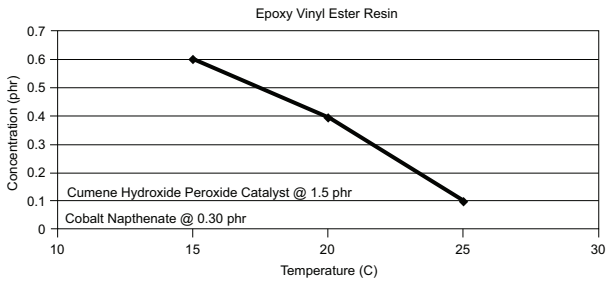
DMA, Cobalt Napthenate and MEKP added on a phr basis.

It is additionally noted that as in Table 1, differing gel times for each respective temperature, could have been achieved through the incorporation of varying amounts of DMA.

C. Impact of DMA on Gel Times of Cumene Hydroperoxide Catalyst in a Vinyl Ester Resin

The graph below details the concentration of DMA required in combination with a cumene hydroperoxide catalyst and cobalt napthenate accelerator to achieve a 15 minute gel time at various temperatures in a epoxy vinyl ester resin.

Concentration of DMA Required at Various Temperatures to Achieve a 15 Minute Gel Time



D. Impact of DMPT on the Low and Ambient Temperature Cure of Vinyl Ester Resins

The addition of 0.1 to 0.5 phr of DMPT, in conjunction with either a benzoyl or methylethyl ketone peroxide catalyst and cobalt napthenate accelerator will accelerate the cure of vinyl ester resins at low and ambient temperatures.

Markets And Recommendations

Both manufacturers of unsaturated polyester resins and fabricators should consider the use of alkyl aniline products to promote the controlled generation of organic peroxide free radicals at ambient and low temperatures to control polymerization, extend workable lifetimes of the resin and achieve optimal resin properties.

Usage Guidelines for Alkyl Aniline Accelerators/ Promoters in Unsaturated Polyester Resins

Temperature Range	Catalyst	Alkyl Aniline Promoter
5 to 40°C	BPO, MEKP or CuHP	0.10 to 0.50 phr DMA or DMPT

Typical usage levels would range between 0.1 and 0.5 phr resin. The choice of catalyst, processing conditions and temperatures also will influence and impact accelerator/promoter levels. Formulations should be tested on a small scale prior to actual commercial usage as many factors can influence performance.

Safety And Toxicity Information

These alkyl aniline products are hazardous materials, and necessary precautions must be taken when working with these products. Please refer to the Material Safety Data Sheet for information on safety and toxicity.

Alkyl aniline promoters should be added to the resin prior to and separate from the catalyst. The promoters must be thoroughly mixed into the resin. The catalyst initiators and alkyl anilines should never be mixed together directly, as violent decomposition may occur.

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