

PRODUCT TECHNICAL BULLETIN

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**TETRAHYDROPHTHALIC ANHYDRIDE
(THPA)
[4-cyclohexene-1, 2 dicarboxylic acid, anhydride (cis)]
CAS Reg. No. 85-43-8
REACH 01-2119486679-14-0001**

Typical Properties

Characteristic	Test Method	Typical
Molecular Weight		152.1
Specific Gravity (molten)	D-102	1.20
Appearance	D-104 (Visual)	Solid white flakes
Color (APHA)	D-103	80 max.
Melting Point (°C)	D-134	99-101
THPA %	D-161	>99

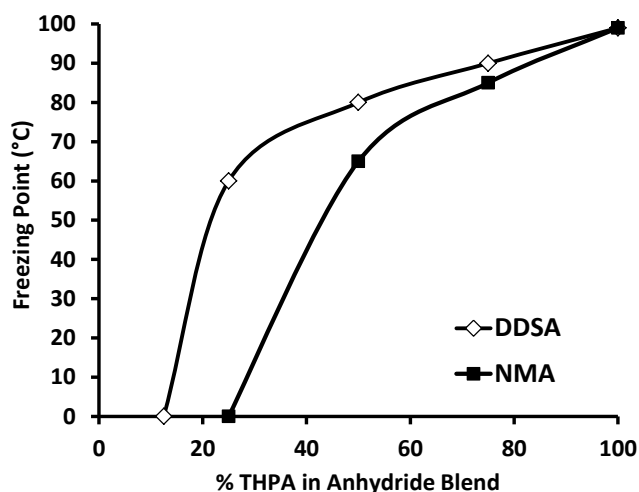
Volatility

Vapor Pressure (mm Hg)		< 0.01 at 20°C 50 at 195°C
Vapor Density (Air = 1)		
Flash Point	ASTM D93	149°C
Autoignition Temperature	ASTM E659	

Anhydride Mixtures

THPA is a relatively high melting solid. However, it may be blended with other anhydrides to facilitate handling by lower the melting point. Blends can be made with liquid anhydrides, such as dodecenylsuccinic anhydride (DDSA) or NADIC® methyl anhydride (NMA). The following graph shows the freezing points of such blends.

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The following table summarizes the eutectic temperatures for binary pairs of anhydrides which include THPA.

% THPA	Other Anhydride	Temperature (°C)
15	Hexahydrophthalic	26
30	Maleic	38
65	Succinic	75
65	Phthalic	79

Epoxy Curing Agent

For more information on the use of anhydrides like THPA as epoxy curing agents, please consult the Technical Bulletin, FORMULATING ANHYDRIDE-CURED EPOXY SYSTEMS, available from Dixie Chemical Company.

Resin Building Block

Alkyd resins can be conveniently divided into three major groups:¹

- (1) Convertible, drying oil-nonreactive resins
- (2) Nonconvertible resins
- (3) Convertible, drying oil-reactive resins

The first of these groups, which could appropriately be called phthalic alkyd resins, comprises about 80% of all alkyds manufactured. Such alkyds are manufactured by the reaction of phthalic anhydride (including modifications in which other polybasic acids are substituted in minor proportions for phthalic) and

¹ W H. Gardner; Paint and Varnish Production, 28-31, 76, Februarv, 1954

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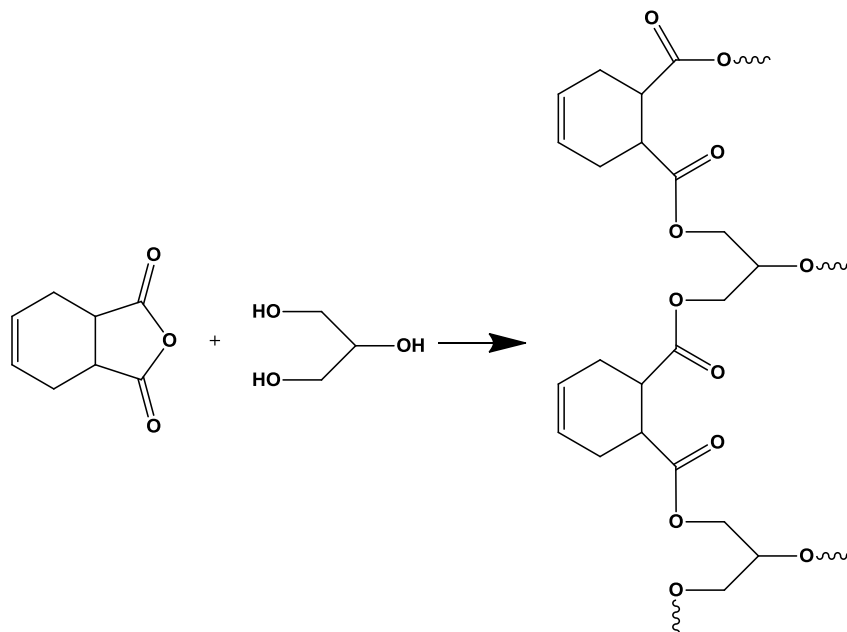
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fatty acids or rosin with polyhydric alcohols and the subsequent incorporation of drying oils.

The second group is obtained by the incorporation of reactants containing two and only two active groups in their molecular structure. Usually a saturated dihydric alcohol, such as glycol, is reacted with a dibasic acid such as phthalic anhydride and further modified with fatty acids and/or non-drying or semi-drying oils.

The third group could be correctly termed maleic alkyd.² Such resins, by definition, require that any polybasic acid or anhydride used in their manufacture contain an unsaturated hydrocarbon group. The presence of the unsaturated group lends itself to a high degree of cross-linking yielding essentially thermosetting resins. These three groupings for alkyd resins are well known in the trade and are only repeated to add clarity to the use of tetrahydrophthalic anhydride in these groups.

It has been reported that tetrahydrophthalic anhydride contains a relatively unreactive double bond.³ It would, therefore, appear to be quite practical to substitute tetrahydrophthalic anhydride for phthalic anhydride in groups (1) and (2) above. The reaction between tetrahydrophthalic anhydride and glycerol yields the following:



² W. H. Gardner; Enc. Chem. Tech. 1,517 (1947).

³ C. Cosgrove & K. A. Earheart, Ind. Eng. Chem. 41, 1492 (1949).

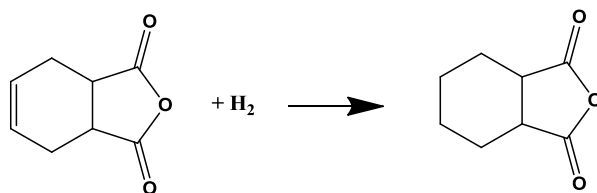
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Resins with better initial color, better color retention⁴ and better adhesion can be obtained with THPA than can be obtained with phthalic anhydride. It has also been found that better initial resin color can be obtained without the use of carbon dioxide or other inert atmospheres in recipes where THPA is substituted for phthalic anhydride. In some recipes, insolubles may be formed. This problem can be avoided by first preparing the glycerol half ester of THPA, subsequently reacting this half ester instead of the anhydride, and then adding the fatty acid to the cook.

The lower melting point of THPA (100°C) as compared to phthalic anhydride (131°C) should help minimize melt time in batch reactions.

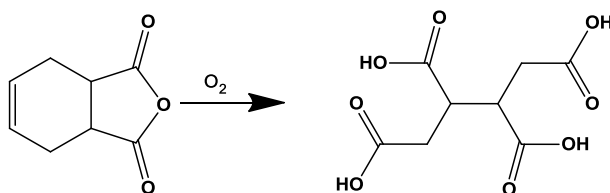
Hexahydrophthalic anhydride can be prepared by direct hydrogenation of tetrahydrophthalic anhydride.⁵



Resins prepared from hexahydrophthalic anhydride show excellent initial color, and excellent color retention without the use of inert atmospheres.

Adducts of tetrahydrophthalic anhydride containing halide groups are possible where fire retarding properties are desired in paints and plastics.⁶

Tetrahydrophthalic anhydride can be oxidized in practically 100% yields to butane-1,2,3,4-tetracarboxylic acid.⁷



Component of Polyester and Styrene Resins

Polyesters are the reaction product of polybasic acid(s) and polyhydric alcohol(s) to form a series of ester linkages, without modification with fatty acids. The

⁴ W. H. Gardner, Am. Paint Jour. 37 No. 28, 56 (1953)

⁵ E. F. Jenkins and E. J. Costello, J.A. C. S-, 68, 2733 (1946).

⁶ R.S. Wilder and G.D. Martin, U.S. Patent 2,550,744 (May 1, 1951).

⁷ E. H. Farmer, and F. L. Warren, J. Chem. Soc., 897 (1929).

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definition does not exclude modification of the polyesters with vinyl monomers. Three applications are included below:⁸

- (1) Unsaturated Polyesters
- (2) Fibers and Films
- (3) Polyester Foams

The first group includes the reaction product of maleic anhydride and phthalic anhydride with polyols. The maleic unsaturation is retained in part in the resin, allowing reaction, and consequently cross-linking, with vinyl monomers such as styrene.^{9,10} The second group includes the well-known Dacron® fiber and Mylar®.¹¹ The third group includes polyesters with a high concentration of hydroxyl groups which are cross-linked with isocyanates to form foams, coatings, etc.

Tetrahydrophthalic anhydride can be used to advantage in the first group as a substitute for phthalic anhydride. As was the case with the alkyd or coating resins, such a substitution results in excellent initial color and color retention in the polyester. The use of a replacement for phthalic anhydride in polyesters yields an exceedingly large number of possible combinations for preparing resins of different properties.¹² A typical reaction for the preparation of an unsaturated polyester might involve maleic and phthalic anhydrides co-esterified with glycols and cross-linked with styrene. It is reported that phthalic anhydride can be entirely replaced with tetrahydrophthalic anhydride to yield better initial color and color retention in such a formulation.^{13,14} Where greater reactivity and cross-linking is desired, the styrene may be replaced with diallyl tetrahydrophthalate,¹⁵ with diallyl chloro tetrahydrophthalate for greater fire resistance, or with triallyl cyanurate for heat resistance.¹⁶ The latter method reportedly results in flexural strengths of two to three times values previously obtained with laminating resins.

Hard baking enamels can be formed from linear polyester containing tetrahydrophthalic anhydride and amino resins (urea formaldehyde or melamine formaldehyde resin) or a polyisocyanate. This coating has excellent flexibility, corrosion, and soiling resistance.¹⁷

⁸ J. R. Lawrence; "Polyester Resins," Chapter 1, Reinhold Publishing Corp., New York, 1960.

⁹ W. H. Gardner, Am. Paint Jour. 37 No. 28, 56 (1953)

¹⁰ E. M. Beavers, "Basic Chemistry of the Polyester Laminating Resins," Paper at 4th Annual Meeting of Reinforced Plastics Div., SPI, Chicago, 1949.

¹¹ DuPont trademarks

¹² K. V. McCullough, J. Wynstra, and R. B. Waters; Off. Digest, Fed. Paint & Varnish Prod. Clubs No. 329, 396 (June 1952).

¹³ W. H. Gardner, Am. Paint Jour. 37 No. 28, 56 (1953)

¹⁴ H. J. Gehart U.S. Patent 2,479,486 (Aug. 16, 1949)

¹⁵ R. J. Agnew, U. S. Patent 2,584,315 (Feb. 5, 1952)

¹⁶ Seventh Annual Tech. Session; Soc. Plastics Ind., Chicago, April, 1952.

¹⁷ Yoichi Murakami, et. al., Ger. Offen. 2103,117 (Aug. 3, 1972)

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Component of Plasticizers

There are several interesting plasticizers which can be made from tetrahydrophthalic anhydride. The following table indicates some of these:

Use	Anhydride	Ester
Vinyl	THPA	dialkyl ¹⁸
Vinyl	HHPA	bis-2-ethylhexyl
Vinyl	THPA	3,5,5-trimethylhexyl ¹⁹
Cellulose	THPA	bis(alkoxyethyl) ²⁰
Vinyl, etc.	THPA	(2-ethylhexyl)-4,5-epoxy ²¹
Vinyl, etc.	THPA	di(isodecyl)-4,5-epoxy ²¹

A number of patents have been received over the years for the epoxy derivatives of tetrahydrophthalic anhydride.^{21,22,23,24,25} The last two plasticizers in the previous table reportedly are designed for use where the plastic is subjected to considerable weathering. Likewise, they are said to have excellent compatibility with vinyl chloride resins at concentrations up to 70 parts plasticizer per 100 parts resin. Further reports indicate that mixed polyesters of tetrahydrophthalic acids make excellent plasticizers with good light stability and non-migration properties.

Butyl and other monoesters of tetrahydrophthalic anhydride, neutral esters of maleic anhydride, and vinyl chloride give resins with good adhesion to metal surfaces²⁶. Benzyl C4-C20 alkyl esters of tetrahydrophthalic anhydride, hexahydrophthalic anhydride, and himic acid have been used as plasticizers for polyvinyl chloride. The softening temperature and color were improved over the use of phthalic esters.^{27,28}

¹⁸ S.A. Miller, U.S. Patent 2,478,299 (Aug. 9, 1949).

¹⁹ Seventh Annual Tech. Session; Soc. Plastics Ind., Chicago, April, 1952.

²⁰ H. J. Barrett and E.F. Izard, U.S. Patent 2,063,144 (Dec. 8, 1937).

²¹ "Epoxy Assists for Vinyls," Chem Week.56, May 9,1959.

²² F. P. Greenspan, and R. E. Light, U.S. Patent 2,929,130 (April 1, 1958).

²³ R. H. Reiff, U.S. Patent 2,928,805 (March 15, 1960).

²⁴ S.O. Greenlee, U.S. Patent 2,907,735 (Oct. 6, 1959).

²⁵ J. E. Gill and J. Munro, J. Chem. Soc., 1952, 4630.

²⁶ Robert A. Piloni, et. al., U.S. Patent 2,979,480 (April, 1961).

²⁷ Yoshuchi Akasome, et. al., Japan Kokai 71, 16,587 (May 7, 1971).

²⁸ Keyokazu Mizutani, et. al., Japan Kokai 74,105,845 (Oct., 1974).

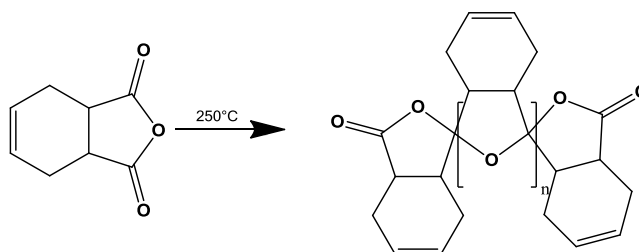
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Other Uses

Tetrahydrophthalic anhydride can be isomerized to 1-cyclohexene-1,2-dicarboxylic acid which holds promise in the field of phthalocyno-type pigments.²⁹

At temperatures above 250°C, tetrahydrophthalic anhydride reacts with itself by splitting off carbon dioxide to form clear, light-colored resins that are believed to have the following structure:



Some tetrahydrophthalic anhydride adducts have useful properties as insecticides, fungicides, and defoliating agents.^{30,31,32,33}

A rubber antioxidant of the diphenylamine type was made using tetrahydrophthalic anhydride.³⁴ A superior tackifier for sulfur curable elastomers was made from the bis(oxiranyl methyl) ester of tetrahydrophthalic anhydride, alkyl phenol novolac resin, and formaldehyde in the presence of xylene and toluene sulfonic acid.³⁵

Bromination of the diglycidyl ester of tetrahydrophthalic anhydride, followed by heating with hexahydrophthalic anhydride gave a self-extinguishing product.³⁶

Handling & Storage

THPA will react with water to form tetrahydrophthalic acid. This is normally undesirable, so THPA should be stored in such a way that it is carefully protected from moisture contamination. When properly stored, THPA has a shelf-life of 24 months.

²⁹ A L. Barney, U.S.2,764,597 (Sep.25, 1956).

³⁰ R. C. Morris and R. M. Horowitz, U.S. Patent 2,489,103 (Nov.22, 1949).

³¹ H. L. Haller; Ind. Eng. Chem. 39, 467 (1947)

³² A. R. Kittleson; Science, 115, 84 (Jan. 25, 1952).

³³ Masahiko Okutus, et. al., Japan 73,07,766 (March 1973).

³⁴ Joseph A. Pawlak, and Frances J. Bayer, Ger. Offen. 2,230,311 (Jan. 18, 1973).

³⁵ Thomas M. Galkiewicz, et. al., Ger. Offen. 2,53718 (July 29, 1976).

³⁶ N. V. Moatschappij, Fr. Demande 2,163,555 (Aug. 31, 1973).

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Safety 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.