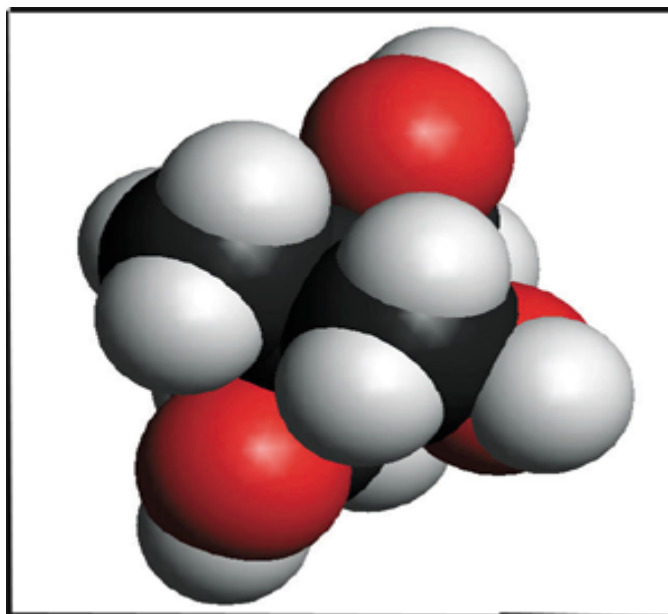


**A  
COMPLETE GUIDE  
TO TRIMET<sup>®</sup>  
BRAND OF  
TRIMETHYLOLETHANE**



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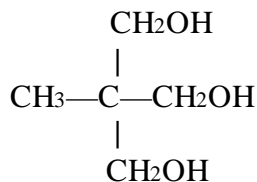
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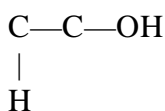
## INTRODUCTION



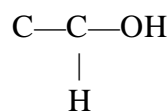
TRIMET® brand of Trimethylolethane (TME)

TRIMET® brand of Trimethylolethane (TME) is a versatile polyol with significant quality features. It is a trihydric alcohol that can be used in all polyol applications. Its compact neopentyl structure provides high hydroxyl content and excellent stability. The TME structure imparts improved heat, light, hydrolysis and oxidation resistance to products. These factors make TME a very desirable component of coating compositions where good weathering characteristics are required.

TME's favorable properties arise from its neopentyl structure. The three hydroxyls of TME are primary. Therefore, they are highly reactive. In addition, the central carbon atom, which is beta to all three hydroxyls, has no hydrogens. The absence of beta hydrogens blocks elimination processes, a common mode of thermal decomposition in polyols. As a result TME provides high thermal stability. Moreover, the hydrogens alpha to the hydroxyls are adjacent to the highly branched central carbon atom. Therefore, the alpha hydrogens are highly hindered. Since alpha hydrogens are a common site of free radical attack, TME has exceptional resistance to the degradation effects of heat and light.



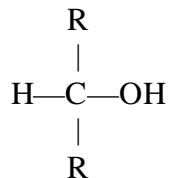
Beta  
Hydrogen



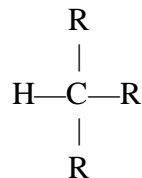
Alpha  
Hydrogen

Similarly, the hindrance provided by the branched carbon chain increases resistance of TME esters to hydrolysis. Ester hydrolysis is a factor in both corrosion resistance and stability. Therefore, TME is a preferred polyol for high performance paint vehicles, especially for those used in water soluble alkyd and polyester enamels.

The TME structure also has no secondary hydroxyls and no tertiary hydrogens. Secondary hydroxyls are slow to react. A secondary hydroxyl requires the presence of a tertiary hydrogen. Tertiary hydrogens are susceptible to free radical attack—especially when on the same carbon as an oxygen. Polyols with secondary hydroxyls are expected to be less resistant to the effects of heat and light.



Secondary  
Hydroxyl



Tertiary  
Hydroxyl

TME has a lower equivalent weight than some polyols because it is a triol with a compact structure. Low equivalent weight means that fewer pounds of TME may be used to provide the hydroxyl equivalents in a given formulation. Therefore, TME can be more economical than other polyols.

Because of its exceptional stability, TME is used for high performance alkyd and polyester resins for paints, polyol ester synthetic lubricants, stabilizers for plastics, plasticizers, and coating agents for pigments. In addition, the nitrates ester of TME is used in explosives and propellants.

Typically the properties imparted by TME are:

- ❖ heat stability
- ❖ hardness
- ❖ resistance to water, alkali, and acids
- ❖ resistance to degradation caused by light
- ❖ resistance to oxidation
- ❖ improved weatherability
- ❖ low color
- ❖ gloss retention
- ❖ stain resistance
- ❖ overbake resistance
- ❖ hydrolytic stability
- ❖ improved corrosion resistance
- ❖ reduced viscosity at high solids

Typical uses of TME in resins for coatings include:

- ❖ Exterior finish coats such as automotive and appliance enamels, farm implement finishes, and marine coatings where durability requirements are demanding.
  - ❖ Silicone-modified polyesters for further improved weather resistance and heat resistance.
  - ❖ High solids reactive diluents and vehicles that meet demanding volatile organic carbon (VOC) requirements in either baked or air dried systems.
  - ❖ Automotive primer surfacer coatings to improve metal primer adhesion, flexibility, corrosion protection and thermal-cycle resistance.
-

- ❖ Industrial finishes for fast air-drying applications requiring excellent weather resistance.
- ❖ Metal finishes capable of exceptionally fast cure by baking with resistance to overbaking.
- ❖ Coil coatings that are flexible, hard, durable.
- ❖ Wire coating that are flexible and extendable (14, 41, 42).
- ❖ Beverage can coatings that are resistant to hydrolysis, acids and bases and have good adhesion.
- ❖ Wood, glass and metal coatings that air-dry to hard, impact resistant, high gloss films.
- ❖ Powder coating binders for thermosetting resins with low softening points that produce chemically resistant coatings.
- ❖ Plasticizers and stabilizers for plastics that resist heat, light, alkali, solvent, and moisture and impart color stability especially for polyvinyl chloride (TME esters, epoxidized esters, and glycidyl esters).
- ❖ Enamels and lacquers (oil and oil-free) for clear or pigmented high gloss coatings with color and gloss stability, particularly TME alkyds in white high bake enamels.
- ❖ Varnishes and enamels for insulating electrical conductors, transformers and magnet wires with good mechanical and electrical properties including resistance to heat shock.
- ❖ Fast air drying water soluble enamels with improved corrosion resistance.
- ❖ Reactive diluents for air drying alkyds.
- ❖ Glycerin replacement to improve dry time, harness, stability, gloss and weatherability.
- ❖ Surface treatment for inorganic pigments such as titanium dioxide for improved dispersability, agglomeration resistance, wettability and optical properties.
- ❖ Photographic films to prevent strain desensitization and tackiness.
- ❖ Photochromic films resistant to tearing, crazing and breaking with good dimensional stability and reduced migration of the photochromic material.
- ❖ Ink formulations that heat cure with good gloss, hardness solvent resistance and heat stability.
- ❖ Synthetic lubricants that withstand the demanding corrosion-oxidation stability test.
- ❖ Textile applications to reduce shrinkage during finishing.
- ❖ Solid phase heat storage in application like solar energy and self-warming textiles.

TME trinitrate (TME TN) has many applications in explosive and propellant formulations. TME TN can be used to contribute the following activities and property modifications:

These uses are described on grester detail in the sections below.

TME is manufactured by GEO Specialty Chemicals, TRIMET Products Group, in Allentown, PA, to rigid specifications for high hydroxyl content, low moisture, low color and low inorganic and other contaminants.

TME is available in three grades: Technical, Pure, and Nitration Grade, and in three forms: briquets, granular, and liquid (aqueous solution). TME Technical is most often supplied in cake resistant briquets. Granular TME Technical can be supplied on special order. TME Technical can also be supplied as an 80% solids aqueous solution.

TME Technical is a high-quality product widely used in the manufacture of alkyd and polyester resins. TME Pure is a special grade that has been processed to a higher purity. TME is also available in a Nitration Grade, a specially purified grade, for use in the manufacture of explosives. The specifications and typical properties of these products are given in Appendix A.

TME appears in the chemical literature under a variety of names. The Chemical Abstracts Service has assigned the CAS Registry Number 77-85-0 and the preferred chemical name 2-(hydroxymethyl)-2-methyl-1,3-propanediol. Other names for TME include: Trimethylolethane, TME, pentaglycerol, PG, pentaglycerine, 1,1,1-trimethylolethane, 1,1,1-trimethaneolethane, and 2,2-di(hydroxymethyl)propanol.

Trimethylolethane is listed on the Chemical Substance Inventory under the U.S. Toxic Substances Control Act and in the European Inventory of Existing Chemical Substances under its Chemical Abstracts Service Registry number 77-85-0. Complex substances containing Trimethylolethane that appear on the TOSCA Inventory are listed in Appendix F. Food use approvals appear in Appendix E.

# **CHEMISTRY**



## NEOPENTYL POLYOLS

TME is a member of the family of materials called neopentyl polyols. The neopentyl polyols are derivatives of neopentane (2,2-dimethylpropane) with two or more of the methyl groups substituted with hydroxyl. Members of the neopentyl family include pentaerythritol (four hydroxyls), Trimethylolethane (three hydroxyls), and neopentyl glycol (two hydroxyls). DMPA® brand of Dimethylolpropionic Acid, also supplied by GEO Specialty Chemicals, TRIMET Products Group, also has a neopentyl structure, but with two hydroxyls and one carboxylic acid group.

Closely related to the neopentyl polyols is Trimethylolpropane (TMP). TMP is technically not a neopentyl polyol because it contains six carbons. However, TMP is often compared to TME, because both are triols. Although they are structurally similar, experimentally the two materials have significantly different properties. TME is a much harder polyol.

Chemists have long recognized the importance of hardness in resin formulations—especially in alkyd formulations. Although molecular weight and the cross-linking capabilities of the oil component are important, hardness of the resin backbone affects the ultimate hardness of the final coating film. Hardness may also be a factor in the drying rate of air drying alkyds. The importance of hardness is recognized in resin specifications requiring a minimum phthalate content.

Hardness has usually been attributed to the aromatic dibasic acids used in resins. The complexity of alkyd formulations makes it difficult to measure the hardness contribution of polyols directly. Oil is a soft component; the aromatic acid is a hard component; together with stoichiometry they define the weight of polyol in the formulation. Addition of a fourth component to allow variation in the polyol content is feasible, but further complicates measurement of the hardness contribution of the polyol.

The hardness of polyols can be estimated from the ball and ring softening point of their esters with dimethylolpropionic acid.\* In esters prepared at 1:1 mole ratio in the presence of butylstannic acid esterification catalyst, results were as follows:

Polyol	Ball & Ring, °C	ICI Viscosity At 100°C Poise
Pentarythritol	109	24
Trimethylolethane	67	7.0
Neopentyl Glycol	waxy	3.3
Trimethylolpropane	liquid	3.7
1,4-Cyclohexane-dimethanol	liquid	2.0
Ethylene glycol	liquid	0.8
2,2,4-trimethyl-pentandiol-1,3	liquid	0.6
1,6-Hexanediol	liquid	0.4

\*Patents Pending

The results indicate that TME is significantly harder than TMP. Its hardness compared to other polyols can be inferred from the ICI viscosity data.

The greater hardness of TME makes it a preferred polyol for air drying alkyds. Substitution of TMP for TME usually has a detrimental effect on drying. This effect is greater than expected from the weight of the longer TMP side chain in the charge. Compensating by removing oil from the formulation results in reduced corrosion protection due to reduced cross-linking.

Moreover, the neopentyl structure of TME provides improved resistance to free radical attack such as on exposure to heat or light. The longer side chain of TMP is less hindered than that of TME. Therefore, reduced resistance is expected. PM data have confirmed faster dry and better gloss retention in air drying alkyds made with TME compared to TMP and better heat resistance in silicone modified polyesters.

Obtaining the benefits of TME in a resin formulation often means substituting it for another polyol like TMP. In a formulation already balanced in terms of hard/soft components, cross-linking potential (e.g. hydroxyl content, oil length), and molecular weight, the substitution should be made on a weight-equivalent basis (46). By the weight-equivalent method, TMP and the hydroxyl equivalents provided by it. The polyols blended should be selected to include components harder and softer than TMP. The weight ratio of the polyols needed can be obtained by simultaneous equations based on total weight and weight per cent hydroxyl (or reciprocal of equivalent weight).

A preferred combination for the replacement of TMP is TME and cyclohexanedimethanol (CHDM). By the weight equivalent method, each pound of TMP in the formulation should be replaced by 0.7648 lb of CHDM. Replacement of TMP with blends of TME and caprolactone has also been suggested. In alkyds, oil length can often be increased when TME is substituted for TMP on a mole basis, again due to the greater hardness of TME. The result can be lower cost, higher performance resins.

The greater hardness provided by TME should also be of value in rosin esters for use in printing inks and in powder coatings.

## TME ALKYD RESINS

**TRIMET®**, brand of Trimethylolethane (TME), is widely used in alkyd resins of all types to give quality products. The outstanding advantages obtained from TME are derived from the inherent properties of this compact neopentyl polyol. Since Trimethylolethane has no beta hydrogens and its alpha hydrogens are all highly hindered, TME esters are very resistant to the destructive influences of heat, moisture, and light. Thus, TME alkyds produce films with excellent weatherability, color and heat stability, gloss retention, overbake resistance and stain resistance. In medium and short oil alkyds, TME is often superior to all other polyols or mixtures of polyols. TME imparts excellent drying and hardness qualities to these alkyds.

Due to TME's high hydroxyl content, excellent thermal stability, and good reactivity, it can be formulated to tailor-make compositions for specific uses (see Table 1). TME alkyds are useful for both air-drying and baking applications.

The methyl group of compact Trimethylolethane molecule has a solubilizing effect compared to pentaerythritol. TME alkyds have good compatibility with other film forming materials and common additives. TME alkyds can be reacted or blended with amine/aldehyde, phenol/aldehyde, vinyl, acrylic, polyurethane and polyester resins. These compositions can meet demanding specifications ranging from those required for automotive finishes to textile decoration.

Good electrical properties coupled with excellent heat resistance make TME alkyds ideal for use in magnet wire enamels and insulating varnishes. The heat resistance imparted by TME makes it the polyol of choice for vehicles in flame-retardant and fire-resistance coatings.

Both solvent and water borne TME alkyds can be prepared. In water soluble alkyds, TME has been shown to provide better hydrolytic stability, drying, gloss retention, hardness and corrosion protection (29b). In addition, TME alkyds can be formulated for fast air-drying baking applications.

### Preparation of TME Alkyds

Alkyd resins are polyesters prepared from polyols and dibasic acids or anhydrides and modified by a fatty acid component (9). The fatty acid may be incorporated as a refined fatty acid, or as a vegetable, i.e., as the glycerin ester of a fatty acid. Typically, an alkyd is prepared from TME, an aromatic dibasic acid such as phthalic anhydride or isophthalic acid, and a drying-oil component. Commonly used oils include tall oil, soybean oil, linseed oil, safflower oil, cottonseed oil and dehydrated castor oil. More complex alkyds are formulated from combinations of the three essential classes of components plus modifiers such as benzoic acid or addition polymer monomers like methyl methacrylate. Many examples of TME alkyds appear in the literature. Representative references are summarized in Table 1.

---

Alkyd resins are readily prepared by the usual esterification procedures (6, 9). The apparatus used must provide for heating, temperature control, agitation, an inert atmosphere and water stripping. Effective modern alkyd resin kettles are available. The resin kettles may be charged in toto or successively with a series of components in a prescribed sequence.

**Table 1. TME Alkyd Compositions, Properties and Applications (a,b)**

EX. REF	Alcohol	Acid	Drying Oil/Acid	Other Components	Cure	Improved Properties	Applications
1. (1)	TME	PA	coconut & cottonseed	--	bake	color & heat stable	enamels, lacquers printing inks
2. (3)	TME, PE	PA	linseed	vinyltoluene acrylonitrile MMA	air dry	rapid cure, non-wrinkling no overspray problems	binders for pigments & TiO <sub>2</sub> ; auto. enamels
3. (4)	TME, PG	ethylhexanoic, IPA	--	amino plastic	bake	hard, low color; alkali, solvent, moisture and color stable	extremely hard high gloss enamel
4. (6)	TME	TMA	safflower	--	air dry	balanced, optimized variables	water soluble air-drying coating comp's.
5. (5)	TME	PA myristic caproic	--	diamide condensate & melamie/formaldehyde	bake	color stable hard, overbake resistance flexible, adherent	baked finishes
6. (7)	TME	PA or PA/BA	tall or soybean	water- & oil-soluble nonyl phenoxy poly-ethylene ethanol emulsifiers	air dry	stable aq. emulsion lower cost, toxicity, odor & hazards	water soluble short & medium alkyd surface coating comp's & pigmented films
7. (12)	TME	PA DMPA	linseed	--	air dry	air-drying, water soluble, low color hard, flexible, translucent films	water soluble coating compositions
8. (20)	TME PE	PA	tall soybean	anthranilic acid	air dry	rapid-drying	short & medium-oil alkyd resin coatings
9. (10)	TME PE	PA BA	dehydrated castor	rutile TiO <sub>2</sub>	air dry	short oil, air-dry fast-dry; good gloss retention color, flexibility & weatherability	white appliance coating
10. (11)	TME or neopentyl polyols	PA succinic anh.	dehydrated castor	--	air dry	water sol. fast dry clear tough films water & salt spray resistance	varnish, semi-gloss paint semi-gloss enamel
11. (14)	TME glycerin	IPA	tall	isopropyl titanate, dicyclopentadiene polymer	air dry bake	elongation, abrasion & solvent resistance, heat shock & thermal stability	varnish for electrical conductors, transformers and current controls

**Table 1. (Continued)**

EX. REF	Alcohol	Acid	Drying Oil/Acid	Other Components	Cure	Improved Properties	Applications
12. (13)	TME	PA p-t-butyl-BA	coconut	modif. acrylic amine/ formaldehyde	bake	balanced gloss, metal primer adhesion impact strength, hardness, moisture & solvent resistance, weather resistance, thermal cycle	automotive coating
13. (19)	TME PE	PA BA	soybean	--	air dry	custom formulation acid & hydroxyl nos. dry time as needed for dry or liquid level. processes	binders for metal oxide coatings for electrophotographic office and business copying products
14. (8)	TME DMPA	chlorendic anh.	tall linseed	mixed with Pb, Co or Mn driers	air dry	air-dry water-soluble flame retardancy and fire resistance	metal coatings, fire resistant application
15. (16)	TME	--	dehydrated castor	copolymer of styrene & methacrolein	air dry	air-drying, clear smooth glossy flexible film	wood, glass, metal coatings
16. (17)	TME neo-pentyl glycol	PA adipic	--	incorporate 10-20% coconut fatty acids	bake	intermediate oil- and oil-free alkyd binders, solvency & compatibility for other resins	pigment binders
17. (18)	TME	TMA & maleic anh.	linseed	salicylic/ formaldehyde	heat curable	water-soluble, heat curable 150°C paints	water-soluble
18. (21)	TME	PA DMPA	tall	MMA & methacrylic acid	air dry	rapid drying light colored water soluble	implement enamels
19. (23)	TME	DMPA	safflower	hexamethylenediisocyanate	air dry	water soluble water resistance high impact	water-thinned coating compositions
20. (24)	TME neo-pentyl glycol	PA tetrahydro-PA	linseed	--	air dry	water soluble workability, high gloss, water resist	compatible polyester and pigmented compositions
21. (22)	TME	PA	linseed	triphenyltin hydroxide	air dry	antifouling storage stability durable	marine coatings
22. (27)	TME	PA	linseed, soybean or dehydrated castor	bis(tributyl tin)oxide, polyvinyl acetate & TDI	air dry	antifouling comps adhesion, hardness, abrasion & leaching resistance, durability	marine coatings
23. (26)	TME	PA	linseed, soybean or dehydrated castor	bis(tributyl tin)oxide, castor oil TDI and mono-alcohols	air dry	antifouling comps adhesion, hardness, abrasion & leaching resistance, durability	marine coatings
24. (28)	TME PG, PE	IPA PA	safflower linoleic acid	m-isoprop-enyl-a,a-dimethylbenzyl isocyanate	air dry	low VOC high solids, air-drying weatherability	reactive diluent or vehicle; cure modifier for acrylics, polyesters, alkyds
25. (25)	TME neo-pentyl glycol hexane-diol	PA	coconut	dibutyltin oxide polyacrylates	bake	sag resistant appearance gloss	thick film coatings

a Other additives and solvents used in these formulations that are commonly used in the art are not reported here.

b Abbreviations: PA = phthalic anhydride, IPA = isophthalic acid, TMA = trimellitic anhydride, BA = benzoic acid, PE = pentaerythritol, PG = propylene glycol, MMA = methyl methacrylate.

When oils rather than fatty acids are used, the oil and the polyol are combined with an alcoholysis catalyst in an initial cooking stage. A transesterification reaction occurs which produces hydroxyl-rich, fatty ester fragments called monoglycerides. The dibasic acid and other components are added after the alcoholysis step to complete the resin preparation. When fatty acids are used, the alcoholysis is omitted; all three components may be combined directly and cooked to completion.

Either fusion or solvent cooking can be used. For solvent cooking, a small amount of an azeotroping solvent, usually xylene, is added. The mixture is gradually brought to temperature. With TME, cooking temperatures in the range of 450-480°F can be used. These exceptionally high temperatures reduce esterification time. The extent of reaction is controlled by monitoring water-of-reaction as it distills out, acid number, resin viscosity and/or cure time.

The use of an inert atmosphere of carbon dioxide or nitrogen to reduce final color is standard practice in alkyd preparations. Nitrogen sparging may decrease the reaction time.

TME esterification proceeds very uniformly. Viscosity can be controlled precisely from batch to batch. For high solids, low viscosity alkyds, a lower cooking temperature should be used to minimize heat bodying of the oil and etherification side reactions that can increase the functionality of polyols. Where high viscosities are required, the cooking temperature may be increased to 480°F or higher. Unlike other polyols, TME resins resist discoloration at these temperatures. TME resins are noted for their low color during cooking and in the ultimate films produced.

TME esters show a high degree of solvency for other ingredients used in alkyd resins. Thus 1:1 molar prepolymers of TME and phthalic anhydride or isophthalic acid can be carried to high degrees of esterification before the fatty acid ingredients in the initial charge because of the solvent action of TME esters as they are formed.

A study of process conditions for the preparation of TME alkyds reports (15) preparation of a prepolymer (75% reacted) from the dibasic acid and polyol in a first step followed by the addition of fatty acid and other components in a second cooking step. The procedure reportedly gives better final properties compared to charging all materials in one step.

Fatty acid cooks are generally recommended to secure the full benefits of TME. If desired, oils can be used. TME will give easy alcoholysis of glycerides at 450°F using a catalyst.

**Catalysts.** Common catalysts can reduce esterification time for TME alkyds. In general, strong acids are effective catalysts, but resin discoloration and corrosion considerations often mean that metal catalysts are preferred. The effects of metal salts of organic acids on the esterification rate of a variety of polyols with acetic acid were in the order: Zn<sup>++</sup>>Mn<sup>++</sup>>Pb<sup>++</sup>>Cd<sup>++</sup>>Mg<sup>++</sup>>Ca<sup>++</sup>>Cu<sup>++</sup>>Hg<sup>++</sup>

(39). Titanium tetrachloride was approximately mid-range in activity. Reaction rates increased with increasing catalyst concentrations but not proportionally.

Catalysts especially suited for formation of TME alkyds include stannous octoate and tetrabutyl titanate. The stannous ion does not darken TME alkyds as it does glycerin alkyds. In addition, TME alkyds made with catalysts give shorter drying times and, due to a higher degree of esterification and lower free hydroxyl and carboxyl content, produce better water resistance. The effect is more significant in medium and long oil alkyds where excess hydroxyl is at a minimum.

Tetrabutyl titanate has been used to catalyze the esterification of terephthalic acid, 1,4-butanediol and TME in the preparation of transparent polyesters (38). Calcium oxide (30) and dibutyltin oxide (37) can be used to catalyze polyester formation in polymeric transesterification reactions.

### **Formulating TME Alkyds**

Alkyd resin formulation requires balancing many factors to attain the specific film properties dictated by the end use. TME alkyds, due to the unique physical and chemical properties of TME, provide the formulator with a versatile resin system. The compatibility and solvency of TME polyesters to common components and a variety of polymer systems makes it possible to produce an array of film properties (see Table 1). In addition, either solvent or water borne coating compositions designed for cure by air-drying or baking can be made.

TME has a low equivalent weight, so one can use less TME to form alkyds of equivalent excess hydroxyl content. In addition, TME has a relatively low vapor pressure. Thus, less TME will be lost in the distillate.

For rapid esterification, only a small (5%) hydroxyl excess is necessary in long oil TME alkyds. As the oil length decreases, the percentage of excess hydroxyl is increased up to 20 to 30% in some cases. This excess polyol gives stability to short amount of stabilizer such as diethylethanol amine or alcohol solvents such as butanols can be added to improve stability in baking enamels.

TME alkyd resins can be further reacted or blended with additives or other polymers under suitable conditions to give the desired final composition (Table 1). Alkyd resins are often modified by addition polymer monomers to improve drying speed. Examples of modified TME alkyds appear in the patent literature. A vinyltoluene/methyl methacrylate modified resin is described in Reference 3.

TME should not be simply substituted mole-for-mole for other polyols. TME alkyds are usually harder than those made with other polyols. Therefore, the oil length of TME alkyds may often be increased to provide similar properties. Since oil is a low-cost component, the result can be reduced raw materials cost. See the Neopentyl Polyols Section for additional discussion of polyol substitution methods.

TRIMET has starting formulations available for TME in most types of alkyds and polyesters. Contact your GEO Specialty Chemicals, TRIMET Products Group representative for copies.

## Compatibility

TME esters show a high degree of solvency for other ingredients used for alkyd cooks. Also, many TME alkyds have excellent solvency and provide vehicles compatible with other film forming materials. The improved compatibility of TME alkyds is attributed to the solubilizing effects of the TME methyl group. Thus, TME alkyds are highly versatile vehicles providing a high degree of formulating flexibility.

The unique TME molecule has a solubilizing effect that allows for the formation of more complex molecular structures without gelation. TME permits formation of higher molecular weight alkyds with faster dry and harder films. In general, TME will allow alkyds of higher phthalic content (less oil) with acceptable acid number and viscosity.

TME alkyds perform important functions in a wide range of coating compositions formulated for specific end uses (see Table 1).

## Quality Features of TME Alkyds

TME imparts many desirable properties into alkyd and alkyd/copolymer coating compositions and their resulting films. In general, TME alkyds have improved weatherability, color and heat stability, and moisture resistance. The films are durable, either as hard, impact resistant baked finishes for automotive or implement coatings or as flexible and extendable wire coatings. TME alkyds are of low color and can be used to produce clear or pigmented high gloss enamels. TME alkyds have excellent compatibility with titanium dioxide and other pigments.

**THERMAL STABILITY AND HEAT RESISTANCE.** TME's excellent thermal stability makes a major contribution to the heat resistance properties of alkyd resin coatings. TME resins may be cured at high temperatures without loss of gloss or discoloration. They are noted for excellent overbake resistance.

Coatings for metal finishes can be baked for 15 minutes at 350-360F. At lower temperatures, the films convert in 20-50 minutes. Reduced baking temperatures may be achieved by post-reacting available hydroxyls with ethylene oxide or caprolactone.

TME can be used as a heat-stable building block for alkyd vehicles that resist overbake. An early application of this principle was to improve heat resistance of automotive topcoats and appliance finishes prepared from TME alkyd/melamine formaldehyde condensate products (5).

Silicone modification can be used to further improve the heat and weather resistance of polyester resins (9). TME offers further improvement for these systems. For more discussion see the Silicone Modified Polyester Section (Page 26).

Examples of TME alkyd formulations and applications requiring thermal stability are shown in Table 1 (Examples 1, 5, 11, 12).

TME alkyd vehicles designed for color retention and heat resistance can be prepared from TME, phthalic anhydride and fatty acids or the methyl esters derived from coconut oil or cottonseed oil. These vehicles are particularly useful in the manufacture of enamels, lacquers, and printing inks (Table 1, Example 1).

TME can be used as a replacement for glycerin in isophthalic polyester alkyd resin for baking use to give improved heat resistance and compatibility (2).

**LOW COLOR AND COLOR AND GLOSS RETENTION.** TME esters are very pale in initial color even when prepared in high temperature cooks at 450-490°F. A small amount of maleic anhydride (0.05 to 0.1%) is often used as a bleach where very low color resins are desired. This procedure is especially effective with TME alkyds. In medium and short oil alkyds, TME will usually give a color of one or two Gardner tubes lower than any other trihydric alcohol or mixtures of polyols such as pentaerythritol/glycol or pentaerythritol/glycerin blends.

TME resins are outstanding for color and gloss retention in the ultimate films produced. Examples of some of these TME alkyd-containing coating compositions are given in Table 1 (Examples 1, 3, 5, 9, 10, 12, 15 & 18). The heat and color stability of TME esters is especially important in baking applications. The neopentyl structure of TME prevents the breakdown of the molecule under the influence of these high temperatures. Thus, TME coatings for metal finishes can be conveniently baked at 350-360°F and in many cases at even higher temperatures without loss of gloss or discoloration. They also provide excellent overbake resistance.

TME alkyds have been very successful in white high bake enamels. In the range of 300-400°F, these alkyds retain excellent color and gloss and resist even severe overbakes.

Fast air-drying short oil TME alkyds reportedly retain gloss and have good flexibility (10). In one example, the resin was prepared by the reaction of TME and pentaerythritol with phthalic anhydride, benzoic acid, and dehydrated number less than six and a cure time of 36 seconds on a 392°F cure plate. The optimum polyol ration of 1:1 parts by weight produced a resin with a Gardner-Holdt viscosity at 50% solids in xylene of ZI, and a tack-free drying time of 20 minutes. Coatings on steel panels were tested for gloss after 330 hours weatherometer exposure. The gloss of the TME alkyd enamel decreased only from 92 to 84 compared to a decrease from 84 to 70 for a similar enamel prepared from a fast-drying premium commercial corn oil alkyd.

When TME is used as the sole polyol in alkyd coating compositions, exterior durability and gloss retention superior to corresponding compositions using combinations of PE/glycerin and PE/glycols are obtained.

Medium oil alkyds in general are noted for outstanding gloss retention, durability, hardness and adhesion. TME medium oil alkyds have excellent initial gloss and gloss retention on exposure to the weather. In medium and short oil alkyds, TME is the polyol of choice.

Superior fast-drying water-soluble acrylic modified long-oil TME alkyd coatings can be prepared for high-gloss enamel top coats. They are especially useful in white and light-colored enamels for application on implements. Alkyds prepared from TME, dimethylolpropionic acid, phthalic anhydride and tall oil fatty acids, were reacted with a blend of addition polymer monomers such as methacrylic acid and methyl methacrylate. These resins could be formulated to dry within 10 minutes and be tack-free after 45 minutes (21).

Improved gloss and weatherability can be obtained by using TME to replace glycerin in alkyd resins when formulated at equivalent or increased oil lengths. In addition, the TME alkyd will show faster dry, a harder film, and possibly cost advantages (see TME Compared to Glycerin).

TME is particularly suited for use in benzoic acid modified alkyds designed for improved gloss, alkali resistance and hardness. In some cases, the film properties are equivalent to epoxy esters but at lower cost.

TME alkyds show good compatibility with amino resins. Baking systems with good gloss retention can be prepared from a TME alkyd vehicle containing short (C6-C9) monobasic acids and melamine or urea resins. Similar resins prepared with glycerin are generally incompatible or show an appreciable loss of gloss on baking.

Exceptionally hard, low bake, low color TME resins for amino resin crosslinking can be prepared by partial condensation of TME and 2-ethylhexanoic acid followed by final cooking with isophthalic acid and propylene glycol at 450°F. When the alkyd was mixed with 15-30% of an amino resin and baked (0.5 hour, 250°F), the resultant films gave Sward values of 46 to 56 with improved color stability, alkali, solvent, and water resistance (4).

**WATER, ALKALI AND ACID RESISTANCE.** The compact neopentyl carbon structure of TME is one of the most stable configurations in organic chemistry. Because esters containing this neopentyl structure are less subject to hydrolysis (11), TME imparts good water, alkali and acid resistance to alkyds which are properly formulated and esterified. Both air-drying and short-oil baking TME alkyds are notably more water and detergent resistant than corresponding glycerin alkyds.

The stability of alkyds increases as the degree of esterification approaches completion and the free hydroxyl and carboxyl content becomes lower. TME alkyds give more complete esterification and better detergent resistance when prepared from fatty acids rather than by glyceride alcoholysis. Stannous ion catalyzed TME alkyd products also have higher degrees of esterification and greater water resistance. Similarly, TME is particularly suited for use in benzoic acid modified alkyds designed to obtain improved alkali resistance, gloss, and hardness.

The rate of acid release is slower in alkyd resins prepared from TME than it is in glycerin alkyds on aging for comparable periods of time. TME alkyds can provide improved resin shelf life.

TME alkyd coating compositions having good water, salt spray, detergent, alkali, acid and/or solvent resistance are shown in Table 1 (Examples 2, 10, 11, 12, 19, 20, 21, 22, & 23).

WEATHER RESISTANCE. TME alkyds have excellent weathering properties. These properties are a combination of the factors discussed concerning the general stability of TME esters (see above). Due to TME's basic neopentyl structure, its esters are highly resistant to degradation caused by heat, moisture, and light. Thus, TME can be beneficially employed in alkyd coating compositions to produce films with excellent weatherability, color, and heat stability.

TME alkyds formed with phthalic anhydride or isophthalic acid are noted for durability to exterior exposure. They resist the effects of moisture and ultraviolet light. Due to their weatherability, gloss retention, high impact strength and toughness they have been accepted in automotive and appliance enamels, farm implement finishes, marine coatings, railroad car paints, etc. (10) (see Table 1). Silicone modification further improves weathering.

An example of a fast air-drying white industrial enamel employing a short oil TME alkyd resin is described above. Accelerated weatherometer tests (330 hours with cycling of 2 hours sun, 18 min. rain, approximately equivalent to six months Florida exposure) of coatings on steel panels were made. The gloss of a TME alkyd enamel decreased only from 92 to 84 compared to a decrease from 84 to 70 for a similar enamel prepared from a fast-drying premium commercial corn alkyd (10).

TME alkyds are useful for formulating compositions to produce a good balance of weather resistance, moisture resistance, thermal-cycle, gloss, adhesion to metal primer coats, impact strength, hardness, and solvent resistance for example, blends of a TME alkyd resin with interpolymers of modified acrylic polymers and an amine/formaldehyde resin provide coating compositions especially useful in automotive applications. An effective alkyd resin is prepared from TME, p-tert-butylbenzoic acid, phthalic anhydride and coconut fatty acids (13).

TME COMPARED TO GLYCERIN. Alkyds were originally developed using glycerin as the polyol. Comparison of TME with glycerin are common. In general, TME provides faster drying, greater hardness and improved chemical, heat and weather resistance when substituted for glycerin. The data in Table 2 demonstrates some of the improvements using TME in equivalent soya and tall oil fatty acid alkyds.

General formulating considerations for substituting TME for other polyols are discussed in the Neopentyl Polyols Section above. The comments below refer to the specific case of substituting TME for glycerin in alkyds.

For best results, TME should not be simply substituted on a mole-for-mole basis for glycerin. Instead, the fatty acid or oil content should be increased slightly to reduce the hydroxyl excess. Some have suggested that using up to 20% fewer excess hydroxyl equivalents will give resin properties comparable to using glycerin. TME has a lower vapor pressure compared to polyols such as glycerin. Thus, substantially less TME will

be lost with the distillate during a resin cook and less may be used in the initial charge. These factors can provide economic advantages for TME resins.

TME produces lower color resins than corresponding glycerin compositions. TME alkyds can be cooked at 480°F or higher with low color formation. Glycerin and most other polyols cannot be cooked at these high temperatures without discoloration. TME resins are outstanding for color retention during cooking and in the ultimate films produced. For example, oil modified alkyd resins useful in the manufacture of enamels, lacquers and printing inks can be prepared from TME, phthalic anhydride and methyl esters of coconut oil fatty acids and cottonseed oil by transesterification at 455°F for four hours followed by three hours at 510°F. The alkyd is soluble in xylene and has a Gardner color of 6. A corresponding alkyd prepared using glycerin in place of TME was unusable due to its dark color and xylene insolubility. The TME composition was particularly useful for applications requiring color retention and heat resistance (1).

**Table 2. TME Alkyd Properties as a Function of Composition**

Molar Ratio Phthalic Anhydride/ Polyol/ Fatty Acid	Viscosity(a) Gardner Scale	Air Dried Film(b)						Caustic Attack on Baked Film(d)	
		Dry Time hours(c)		Sward Hardness			First Attack	Denude Time	
		STT	TF	1 day	14 days	28 days			
Soya fatty acid alkyds									
Glycerin	1.04/1.0/0.87	U	3.3	6.5	6	20	--	--	5:00
	1.0/1.0/0.91	P	1.8	6.5	6	22	--	--	0:40
	0.96/1.0/0.95	G	3.0	8.5	4	8	--	--	0:30
TME	1.04/1.0/0.87	Z	1.3	3.0	4	28	--	--	85:00
	1.0/1.0/0.91	A	1.8	6.0	4	24	--	--	31:00
	0.96/1.0/0.95	H	3.2	8.5	4	18	--	--	7:00
Tall Oil Acid Alkyds									
Glycerin	1.0/1.0/0.70	J	0:45	4:00	4	18	20	0:15	86:00
TME	1.0/1.0/0.60	T	0:20	1:00	8	20	38	3:00	269:00
	1.0/1.0/0.70	G	0:35	1:50	6	18	34	8:00	120:00
	1.0/1.0/0.75	E	1:30	4:00	6	16	32	8:00	200:00

a 50% nonvolatiles in mineral spirits.

b Film contained 0.5% Pb plus 0.05% Co as naphthanantes based on solids.

c STT = set to touch, TF = tack free.

d Baked films contained 0.02% Mn; baked at 150C for 30 minutes,

exposed at room temperatures to 3% NaOH.

Source: Reference 9.

In isophthalic alkyd resins for baking, the use of TME in place of glycerin improves compatibility with xylene in short oil vehicles (2).

The use TME to replace glycerin in fatty acid ester based lacquers imparts improved characteristics and especially improved stability on atmospheric exposure (40).

In general, TME alkyds dry faster, give better hardness and are of lower color than corresponding glycerin alkyds at equal phthalic content. TME alkyds have excellent resistance to water, detergents, alkalis, acids and other reagents. They are notably better than corresponding glycerin alkyds in all these resistance tests. Alkyd resins prepared from TME show a slower

increase in acid value than do glycerin alkyds on aging for comparable periods.

**HIGH SOLIDS ALKYDS.** TME has been used in the preparation of low viscosity reactive diluents for use in high solids, air-drying alkyd. The compositions are prepared by the reaction of TME with linoleic acid and the hemi-ester of cyclohexanol with maleic anhydride (29). A starting formulation of this type is available as a GEO Specialty Chemicals, TRIMET Products Group Product Guide. Copies may be obtained through your GEO Specialty Chemicals representative. A low cost high-solids alkyd starting formulation appears in Appendix B.

High-solids air-drying alkyds based on tem and chlorendic anhydride have been reported (29c).

High-solids alkyds have been prepared by reacting a hydroxyl functional resin prepared with TME with isocyanatoethyl methacrylate (28). The products were suitable for use either as vehicles, reactive diluents or as cure modifiers.

TME has been shown to produce lower viscosity when substituted for TMP in a typical high solids formulation.

**WATER SOLUBLE ALKYDS.** The literature includes numerous examples of water soluble alkyds made with TME (4, 7, 8, 11, 12, 17, 18, 21, 23, 24, 37, 45, 128). In addition, GEO Specialty Chemicals provides starting formulations for them in TME bulletins 5 and 9. GEO Specialty Chemicals also has additional information on water soluble coating in conjunction with DMPA® brand of Dimethylolpropionic Acid. A companion volume, "DMPA® brand of Dimethylolpropionic Acid: A complete Guide" contains extensive references to that literature in addition to information on urethane dispersions and other water borne coatings. Additional water soluble alkyd starting formulations are provided in DMPA® Bulletins 1 and 3 and in a Product Guide describing WA-78. A recent study showing the advantages of TME in water soluble alkyds has been published (29b).

## TME POLYESTER RESINS

TRIMET, Trimethylolethane (TME), is an effective polyol for the preparation of quality oil-free polyester resins. As discussed in the Introduction, the outstanding qualities imparted to TME polyester arise from the compact neopentyl structure of the Trimethylolethane molecule. Because there are no beta hydrogens and the alpha hydrogens are highly hindered, TME esters are highly resistant to deterioration due to heat, moisture, light and oxidation. Thus, enhancement of properties such as weatherability, color and heat stability, durability, gloss retention, overbake resistance and stain resistance can generally be achieved by the use of TME. The esters derived from TME, due to the hindered alpha-carbons, are exceptionally resistant to hydrolysis and oxidative degradation.

Polyesters are sometimes modified with short synthetic fatty acids (up to 20%) for improved compatibility and wetting properties (17). TME resins made with 2-ethylhexoic acid have excellent compatibility with amino resins and produce films that are extremely hard and tough with 15 to 30% amino resin modification (4).

Epsilon caprolactone will react with free hydroxyl and is an excellent modifier for TME polyesters. It can be used with TME to replace TMP. Since TME has a lower equivalent weight, it can be substituted on a mole-for-mole basis and the weight difference made up with caprolactone.

Improved rigidity of films of polyarylates of isophthalic acid and phenolphthalein can be accomplished by incorporation of a small amount (0.05-0.1 mole %) of TME to introduce active free hydroxyls that can be used for cross-linking (33).

### Preparation of TME Polyesters

Polyesters are readily prepared from polyols and di- or tribasic acids or suitable derivatives by direct esterification. Other common ester forming methods (9), transesterification, ester interchange and use of acid chlorides, may also be used.

The manufacturing procedures for polyesters are similar to those used for the preparation of alkyds (see Alkyd Resin Section). Effective resin kettles are available that provide for heating, temperature control, agitation, stripping of volatile products and an inert atmosphere. Typically, a polyester can be prepared from TME and dibasic acids and/or esters by heating the components at temperatures in the range 350-470°F with removal of volatile reaction is controlled by monitoring the amount of elimination product (water-or alcohol-of reaction) or the acid number. In some cases, it may be beneficial to heat the components neat under reflux initially at 445-465°F followed by xylene addition and azeotropic removal of water (31).

Increasing the esterification temperature has a lesser effect on ultimate molecular weight than with alkyds, but does increase the rate of reaction. Exceptionally high reaction temperatures of 450°F to 470°F with resultant shorter cooking times are possible when TME is the chosen polyol because of its thermal stability and **the stability of the resultant polymer. TME polyesters prepared at these high temperatures are generally of significantly lower color than corresponding resins prepared with alternative polyols. In addition, the relatively low volatility of TME reduce loss of the polyol to the distillate.**

TME esters show a high degree of solvency for many of the components used in polyester resins. Thus 1:1 molar prepolymers of TME and phthalic anhydride or isophthalic acid can be carried to high degrees of esterification before the other components are added. Cooks can be conducted with a minimum of liquid ingredients initially because of the solvent action of the TME esters as they are formed.

### **Quality Features of TME Polyesters**

TME imparts many desirable qualities into polyester coating compositions and their resulting films. In general, TME improves weatherability, color and heat stability, and moisture resistance. The films are useful as durable, hard, impact resistant baked industrial finishes. TME polyesters are of low color and can be used to produce transparent films, or pigmented to form high gloss, light colored enamels.

TME is an excellent polyol for incorporation into oil-free polyester resins to provide superior thermal stability and overbake resistance. Baking enamel compositions can be formulated using TME polyesters as base resins. For example, TME is partially esterified with benzoic acid leaving two free hydroxyls. This product is then reacted with trimellitic anhydride and adipic acid at 352°F to produce the resin. Enamels formulated with this resin have good alkali resistance (32).

Combinations of TME/glycol polyesters with aminealdehyde resins produce baked coatings which have high resistance to overbake and good gloss and color retention (31). In addition, these coatings have excellent resistance to detergents, alkali, soaps and solvents, toughness, flexibility, scratch resistance and stability to discoloration. An example, polyester resin is prepared from isophthalic acid, fumaric acid, pelargonic acid, TME and neopentyl glycol. The temperature of the cook is slowly raised to 240°C. After cooling to 145°C and adding xylene, the cook is continued at 230-240°C until an acid number of 10 or less is obtained (3-4 hours). The resin is let down to 60% solids with xylene giving a solution with a viscosity of H (Gardner-Holdt) and an acid number of 9. Blending of this polyester (six parts) with a butylated melamine-formaldehyde resin (Resimene 875, four parts) produced a composition that was curable by baking for 30 minutes at 177°C. The cured coatings showed good gloss and color retention on rebaking for one hour at 204°C.

A thermosetting baking resin with good cure, high gloss, good color, good hardness and

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excellent resistance to soaps, detergents and solvents is formed by blending a TME polyester base resin, an acrylic resin and an amine-formaldehyde resin (34). An example vehicle is prepared from: a polyester formed from isophthalic acid, fumaric acid, pelargonic acid, TME and neopentyl glycol and let down to 70% solids with additional xylene; an acrylic resin prepared from butyl acrylate, methyl methacrylate and methacrylic acid; and a butylated benzoguanamine-formaldehyde resin.

A polyester with superior color stability on baking can be prepared by reaction at 350-450°F of an aliphatic polyol containing at least three hydroxyl groups on nonadjacent carbons, a dialkyl ester of an aromatic diacid and an aliphatic diacid in proportions such that the ratio of hydroxyls to carboxyls is 1.2-1.5. The preferred polyol is TME (30).

TME polyesters can be prepared with low color. TME is useful in the formation of low color and transparent polyester films. Resins for this purpose can be prepared from terephthalic acid, TME, 1,4-butanediol and catalytic amounts of tetrabutyl titanate heated at 180-230°C (38).

A hydrolytically stable lacquer can be formulated by blending a TME/phthalic anhydride/isodecyl alcohol polyester with a methylated melamine-formaldehyde resin (35).

Films with good adhesion and resistance to water, solvents chemicals and soiling can be formed by baking coating compositions containing water-thinned TME polyester bases mixed with melamine resins. The polyester is prepared with hydroxyl values 300-800, acid numbers less than 30 and number-average molecular weights of 500-3000. An example polyester is prepared by heating TME (500), DL-malic acid (500) and dibutyltin oxide (0.4 part) at 170°C for five hours and at 180°C for seven hours (37).

### **TME Polyesters for Powder Coating**

TME polyesters can be used to formulate binders for use in powder coating applications. For example (36), a polyester, prepared from TME, polyethylene terephthalate, 3,5,5-trimethylhexanoic acid and phthalic anhydride is heated at 115-125°C with 5% hexakis(methoxymethyl)melamine under reduced pressure. The product is a thermosetting resin with a softening point of 75°C that produces a chemically resistant, thermosetting coating.

## **SILICONE MODIFIED POLYESTER**

Silicone modification can be used to further improve the properties of oil-modified alkyds and polyester resins. TME can be used to formulate polyesters with superior properties for use as “bases” for condensation with methoxysilanes.

Silicone modification of TME polyesters provides improved heat, abrasion and weather resistance and gloss retention. Thus, silicone modified TME alkyds are employed mainly in air-drying maintenance finishes and are suitable for use in exterior coatings and for coatings on hot surfaces such as hot water heaters, furnaces, motors, etc. Silicone modified polyesters are employed in thermosetting industrial finishes, with or without small quantities of melamine-formaldehyde cross-linkers.

Silicone modification levels of 15 to 50% by weight of the resin provide useful property improvements. Optimum performance properties are typically observed when organic resins are formulated to contain 30% silicone modification.

For silicone modification, the choice of the polyester or alkyd is very important. Superior results are generally obtained with products based on isophthalic acid, TME and a glycol such as neopentyl glycol. Modifying acids that provide varying degrees of flexibility are non-drying fatty acids, dimer, adipic, sebacic and azelaic acids. Short-oil alkyds prepared from drying oils such as soybean, dehydrated castor and linseed oil are also suitable for silicone modification. Cross-linking can be effected with melamine resins.

The thermal stability and effect of polyols on the properties of silicone-alkyd copolymers has been studied (41). Formulations containing TME produced resins with overall properties superior to those prepared with other triols. Copolymers with TME and neopentyl glycol showed superior thermal stability. On exposure to air at 275°F for hundreds of hours, the TME resins retained good gloss, color, film integrity and flexibility.

In a comprehensive series of studies, Earhart (46) has evaluated the parameters involved in formulating polyester bases for silicone modification. To compare polyester formulations, the equivalents of excess hydroxyl and either the molecular weight or the number of ester pairs in the backbone should be kept constant. These factors assure comparable condensation with the silane condensation and melamine resin cross-linking. The studies showed that silicone modified TME/glycol polyesters were superior in hardness, equivalent in flexibility, improved in adhesion and lower in cost than comparable TMP polyesters.

From his studies of TME and TMP resin pairs, Earhart (46) noted that the resin chemist has a practical means of improving on TMP polyesters. This is accomplished by the simple expedient of replacing the TMP with TME and small amounts of any glycol while holding the free hydroxyl and phthalic content constant. Resins formulated in this manner have improved properties and are more economical.

In a study (43) on the effects of polyols on the properties of silicone-alkyd copolymers, TME formulations produced resins with overall superior properties to those prepared with other triols. Copolymers with TME and neopentyl glycol showed superior thermal stability. TME resins retained good gloss, color, film, integrity and flexibility on exposure to air at 275F during hundreds of hours. These polymerizations could be catalyzed by strong organic acids.

Isophthalic acid tends to give harder but less flexible polyester films than phthalic anhydride. This inverse relationship is apparently shifted by the addition of silicones which improves hardness while maintaining of slightly improving flexibility.

TME is effective in high gloss retention silicone-modified polyester finishes (31). The polyesters incorporated into such coating compositions can be formed from TME, isophthalic acid, azelaic or adipic acids, and small amounts of other additives. It is recommended that small amounts of a glycol be added with the TME for even better results. These coatings had good hardness, flexibility and adhesion.

**Table 3. Formulation and Properties of Silicone Modified TME Resins**

<b>EX. REF</b>	<b>Alcohol</b>	<b>Acid</b>	<b>Drying Oil/Acid</b>	<b>Other Components</b>	<b>Improved Properties</b>	<b>Application</b>
1. (43)	TME neopentyl glycol	oil modified	alkyd	silicone	heat stable color, gloss, film integ. flexibility	heat resistant coatings
2. (45)	TME	phthalic, dimethylol- propionic	linseed	organosiloxane cyclopentadiene/ linseed copolymer, organopolysiloxane	water soluble air- drying preservative conditioner	automotive vinyl tops, seats
3. (44)	TME neopentyl glycol	isophthalic	castor	silicone resin amino/HCHO	strong, flexible stable, inexpensive binder	glass paper impregnator for mica tapes for electrical; insulation
4. (42)	TME ethylene glycol	methyl terephth- alate	drying oils or fatty acid	diphenyl siloxane w. 20% SiOMe	no crazing on coiling	wire coating
5. (41)	TME ethylene glycol	methyl terephth- alate		diphenyl siloxane w. 20% SiOMe	dielectric strength craze resistance	electrical conductor insulation wire coatings

## TME URETHANES

TME polyesters can be formulated to provide excellent polyester polyols for use in urethane coatings. A large number of dibasic acids such as adipic, sebacic, azelaic or dimer acids can be condensed with TME to form suitable polyesters. One-part moisture-cure polyurethane coatings may be prepared from isocyanate terminated TME polyesters. One-part urethane oils (uralkyds) that air dry in the presence of metallic driers may be prepared from alkyd precondensates made with TME. They reportedly can be formulated for fast drying, improved toughness and good in-can stability.

Two-part polyurethane coatings require TME polyesters with sufficient excess hydroxyl to combine with a polyisocyanate adduct or isocyanate terminated polymer in stoichiometric proportions. For example, the first component can be prepared from TME and adipic acid; the second component can be prepared from TME and adipic acid; the second component can be prepared from 1,3-butanediol, TME and toluene diisocyanate. A wide variation in properties for the finished coatings can be obtained through proper formulation of the components. Thus, finished coating may be varied from soft and flexible to hard and tough depending on the hydroxyl number and chain length of the polyester portion.

Water-thinned fatty acid-modified polyurethane compositions are prepared from the reaction of a partially esterified TME/safflower oil fatty acids intermediate with dimethylolpropionic acid and hexamthylenediisocyanate. A typical polyurethane has a fatty acid content of 30% and a diisocyanate content of 40%. On neutralization with triethylamine/water a solution containing 25% solids is obtained. Coatings had a pencil hardness of B, Gardner impact test of 160 in. lb., Erichsen value greater than 8 mm, and water immersion test greater than one day (23).

An isocyanate modified tin containing TME alkyd composition is reported (27) to have excellent properties for marine coatings applications. These compositions are prepared from components having a combination of hydrophilic and hydrophobic components and containing a high tin content. An initially formed TME, phthalic anhydride and linseed fatty acid alkyd resin is further reacted with additional phthalic anhydride and di(butyltin) oxide to give a polymer of 80% solids in xylene containing 9.65% tin. The tin alkyd is then further heated with an equivalent molar weight of polyvinyl acetate, ethylene glycol monobutyl ether and toluene diisocyanate in mixed solvents. The coatings had good adhesion, hardness, abrasion resistance, leaching resistance, and useful life.

High solids resins can be obtained by reacting at least a portion of the available hydroxyl groups on a resin with isocyanatoethyl methacrylate. Such a resin can then be used as the major vehicle in high-solids coatings or as a reactive diluent and cure modifier of oxidatively curable alkyd polyesters and acrylic resins. When this alkyd was used as a reactive vehicle for a sunflower-and tall oil-acid TME alkyd, a coating was formed that showed weather resistance and good drying properties (28).

## TME EPOXY RESINS

TME can be reacted with epichlorohydrin to produce epoxy intermediates and resins. These resins may be used as foundry sand binders, wet strength additives for paper, and for adhesive applications. Epoxidized esters of polyols including TME may be useful as coating resins for baking. The films resist water, corrosion, alkalis and solvents.

TME or esters TME can be used as epoxy polymerization initiators or modifiers in epoxy/urethane foams and resins (116).

TME glycidyl esters and ethers are effective intermediates and components in resin compositions. Glycidyl ethers are readily prepared from epichlorohydrin and TME (109). The glycidyl ethers can be esterified with fatty acids to yield products useful as plasticizers and stabilizers for polyvinyl chloride resins. Glycidyl ether modified polyol coating compositions can be prepared that are water-thinnable and have good storage properties (128). These coating compositions, which are useful on wood or printed wood products, are prepared by reaction of TME (1 mole) with a glycidyl ether such as allyl glycidyl ether (0.2-2.0 mole) and addition of a suitable catalyst such as boron trifluoride-etherate.

Halogen containing ether epoxides are suitable as binders and intermediates for a wide range of uses (104). They are prepared by partial dehydrohalogenation of the reaction product of a polyol such as TME with an epihalohydrin. These products are useful drying varnishes, infusible resins, detergents, dyes, insecticides, pharmaceuticals, wire coatings and lubricating-oil additives.

An epoxy resin having a cationic charge can be designed for paper industry and foundry applications (106). The resin is prepared by initial reaction of TME (1 mole) with epichlorohydrin (2mole) followed by further reaction with diethylenetriamine and incorporation of the final condensate into a urea/formaldehyde resin. The product was useful as a foundry sand core binder, in the manufacture of wet strength paper from kraft pulp, and as adhesive in corrugated paper.

An epoxy resin producing rigid heat-resistant coatings can be prepared from dicyclopentadiene dioxide, a 1,2-epoxy compound, TME and maleic anhydride (117). The resin was useful as a laminating resin, adhesive, potting and encapsulating material, molding compound and coating composition.

## **ACRYLATE AND METHACRYLATE ESTERS IN ADDITION POLYMERS**

TME can be esterified with unsaturated acids to yield useful polyunsaturated esters. The inclusion of TME triacrylate and a plastomeric polymer in vinyl chloride molding polymer formulation and irradiation of the molded products produced films with improved impact strengths and higher softening points (122). TME trimethacrylate is used with chloroprene to prepare a gel polymer that has improved extrudability over the unmodified chloroprene rubber (121). TME dimethacrylate has been used as the adhesive in a UV sensitive photopolymerizable formulation for laminating a polymer coated cellophane film to an oriented polypropylene film (124). Acrylate and methacrylate esters of TME derived 5-hydroxymethyl-5-methyl-1,3-dioxanes can be used to introduce interesting side groups into polyenes (105).

## **POLYANHYDRIDES**

The polyanhydride trimethylolethane tris(trimellitate anhydride) can be used as a cross-linking agent or to form polymers such as polyimides (112). This polyanhydride can be prepared by transesterification between three moles of trimellitic anhydride and one mole of TME triacetate. The reaction is carried out at elevated temperatures (300°C) in a solvent such as chlorinated biphenyl with removal of the liberated acetic acid until complete (a few hours). The product is isolated as a solid, m.p. 85-87°C.

## SYNTHETIC LUBRICANTS

Trimet, Trimethylolethane (TME), because of its exceptionally stable neopentyl structure, is a suitable polyol for the manufacture of polyol ester synthetic lubricant base stocks. Polyol ester base stocks provide a unique combination of properties—particularly good high temperature stability coupled with low temperature viscosity. They are the preferred base stocks for use in demanding applications such as jet engine lubricants.

Esters prepared from TME and short chain aliphatic acids are useful in synthetic lubricants which must withstand high temperatures. Blends of fatty acids are often used to achieve the low temperature viscosity properties required in jet engine lubricants. Small amounts of antioxidants and corrosion inhibitors are incorporated into the finished lubricant to improve their performance at high temperatures.

TME esters are also of value as textile lubricants and are reportedly useful as non-caloric shortenings for food.

Various TME esters have been reported. The lubricant properties of these esters are shown in Table 4. Mixed esters of TME appear to meet the requirements of Military Specification MIL-L-7808J, dated May 11, 1982.

**Table 4. Lubricant Properties of TME Esters**

Esters	Viscosity cs, °F			Pour Point (°F)	Visc. Index	ASTM Slope	Flash Point (°F)	Flame Point (°F)	Coefficient of Friction			
	212	100	-40 -65						Static	Kinetic	us/uk	Ref
Dibutyrate monolaurate	--	--	solid	+20	--	--	--	--	--	--	--	B
Dibutyrate monopelargonate	3.0	12.2	11900	-92	103	--	410	441	--	--	--	A
Dicaproate monoheptanoate	3.0	11.8		-86	118	--	460	484	--	--	--	A
Dicaproate monopelargonate	2.0	11.0		-96	124	--	422	462	--	--	--	A
Dicaproate monovalerate	2.7	10.3		-92	105	--	421	468	--	--	--	B
Divalerate monocaproate	2.5	9.7		-94	99	--	428	473	--	--	--	B
Divalerate monocaprylate	3.0	11.6		-90	114	--	428	473	--	--	--	A
Divalerate monoheptanoate	3.4	14.2		-88	130	--	471	500	--	--	--	A
Divalerate monolaurate	--	--		+23	--	--	460	484	--	--	--	B
Divalerate monopelargonate	3.15	12.98		-86	119.6	--	450	482	--	--	--	A
Tri-2-ethylhexanoate	3.93	--	>10000	-65	--	--	--	--	--	--	--	F
Tricaprate	5.12	24.5		+10*	150	0.68	535	--	0.104	0.126	0.83	D
Tricaproate	2.9	11.0		-90	111	0.75	433	482	--	--	--	A, C
Tricaprylate	3.89	--		-45*	--	--	--	--	--	--	--	F
Triheptanoate	3.24		2300*	-65*	--	--	--	--	--	--	--	F
Tripelargonate	4.5	21.0	solid	35	147	0.70	535	--	0.109	0.12	0.79	A, D

Notes: \*

Solidified at one hour

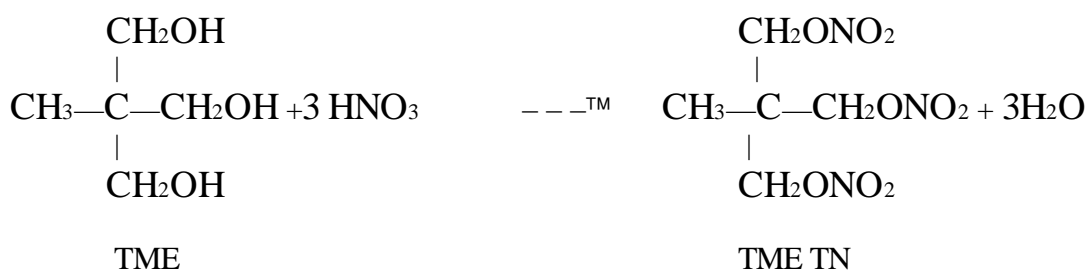
- (A) Brit. Pat. 951,939, (3/11/64), to Heyden Newport Corp.; and W.M. Kraft and R.H. Barth. Ger. Pat. 1,444,852, (12/2/71), to Tenneco Chemicals, Inc.
- (B) Brit. Pat. 951,937, (3/11/64) to Heyden Newport Corp.; M.A. Gladsten, W.M. Kraft and R.H. Barth. Ger. Pat. 1,44,851, (12/2/71), to Tenneco Chemicals, Inc.
- (C) G. Cohen et al., Ind. Eng. Chem. 45,1766 (1953)
- (D) M.Z. Fainman, U.S. Pat. 2,950,250, (8/23/60), to Standard Oil Company of Indiana; R.S. Barnes and M.Z. Fainman, Lubrication Engineering. Aug. 1957, p. 454.
- (E) W.F. Bernholz and T.C. Cox, U.S. Pat. 3,464,922, (9/2/69), to Drew Chemical Corp.
- (F) GEO Specialty Chemicals, TRIMET Products Group.

## EXPLOSIVES AND PROPELLANTS

TME can be nitrated to produce a liquid nitrate ester, Trimethylolethane trinitrate (TME TN), with unique properties for use in explosive and propellant compositions.

TME TN has a high rate of detonation and low sensitivity to impact. Compared to nitroglycerin, TME TN has a lower freezing point and does not cause headaches. Accordingly, it may be used to reduce the impact sensitivity of sensitizers for ammonium nitrate, or as a component of headacheless and nonfreezing industrial dynamites. TME TN can also be used as an energetic plasticizer in various propellants and plastic explosives. TME TN can be formulated into explosives to improve properties such as water resistance, plasticity, detonation rates, temperature stability, electrostatic sensitivity, and mechanical strength.

### Preparation of TME TN



TME TN is easily prepared in a manner similar to the process for glycerin trinitrate. High yields (93%) are obtained by treatment of TME at 10°C with an acid mixture containing 45% nitric acid and 55% sulfuric acid. Fortifying the mixed acids with 20% oleum reportedly increases yields to 97-98% (52). A solvent system such as glacial acetic acid and acetic anhydride can be used for the nitration reaction (53).

**Table 5. Properties of TME TN (52, 54)**

Melting point	51°C
Freezing point	-60°C
Specific gravity (20°C)	1.4685
Refractive index (17.5°C)	1.4760
Water solubility (19°C)	0.516 g/L
(36°C)	0.685 g/L
Viscosity;	
discharge of a 10 mL. pipet at 20°C	148 sec.
Lecocche Lambert viscometer	1.56 polees
Volatility at 60C	1.3 mg/dm <sup>2</sup> /h
Impact sensitivity for 50% detonation	0.59 kg
Heat of explosion	1270 kcal/kg
Lead block expansion	85 % of PETN
	115 % of PA

PETN = pentaerythritol tetranitrate; PA = picric acid

An industrial scale continuous process for production of TME TN involves direct addition of a solution TME in sulfuric acid to >97% nitric acid or nitric acid/sulfuric acid (containing 20% excess HNO<sub>3</sub>) and collection of the insoluble oil (52).

Conitration of polyols can be accomplished by addition of mixtures such as TME and starch or diethylene glycol to nitrating baths containing nitric acid and sufficient sulfuric acid to inhibit solution of the nitrates in the medium (60, 62, 85).

### **Explosive Applications of TME TN**

TME TN can be used to effectively modify and improve the characteristics of explosive compositions. Its high rate of detonation and low impact sensitivity permit incorporation into explosive formulations for increased blasting power with little or no effect on detonation sensitivity.

**Table 6. TME TN Detonation Rates (54)**  
(nonconfined TME TN cartridges, 30 mm. Dia.)

density g/cm <sup>3</sup>	1.49	1.48	1.50
rate, m/sec	6750	7040	7060

**TME TN SENSITIZERS.** TME TN can be used as a sensitizer for ammonium nitrate explosive compositions. TME TN/ammonium nitrate explosives with increased sensitivity and an increased rate of detonation can be prepared by blending at temperatures in the range 100 to 150°F (70). TME TN can be used as the sensitizer for an extrudable ammonium nitrate slurry explosive prepared using fibrous plant pulp as both fuel and thickener (63).

**TME TN BLENDED SENSITIZER.** TME TN can be blended with other polyol nitrate esters to provide an explammonium nitrate dynamites. Combinations have been used containing TME TN and nitroglycerin (65), ethylene glycol dinitrate (65), PETN (62), or neopentyl glycol dinitrate (55). The blends may be prepared by conitration of blended polyols (65).

**ENERGETIC PLASTICIZERS FOR EXPLOSIVES AND PROPELLANTS.** TME TN may be used to plasticize binders used in propellant formulations. In this application TME TN replaces oxygen deficient components. Since TME TN is an energetic component, the total energy content of the propellant is increased.

TME TN is used as an energetic plasticizer for high-viscosity nitrocellulose in high power plastic demolition explosives. This combination functions as a binder for a finely divided high explosive such as RDX, HMX or PETN producing a flexible, rubbery composition of entirely active ingredients (79).

TME is employed in propellant compositions as an energetic plasticizer for binders such as nitrocellulose (50, 62, 77, 80, 84), nitro starch (82), pentaerythritol trinitrate acrylate

co-polymer (74, 76) and cellulose acetate (73). Blends of TME TN with triethylene glycol TN with triethylene glycol dinitrate, diethylene glycol dinitrate (78a), or 1,2,4-butanetriol trinitrate (78b) have been used as nitrocellulose plasticizers.

Propellant applications of TME TN plasticized nitrocellulose binders include a plateau burning propellant composition (80); a high power smokeless powder as for use in tank guns (84); and a propellant composition containing solid aluminum hydride and ammonium perchlorate (77).

Higher energy, low flame temperature propellant compositions are formulated with blends of TME TN and diethylene glycol dinitrate or triethyleneglycol dinitrate as an energetic plasticizer for nitrocellulose (75, 78). Similar propellants with superior strength under severe low temperature conditions were prepared using a blend of TME TN/ triethyleneglycol dinitrate/1,2,4-butanetriol trinitrate as the plasticizer (78b).

Applications for TME TN plasticized cellulose acetate binders include a slow clean burning propellant useful as a power source for guided missile accessories (61); and a propellant composition based on cellulose acetate using TME TN as an energetic plasticizer (73).

TME TN plasticized pentaerythritol trinitrate acrylate co-polymer binders were employed in a high energy, high solids content, low sensitivity propellant composition (74) and in a high energy, low burn rate double base propellant containing HMX (76). The latter propellant was designed for use in the upper stages of large solid propellant rockets.

TME TN was used as a plasticizer for nitro starch binder in a plastic explosive containing RDX (82).

**FLEXIBLE/PLASTIC EXPLOSIVES.** A high power plastic demolition explosive can be prepared employing TME TN as an energetic plasticizer for high-viscosity nitrocellulose. This combination functions as a binder for a finely divided high explosive such as RDX, HMX or PETN producing a flexible, rubbery composition of entirely active ingredients (79).

An RDX containing plastic explosive can be prepared with TME TN and tribally acetyl citrate plasticized nitrocellulose binder (64).

Gelatin dynamites are prepared with TME TN and nitrocellulose employing a nitroparaffin such as nitromethane, nitroethane or 2-nitropropane as solvent (68).

**WATER RESISTANCE.** Jellylike adhesive mixtures containing 5—49% nitrostarch gelatinized with 0.5-30% TME TN serve to moisture proof explosive compositions containing water soluble nitrates. Water resistant dynamite blasting compositions are prepared in this way. The solubility of nitrostarch in TME TN is ca. 1.5% (56).

Water resistant permissible explosives can be prepared with a TME TN/petroleum blended sensitizer for ammonium nitrate dynamites (69).

**IMPACT SENSITIVITY CONTROL.** The low sensitivity of TME TN to mechanical shock (Table 5) provides the explosives formulator with a way to lower the impact sensitivity of explosive compositions. TME TN has been used in this manner to reduce the impact sensitivity of nitroglycerin or ethylene glycol dinitrate sensitizers for ammonium nitrate dynamites (65).

The blends are most effectively prepared by conitration of blended polyols (65). Similarly, starch can be nitrated in the presence of TME producing a conitrate with reduced impact sensitivity and reduced tendency to segregate compared to mechanical blends. The starch/TME conitrates were used in ammonium nitrate slurries (60).

TME TN can be blended with PETN to provide an explosive sensitizer with reduced impact sensitivity, but no significant reduction in detonator sensitivity (62).

Blends of TME TN and neopentyl glycol dinitrate can be used to produce dynamites with reduced shock sensitivity, lower freezing points, higher viscosity and better stability than dynamites prepared using nitroglycerin and ethylene glycol dinitrate blends (55).

**CONTROLLED DETONATION RATE.** The detonation rate of ammonium nitrate dynamites sensitized with TME TN can be controlled by blending the TME TN with small amounts of fuel oil. The detonation rate of these explosive compositions is adjusted by the petroleum content. The method can be applied to the preparation of water resistant permissible explosives, ammonium dynamites and gelatin dynamites (69).

The rate of detonation of ammonium nitrate/ TME TN explosives can be reduced by blending in small amounts of water (71).

Incorporation of aluminum flake into an ammonium nitrate/ TME TN composition increases the rate of detonation (72). TME TN ammonium nitrate explosives with increased sensitivity and an increased rate of detonation can be prepared by blending at temperatures in the range 100 to 150 degrees F (70).

**TEMPERATURE STABILITY.** The freezing point of nitroglycerin (reported for stable form, ca. 13 degrees C (48,49,50). Thus, TME TN has been incorporated into explosive and propellant compositions to provide low temperature stability.

Blends of TME TN and neopentyl glycol dinitrate when used as an alternative to nitroglycerin and ethylene glycol dinitrate blends in dynamites produced explosives with lower freezing points, reduced shock sensitivity, higher viscosity, and better stability (55).

Particulate propellant explosives of conventional nitrocellulose, after treatment with a solution of TME TN (4.2 parts / final wt.), maintain substantially constant effectiveness over a wide range of temperature (57b). Similarly, TME TN (4-24 parts by wt.) is used to surface-coat dry gunpowder (100 parts) in smokeless propulsion agents with low temperature coefficients (57b).

Compositions using blends of TME TN with triethyleneglycol dinitrate and 1,2,4-butanetriol trinitrate used as a plasticizer for nitrocellulose in a higher energy, low flame temperature, armor piercing mortar propellant had superior strength under arctic temperature conditions and consistent performance properties (78b).

**TME TN AS A NITROGLYCERIN SUBSTITUTE.** Hertz (51) first suggested that, as an explosive, TME TN is capable of partly or entirely replacing nitroglycerine. TME TN is capable of partly or entirely replacing nitroglycerine. TME TN gelatinizes nitrocellulose (11.7% N) only slightly and can be used satisfactorily to replace nitroglycerin in double-base powders (52). Blends of TN and neopentyl glycol dinitrate were claimed for use in dynamites as an alternative to nitroglycerin and ethylene glycol dinitrate blends. The novel blends were said to have lower freezing points, reduced shock sensitivity, higher viscosity and better stability (55).

**REDUCED ELECTROSTATIC SENSITIVITY.** The sensitivity of a primary high explosives such as lead azide to electrostatic discharges can be reduced by blending up to 6% TME TN into the composition (66).

### Miscellaneous TME TN Uses

**SMOKELESS POWDER.** In World War II, Germany manufactured some 1,1,1-(Trimethylolthane for use in smokeless double-base powders (47). TME TN (4-24 parts by wt.) is used to surface-coat dry gunpowder (100parts) in smokeless propulsion agents with low temperature coefficients (57a). Smokeless powders can be prepared with TME TN and nitrocellulose employing a nitroparaffin such as nitromethane, nitroethane or 2-nitropropane as solvent (68).

**GAS GENERATOR.** Nitrogen gas generating compositions for inflating safety devices are prepared by coating pellets of alkali metal azides and an oxidant with a TME TN plasticized nitrocellulose lacquer (83).

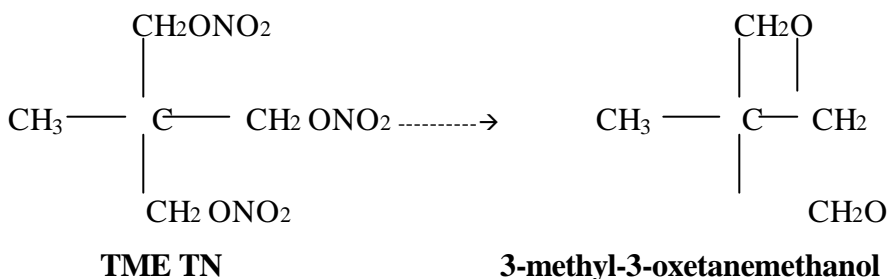
**MECHANICAL STRENGTH.** TME TN alone or in combination with other polyol nitrates are added to solid propellant compositions to provide high mechanical and impact strength at low temperatures (81).

**DEFLAGRATING FUSE.** Deflagrating fuse can be prepared with TME TN and nitrocellulose employing a nitroparaffin such as nitromethane, nitroethane or 2-nitropropane as solvent (68).

**PETN PURIFICATION.** The removal of residual acidity from crude PETN by water washing was facilitated by blending with liquid explosives such as TME TN. Conitration of TME with PE produced a mixture of nitrates which was easily washed to low acidity (67).

### Hydrolysis of TME TN

Hydrolysis of TME TN in 50-60 degrees C aqueous ethanolic sodium hydroxide has been studied. Three moles of base react with one mole of TME TN. The major product is 3-methyl-3-oxetanemethanol with only trace amounts of TME FORMED (86).



## HEAT STORAGE APPLICATIONS

### Background

TME is one of an interesting class of compounds known as plastic crystals. Plastic crystals may be used in heat storage applications (87,88,90,94). This class of compounds stores and releases heat through a reversible solid-solid transition from an ordered crystal to a less ordered plastic crystal state. The transitions involve large changes in energy, by definition greater than the heat of fusion.

Differential scanning calorimetry (DSC) and infrared studies (100) on crystalline TME taken during heating and cooling cycles in the range 25-100 degrees C have shown that TME exhibits a reversible plastic crystal phenomenon at approximately 80 degrees C with an enthalpy change of 46 cal / g. Another DSC study showed the endothermic transition temperature to be 83 degrees C with associated heat exchange of 34 cal / g. The endothermic transition temperature has also been reported as 81 degrees C, with an entropy change of 15.6.e.u. (89a). The phase transition to a plastic crystal has been investigated (90).

### Formulation of Heat Storage Materials

When the solid-state transition temperatures ( $T_{tr}$ ) are suitable for a specific end use, the transition temperature may be altered by admixture with other material (doping). Binary mixtures of latent heat storing polyols can be used to modify the transition temperature (95, 97). The substitutional or interstitial dopants are incorporated in large amounts to form solid solutions. Binary mixtures of pentaerythritol ( $T_{tr}$  182-3 degrees C, melting point 258 degrees C) and TME ( $T_{tr}$ , 81 degrees C, melting point 197 degrees C) are melted together to form heat storage materials. At a concentration of 35 wt % TME, the solid state transition temperature was ca. 140 degrees C. No supercooling occurred. The transition temperature of the binary material decreased as the concentration of TME was increased.

The reversible transitions from crystal solid to plastic crystal in binary mixtures of neopentyl glycol with TME and with pentaerythritol have been examined calorimetrically (98). The transition temperature corresponding to neopentyl glycol (ca. 40 degrees C) can be increased by addition of TME or pentaerythritol. At concentrations up to 40%, there is a total inhibition of the transition corresponding to the minority compound.

The cycling ability of heat storage polyol mixtures is markedly extended by the addition of a phenol or an amine dopant (96). Melting mixture of TME (35 wt %), pentaerythritol (59% wt) and 2,6-di-tert-butyl-p-cresol (6 wt %) produces a heat storage material having a phase transfer temperature of ca. 140 degrees C. This material showing no loss in heat storage capacity after two months of cycling once a day between the temperatures of 30-180 degrees C. The heat storage capacity of the binary material without the phenolic additive dropped to zero during the test period.

Plastic crystals of the polyol type are hygroscopic and water soluble. For effective use, they must be contained in a manner excluding moisture. For example, heat storing capsules (0.5-10 mm diam.) can be prepared by impregnating absorbent



The reversible change from order to disorder in the solid-state transition phenomenon can be graphically demonstrated by IR analysis (100). Organic compounds such as TME form molecular crystals in which the molecule retains its identity in the crystal. For molecular crystals, the perturbations induced by the crystalline environment are realized in the IR spectrum by changes in band intensities, shifts in band positions, and splitting of bands. Infrared spectra of crystalline TME taken during heating and cooling in the range 25-100 degrees C had sharp absorption peaks below the transition temperature. The spectrum peaks coalesced into featureless broad bands through the transition temperature range and above it. The sharp structural features returned on cooling the sample.

The solid-state transformations of pentaerythritol, TME, neopentyl glycol and their binary mixtures have been studied thermodynamically (91). The observed thermodynamic properties of these neopentyl alcohols during transition support a mechanism for the transformation involving reversible breaking of nearest temperature. The same mechanism appears to hold for the solid-state transformations result in many reorientation possibilities, the transition entropies may be very high (89a).

The introduction of new conformational disorder into a plastic crystal structure by replacing a substituent with a more complex substituent within a series would be expected to increase the transitional entropy (89c). This holds true for the substitution of hydroxymethyl for methyl groups within the series of neopentane (entropy change 4.4 e.u.), Trimethylolethane (entropy change 21.5 e.u.) (89a, 89b). However, in other series of neopentyl alcohols containing a carboxyl or nitro substituent, the replacement of a methyl by a hydroxymethyl group lowered the transitional entropy. Steric hindrance and/or polar effects are the probable cause of the restrictions in conformational order.

## TIME SURFACE TREATMENT FOR PIGMENTS

Inorganic pigments such as titanium dioxide are often coated with organic surface treatments that improve their dispersibility, especially in plastic molding resins. TME itself is a preferred surface treatment. It is highly soluble in water making it easy to apply. Its neopentyl triol structure gives complexation with the oxide surface of the pigment providing improved properties that do not wash off—even in waterborne paints. In addition, TME is not basic and does not interfere with the catalyst systems used in amino resin cross-linked paints.

Properties reported to be improved by treatments of titanium dioxide pigments with TME are:

- ❖ Dispersibility; coating compositions (123), air-drying alkyd paints (120)
- ❖ Agglomeration resistance (120)
- ❖ Wettability (123)
- ❖ Optical properties (120,123)

Direct comparisons have shown TME to produce treated titanium dioxide with wettability and optical properties superior to those producible with trimethylolpropane (123).

When TME is used in combination with aluminum oxide to coat titanium dioxide (up to 0.3% aluminum oxide and up to 0.5% of TME), a pigment is produced that has superior properties for polyethylene coatings (129). This treatment produced better whiteness, dispersibility, hiding power, and heat resistance than the formulation with untreated pigment. Similarly, titanium dioxide pigments can be treated with TME and adducts of organic phosphates with alkanolamines (130). This coating suppresses yellowing in polymers. Treated pyrogenic titanium dioxide (2%) in polystyrene, when pressed at 425 degrees F and 35 tons pressure, produced a product with improved brightness and color tone as compared to untreated product.

Filter cakes of recycled titanium dioxide milling fines can be reslurried with Nalco 78J913 and dry titanium dioxide and used in acrylic coatings of Gardner gloss number 71%. Addition of 0.09% TME raised the Gardner gloss value to 74% (126).

## **TIME PLASTICIZERS**

Esters of TME may be used as plasticizers for special applications. For example, the triacetate of TME has several advantages over triacetin made with glycerin. It is more stable to the destructive influences of heat, light, and hydrolysis.

The longer chain esters of TME described in the Synthetic Lubricants section, p. 32, may also have utility as plasticizers. TME esters made with long chain fatty acids can be epoxidized to yield vinyl stabilizers and plasticizers. Polymeric plasticizers can often be improved by using TME in connection with diols.

TME glycidyl ethers can be esterified with fatty acids such as stearic acid to yield products useful as plasticizers and stabilizers for polyvinyl chloride resins (109).

## PHOTOGRAPHIC, PHOTOCHROMIC AND INK APPLICATIONS OF TME

The use of TME in photographic, photochromic and ink compositions has been widely reported. A few examples are described below.

TME, when added to typical gelatin silver halide photographic emulsions, prevents desensitization due to strain ("stick-mark") and tackiness of the coating. In comparative emulsions, TME was more effective than glycerin (119).

A TME polyester that imparts improved properties to photochromic thermoplastic products can be prepared from TME and tetrahydrophthalic anhydride in reaction with adipic acid and neopentyl glycol or with dimer acid and 1,5-pentanediol (115). This polyester can be incorporated into the layer of film-forming thermoplastic resin and maintain its molecularly dispersed state. Reversible color changes on exposure to visible or ultraviolet radiation are unaffected, including intramolecular hydrogen transfer, molecular realignment, valence-tautomerization, geometrical realignment and/or dissociation photochromic phenomena.

TME polyester/ melamine resins can be used to prepare heat curing ink formulations with good gloss, hardness, solvent resistance, and heat stability during pasteurization (127). Initially, a polyol such as TME is partially esterified (acid no. 1-10) with an alkanolic acid (lauric acid) and tall-oil rosin. This ester is then reacted with a polycarboxylic acid or anhydride such as trimellitic anhydride to acid no.20-90, hydroxyl no. 20-400 and mol. wt. 100-1600). The polyester is then formulated with hexakis(methoxymethyl)melamine and commonly used dyes, pigments, and ink formulating ingredients.

## TME ADHESIVES APPLICATIONS

TME is often used as a component of adhesives. It may be used as part of the polymer, or as a plasticizing additive.

Polymeric materials having good adhesive properties and being unaffected by moisture can be prepared by the reaction of diisocyanates or diisothiocyanates with diols formed by monoesterification of TME with a diboronic acid derivative (108). For example, bis(trimethylolethane)p-phenylenediboronate is reacted with 4,4'-diisocyanatodiphenylmethane.

TME dimethacrylate was employed as the adhesive in a photopolymerizable formulation for laminating a polymer coated cellophane film to a oriented polypropylene film (124).

Methyl hydroxypropyl cellulose based thermosetting adhesives can be plasticized effectively by inclusion of 0.5-3% of TME in the formulation (110).

A low molecular weight (4500, hydroxyl no.7) polyester prepared from TME, neopentyl glycol, tetrahydrophthalic anhydride and adipic acid combined with hexakis(methoxymethyl)melamine can be used to form a strongly adherent heat-sealed film on oxidized polyolefin surfaces (114).

## MISCELLANEOUS APPLICATIONS OF TME

### **Surfactants**

Useful surface-active agents can be prepared from TME. For example, polyoxy derivatives of monoesters of TME are useful in cosmetics and pharmaceuticals as emulsifying agents for oil-in-water emulsions (107). The two free hydroxyls of TME monoesters such as stearate, laurate, myristate and oleate are reacted with an alkylene oxide such as ethylene oxide. By controlling the length of the polyoxy side chains, products can be obtained ranging from solids to liquids.

### **Nucleating Agent for Fog Dispersal**

TME can be used as a nucleating agent for dispersal of fogs (125). Spraying aqueous solutions (50-60 degrees C) of TME into warm (>-5 degrees C) fogs can effect dispersal. Cold fogs are dispersed by passing into them a smoke containing submicron particles of TME.

### **Biologicals**

The tripropiolate ester of TME inhibits the growth of fungi and bacteria (111).

### **Fabric Finishing**

Shrinkage is reduced when a combination of irradiation and TME is used during the finishing process for low twist polyamide fibers (131). The fibers are irradiated under tension followed by treatment with a 1-5% aqueous solution of TME. Fabric treated in this manner had residual warp and weft shrinkage of 1.6 and 2.0% and warp and weft tensile stress of 54 and 32 compared with 4.4, 5.6, 26 and 25 respectively when the fabric was conventionally finished.

## DERIVATIVES OF TME

TME is a useful starting material for synthesis of other compounds. It has three reactive primary alcohol groups with a compact neopentyl structure. It will undergo most common reactions of alcohols, i.e., esterification, etherification, additions to active groups, replacement, etc. Derivatives of TME have exceptionally good stability since there are no beta hydrogens available to facilitate elimination reactions. The 1,3-propanediol portion of TME can enter into cyclization reactions with aldehydes and ketones to cyclic acetals and ketals or with phosphorus acids to yield cyclic esters. Some derivatives of TME are listed in Table 7.

**Table 7. TME Derivatives**

Formula	Preparation	Phys.Constants*	Ref.
1. tribromide	TME/PBr <sub>3</sub>	b7-8, 106-109% <sub>00</sub> b4-6, 104% <sub>00</sub> b1 94-95% <sub>00</sub> b6 108% <sub>00</sub> , f.p. 9.2% <sub>00</sub> n /D 1.5593, d 2.0917, b10, 115% <sub>00</sub>	102   101  103
2. triiodide	1. /NaI	b10 168-170% <sub>00</sub> , m. 32% <sub>00</sub>	103
3. tritosylate	TME/TsCl	needles m. 108-8.5% <sub>00</sub> m. 106.5-107% <sub>00</sub>	103 113
4. triamine.HCl	3. /C <sub>6</sub> H <sub>4</sub> (CO) <sub>2</sub> NH	leaflets, m.ca. 270% <sub>00</sub>	103
5. triamine	4. /alkali	oil b10 105-106% <sub>00</sub> b 219-220% <sub>00</sub> , fumes in air, strongly absorbs CO <sub>2</sub> , hygroscopic	103    103
6. triamine picrate		m. 152% <sub>00</sub>	103
7. triethylthio ether	1. /EtSH, EtNa	b7, 140-141% <sub>00</sub>	102
8. monostearate	TME/acid/NaOH	m. 43-46% <sub>00</sub>	107
9. monolaurate	TME/acid/NaOH	m. 30-34% <sub>00</sub>	107
10. monomyristate	TME/acid/NaOH	m. 40-44% <sub>00</sub>	107
11. monooleate	TME/acid/NaOH	an oil	107
12. tripropiolate	TME/acid/NaOH	m. 83-84% <sub>00</sub>	111
13. trimethylolethane-tris		m. 85-87% <sub>00</sub>	112
14. monoallyl ether		b1 108-110% <sub>00</sub>	118
15. diallyl ether		b7 96-108% <sub>00</sub>	118
16. triacetate		oil b0.05 103% <sub>00</sub>	132
17. tribenzoate		m. 82% <sub>00</sub>	132
18. trithiobenzoate		m. 44% <sub>00</sub>	132
19. tri-p-nitrobenzoate		m. 152% <sub>00</sub>	132
20. orthoformate		m. 106% <sub>00</sub>	132
21. mercaptan		odoriferous liquid, b18 142% <sub>00</sub>	132
22. trimethylsulfone		m. 155	132

## TOXICITY INFORMATION

Trimethylolethane is classified as “non-toxic” by both oral and intraperitoneal acute toxicity tests in mice. No animals died by either route of administration at the 5g/kg level. Thus the LD<sub>50</sub> is greater than 5000 mg/kg.

When applied to the skin of rabbits according to the method of Draize et al. (16 CFR 1500.41), TME was mildly irritating to the abraded skin with a score of 0.6.

When applied in the eyes of rabbits according to the method of Draize et al. (16 CFR 1500.42), TME is not irritating to the eye, with a score of 0.0.

# **SAFETY AND HANDLING**



HMIS Rating. The NFPA Hazardous Materials Identification System rating for TME is: Health Hazard – 1; Flammability – 1; Reactivity – 0; Personal Protection – E (goggles, gloves, dust respirator). This rating indicates that TME is a minimal hazard substance.

#### First Aid

Eyes: Flush thoroughly with water for at least 15 minutes. See a physician

Skin: Wash thoroughly with soap and water.

Ingestion: Induce vomiting. See a physician immediately.

Fire Extinguishing. Use water, dry chemical, foam, or carbon dioxide. Use water to keep fire-exposed packaging cool.

Storage. TME is a combustible solid, flashpoint (Cleveland open cup) 320 degrees F. Store in a cool dry area. Do not store near oxidizers.

Briquetted TME may be stored indefinitely without change provided packaging remains intact and is protected from water damage. The moisture content of TME may increase slowly on extended storage.

Granulated TME storage should be limited to six months or less due to a tendency of the product to cake. To minimize caking, pallets of TME should not be stacked on top of each other, and storage temperatures should be minimized. High humidity conditions may accelerate caking especially if packaging has been opened.

Liquid TME should be stored in tanks heated to maintain the liquid temperature at 80 degrees C. Crystallization will occur at lower temperatures.

Handling. Approved safety goggles, gloves, and a dust respirator are recommended as minimum personal protective equipment when TME is being handled. A permissible dust exposure limit or TLV has not been established for TME. We suggest the OSHA nuisance dust limit of 15 milligrams per cubic meter as total dust as the maximum recommended eight-hour time-weighted average. If dust concentrations exceed permissible limits, NIOSH approved dust respirators, with approval TC-21C-XXX and tight-fitting goggles should be worn until engineering controls are completed.

Due to its granular nature, TME is not likely to form explosive dusts. Care should be taken to avoid the accumulation of dusts.

Waste Disposal. TME may be disposed of in an approved disposal facility in accordance with applicable federal, state, and local regulations. The nature and extent of contamination, if any, may require the use of specialized disposal methods.

Packaging. TME is packaged in 50 lb. multiwall paper bags. The bags are color coded, blue and red, for easy identification. Big bags containing up to 2000 lb can be supplied.

Shipping. TME is classified as a non-hazardous material by the U.S. Department of Transportation. No special labeling is required for shipment.

Material Safety Data sheet. Consult the Material Safety Data Sheet on TME for current information on this product.

Technical Services. TRIMET Products Group maintains a staff of Technical Service experts who can provide assistance on TME handling questions.

# REFERENCES

## Alkyds

1. *L.E. Cadwell and C. Frazier, U.S. Patent 2,618,617, to American Cyanamid Co., Nov. 18, 1952*—Oil modified alkyd resins useful in the manufacture of enamels, lacquers and printing inks were prepared by reaction of TME, phthalic acid anhydride and non-hydroxylated oil fatty acids such as methyl esters of coconut oil fatty acids or cottonseed oil. Alkyd resins of this type were soluble in xylene and had a Gardner color of 6.
2. *E.F. Carlston, Am. Paint J., 42(1), 40-50 (1957), Chem. Abstr. 52:748g*—The use of TME in place of glycerin in an isophthalic polyester alkyd resin for baking use improved compatibility with xylene in short oil vehicles.
3. *J.H. Sample and C.H. Williams, U.S. Patent 2,890,185, to Sherwin Williams Co., Jun. 9, 1959*—A nongelled interpolymer useful for automotive finishing was made from an oil-modified alkyd and at least 3 monomers: a monomeric monovinyl aromatic compound, a monomeric ester of an unsaturated aliphatic acid, and a monomeric vinyl cyanide. A modified alkyd resin was made by reaction of linseed fatty acid, TME, pentaerythritol, phthalic anhydride, vinyltoluene, methylmethacrylate and acrylonitrile. Enamels for automotive coatings, when formulated using this modified alkyd resin as the vehicle for pigments and TiO<sub>2</sub>, had the advantages of shorter dry time, nonwrinkling and no overspray problems.
4. *E.F. Carlston and G.B. Johnson, U.S. Patent 2,991,274, Jul.4, 1961*—Oiless alkyd plasticizers for amino plastic coating resins were prepared by partial condensation of TME and 2-ethylhexanoic acid (434 degrees F, 2.5 hours) and then condensation with isophthalic acid and propylene glycol by cooking at 450 degrees F.
5. *Rohm & Haas Co., Neth. Appl. 6,413,721, May 31, 1965, U.S. Appl. Nov. 29, 1963; Chem. Abstr. 64:3848h*—A coating composition that produces hard, flexible and strongly adherent films was prepared from a TME/phthalate alkyd and alkylated condensation products of formaldehyde and diamides (C4-12). Replacement of 5-30% of the diamide condensate by a formaldehyde/melamine condensate provided resistance to discoloration in the event of overbake.
6. *C.E. Bruggeman, J. Paint Technol. 37 (489) 1186-203 (1965); Chem. Abstr. 64:914a*—An alkyd system is described that attempts to balance or optimize all the variables. The alkyd is based on trimellitic anhydride, TME and safflower oil.
7. *W.M. Kraft and J. Weisfeld, U.S. Patent 3,223,658, to Tenneco Chemicals Co., Dec. 14, 1965*—Stable aqueous emulsions were prepared from short-oil and medium-oil TME based alkyds. The corresponding coating compositions had properties equivalent to solvent-based compositions prepared from the same alkyd.
8. *J.M. Menke, U.S. Patent 3,380,942, to Velsicol Chemical Corp., Apr. 30, 1966*—Air-drying, water-soluble, halogen-containing alkyds were prepared from TME and

chlorendic anhydride. Metal coatings prepared from the resins had high flame retardancy and fire resistance.

9. W.M. Kraft, E.G. Janeuz and D.J. Sughrue, Chapter 3, "Film Forming Compositions," Vol.1, part 1, Edit. R.R. Myers and J.S. Long, Marcel Dekker Inc., New York, 1967, p. 71; D.H. Solomon, "The Chemistry of Organic Film Formers," Robert E. Kreiger, Huntington, NY, 1977, p. 75; "How to Process Better Coating Resins with Amoco IPA and TMA," Bulletin IP-65, Amoco Chemicals Company, Chicago, IL; H.J. Lanson, Chapter 49, "Applied Polymer Science," ACS Symposium Series No. 285, Edit. R.W. Tess and G.W. Poehlein, American Chemical Society, Washington, D.C., 1985; P.K.T. Oldring and G. Hayward, Editors, Chapter VI, "A Manual of Resins for Surface Coatings," Second Edition, Vol.1, SITA Technology, London, 1987, p.129

10. *C.J. McWhorter and E.L. Clark, U.S. Patent 3,329,634, to Commercial Solvents Corp., Jul. 4, 1967*—Short oil TME alkyd resins with short air-drying times were suitable for formulating white appliance coatings that retained gloss and had good flexibility. The alkyds were prepared as the reaction product of equal parts by weight of TME and pentaerythritol with an acid mixture containing phthalic anhydride, benzoic acid, and dehydrated castor oil fatty acids. A paint formulation was prepared using cobalt and zirco driers.

11. *T.J. Miranda, U.S. Patent 3,329,635, to O'Brien Corp., Jul.4, 1967*—Water soluble condensation polymers were prepared from neopentyl polyols such as TME and formulated into a varnish, a semi-gloss enamel and a fast drying semi-gloss paint. A succinic anhydride group was reacted with each hydroxyl group of a neopentyl alcohol to provide a product containing one free carboxyl group and three ester groups per molecule. This intermediate was then condensed with TME, phthalic anhydride and dehydrated castor oil fatty acid in proportions calculated to give an acid number of approximately 55-60.

12. *R.J. Ruhf, E.J. Russell and W.S. Egge, U.S. Patent 3,345,313, to Trojan Powder Co., Oct. 3, 1967*—Water soluble alkyd resins were prepared from a polyol, a polycarboxylic acid, and a polymethylolalkanoic acid. An air-drying alkyd resin was prepared by reacting dimethylolpropionic acid, phthalic anhydride TME and linseed oil fatty acids forming a solution of 35 wt % solids in aqueous tertiary-butanol and adjusting the pH to 7.5 with triethylamine.

13. *R.M. Christenson and BAN. McBain, U.S. Patent 3,345,313, to Trojan Powder Co., Oct 3, 1967*—Blends of an alkyd resin, a modified acrylic polymer and an amine/formaldehyde resin provided coating compositions especially useful in automotive applications. An effective alkyd resin was prepared from TME, p-tert-butylbenzoic acid, phthalic anhydride and coconut fatty acids. Several formulations for the inter polymers are presented.

14. *L.C. Scala and F.A. Sattler, U.S. Patent 3,380,015, to Westinghouse Electric Co., Jun.18,1968, (Brit. 1,088,323, Oct.25, 1967)*—TME was used in alkyd resin

compositions useful as wire enamels and varnishes for motors, electrical conductors, transformers and current controls. The compositions were prepared by combining an alkyd resin contain TME, glycerin, isophthalic acid, tall oil fatty acids and isopropyl titanate with a dicyclopentadiene polymer.

15. *K.A. Earhart, Paint and Varnish Products, 58(10), 79-88 (1968); Chem. Abstr. 70:5244a*—Improved properties for baking coatings and air-drying white enamels were obtained by forming a prepolymer of TME with phthalic anhydride or isophthalic acid before addition of fatty acids.

16. *W.E. Smith, G.J. Mantell and E.C. Chapin, U.S. Patent 3,449,277, to Gulf Oil Corp., Jun. 10, 1969*—A clear smooth glossy film that did not craze on bending was prepared from the product of the reaction of a styrene-methacrolein copolymer, TME and dehydrated castor oil acid.

17. *H. Kozu, M. Kimura, T. Watanabe, N. Iwasawa and M. Yoshida, Ger. Offen. 2,013,988, to Kansai Paint Co., Oct. 1, 1970; Chem. Abstr. 74:32756y*—TME-containing polyester binders for pigments with properties intermediate between alkyd and oil-free alkyd binders with good solvent compatibility and compatibility with other resins were prepared. The resins contained 10-20% of a fatty acid.

18. *S. Isuru, K. Ionue, M. Shigematsu, (Kanae Paint Co., Ltd.) Japan Patent 70 35,434, Nov.12, 1970; Chem. Abstr. 75:50536y*—Heat curable water-soluble resins were prepared from linseed oil, maleic anhydride, TME, trimellitic anhydride and salicylic acid-formaldehyde.

19. *R.D. Holzinger and J.D. Miller, U.S. Patent 3,595,650, to Sherwin-Williams Co., Jul.27, 1971*—Alkyd resins for electrophotographic coatings and coated substrates containing metal oxides were prepared from TME, pentaerythritol, phthalic anhydride, benzoic acid and soybean oil. The compositions were useful in office and business copying products.

20. *R.D. Holzinger and J.D. Miller, U.S. Patent 3,595,650, to Sherwin-Williams Co., Mar. 6, 1973*—Rapid-drying TME-containing short-oil and medium-oil alkyd resins modified with an aminoaromatic carboxylic acid had tack-free drying times of 15-110 minutes. The alkyds were prepared from phthalic anhydride, TME, pentaerythritol, anthranilic acid, tall oil fatty acids, and alkali refined soybean oil.

21. *R.R. Harris and W.J. Pollack, U.S. Patent 4,133,786, to McWhorter, Inc., Jan. 8, 1979*—Fast-drying water-soluble acrylic modified long-oil TME alkyd coating compositions were prepared for high-gloss enamel top coats. They were especially useful in white and light-colored enamels for application on implements.

22. *K. Nakagawa, K. Yamano, T. Watanabe, K. Yamamoto and S. Inomata, Japan Patent 79 136,223, to Kanasi Paint Co., Sep. 28, 1979; Chem. Abstr. 92:95754k*—Antifouling coating compositions with good stability were formed by the reaction of TME,

Phthalic anhydride, linseed oil and triphenyltin.

23. *Kanasi Paint Co., Japan Patent 81 10,572, Feb. 3, 1981; Chem. Abstr. 94:210424h*—Water-thinned fatty acid-modified polyurethane compositions were prepared from the reaction of a partially esterified TME/safflower oil fatty acids intermediate with dimethylolpropionic acid and hexamethylene-diisocyanate.

24. *Nippon Paint Co., Ltd., Japan Patent 57 135,874, Aug. 21, 1982; Chem. Abstr. 98:55706m*—Aqueous coating compositions containing alicyclic or aromatic structures, a polyester and an alkyd were prepared that produced coatings with good workability, high gloss and water resistance. The resins were prepared by partial esterification of TME with linseed oil fatty acids followed by addition of neopentyl glycol, phthalic anhydride, and tetrahydrophthalic anhydride.

25. *N. Sakaguchi, T. Hamada, Y. Ito and G. Nagoao, Japan Patent 60 210,673, to Nippon Paint Co., Ltd., Oct. 23, 1985; Chem. Abstr. 104:150887*—Sag resistant thick film coating compositions giving films with good gloss and appearance were prepared from vehicles containing a TME alkyd containing less than 25% oil and polyacrylates.

26. *T. Lane and M. Rosen, U.S. Patent 4,554,185, to Marine Shield Corp., Nov. 19, 1985*—Antifouling marine coatings with good adhesion, hardness, abrasion resistance, leaching resistance, and useful life were prepared from a polyurethane and a tin containing alkyd.

27. *T. Lane and M. Rosen, U.S. Patent 4,596,724, to Marine Shield Corp., Jun. 24, 1986*—Antifouling marine coatings with good adhesion, hardness, abrasion resistance, leaching resistance, and useful life were prepared from high tin compositions made up of a blend of hydrophilic and hydrophobic polymers.

28. *D. Bode and H. DeGraaf, U.S. Patent 4,609,706, to SCM Corp., Sep. 2, 1986*—High-solids alkyd resins were obtained by reaction of at least a portion of the available hydroxyl groups on a resin with an ethylenically unsaturated monoisocyanate monomer. The alkyd could be used as the major vehicle in high-solids coatings or as a reactive diluent and cure modifier of oxidation curable alkyd polyesters and acrylic resins.

29.a. *P.E. Eckler, U.S. Patent 4,689,266, to International Minerals & Chemical Corp., Aug. 25, 1987*—Reactive diluents for air-drying alkyds were prepared by partially reacting cyclohexanol with maleic anhydride and then with linoleic acid and TME. The finished product was a low viscosity liquid, which could replace part of the resin solids in a conventional alkyd paint formulation with no effect on drying.

29.b. *P.E. Eckler, American Paint & Coatings Journal, Feb. 1, 1988, p. 37*—A comparison of nineteen water soluble air-drying alkyds indicated that TME provided better hydrolytic stability, drying, gloss retention, hardness and corrosion protection.

29c. A.C. Abbott, "Ambient Cure Resins," and "Baking Alkyd Formula," Velsicol Chemical Corp., Rosemont, IL.

### **Polyesters**

30. *J.H. Sample, U.S. Patent 2,901,465, to Sherwin-Williams Co., Aug. 25, 1959*—A polyester with superior color stability on baking could be prepared by reacting at 350-450 degrees F of an aliphatic polyol with at least three hydroxyl groups on nonadjacent carbons, a dialkyl ester of an aromatic diacid and an aliphatic diacid in proportions such that the ratio of hydroxyls to carboxyls is 1.2-1.5. The preferred polyol was TME.

31. *D.J. Carlick, N.J. Kennedy, L. Kutik and H.T. Roth, U.S. Patent 3,039,979, to Interchemical Corp. Jun. 19, 1962*—Combinations of TME/glycol polyesters with amine-aldehyde resins produced baked coatings which had high resistance to detergents, alkali, soaps and solvents in addition to toughness, flexibility, scratch resistance and stability to discoloration. An example polyester was prepared from isophthalic acid, fumaric acid, pelargonic acid, TME and neopentyl glycol.

32. *A.B. Benjamin, U.S. Patent 3,067,158, to Standard Oil Co. of Indiana, Dec. 4, 1962*—Partial esterification of TME with benzoic acid to leave approximately two free hydroxyls followed by reaction with trimellitic anhydride and adipic acid (352 degrees F, 7 hours) produced a resin base which could be formulated into a baking enamel with good alkali resistance.

33. *V.V. Korshack, S.V. Vinogradova and S.A. Siling, Vysokamolekul. Soedin., 7(4), 701 (1965); Chem. Abstr. 63:3123g*—Improved rigidity of films of polyarylates of isophthalic acid and phenolphthalein could be accomplished by incorporation of a small amount (0.05-0.1 mole %) of TME to introduce active free hydroxyls that were used for cross-linking.

34. *N.G. Gaylord, U.S. Patent 3,098,835, to Interchemical Corp., Jul. 23, 1965*—A thermosetting baking resin with good cure, high gloss, good color, good hardness and excellent resistance to soaps, detergents and solvents was formed by blending a TME polyester, an acrylic resin and an amine-formaldehyde resin.

35. *Imperial Chemical Industries, Ltd., Neth. Appl. 6,503,380, Sep. 20, 1965; Chem. Abstr. 64:8493c*—A hydrolytically stable coating could be prepared by blending a TME/phthalic Anhydride/isodecyl alcohol polyester with a methylated melamine-formaldehyde resin.

36. *H. Fischer and H.J. Schubert, Ger. Offen., 1,926,035, to Reichold-Albert-Chemie A.G., Nov. 26, 1970; Chem. Abstr. 74:43631b*—Thermosetting resins suitable as binders for use in powder coating applications were formulated with TME polyesters and a melamine resin.

These thermoplastic coatings had good chemical resistance.

37. *K. Mori and Y. Murakami Japan Patent 78 17,642, to Dainippon Ink and Chemicals, Inc., Feb. 17, 1978; Chem. Abstr. 89:112668t*—TME was useful in preparing water-thinned polyester base resins for coating compositions with hydroxyl values 300-800, acid numbers less than 30 and number-average molecular weights of 500-3000. These polyester bases when mixed with melamine resins produced baked films with good adhesion and resistance to water, solvents, chemicals and soiling. An example polyester was prepared from TME, DL-malic acid and dibutyltin oxide.
38. *Toray Industries, Inc., Japan Patent 82 38,818 & 82 38,819, Mar.1, 1982; Chem. Abstr. 97:93036g & 97:128316c*-- TME, as a result of its exceptional heat and color stability, was useful in the formation of low color and transparent polyester films. The polyester was prepared by reacting terephthalic acid, 1,4-butanediol/triol and catalytic amounts of tertabutoxy titanium at 180-230 degrees C.
39. *L.H. Dunlap and J.S. Heckles, J. Am. Oil Chemists' Soc., 37,281 (1960); Chem. Abstr. 54:15465f*—Types and concentrations of catalysts for the esterification of oleic acid with a variety of polyols were investigated.
40. *G.V. Rudnaya and N.A. Slovokhotova, Zh. Prikl. Spektroskop., 7,70 (1967); Chem. Abstr. 67:118159m*—The replacement of glycerin by TME in fatty acid ester based lacquers imparted improved characteristics – especially improved stability to atmospheric exposure.

### **Silicone Modified Polyesters**

41. *Midland Silicones Ltd., Brit. Patent 765,662, Jan. 9, 1957; Chem. Abstr. 51:10951i*—An alkyd-silicone resin with improved dielectric strength and craze resistance suitable for application to electrical conductors was prepared by reaction of a mixture of and organosilicone resin with glycols and dicarboxylic acids.
42. *D.R. Sylvester, Ger. Offen. 960,505, to Dow Chemical Co., Mar. 21, 1957; Chem. Abstr. 54:12651i*—Alkyd resins are described containing 10-35% by weight of TME modified with organosiloxanes suitable for wire coatings which did not craze on coiling.
43. *A. Abdul-Karim and N. Irani, Am. Paint J. 46 (51), 17, 20, 22, 24-25, 28-9, 32 (1962); Chem. Abstr. 57:1265*—A study of the thermal stability of silicone/alkyd copolymers and the effect of strong organic acids on the alkyd components is reported.
44. *D.A. Rogers, Jr. and L.W. Frost, U.S. Patent 3,342,763, to Westinghouse Electric Corp., Sep. 29, 1967*—A partially cross-linked vegetable oil modified polyester binder composition was blended with an amino/formaldehyde resin or with a silicone

Intermediate resin to form a useful varnish. The alkyd resin contained a combination of polyols (TME/neopentyl glycol), a hydroxyl containing oil (castor oil), and an aromatic dicarboxylic acid (isophthalic acid).

45. *J.A. Stroh and R.J. Wesala, U.S. Patent 3,527,723 to Park Chemical Co., Sep. 8, 1970*—TME compositions suitable for preservative or conditioning coatings for automobile vinyl tops, seats, etc. were prepared from an air-drying alkyd (TME, phthalic anhydride, linseed oil fatty acids and dimethylolpropionic acid), a water soluble cyclopentadiene/linseed oil copolymer vehicle, and emulsified organopolysiloxane oil, an optional drier and a carrier fluid.

46. *K.A. Earhart, Paint Varn. Prod. 63 (1), 35-43 (1972); 63(2), 37-43 (1972)*—A comparative study of TME and TMP in silicone modified polyesters is reported. Polyesters were prepared from the triols with isophthalic acid and azelaic or adipic acids and small amounts of other additives. The polyesters were modified with 30% and 50% methoxysilane. TME/glycol coatings were lower in cost than comparable TMP coatings.

### **Explosives**

47. T. Urbanski, *Chemistry and Technology of Explosives, Vol. II.* Pergamon Press, New York, 1965, p. 197.

48. S. Nauckhoff, *Z. Anew. Chem., 11, 53 (1905): Ref. 47.*

49. H. Kast *Z. ges. Schiess – u. Sprengstoff. 1, 225 (1906): Ref 47.*

50. H. Hibbert, *U.S. Patents 994,841-2 (1911).*

51. E. Hertz, *Ger. Offen. 474173 (1927): Ref. 47.*

52. *T. Colson, Mem. Poudres 30, 43 (1948); Chem. Abstr. 45:8249f;--* TME TN only slightly gelatinized nitrocellulose (11.7% N) and was used satisfactorily to replace nitroglycerin in double-base powders. A commercial-scale continuous process for the preparation of TME TN is described. Physical data and explosive characteristics of TME TN are reported.

53. *R.R. Barnhart and R.M. Cavanaugh, U.S. Patent 2,545,536, to E.I. du Pont de Nemours, Mar. 20, 1951*—Trimethylolethane was nitrated in glacial acetic acid and acetic anhydride to give TME TN.

54. L. Medard and M. Thomas, *Mem. Poudres 36, 97 (1954): Ref. 47.*

55. *W.H Rinkenbach, U.S. Patent 2,709,130, to Trojan Powder Co., May 24, 1955*—Blends of TME TN and neopentyl glycol dinitrate were claimed for use in dynamites as an alternative to nitroglycerine and ethylene glycol dinitrate blends. The novel blends were said to have lower freezing points, reduced shock sensitivity, higher viscosity

and better stability. Seven dynamite compositions are described.

56. *E.J. Russell, U.S. Patent 2,821,466, to Trojan Powder Co., Jan. 28, 1958*—Jelly-like adhesive mixtures containing 5-49% nitrostarch gelatinized with 0.5-30% TME TN served to moistureproof explosive compositions are presented.

57a. *Recherches Chimiques S.A., Belg. Patent 566,271 (1958); Chem Abstr. 53:107766b*-Smokeless powder. TME-TN (4-24 parts by wt.) was used to surface-coat dry gunpowder (100 parts) in smokeless propulsion agents with low temperature coefficients.

57b. *Recherches Chimiques S.A., Brit. Patent 832,137 (1960), Apr. 6, 1960; Chem. Abstr. 54:14690g* – Particulate propellant explosives of conventional nitrocellulose, after treatment with a solution of TME TN (4.2%), maintained substantially constant effectiveness over a wide range of temperatures.

58. *J.P. Flynn, G.A. Lane, J.J. Plomer, U.S. Patent 3,865,654, to Adamas Carbide Corp., Jun. 16, 1965* – TME TN was employed as a plasticizer in nitrocellulose binders for propellant compositions.

59. *G.L. Griffith, G.L. Knotts, and W.L. Scwoyer, U.S. Patent 3,238,074, to Trojan Powder Co., May 1, 1966* – TME TN was used as a sensitizer for an extrudable ammonium nitrate explosive useful in seismic exploration charges.

60. *G.L. Griffith, U.S. Patent 3,300,348, to Trojan Powder Co., Jan. 24, 1967* – Starch was nitrated in the presence of TME producing a conitrate with reduced impact sensitivity and tendency to segregate compared to mechanical blends. The co-nitrates were used in ammonium nitrate slurries.

61. *F.G. Crescenzo, R.L. Dow and B.Y.S. Lee, U.S. Patent 3,306,790, to U.S. Navy, Feb. 28, 1967* – A slow, clean-burning propellant useful as a power source for guided missile accessories was prepared using TME TN as a plasticizer for a cellulose acetate binder.

62. *J.B. Bronstein and G.L. Griffith, U.S. Patent 3,344,005, to Trojan Powder Co., Sep. 26, 1967* – TME TN was blended with PETN to provide an explosive sensitizer with reduced impact sensitivity, but no significant reduction in detonator sensitivity. See also: G.L. Griffith, S. African Pat. 69 00,040, to Commercial Solvents Corp., Jun 25, 1969.

63. *G.L. Griffith, U.S. Patent 3,361,604, to Trojan Powder Co., Jan. 2, 1968* – An ammonium nitrate slurry explosive was prepared using fibrous plant pulp as both fuel and thickener. TME TN was used as a sensitizer.

64. *J.D. Hopper, U.S. Patent 3,400,025, to U.S. Army, Sep. 3, 1968* -- A plastic explosive was prepared using TME TN and tributyl acetyl citrate as plasticizers for nitrocellulose binder in an RDX containing composition.

65. *G.L. Griffith, U.S. Patent 3,423,256, to Commercial Solvents Corp., Jan. 21, 1969* --

TME TN was used to reduce the impact sensitivity of nitroglycerine or ethylene glycol dinitrate. The blends were prepared by co-nitration of blended polyols and were used as sensitizers for ammonium nitrate dynamites.

66. *W.L. Schwoyer, U.S. Patent 3,461,007, to Commercial Solvents Corp., Aug. 12, 1969* – Up to 6% TME TN was blended with primary high explosive such as lead azide to reduce the sensitivity of the composition to electrostatic discharges.

67. *G.L. Wyler, U.S. Patent 3,479,236, to Commercial Solvents Corp., Nov. 18, 1969* -- Free nitric acid is removed from PETN by dispersing in a liquid, low impact sensitivity explosive such as TME TN and drowning out the product. Conitration of TME with PE produced a mixture of nitrates which was easily washed to low acidity.

68. *G.L. Griffith, W.J. Carrol and W.L. Schwoyer, U.S. Patent 3,489,623, to Commercial Solvents Corp., Jan.13,1970* – Gel explosives were prepared with TME TN and nitrocellulose employing a nitroparaffin as solvent. The technique was used to prepare gelatin dynamites, smokeless powders and deflagrating fuse. The nitroparaffins used included nitromethane, nitroethane and 2-nitropropane.

69. *G.L. Griffith, U.S. Patent 3,580,750, to Commercial Solvents Corp., May 25, 1971* – TME TN blended with small amounts of fuel oil was used as a sensitizer for ammonium nitrate dynamites. The detonation rate of these explosive compositions could be controlled by the petroleum content. Examples describe the preparation of water resistant permissible explosives, ammonium dynamites and gelatin dynamites.

70. *G.L. Griffith, U.S. Patent 3,580,751, to Commercial Solvents Corp., May 25, 1971*— TME TN ammonium nitrate explosive with increased sensitivity and an increased rate of detonation were prepared by blending at temperatures in the range 100 to 150 degrees F.

71. *G.L. Griffith, U.S. Patent 3,580,752, to Commercial Solvents Corp., May 25, 1971*— In TME TN/inorganic nitrate explosive compositions, the detonation velocity can be modified by adjusting the water content of the composition.

72. *G.L. Griffith, U.S. Patent 3,580,753, to Commercial Solvents Corp., May 25, 1971*— Aluminum flake was incorporated into an ammonium nitrate/TME TN explosive to increase the rate of detonation.

73. *F.G. Crescenzo and S.L. Dow, U.S. Patent 3,639,183, to U.S. Navy, Feb. 1, 1972* – A propellant composition is described based on cellulose acetate using TME TN as an energetic plasticizer.

74. *M.G. Baldwin and P.H. Gelhaus, U.S. Patent 3,785,887, to U.S. Army, Jan. 15, 1974*— A high energy, high solids content, low sensitivity propellant composition was prepared. TME TN was used as an energetic plasticizer for a pentaerythritol trinitrate acrylate copolymer binder.

75. *J.P. Flynn, G.A. Lane and J.J. Plomer, U.S. Patent 3,865,656, to Adamas Carbide Corp., Feb. 11, 1974* – An 85/15 blend of TME TN diethylene glycol dinitrate was used as an energetic plasticizer for nitrocellulose in a higher energy propellant.

76. *M.G. Baldwin and P.H. Gelhaus, U.S. Patent 3,804,603, to U.S. Army, Apr. 16, 1974*– TME TN was used as an energetic plasticizer for pentaerythritol trinitrate acrylate copolymer in a high energy, low burn rate double base propellant. HMX was used as the oxidizer. The propellant was designed for use in the upper stages of large solid propellant rockets.

77. *J.P. Flynn, G.A. Lane and J.J. Plomer, U.S. Patent 3,844,856, to Dow Chemical Co., Oct. 29, 1974* – TME TN was used as an energetic plasticizer for a nitrocellulose binder in a propellant composition containing solid aluminum hydride and ammonium perchlorate.

78a. *J. Zucker, B. Trask and F. Costa, U.S. Patent 3,867,214, to U.S. Army, Feb. 18, 1975* – A blend of TME TN with triethyleneglycol dinitrate and sometimes diethylene glycol dinitrate was used as a plasticizer for nitrocellulose in a higher energy, low flame temperature artillery propellant.

78b. *J. Zucker, B. Trask and F. Costa, U.S. Patent 3,867,214, to U.S. Army, Feb. 18, 1975* – A blend of TME TN with triethyleneglycol dinitrate and 1,2,4-butanetriol trinitrate was used as a plasticizer for nitrocellulose in a higher energy, low flame temperature, armor piercing mortar propellant. The compositions had superior strength under arctic temperature conditions and consistent performance properties.

79. *F.H. Wells, U.S. Patent 3,943,017, to U.S. Army, Mar. 9, 1976* – A higher power plastic demolition explosive is described employing TME TN as an energetic plasticizer for high-viscosity nitrocellulose.

80. *J.B. Eldridge, U.S. Patent 3,951,706, Apr. 20, 1976* – TME TN was described as a plasticizer for nitrocellulose in a plateau burning propellant composition.

81. *M. Shinohara, F. Matsui and M. Nakayama, Japan Patent 76 48,129, to Nippon Oils and Fats Co., Nov. 1, 1976; Chem. Abstr. 98:1238211* – TME TN alone or in combination with other polyol nitrates was added to solid propellant compositions to provide high mechanical and impact strength at low temperatures.

82. *F.D. Wells, U.S. Patent 4,014,719, to U.S. Army, Mar. 29, 1977* – TME TN was used as a plasticizer for nitro starch binder in a plastic explosive containing RDX.

83. *A.T. Camp and P. Stang, U.S. Patent 4,339,288, Jul. 13, 1982* – Nitrogen gas generating compositions for inflating safety devices were prepared by coating pellets of alkali metal azides and an oxidant with a TME TN plasticized nitrocellulose lacquer.

84. H.M. Zeller, R.J. Couturier and R.A. Tribot, U.S. Patent 4,347,087, to Societe Nationale des Poudres et Explosifs, Aug. 31, 1982 – A high power smokeless powder for use in tank guns is described. TME TN is described as an alternative plasticizer for nitrocellulose in the formulation.

85. E.H. Zeigler, Jr., U.S. Patent 4,352,699, to Hercules, Inc., Oct. 5, 1982 – A process for the co-nitration of TME and diethylene glycol is described. The process used an excess of nitric acid which is claimed to result in a spent acid liquor with improved stability.

86. J.C. Hoffsommer, D.J. Glover, N.F. Burlinson, *J. Org. Chem.*, 48, 315 (1983) – Hydrolysis of TME TN in 50-60 degrees C aqueous ethanolic sodium hydroxide was studied.

### Heat Storage Applications

87. E.F. Westrum, Jr. and J.P. McCullough in "Physics and Chemistry of the Organic Solid State," Volume 1, D. Fox, M.M. Labes and A. Weissberger (Editors), Interscience, New York, 1963, Chapter 1, pp. 85-102.

88. J.G. Aston, *ibid.*, Chapter 9, pp. 543-582.

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89b. E. Murrill and L.W. Breed, *ibid.*, 1, 409 (1970) – New substituted ethanes that exhibit the solid-state transition phenomenon were identified.

89c. E. Murrill, M.E. Whitehead and L.W. Breed, *ibid.*, 3, 311 (1972) – New compounds of the neopentyl type were identified as having plastic crystal properties. Thermodynamic data were reported and mechanisms for the solid-state phase transition phenomenon are discussed.

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91. D.K. Benson, *Energy Technol.* 712 (1983); *Chem. Abstr.* 99:31061d – Three types of solid-state phase-change materials including neopentyl alcohols such as TME were studied. Data are presented and their technical and economical potential in passive solar architectural applications are discussed.

92. D.K. Benson, R.W. Burrows and J.D. Webb, *Sol. Energy Mater.*, 13, 133 (1986); *Chem. Abstr.* 104:136988 – The mechanism for solid state phase transitions in neopentyl polyols such as TME was determined.

93. *T.M. Vigo and C.M Frost, Thermochim Acta, 76, 333 (1984); Chem. Abstract 101:112296m: see also T.I. Vigo and C.M. Frost, U.S. Pat. Appl. 818,567, to U.S. Dept. of Agr., Aug., 1986; Chem. Abstr. 106:019910* – Incorporation of materials that have a high heat of transformation for reversible solid-state phase changes into fiber for the creation of temperature adaptable fabrics was studied.

94. Chemical Week, Aug.1, 1984, p.22, “Plastic Crystals that Store and Release Heat.”

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96. *H. Taoda, et al., Japan Patent 86 218, 683, to Agency of Industrial Sciences and Technology, Sep. 29, 1986; Chem. Abstr. 106:105533* – The cycling ability of a heat storage material such as TME/pentaerythritol was markedly extended by the addition of a phenol or an amine.

97. *H.Taoda, et al., Japan Patent 86 218,682, to Agency of Industrial Sciences and Technology, Sep. 29, 1986; Chem Abstr. 106:105533* – Binary mixtures of pentaerythritol and TME were melted together to form heat storage materials with intermediate solid-state transition temperatures.

98. *J. Font et al., Sol. Energy Mater., 15, 299 (1987) Chem Abstr. 107:026032* – The reversible transitions from crystal solid to plastic crystal in binary mixtures of neopentyl glycol with TME and with pentaerythritol were studied calorimetrically.

99. *A. Horie, K. Kaneoka and F. Takenaka, Japan 87 52,153, Matsushita Electrical Works, Ltd., Mar. 6 1987; Chem Abstr. 106:200922* – Heat storing capsules (0.5-10 mm diam.) were prepared by impregnating absorbent particles with a latent heat storing material such as TME and coating with a water-impermeable thermoplastic resin such as polyethylene.

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113. *M.F. Shostakovakii, AS. Atovin and A.N. Mirakova, Zh. Obskck. Khim, 35, 804 (1965); Chem. Abstr. 63:7002c* – Trimethylolethane tris-(p-toluenesulfonate), mp 106.5-107 degrees C was prepared.
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115. *American Cyanamid Co., Neth. Appl. 6,507,328, Dec. 13, 1965; Chem. Abstr. 65:1085e* – A TME polyester that imparted improved properties to photochromic thermoplastic products was readily prepared from TME and tetrahydrophthalic anhydride in reactin with adipic acid and neopentyl glycol or with a dimer acid and 1,5-pentanediol. This polyester could be incorporated into the layer of film-forming thermoplastic resin containing a photochromic material and/or used as a separating barrier between the support surface and the photochromic layer.
116. *C.W. McGary, Jr. and C.T. Patrick, Jr., U.S. Patent 3,242,106, to Union Carbide Corp., Mar. 22, 1966* – TME or esters of TME were used as epoxy polymerization initiators or modifiers in epoxy/urethane foams and resins.
117. *V.A. Chase and S.A. Miller, U.S. Patent 3,296,322, to Brunswick Corp., Jan. 3, 1967* – An epoxy resin producing rigid heat-resistant coatings was prepared from dicyclopentadiene dioxide, a 1,2-epoxy compound, TME and maleic anhydride.
118. *H. Delius, U.S. Patent 3,355,502, to Reichold Chemicals, Inc., Nov. 28, 1967; Chem. Abstr. 68:77736f* – Mono- and diethers of TME were prepared by reaction of excess TME with 2,3-unsaturated alkenols using mercuric salts and boron trifluoride as etherification catalysts.
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120. *British Titan Products Co., Ltd., Fr. 2,045,426, Feb. 26, 1971; Chem. Abstr. 76:15827g* – Treatment of titanium dioxide pigments with TME imparted

Agglomeration resistance and improved dispersibility in air-drying alkyd paints. The products had excellent optical properties.

121. *T. Kadowaki, M. Dohi and K. Yobobori, Ger. Offen. 2,329,215, to Denki Kagaku Kogyo K.K., Jan. 24, 1974; Chem. Abstr. 82:87402x* – TME Trimethacrylate was used with chloroprene to prepare a gel polymer that had improved extrudability over unmodified chloroprene rubber.
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124. *R.H. Kester and R. Rosen, U.S. Patent 3,992,363, to Sun Chemical Co., Nov. 16, 1976* – TME dimethacrylate was used as the adhesive in a uv sensitive photopolymerizable formulation for laminating a polymer coated film to an oriented polypropylene film.
125. *A.N. Fletcher, U.S. Patent 4,009,828, to U.S. Navy, Mar. 1, 1977* – TME acted as a nucleating agent for dispersal of fogs. Spraying aqueous solutions (50-60 degrees C) of TME into atmospheric fog at temperatures greater than 5 degrees C was effective in dispersing the fog. Colder fogs were dispersed with smoke containing submicron particles of TME.
126. *D.W. Blake, G.A. Shaehan, J.W. Rowland, G. L. Roberts, U.S. Patent 4,178,485, to American Cyanamid Co., Oct. 9, 1979* – Filter cakes of recycled titanium dioxide milling fines could be reslurried with Nalco 78J913 and dry titanium dioxide and used in acrylic coatings of Gardner gloss number 71%. Addition of 0.09% TME raised the Gardner gloss value to 74%
127. *S.L. Laddha and T. Solzbert, French Patent 2,483,434, to Sun Chemical Co., Dec. 4, 1981; Chem. Abstr.96:144705p* – TME polyester/melamine resins were used to prepare heat curing ink formulations with good gloss, hardness, solvent resistance and heat stability during pasteurization.
128. *W.H. Chang, R. Piccirilli and D. Dehl, U.S. Patent 4,314,923, to PPG Industries, Inc., Feb. 9, 1982* – Glycidyl ether modified polyol coating compositions were prepared that were water-thinnable and had good storage properties. These coatings which we useful on wood or printed wood products, were prepared by

reaction of TME (1mole)with a glycidyl ether such as allyl glycidyl ether (0.2-2.0 mole) and addition of a suitable aminoplast curing agent such as boron trifluoride-etherate.

129. *Ishihara Sangyo Kaisha Ltd., Japan Patent 82 36,157, Feb. 26, 1982; Chem. Abstr. 96:218810* – TME was used in combination with aluminum oxide to coat titanium dioxide (up to 0.3% aluminum oxide and up to 0.5% of TME). The treated pigment had superior properties for polyethylene coatings such as better whiteness, dispersibility, hiding power and heat resistance than in the same formulation with untreated pigment.
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131. *K.D. Pismannik, et al., East German Patent 232,406, Jan. 29, 1986; Chem. Abstr.106:019910* – Shrinkage was reduced by the use of irradiation and TME during the finishing process for low twist polyamide fibers. The fibers were irradiated under tension followed by treatment with a 1-5% aqueous solution TME.
132. *W.V.E Doering and L.K. Levy, J. Am. Chem. Soc. 77,509 (1955)* – The triacetate, tribenzoate, orthoformate, trimercaptan, trithiobenzoate, tri-p-nitrothiobenzoate, and trimethylsulfone derivatives of TME were prepared.

# **APPENDIX**

## APPENDIX A

### Specifications and Properties of TME

CAS Registry Number 77-85-0

	Technical	Pure	Nitration	Liquid*
<b>Specifications:</b>				
Hydroxyl Content, %, min	41.0	41.75	41.75	41.0
Ash, %, max	0.01	0.01	0.01	0.01
Water Insolubles, ppm, max	50	50	50	50
Moisture, %, max (Karl Fischer Method)	0.30**	0.30**	0.30**	*
Phthalate Ester Color, Gardner, max (ASTM D-2195)	1	1	--	1
<b>Typical Properties:</b>				
Appearance	White	Crystalline	Solid	Colorless Solution
Melting Range, Deg.C	190-200	199-203	199-203	190-200*
Density, briquets, lbs/gal	6.3	6.6	6.6	9.04***
Granular, lbs./gal	6.2	6.5	6.5	--
Combining Weight	41	40.5	40.5	41
Combing Weight, theory	40.05			
Hydroxyl Content, wt %, theory	42.47			
Flashpoint, Cleveland Open Cup, Deg. F	320			
Thermodynamic Properties (Ref 89a)				
Plastic Crystal Transition				
Temperature, Deg. C	81			
Enthalpy, cal/g	46.1			
Entropy, eu	15.6			
Fusion				
Enthalpy, cal/g	10.7			
Entropy, eu	2.7			
Specific heat (solid), 25 Deg. C, cal/g.-K	0.353			
Specific heat (solid), 50 Deg. C, cal/g.-K	0.372			
Solubility, grams per 100g. solvent				
Water at 25 Deg. C	140			
Methanol at 25 Deg. C	75.2			
Ethanol at 25 Deg. C	27.9			

\* Solids basis, supplied as 80% solids in water

\*\* As packed

\*\*\* 80 Deg. C, gross wt. basis

## Appendix B

### Processes for Preparing TME Alkyds

#### High-solids Baking Enamels

TME Trimethylolethane can be used in the manufacture of high-performance, high-solids polyester baking enamels. The following formulation demonstrates a reduced cost, high-solids resin with good performance properties. In addition, TME provides improved overbake resistance.

Charge	Resin moles	A grams	Resin moles	B grams
Tall oil fatty acid (A)*	0.365	105	--	--
Trimethylpentanediol (TMPD) (B)	2.874	440	3.976	583
TME Trimethylolethane (C )	0.943	116	--	--
Trimethylolpropane (D)	--	--	0.422	57
Phthalic Anhydride (E)	1.529	225.5	1.615	239
Adipic Acid (E)	1.529	223.5	1.610	235
Dibutyl Tin Oxide (F)		2.0		2
		<hr/>		<hr/>
		1112.0		1116
Water of reaction		89		86
Allowances for TMPD losses		21		28
		<hr/>		<hr/>
		1002.0		1002

\* letters in parentheses refer to suppliers found on p. 82.

#### Procedure

Charge the fatty acid and dimethylpentanediol and warm to melt. Then add the remaining materials with agitation. Heat to 225-230 Deg. C under a nitrogen blanket with a steam heated partial condenser. Hold for an acid number of 15.5. Cool to 140 Deg. C and let down to 90% solids with ethylene glycol monoethyl ether acetate.

### Resin Properties\*

Solvent	Viscosity
n-Butyl alcohol	z2.5-z3
Methyl ethyl ketone	z2.5-z3
Methyl n-amyl ketone	z4-z4.5
n-Butyl acetate	z4.5-z5
Aromatic 100 (L)	z5
Ethylene	z5.5-z6

### High Solids Gloss White Baking Enamels

	Pounds	Gallons
High solids resin A or B*	471.1	52.35
Titanium dioxide pigment (G)	404.3	12.14
Hexamethoxymethyl melamine (H)	181.8	18.18
Flow control agent (J)	5.9	0.70
Ethylene glycol monoethyl ether acetate	24.3	3.01
n-Butyl alcohol	26.3	3.90
Disperse, then add		
Catalyst (K)	6.0	0.75
Ethylene glycol monoethyl ether acetate	72.3	8.97
	<hr/>	<hr/>
	1191.9	100.00
Solids by weight	85.0%	
Solids by volume	77.3%	
Resin/cross-linker ratio	70/30	
Catalyst on total resin	1%	
Pigment/binder ratio	0.67/1	
Pounds of TiO <sub>2</sub> /100 gallons	4.0	
Viscosities*	Resin A	Resin B
#4ZahnCup,seconds	25	24
#4 Ford Cup, seconds	110	105

\* 90% by weight in ethylene glycol monoethyl ether acetate.

### Physical Properties of Coated Enamels

For dry film of 1-1.5 mil thickness on 24-gauge Bonderite 1000 (M) CRS panels.

Cure cycle –10 min. at 350 deg. F

	Resin A	Resin B
60% gloss	91	89
Pencil Hardness	2H	2H
MEK double rub	100+	100+
Reverse impact, in.-lb.	50	40
Direct Impact, in.-lb.	110	100
Cross hatch adhesion, removal	none	none

At 100% overbake (20 min. at 350 deg. F), enamel A discolored less.

### Raw Materials Suppliers

- (A) Arizona Chemical Co.; Acintol FA-1
- (B) Eastman Chemical Products
- (C) GEO Specialty Chemicals, TRIMET Products Group
- (D) Celanese
- (E) Monsanto, Inc.
- (F) M&T; Fascat 4201
- (G) DuPont; Ti-Pure R-900
- (H) American Cyanamid; Cymel 303
- (I) 3M Co.; 20% Fluorad FC-430 in ethylene glycol monoethyl ether acetate
- (J) American Cyanamid; Cycat 4040
- (K) Exxon
- (L) Parker Rustproof Division of Oxy Metal Industries Corp.

## Appendix C

### Processes for Preparing TME Polyesters transesterification Fusion Cooking Method

A polyester with superior color stability on baking can be prepared by the following transesterification fusion cooking method (30).

#### Materials

Dimethyl isophthalate . . . . .	808g.
TME . . . . .	600
Adipic acid . . . . .	1.53
Calcium oxide . . . . .	2

#### Procedure

The charge is heated to 350 degrees F in 30 minutes and held there for three hours. The temperature is raised to 390 degrees F, held for 2.5 hours and then raised to 420 degrees F. The cook is continued until the desired acid number is reached, i.e., 3.7 after 5.5 hours, 0.8 after 7hours. The batch can be cut to 55% solids in a mixture of two parts butoxyethanol to one part xylene. The base yield of the polyester is 1340 g. and the Gardner-Holdt viscosity is T+

### Solvent Cooking Method

A polyester suitable for use with amine-aldehyde resins to produce films with superior resistance to overbake and corrosive elements can be prepared by the following solvent cooking method (31).

#### Materials

Isophthalic acid . . . . .	200 parts
Fumaric acid . . . . .	104
Pelargonic acid . . . . .	288
Neopentyl glycol . . . . .	220
TME . . . . .	162

#### Procedures

The charge is heated to 160 degrees C under a carbon dioxide atmosphere. The temperature is slowly raised during three hours to 240 deg.C. The temperature is temporarily reduced and xylene (54 parts) is added. The water-of-esterification is azeotroped off at 230-240 deg. C until the acid number is 10. The solids content is adjusted to 60% with additional xylene (Gardner-Holdt viscosity H, acid number 9). Blending of six parts of this polyester with four parts of a butylated melamine-

## APPENDIX D

### Processes for Preparing Trimethylolethane Trinitrate, TME TN

TME TN can be prepared by the nitration of Trimethylolethane as follows (53).

#### Charge:

TME, Nitration Grade, 20 mesh . . . . . 5 lb. 12 oz.  
Acetic acid . . . . . 12 lb. 2 oz.  
Nitric acid, 98% . . . . . 11 lb. 2 oz.  
Acetic anhydride, 95% . . . . . 20 lb. 3 oz.

#### Procedure

The Trimethylolethane is dissolved in the acetic acid at 35 deg. C. This solution is cooled to 25 deg. C and fed together with the nitric acid into the acetic anhydride with stirring at 20-26 deg.C. After 30 minutes, the mixture is cooled to 10 degrees C. and drowned in well-agitated water. A 90% yield of TME TN is obtained.

Alternatively (52), Trimethylolethane can be added incrementally to an amount of fuming nitric acid (>97%, approximately three times the theoretical amount) at 10 deg. C. On cooling, the yellow viscous oil that is deposited is collected via methylene chloride extraction. A nitrating solution comprising 400 grams of 97% nitric acid, 470 grams of 100% sulfuric acid and 100 grams of oleum (20% SO<sub>3</sub>) effected a 97-98% conversion of 100 grams TME to TME TN.

## APPENDIX E

### Food Additive Applications

Trimet Trimethylolethane (TME) has been cleared by the U.S. Food and Drug Administration for food additive applications as follows:

Application	FDA Regulation
Adhesives	21 CFR 175.105
a. as a component of polyester resins (including alkyds and rosin esters) by cross reference to 175.300(b) (3) (vii)	
b. as the tribenzoate ester	
Resinous and polymeric coatings for metal substrates	21 CFR 175.300
Resinous and polymeric coatings for polyolefin films	21 CFR 175.320
Xylene-formaldehyde resins	21 CFR 175.380
Zinc-silicon dioxide coatings	21 CFR 175.390
Components of paper and paperboard coatings in contact with aqueous and fatty foods	21 CFR 176.170
Defoaming agents used in the manufacture Of paper and paperboard	21 CFR 176.2107
Sealing gasket closures	21 CFR 177.1210
Cross-linked polyester resins	21 CFR 177.2420
Animal glue	21 CFR 178.3120

The following complex substances containing TME appear in the Inventory of Chemical Substances under the U.S. Toxic Substances Control Act:

Complex Substance	CAS Registry Number
Trimethylolethane, adipic acid and coconut oil	68604-24-0
diethylene glycol	63164-02-3
diethylene glycol and polyethylene glycol	67907-28-2
hydrogenated bisphenol A, glutaric, succinic, and Pelargonic acid (methyl esters)	68551-00-8
NPG, TMA, and hydrogenated coconut fatty acid	68915-49-1
NPG, TMA, and pelargonic acid	68072-49-1
TMPD, TMA	33807-61-3
TME, capric, and caprylic acids	69226-98-8
TME, capric, caprylic, and lauric acids	68411-73-4
TME, C <sub>8</sub> -C <sub>10</sub> carboxylic acids	68920-22-9
TME, chlorendic acid, benzoic acid, linseed oil, and tung oil	68938-38-5
TME, C <sub>18</sub> dimer acid, and ethylene glycol	68939-19-2
TME, dimethylbiphenyldiisocyanate, 1,6-hexanediol, 4,4'-(methanetetrayl)dinitro[bis(3,5-bis-1-methylethyl)-Phenol], PEG, caprolactone, and phosgene	68189-48-0
TME, epichlorohydrin	68460-21-9
TME, ethoxylated nonylphenol, TOFA, epoxidized soya oil, and styrene	68015-46-3
TME, and fumarated rosin	68082-94-0
TME, glycidyl allyl ether	71839-56-0
TME, heptanoic acid	23336-49-4
Trimethylolethane, isophthalic acid and adipic acid, castor oil	68855-64-1
azelaic acid, linseed oil	68553-22-0
benzoic acid and conjugated safflower oil	68457-93-2
dehydrated castor FA, methyl methacrylate	66071-51-0
soya oil	68083-21-6
tall oil fatty acid	68552-62-5
vegetable oil fatty acid	68514-11-4
Bisphenol A, soya oil, p-t-butylbenzoic acid, and formaldehyde	68410-85-5
p-t-butylbenzoic acid, soya oil	68918-49-0
CHDM and Adipic acid, vegetable oil fatty acid	70025-10-4
TMA, benzoic acid, soya fatty acid	68188-58-9
TMA, benzoic acid, tall oil fatty acid	72066-68-3
TMA, tall oil fatty acid	72480-54-7
Dehydrated castor oil FA, TOFA, methyl methacrylate, styrene	68333-41-5
Diethylene glycol, TMP, adipic acid	67674-64-0

Complex Substance	CAS Registry Number
diethylene glycol, TMPD	68133-12-0
diethylene glycol, TMPD, adipic acid	67906-90-5
C <sub>18</sub> acid, benzoic acid, safflower oil	68213-32-1
dipropylene glycol, propylene glycol, maleic anhydride, and terephthalic acid	68541-41-3
Trimethylolethane, isophthalic acid, glycerine and dehydrated castor oil	70983-70-9
safflower oil	68333-61-9
soya oil	68410-78-6
tall oil	68608-29-7
terephthalic acid and coconut oil	68921-05-1
linseed oil	68783-68-6
soya oil	68783-39-7
tall oil fatty acid	68650-20-4
TOFA, tallow fatty acid	68919-69-7
tallow fatty acid	68650-60-2
trimellitic anhydride, vegetable oil fatty acid	68856-00-8
TME, IPA, 1,6-hexanediol, and adipic acid	67906-24-5
TME, isophthalic acid, hydrogenated bisphenol A and trimellitic anhydride, linseed oil fatty acid	67989-58-6
trimellitic anhydride, vegetable oil fatty acid	68915-21-9
TMPD, TMA, and linoleic acid	67939-13-3
TME, isophthalic acid, and linseed oil	68309-47-7
linseed oil, rosin	68458-36-6
maleic anhydride, benzoic acid, soya oil	67923-27-7
maleic anhydride, soya oil, rosin	68814-66-4
neopentyl glycol and adipic acid	31048-26-7
adipic acid, trimellitic anhydride	68715-92-4
adipic acid, vegetable oil fatty acid	70025-11-5
azelaic acid, trimellitic anhydride	71050-60-7
maleic anhydride, pelargonic acid	67989-04-2
propylene glycol capped bisphenol A and adipic acid	64521-28-4
safflower oil	68554-45-0
tall oil fatty acid	70528-76-6
TMA, benzoic acid, soya fatty acid	68605-23-2
TMA, soya oil	68814-36-8
TMP, adipic acid	68299-12-7
TMP, adipic, isononanoic acid	68439-34-9
TMP, adipic, TMEhoxydimethyltriphenyltrisiloxane	68540-53-4
TMP, azelaic	64365-59-9

Complex Substance	CAS Registry Number
TMP, azelaic, polydimethylsilene oxide polymethyl-(2-phenylethyl)-silene oxide	66085-52-7
TME, isophthalic acid, and pelargonic acid	68186-58-3
pentaerythritol, benzoic acid, and linseed oil	68533-24-2
pentaerythritol and coconut fatty acid	70879-69-5
PE, fumaric acid, linseed oil, menhaden oil, and rosin	68410-51-5
pentaerythritol, and soya oil	68152-86-3
pentaerythritol, trimellitic anhydride, and linseed oil	68514-57-8
(dimethyl ester) and propylene glycol	68867-74-3
propylene glycol, maleic anhydride, and terephthalic acid	68541-27-5
propylene glycol and terephthalic acid	68541-29-7
propylene oxide capped bisphenol A, TMPD, and adipic acid	64521-27-3
safflower oil	68476-93-7
soya oil	66070-63-1
soya oil, linseed oil, formaldehyde, phenol, and rosin	68476-68-6
stearic acid	68186-77-6
tall oil fatty acid	68526-37-4
trimethylolethane, isophthalic acid, terephthalic acid and acrylic acid, linoleic acid, styrene, and methyl methacrylate	67712-02-1
benzoic acid, linseed oil, and tall oil	68783-67-5
benzoic acid, polymerized safflower oil, and safflower oil	70084-95-6
benzoic acid, soya oil, and tung oil	68918-50-3
benzoic acid, tall oil fatty acid, tallow fatty acid, and tung oil	68919-56-2
linseed oil and rosin	68919-30-2
soya fatty acid and vegetable oil fatty acid	68650-27-1
soya oil and rosin	68938-49-8
tall oil	68650-33-9
tall oil fatty acid and rosin	68919-72-2
trimellitic anhydride, linoleic acid, methyl methacrylate, and styrene	70529-00-9
Trimethylolethane, isophthalic acid, trimellitic anhydride and linoleic acid, methyl methacrylate, and styrene	70529-00-9
benzoic acid and castor oil	68154-17-6
benzoic, castor oil, and coconut oil	71243-52-2
benzoic and linseed oil	68553-25-3
ditto	68606-49-5
benzoic, safflower FA, soya FA, and TOFA	70750-35-5
benzoic and soya oil	68152-84-1
benzoic and soya fatty acid	68552-40-9
benzoic and tall oil	69013-27-0
benzoic and tung oil	68333-64-2
benzoic and vegetable oil fatty acid	68783-59-5

Complex Substance	CAS Registry Number
soya oil	68647-69-8
soya fatty acid, and vegetable fatty acid	68650-26-0
tall oil	68513-82-6
tall oil fatty acid	68139-52-6
Trimethylolethane, isophthalic acid and	
Trimethoxydimethyltriphenyltrisiloxane	68311-07-9
TMP	64365-54-5
TMP, adipic, pelargonic acid, and Trimethoxydimethyl- triphenyltrisiloxane	68647-10-9
TMP, adipic acid, and Trimethoxydimethyltriphenylsiloxane	68540-52-3
TMP and azelaic acid	64365-55-5
TMP and soya oil	70879-78-6
TMP, trimellitic anhydride, and vegetable oil FA	70914-01-1
TMP and Trimethoxydimethyltriphenyltrisiloxane	68540-50-1
TMPD and adipic acid	68813-99-0
TMPD, adipic acid, and vegetable oil fatty acid	70025-12-6
TMPD, trimellitic anhydride, and tall oil fatty acid	67989-31-5
TMPD and adipic acid	55100-63-5
Trimethylolethane and maleic anhydride	72829-16-4
Trimethylolethane, maleic anhydride, and benzoic acid	68071-26-1
Trimethylolethane, phthalic anhydride, adipic acid, and soya fatty acid and styrene	68605-20-9
p-t-butyl benzoic acid	68186-76-5
p-t-butyl benzoic, capric, and myristic acids	68130-16-5
coconut oil	68650-70-4
C <sub>9</sub> -C <sub>16</sub> dicarboxylic acids	69011-91-2
maleic anhydride and p-t-butyl benzoic acid	68002-45-9
maleic anhydride and coconut oil	68082-19-9
maleic anhydride and pelargonic acid	68070-97-3
pelargonic acid	68647-12-1
TME, PA, azelaic acid, p-t-butyl benzoic acid, and pelargonic acid	69029-31-8
Trimethylolethane, phthalic anhydride, benzoic acid	68646-97-9
Trimethylolethane, phthalic anhydride, benzoic acid and	
castor oil	68409-89-2
coconut oil	66071-24-7
conjugated safflower oil	68457-94-3
dehydrated castor oil	68131-62-4
linseed oil fatty acid	68526-24-9
safflower oil	68132-15-0
safflower oil an tung oil	68814-24-4
soya oil	68937-58-6
tall oil fatty acid	68082-44-0

Complex Substance	CAS Registry Number
tall oil fatty acid and rosin	68082-45-1
vegetable oil fatty acid	68082-62-2
Trimethylolethane, phthalic anhydride, bisphenol A and benzoic acid, soya fatty acid, and epichlorohydrin	68920-29-6
lauric acid and epichlorohydrin	64365-52-2
myristic acid and epichlorohydrin	64653-91-4
TME, phthalic anhydride, and butylbenzoic acid	64415-30-1
TME, phthalic anhydride, and p-t-butylbenzoic acid	68814-19-7
TME, phthalic anhydride, and p-t-butylbenzoic acid and castor oil	70913-95-0
dehydrated castor oil	66071-44-1
isononanoic acid	67989-05-3
linseed oil and soya oil	68122-94-1
pelargonic acid	67906-87-0
ditto	67989-21-3
ditto	68186-48-1
ditto	68936-79-8
soya oil	66071-22-5
TME, phthalic anhydride, and capric acid	67906-89-2
TME, phthalic anhydride, and C <sub>10</sub> -C <sub>18</sub> caroxylic acids	68583-91-5
TME, phthalic anhydride, and castor oil	68409-93-8
TME, PA, castor oil, and coconut oil	69013-26-9
TME, PA, castor oil, and tall oil	68952-26-1
TME, phthalic anhydride, and coconut fatty acid	68647-52-9
TME, phthalic anhydride, and coconut oil	68082-21-3
ditto	68082-22-4
TME, PA, coconut oil, benzoguanamine, formaldehyde, and styrene	68783-32-4
TME, phthalic anhydride, coconut oil, and styrene	68783-33-5
TME, phthalic anhydride, and cottonseed oil fatty acid	66070-99-3
dehydrated castor oil, soya oil, and vinyltoluene	68551-64-4
C <sub>9</sub> -C <sub>16</sub> and C <sub>9</sub> -C <sub>14</sub> dicarboxylic acids, and palmitic acid	69011-93-4
TME, phthalic anhydride, diethylene and glycol and benzoic acid and styrene	68987-76-8
castor oil	68783-29-9
maleic anhydride and tetrabromophthalic anhydride	70833-56-6
TME, PA, C <sub>18</sub> dimer acid, and dehydrated castor oil	68551-99-5
TME, PA, C <sub>18</sub> dimer acid, dehydrated castor oil methyl methacrylate, and styrene	68551-98-4
TME, phthalic anhydride, dipentaerythritol and ethylene glycol, pentaerythritol, fumaric acid, and tall oil fatty acid	68139-43-5

Complex Substance	CAS Registry Number
pentaerythritol, benzoic acid, and soya oil	68122-65-6
pentaerythritol, benzoic acid, and tall oil FA	68459-62-1
pentaerythritol, fumaric acid, and tall oil	68783-99-3
Trimethylolethane, phthalic anhydride, ethylene glycol and glycerine, pentaerythritol, polypropylene glycol, TMP, and C <sub>16</sub> -C <sub>18</sub> and C <sub>18</sub> unsaturated oil	68514-24-9
glycerine, pentaerythritol, propylene glycol, TMP, and C <sub>16</sub> -C <sub>18</sub> and C <sub>18</sub> unsaturated oil	68915-79-7
pentaerythritol and benzoic acid, tall oil fatty acid, and linseed oil	68605-46-9
coconut fatty acid	68459-36-9
maleic anhydride and walnut oil	68015-23-6
trimellitic anhydride and safflower oil	68649-77-4
TMA, and C <sub>16</sub> -C <sub>18</sub> and C <sub>18</sub> unsaturated oil	68606-14-4
propylene glycol and adipic acid and conjugated safflower oil	68607-57-8
isophthalic acid, and oleic dimer acid	68016-24-0
ditto	68425-71-8
sebacic acid and conjugated safflower oil	68213-64-9
C <sub>18</sub> dimer acid	68938-20-5
Trimethylolethane, phthalic anhydride, fumaric acid and benzoic acid and tall oil fatty acid	68920-34-3
coconut oil	68604-26-2
linseed oil and tall oil	68139-21-9
pelargonic acid	67989-02-2
Trimethylolethane, phthalic anhydride, glycerine and adipic acid, isophthalic acid, benzoic acid, and coconut fatty acid	68459-33-6
benzoic acid and linseed oil	68122-91-8
benzoic acid and safflower oil	73138-84-8
castor oil	68459-76-7
coconut oil	68525-83-7
dehydrated castor oil and soya ail	68605-01-6
linseed oil and soya oil	68606-67-7
linseed oil and tung oil	68139-22-0
Trimethylolethane, phthalic anhydride, glycerine and maleic anhydride, and castor oil	68038-04-0
pentaerythritol and benzoic acid and soya oil	68918-48-9
maleic anhydride and castor oil	68459-73-4
maleic anhydride, linseed oil, and rosin	68991-14-0
maleic anhydride, palmitic, pelargonic, and stearic acids	69029-17-0
maleic anhydride and soya oil	68512-82-3

Complex Substance	CAS Registry Number
vegetable oil fatty acid	68476-21-1
trimethylolethane, phthalic anhydride and 1,6-hexanediol, neopentyl glycol, adipic acid, and fumaric acid	70615-20-2
1,6-hexanediol, neopentyl glycol, and isophthalic acid	67487-65-4
isophthalic acid and dehydrated castor oil	68513-57-5
dehydrated, polymerized castor oil, and safflower oil	68409-85-8
vegetable oil fatty acid and linseed oil	68410-43-5
vegetable oil fatty acid and safflower oil	68476-22-2
vegetable oil fatty acid, soya oil, and tung oil	68476-23-3
itaconic acid, safflower oil and tung oil	66070-67-5
tung oil, acrylonitrile, and styrene	68649-78-5
tung oil and styrene	66071-54-3
lauric acid	64385-83-7
lauric acid and palmitic acid	68511-06-8
linseed oil	68553-56-0
linseed oil, p-t-butylphenol, formaldehyde, and rosin	68910-75-8
linseed oil and soya oil	68514-59-0
linseed oil and tall oil	68188-57-8
maleic anhydride and benzoic acid and tall oil fatty acid	68038-20-0
coconut fatty acid	68920-16-1
dehydrated castor oil fatty acid	68308-98-5
pelargonic acid	68890-71-1
sorbic acid and tall oil fatty acid	73138-56-4
tall oil and abitol	68957-19-7
tall oil fatty acid	68139-54-8
TOFA, HMMM, formaldehyde, urea	67989-39-3
myristic acid	64653-92-5
neopentyl glycol	68586-08-3
neopentyl glycol, adipic acid, and isophthalic acid	67815-72-9
neopentyl glycol, adipic acid, isophthalic acid and p-t-butylbenzoic acid	73049-33-9
pelargonic acid and cottonseed oil	68390-43-2
Pentaerythritol	32876-35-0
pentaerythritol, adipic acid, tall oil fatty acid, and soya oil	68333-46-0
Trimethylolethane, phthalic anhydride, pentaerythritol, benzoic acid and soya oil	66070-93-7
ditto	68552-41-0
ditto	68083-23-8
stearic acid and vegetable oil fatty acid	68814-86-8
tall oil	68918-08-1

Complex Substance	CAS Registry Number
tung oil, dimethylethanolamine	68410-89-9
Trimethylolethane, phthalic anhydride, pentaerythritol	
p-t-butylbenzoic acid and	
Coconut oil	68921-21-1
2-ethylhexanoic acid, allyl alcohol, and styrene	68389-69-5
soya fatty acid and castor oil	66071-42-9
tall oil fatty acid, allyl alcohol, and styrene	68605-43-6
Trimethylolethane, phthalic anhydride, pentaerythritol, and	
C <sub>6</sub> -C <sub>12</sub> carboxylic acid	68082-01-9
castor oil, methyl methacrylate, and styrene	68308-84-9
coconut oil	68459-30-3
conjugated safflower oil and soya oil	68309-63-7
cottonseed oil fatty acid	68991-00-4
dehydrated castor oil fatty acid	66071-02-1
dehydrated castor oil, methyl methacrylate, and styrene	66071-73-6
dehydrated castor oil and soya oil	68132-73-0
dehydrated castor oil fatty acid and soya oil	68459-48-3
dehydrated castor oil and propylene oxide	68552-30-7
2-ethylhexanoic acid	67875-48-3
fumaric acid and tall oil fatty acid	68814-82-4
fumaric acid and walnut oil	68015-22-5
isophthalic acid and	
dehydrated castor oil	68513-56-4
linseed oil	68410-56-0
maleic anhydride and soya oil fatty acid	68513-33-7
maleic anhydride and	
benzoic acid and soya oil	68458-04-8
benzoic acid and tall oil fatty acid	68139-38-8
palmitic, pelargonic, and stearic acids	69020-16-9
safflower oil and walnut oil	70879-75-3
soya oil	68390-07-8
soya oil and walnut oil	68607-05-6
walnut oil	67700-53-2
propylene glycol and coconut oil	68513-61-1
safflower oil	68554-46-1
safflower oil and soya oil	66071-00-9
soya oil	68072-26-4
tall oil fatty acid	67762-03-2
tall oil fatty acid and vinyltoluene	68911-46-6
trimellitic anhydride, benzoic acid, and tall oil fatty acid	68139-39-9
Trimethylpentanediol and tall oil fatty acid	68139-55-9
tripentaerythritol and tall oil	68650-35-1
vegetable oil fatty acid, acrylonitrile, methyl	
methacrylate,	
and vinyltoluene	68783-58-4

Complex Substance	CAS Registry Number
walnut oil	70248-41-8
Trimethylolethane, phthalic anhydride and propylene glycol and soya oil	68122-50-9
propylene glycol and tetrabromophthalic anhydride	68992-09-6
safflower oil and styrene	68783-86-8
soya fatty acid	68605-29-8
soya oil	68140-06-7
tall oil fatty acid	66070-83-5
tall oil fatty acid and castor oil	68921-20-0
trimellitic anhydride, benzoic acid, and tung oil	68410-90-2
trimellitic anhydride and soya oil	68477-06-5
trimethylolpropane, maleic anhydride, benzoic acid, and soya oil	67923-29-9
trimethylpentanediol, adipic acid, and trimellitic anhydride	67939-51-9
vegetable oil fatty acid and tung oil	67989-34-8
Trimethylolethane and conjugated safflower oil	68152-79-4
TME, tall oil fatty acid, epoxidized soya oil, and ethoxylated nonylphenol	68783-51-7
Trimethylolethane terephthalic acid and diethylene glycol, trimethylolpropane, and adipic acid	70729-93-0
dimethyl ester, ethylene glycol, linoleic acid, dimethoxydiphenylsilane	68958-13-4
neopentyl glycol	68413-95-6
pentaerythritol and soya oil	68608-06-0
trimellitic anhydride, benzoic acid, castor oil, and coconut oil	68991-63-9
Trimethylolethane, toluene diisocyanate and ethylene glycol, neopentyl glycol, phthalic anhydride, and tall oil fatty acid	68333-43-7
isophthalic acid, trimellitic anhydride, and tall oil fatty acid	72623-79-1
neopentyl glycol, phthalic anhydride, and TOFA	67922-89-8
pentaerythritol, isophthalic acid, phthalic anhydride, and linseed oil	68410-55-9
linseed oil	68553-59-3
tung oil	68555-26-0
Trimethylolethane, trimellitic anhydride, bisphenol A, benzoic acid, vegetable oil fatty acid, and epichlorohydrin	68956-45-6

## Abbreviations

CHCM, 1,4-cyclohexanedimethanol  
FA, Fatty Acid  
HMMM, hexamethoxymethylmelamine  
IPA, isophthalic acid  
NPG, neopentyl glycol  
PA, phthalic anhydride  
PE, pentaerythritol  
PEG, polyethyleneglycol  
TMA, trimellitic anhydride  
TME, Trimethylolethane  
TMP, trimethylolpropane  
TMPD, 2,2,4-Trimethylpentanediol-1,3  
TOFA, tall oil fatty acid

## **TRADEMARKS**

Acintol®, Arizona Chemical Co.

Bonderite®, Oxy Metals Co.

Cycat®, American Cyanamid Co.

Cymet®, American Cyanamid Co.

DMPA® GEO Specialty Chemicals, TRIMET Products Group

Fascat®, M&T Chemical Co.

Fluorad®, 3M

Resimene®, Monsanto, Inc.

Ti-Pure®, EI DuPont de Nemours & Co., Chemicals & Pigments Dept.

TRIMET®, GEO Specialty Chemicals, TRIMET Product Group