ALCOHOLS, POLYHYDRIC

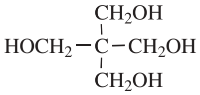
1. Introduction

Polyhydric alcohols or polyols contain three or more CH_2OH functional groups. The monomeric compounds have the general formula $R(CH_2OH)_n$, where $n = 3$ and R is an alkyl group or CCH_2OH; the dimers and trimers are also commercially significant. Related species where $n = 2$ are discussed elsewhere (see GLYCOLS).

The most important polyhydric alcohols are shown in Figure 1. Each is a white solid, ranging from thecrystalline pentaerythritols to the waxy trimethylol alkyls. The trihydric alcohols are very soluble in water, as is ditrimethylolpropane. Pentaerythritol is moderately soluble and dipentaerythritol and tripentaerythritol are less soluble. Table 1 lists the physical properties of these alcohols. Pentaerythritol and trimethylolpropane have no known toxic or irritating effects (1,2). Finely powdered pentaerythritol, however, may form explosive dust clouds at concentrations above 30 g/m^3 in air. The minimum ignition temperature is 450°C (3).

2. Reactions

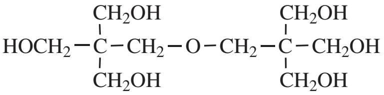
Direct acetylation of pentaerythritol using acetic acid in aqueous solution or in toluene produces a mixture of acetates which can be fairly readily separated by chromatographic methods or distillation (8,9). The final product composition can be varied somewhat by altering the amount of water present. Esters of higher homologues and trimethylolpropane can also be synthesized using this procedure. Acrylate and methacrylate monoesters may be produced (10,11) when protecting groups are placed on three of the pentaerythritol hydroxyls. The protected intermediate then reacts with either acryloyl chloride [814-68-6] or



$HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$

(**1**)

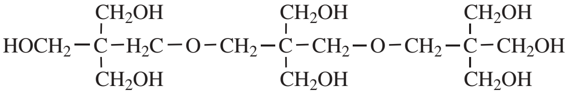
pentaerythritol, tetramethylolmethane



$HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2-O-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$

(**2**)

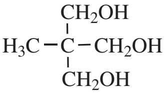
dipentaerythritol



$HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-H_2C-O-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2-O-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$

(**3**)

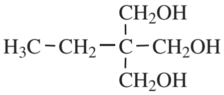
tripentaerythritol



$H_3C-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$

(**4**)

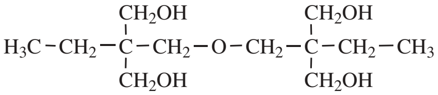
trimethylolethane



$H_3C-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$

(**5**)

trimethylolpropane



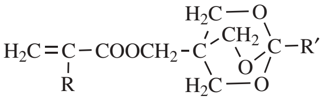
$H_3C-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2-O-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2-CH_3$

(**6**)

ditrimethylolpropane

Fig. 1. Polyhydric alcohols. Systematic names are (**1**) 2,2-bis(hydroxymethyl)-1,3-propanediol; (**2**) 2,2-[oxybis(methylene)]-bis[2-hydroxymethyl]-1,3-propanediol; (**3**) 2,2-bis{[3-hydroxy-2,2-bis(hydroxymethyl)propoxy]methyl}-1,3-propanediol; (**4**) 2-hydroxy-methyl-2-methyl-1-2-methyl-1,3-propanediol; (**5**) 2-ethyl-2-hydroxymethyl-1,3-propanediol; and (**6**) 2,2-[oxybis(methylene)]-bis(2-ethyl)-1,3-propanediol.

methacryloyl chloride [27550-72-7] to give products of the type



An alternative synthesis converts monobromopentaerythritol to the ortho ester, followed by reaction with cuprous acrylate.

Long-chain esters of pentaerythritol have been prepared by a variety of methods. The tetranonanoate is made by treatment of methyl nonanoate [7289-51-2] and pentaerythritol at elevated temperatures using sodium phenoxide alone, or titanium tetrapropoxide in xylene (12). Phenolic esters having good antioxidant activity have been synthesized by reaction of phenols or long-chain aliphatic acids and pentaerythritol or trimethylolpropane (13). Another ester synthesis employs the reaction of a long-chain ketone and pentaerythritol in xylene or chlorobenzene (14). Mixed esters have been produced using mixed isostearic and cyclohexane carboxylic acids in tribromophosphoric acid, followed by reaction with lauric acid (15).

Polyhydric alcohol mercaptoalkanoate esters are prepared by reaction of the appropriate alcohols and thioester using *p*-toluenesulfonic acid catalyst under nitrogen and subsequent heating (16, 17). Organotin mercapto esters are similarly produced by reaction of the esters with dibutyltin oxide (18).

Table 1. **Physical Properties of Polyhydric Alcohols**

Property	Penta-erythritol	Dipenta-erythritol	Tripenta-erythritol	Trimethylol-ethane	Trimethylol-propane	Ditrimethylol-propane[a]
CAS Registry Number	[115-77-5]	[126-58-9]	[78-24-0]	[77-85-0]	[77-99-6]	[23235-61-2]
molecular formula	$C_5H_{12}O_4$	$C_{10}H_{22}O_7$	$C_{15}H_{32}O_{10}$	$C_5H_{12}O_3$	$C_6H_{14}O_3$	$C_{12}H_{26}O_5$
melting point, °C	261–262[b]	221–222.5[b]	248–250[b]	202[c]	58.8[d]	112–114
boiling point, °C	276 (4 kPa)			283[c]	289[d]	210 (0.12 kPa)
solubility, g/100 g water						
25°C	7.23[b]	0.28[e]	0.018[e]	soluble	soluble	2.6
50°C	16.1[e]	1.1[e]	0.07[e]			8.3
90°C	51.9[e]	6.1[e]	0.51[e]		>200 (completely soluble)	
flash point, °C (Cleveland open cup)	260[f]				180[d]	>150
density, g/mL	1.396[f]	1.369[f]	1.30[f]		1.09[d]	1.18
refractive index	1.55 (20°C)[g]				1.472 (70°C)[g]	

[a] Data supplied by Perstorp AB.

[b] Ref. 1.

[c] Refs. 4 and 5.

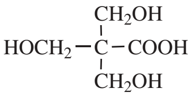
[d] Ref. 2.

[e] Estimated value.

[f] Ref. 6.

[g] Ref. 7.

Pentaerythritol can be oxidized to 2,2-bis(hydroxymethyl)hydracrylic acid [2831-90-5], $C_5H_{10}O_5$,



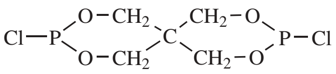
$$HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-COOH$$

by direct air oxidation in aqueous solution using a palladium–carbon catalyst (19), or by biological oxidation using corynebacterium or arthrobacter cultures (20).

Bromohydrins can be prepared directly from polyhydric alcohols using hydrobromic acid and acetic acid catalyst, followed by distillation of water and acetic acid (21). Reaction conditions must be carefully controlled to avoid production of simple acetate esters (22). The raw product is usually a mixture of the mono-, di- and tribromohydrins.

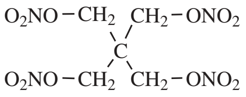
Borolane products of mixed composition can be synthesized by direct addition of boric acid to pentaerythritol (23).

Reaction between pentaerythritol and phosphorous trichloride [7719-12-2] yields the spirophosphite, 3,9-dichloro-2,4,8,10-tetraoxa-3,9,-diphosphaspiro [5,5]-undecane [3643-70-7], $C_5H_8Cl_2O_4P_2$,



in the presence of benzene or a methyl acid phosphate catalyst (24,25) followed by removal of hydrogen chloride. Substituents may then replace the remaining chloride on treating the product with an alcohol or phenol (26) in the presence of a hydrogen chloride binding base such as triethylamine. Direct reaction of triethyl phosphite [122-52-1] and pentaerythritol is also possible (27). Pentaerythritol phosphate is similarly prepared by the reaction of pentaerythritol and phosphorus oxychloride [10025-87-3], $POCl_3$, in dioxane (28). Substituted diphosphaspiro compounds are made by reaction of pentaerythritol and either phosphonic anhydrides or trialkyl phosphites and trialkylamine (29,30).

The commercially important explosive pentaerythritol tetranitrate [78-11-5] (PETN), $C_5H_8N_4O_{12}$,

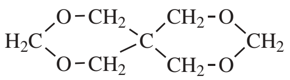


is produced by direct reaction of pentaerythritol in nitric or nitric–sulfuric acid media (31–33).

Aminoalkoxy pentaerythritols are obtained by reduction of the cyanoethoxy species obtained from the reaction between acrylonitrile, pentaerythritol, and lithium hydroxide in aqueous solution. Hydrogen in toluene over a ruthenium catalyst in the presence of ammonia is used (34). The corresponding aminophenoxyalkyl derivatives of pentaerythritol and trimethylolpropane can also be prepared (35).

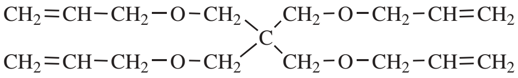
Tosylates of pentaerythritol and the higher homologues can be converted to their corresponding tetra-, hexa-, or octaazides by direct reaction of sodium azide (36), and azidobenzoates of trimethylolpropane and dipentaerythritol are prepared by reaction of azidobenzoyl chloride and the alcohols in pyridine medium (37).

Pentaerythritol can be converted to the biscyclic formal, 2,4,8,10-tetraoxaspiro[5,5]undecane [126-54-5], $C_7H_{12}O_4$,



by heating in the presence of formaldehyde or paraformaldehyde and an acid catalyst (38). Alternatively, a cation-exchange resin catalyst may be used and excess water removed by azeotropic distillation (39). Higher aldehydes have also been used to prepare long-chain alkyl and aryl cyclic acetals (40–43).

Simple alkyl and alkenyl ethers of pentaerythritol are produced on direct reaction of the polyol and the required alkyl or alkenyl chloride in the presence of quaternary alkylamine bromide (44). Allyl chloride produces the pentaerythritol tetrallyl ether [1471-18-7],

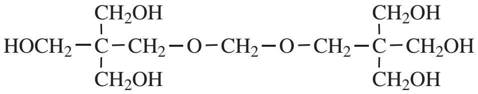


in high yield by this method (45,46) or by using sodium hydroxide catalyst (47). Polycyclic crown looped and starburst dendrimer ethers are synthesized utilizing blocking-deblocking and high dilution cyclization techniques in reactions of dialcohols and ditosylates (48,49).

3. Manufacture

Pentaerythritol is produced by reaction of formaldehyde [50-00-0] and acetaldehyde [75-07-0] in the presence of a basic catalyst, generally an alkali or alkaline-earth hydroxide. Reaction proceeds by aldol addition to the carbon adjacent to the hydroxyl on the acetaldehyde. The pentaerythrose [3818-32-4] so produced is converted to pentaerythritol by a crossed Cannizzaro reaction using formaldehyde. All reaction steps are reversible except the last, which allows completion of the reaction and high yield industrial production.

The main intermediates in the pentaerythritol production reaction have been identified and synthesized (50,51) and the intermediate reaction mechanisms deduced. Without adequate reaction control, by-product formation can easily occur (52,53). Generally mild reaction conditions are favored for optimum results (1,54). However, formation of by-products cannot be entirely eliminated, particularly dipentaerythritol and the linear formal of pentaerythritol, 2,2′-[methylenebis(oxymethylene)]bis(2-hydroxymethyl-1,3-propanediol) [6228-26-8]:



$$HOCH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2-O-CH_2-O-CH_2-\underset{CH_2OH}{\overset{CH_2OH}{C}}-CH_2OH$$

The quantities of formaldehyde and base catalyst required to produce pentaerythritol from 1 mol of acetaldehyde are always in excess of the theoretical amounts of 4 mol and 1 mol, respectively, and mole ratios of formaldehyde to acetaldehyde vary widely. As the mole ratio increases, formation of dipentaerythritol and pentaerythritol linear formal is suppressed. Dipentaerythritol formation may also be reduced by increasing the formaldehyde concentration, although linear formal production increases under those conditions (55,56).

The most common catalysts are sodium hydroxide and calcium hydroxide, generally used at a modest excess over the nominal stoichiometric amount to avoid formaldehyde-only addition reactions. Calcium hydroxide is cheaper than NaOH, but the latter yields a more facile reaction and separation of the product does not require initial precipitation and filtration of the metal formate (57).

A typical flow diagram for pentaerythritol production is shown in Figure 2. The main concern in mixing is to avoid loss of temperature control in this exothermic reaction, which can lead to excessive by-product formation and/or reduced yields of pentaerythritol (55,58,59). The reaction time depends on the reaction temperature and may vary from about 0.5 to 4 h at final temperatures of about 65 and 35°C, respectively. The reactor product, neutralized with acetic or formic acid, is then stripped of excess formaldehyde and water to produce a highly concentrated solution of pentaerythritol reaction products. This is then cooled under carefully controlled crystallization conditions so that the crystals can be readily separated from the liquors by subsequent filtration.

The first stage crystals are rich in pentaerythritol linear formal and may be treated (60, 61) to convert this species to pentaerythritol and formaldehyde, which can then be recovered. The concentrated liquors obtained after redissolving are then recrystallized and filtered prior to drying of the final product.

The exact order of the production steps may vary widely; in addition, some parts of the process may also vary. Metal formate removal may occur immediately after the reaction (62) following formaldehyde and water removal, or by separation from the mother liquor of the first-stage crystallization (63). The metal formate may be recovered to hydroxide and/or formic acid by ion exchange or used as is for deicing or other commercial applications. Similarly, crystallization may include sophisticated techniques such as multistage fractional crystallization, which allows a wider choice of composition of the final product(s) (64,65).

Staged reactions, where only part of the initial reactants are added, either to consecutive reactors or with a time lag to the same reactor, may be used to reduce dipentaerythritol content. This technique increases the effective formaldehyde-to-acetaldehyde mole ratio, maintaining the original stoichiometric one. It also permits easier thermal control of the reaction (66,67). Both batch and continuous reaction systems are used. The former have greater flexibility whereas the product of the latter has improved consistency (55,68).

Dipentaerythritol and tripentaerythritol are obtained as by-products of the pentaerythritol process and may be further purified by fractional crystallization or extraction. Trimethylolethane and trimethylolpropane may be prepared by a similar aldol–cross Cannizzaro reaction scheme using propionaldehyde or butyraldehyde, respectively (58) in place of acetaldehyde. Formaldehyde and catalyst requirements are somewhat reduced because of the lower hydrogen content. Ditrimethylolpropane is obtained as a by-product of the trimethylolpropane synthesis (59).

4. Economic Aspects

Production of pentaerythritol in the United States has been erratic. Demand decreased in 1975 because of an economic recession and grew only moderately to 1980 (69). The range of uses for pentaerythritol has grown rapidly in lubricants (qv), fire-retardant compositions, adhesives, and other formulations where the cross-linking capabilities are of critical importance.

The world's largest producers are Perstorp AB (Sweden, United States, Italy), Hoechst Celanese Corporation (United States, Canada), Degussa (Germany), and Hercules (United States) with estimated 1989 plant capacities of 65,000, 59,000, 30,000, and 22,000 t/yr, respectively. Worldwide capacity for pentaerythritol production was 316,000 t in 1989, about half of which was from the big four companies. Most of the remainder was produced in Asia (Japan, China, India, Korea, and Taiwan), Europe (Italy, Spain), or South America (Brazil, Chile). The estimated rate of production for 1989 was about 253,000 t or about 80% of nameplate capacity.

The world's largest producers of trimethylolpropane are Perstorp AB at 50,000 t/yr, Hoechst Celanese at 23,000 t/yr, and Bayer at 20,000 t/yr. Estimated worldwide capacity is 139,000 t and actual production is on the order of 88,000 t.

Dipentaerythritol is sold by Perstorp AB and by Hercules (United States), ditrimethylolpropane by Perstorp AB both in relatively pure form. Tripentaerythritol is also available; however, the purity is limited. Trimethylolethane is produced commercially by Alcolac (United States) and Mitsubishi Gas Chemicals (Japan).

Pentaerythritol is produced in a variety of grades having differing amounts of dipentaerythritol and small quantities of linear formal. Mono pentaerythritol contains a minimum of 98.0% pentaerythritol with most of the remaining material being dipentaerythritol. Nitration-grade pentaerythritol composition is dependent on the individual customer's demands. The product may be highly pure (>99.5% pentaerythritol) or may contain up to about 1.6% dipentaerythritol. Technical-grade pentaerythritols generally contain at least 8% dipentaerythritol and the normal limit is about 12%, although some specialty products may be even higher. Pure dipentaerythritol may be added to standard technical-grade pentaerythritol. Tripentaerythritol is also present in most technical-grade product.

5. Analytical Methods

Pentaerythritol may be analyzed by nonspecific wet chemical means such as the hydroxyl method, the results of which include all the usual impurities such as dipentaerythritol, tripentaerythritol, and the formals (70), or the benzal method. A number of gas chromatographic methods allowing facile analysis of the more volatile ethers and esters formed by a number of reagents as well as simultaneous determination of other normal constituents are also available. Acetate esters (71), trimethylsilyl ethers (72), and trifluoroacetate esters (73) give highly satisfactory analyses. ASTM methods D2195 (wet chemical) and D2999 (gas chromatographic) are recognized standards for industrial use.

6. Health and Safety Factors

Pentaerythritol and trimethylolpropane are classified as nuisance particulate and dust, respectively. They are both nontoxic to animals by ingestion or inhalation and are essentially nonirritating to the skin or eyes (2,74).

7. Uses

The most important industrial use of pentaerythritol is in a wide variety of paints, coatings, and varnishes, where the cross-linking capability of the four hydroxy groups is critical. Alkyd resins (qv) are produced by reaction of pentaerythritol with organic acids such as phthalic acid or maleic acid and natural oil species.

The resins obtained using pentaerythritol as the only alcohol group supplier are noted for high viscosity and fast drying characteristics. They also exhibit superior water and gasoline resistance, as well as improved film hardness and adhesion. The alkyd resin properties may be modified by replacing all or part of the pentaerythritol by glycols, glycerol, trimethylolethane, or trimethylolpropane, thereby reducing the functionality. Similarly, replacing the organic acid by longer-chain acids such as adipic or altering the quantities of the oil components (linseed, soya, etc) modifies the drying, hardness, and wear characteristics of the final product. The catalyst and the actual cooking procedures also significantly affect overall resin characteristics.

Rosin esters of pentaerythritol prepared from varying amounts of oil yield varnishes of the required oil length for a wide range of outlets such as wood and metal finishing, sealing and jointing formulations, and sand binders for molds. Formulations for some of these complex resins have been described in great detail in the literature, although exact production details are normally guarded jealously by the manufacturers because the order of reaction can also alter the properties of the final product (75–78).

Long-chain esters of pentaerythritol have been used as pour-point depressants for lubricant products, ranging from fuel oils or diesel fuels to the high performance lubricating oils required for demanding outlets such as aviation, power turbines, and automobiles. These materials require superior temperature, viscosity, and aging resistance, and must be compatible with the wide variety of metallic surfaces commonly used in the outlets (79–81).

The explosives and rocket fuels formed by nitration of pentaerythritol to the tetranitrate using concentrated nitric acid (33) are generally used as a filling in detonator fuses. Use of pentaerythritol containing small amounts of dipentaerythritol produces crystallization behavior that results in a high bulk density product having excellent free-flow characteristics, important for fuse burning behavior (82). PETN is also used for medicinal purposes as a vasodilator in the treatment of angina. This product is a dry mixture of pure PETN and an inert carrier, for example, lactose or mannitol, to minimize the usual explosive potential. For the same reason, only small quantities are normally shipped and rigorous packaging is recommended (83).

Pentaerythritol is used in self-extinguishing, nondripping, flame-retardant compositions with a variety of polymers, including olefins, vinyl acetate and alcohols, methyl methacrylate, and urethanes. Phosphorus compounds are added to the formulation of these materials. When exposed to fire, a thick foam is produced, forming a fire-resistant barrier (see FLAME RETARDANTS) (84–86).

Polymer compositions containing pentaerythritol are also used as secondary heat-, light-, and weather-resistant stabilizers with calcium, zinc, or barium salts, usually as the stearate, as the prime stabilizer. The polymers may be in plastic or fiber form (87–89).

Pentaerythritol in rosin ester form is used in hot-melt adhesive formulations, especially ethylene–vinyl acetate (EVA) copolymers, as a tackifier. Polyethers of pentaerythritol or trimethylolethane are also used in EVA and polyurethane adhesives, which exhibit excellent bond strength and water resistance. The adhesives may be available as EVA melts or dispersions (90, 91) or as thixotropic, one-package, curable polyurethanes (92). Pentaerythritol spiro ortho esters have been used in epoxy resin adhesives (93). The EVA adhesives are especially suitable for cellulose (paper, etc) bonding.

Pentaerythritol and trimethylolpropane acrylic esters are useful in solventless lacquer formulations for radiation curing (qv), providing a cross-linking capability for the main film component, which is usually an acrylic ester of urethane, epoxy, or polyester. Some specialty films utilize dipentaerythritol and ditrimethylolpropane (94,95).

Titanium dioxide pigment coated with pentaerythritol, trimethylolpropane, or trimethylolethane exhibits improved dispersion characteristics when used in paint or plastics formulations. The polyol is generally added at levels of 0.1–0.5% (96).

Photocurable materials for photographic films contain pentaerythritol and dialkylamino and/or nitrile compounds, which have good adhesion and peelability of the layers, and produce clear transfer images (97,98).

Electroless plating on metal substrates can be improved by addition of pentaerythritol, either to a photosensitive composition of a noble metal salt (99), or with glycerine to nickel plating solutions (100). Both resolution and covering power of the electrolyte are improved.

Binary mixtures of pentaerythritol with many other polyol species can produce heat or electrical storage media having excellent retention properties based on the solid–solid, crystal–plastic–crystal phase-transition phenomena. The solid solutions of these mixtures can also be tailored, by adjusting the ratios of the individual components, to exhibit phase transformation and energy release under the required conditions. These media are applicable to domestic hot water, solar heat, and industrial process heat storage and recovery (101–103).

BIBLIOGRAPHY

"Pentaerythritol" in *ECT* 1st ed., Vol. 10, pp. 1–6, by H. Weinberger, Fine Organics, Inc., "Other Polyhydric Alcohols" under "Alcohols, Polyhydric," in *ECT* 2nd ed., Vol. 1, pp. 588–598, by E. Berlow, Heyden Newport Chemical Corp.; in *ECT* 3rd ed., Vol. 1, pp. 778–789, by J. Weber, Celanese Canada, Ltd., and J. Daley, Celanese Chemical Company; in *ECT* 4th ed., Vol. 1, pp. 913–925, by William N. Hunter, Celanese Canada, Inc.

CITED PUBLICATIONS

1. E. Berlow, R. H. Barth, and E. J. Snow, *The Pentaerythritols*, Reinhold Publishing Corp., New York, 1958.
2. *Material Safety Data Sheet C41, Trimethylolpropane, Flake*, Celanese Canada Inc., Montreal, 1990.
3. I. Harttmann and J. Nagy, *U.S. Bureau of Mines Report of Investigation No. 3751*, 1944.
4. *Product Bulletin PE-10-55*, Heyden Newport Chemical Corp.
5. *Technical Data Sheets TDS-1 and TB-1*, Commercial Solvents Corp.
6. *Product Bulletin, Pentaerythritol*, Sam Yang Chemical Co., Korea.
7. *Physical Properties Manual*, Celanese Chemical Company, Dallas, Tex., 1981.
8. N. S. Bankar, P. N. Chaudhari, and G. H. Kulkarni, *Indian J. Chem.* **13**, 986–987 (1975).
9. Jpn. Pat. 53/63,306 (June 6, 1978), K. Takeuchi, Y. Matsui, H. Kano, and T. Motohashi (to Ajinomoto Co., Ltd.).
10. A. B. Padias and H. K. Hall, Jr., *Macromolecules* **15**, 217–223 (1982).
11. U.S. Pat. 4,405,798A (Sept. 20, 1983), H. K. Hall and D. R. Wilson (to Celanese Corp.).
12. Brit. Pat. 1,374,263 (Nov. 20, 1974), T. Keating (to Imperial Chemical Industries Ltd.).
13. T. S. Chao, M. Kjonaas, and J. DeJovine, *Preprints Div. Pet. Chem. Am. Chem. Soc.* **24**, 836–846 (1979).
14. U.S. Pat. 3,932,460 (Jan. 13, 1976), D. R. McCoy, T. B. Jordan, and F. K. Ward (to Texaco Inc.).
15. Ger. Pat. 2,758,780 (July 12, 1979), K. H. Hentschel, R. Dhein, H. Rudolph, K. Nuetzel, K. Morche, and W. Krueger (to Bayer A.G.).
16. Jpn. Pat. 57/38,767 A2 (Mar. 3, 1982), (to Asahi Denka Kogyo K.K.).
17. Jpn. Pat. 57/11,959 A2 (Jan. 21, 1982), (to Asahi Denka Kogyo K.K.).
18. Brit. Pat. 1,439,753 (June 16, 1976), H. Coates, J. D. Collins, and I. H. Siddiqui (to Albright and Wilson Ltd.).
19. Jpn. Pat. 52/100,415 (Aug. 23, 1977), T. Kiyoura (to Mitsui Toatsu Chemicals, Inc.).
20. Jpn. Pat. 52/72,882 (June 17, 1977), T. Ooe, T. Nakazato, and R. Yoshikawa (to Mitsubishi Gas Chemical Co., Inc.).
21. Ger. Pat. 2,440,612 (Mar. 6, 1975), Y. Christidis (to Nobel Hoechst Chimie).
22. Ger. Pat. 3,125,338 A1 (Jan. 13, 1983), K. Koenig and M. Schmidt (to Bayer A.G.).
23. A. Kamors, *Tezisy Dokl. Konf. Molodykh Nauchn. Rab. Inst. Neorg. Khim., Akad. Nauk Latv. SSR, 5th*, 17–20.
24. Czech. Pat. 190,732 B (Dec. 15, 1981), J. Holcik, M. Karvas, and J. Masek.
25. Eur. Pat. Appl. EP 113,994 A1 (July 25, 1984), B. E. Johnston and P. R. Napier (to Mobil Oil Corp.).
26. Jpn. Pat. 61,225,191 A2 (Oct. 6, 1986), K. Tajima, M. Takahashi, K. Nishikawa, and T. Takeuchi (to Adeka Argus Chemical Co., Ltd.).

27. Ger. Pat. 2,630,257 (Jan. 12, 1978), H. Habarlein and F. Scheidl (to Hoechst A.G.).
28. U.S. Pat. 4,454,064 A (June 12, 1984), Y. Halpern and R. H. Niswander (to Borg-Warner Corp.).
29. Fr. Pat. 2,489,333 A1 (Mar. 5, 1982), J. Kiefer (to Ciba-Geigy A.G.).
30. U.S. Pat. 4,152,373 (May 1, 1979), M. L. Honig and E. D. Weil (to Stauffer Chemical Co.).
31. L. Desvergnes, *Chim. Ind.* **29**, 1263 (1933).
32. Jpn. Pat. 51/118,708 (Oct. 18, 1976), S. Oinuma and M. Kusakabe (to Agency of Industrial Sciences and Technology).
33. Czech Pat. 221,031 B (Mar. 15, 1986), S. Zeman, M. Dimun, and Z. Cervenka.
34. U.S. Pat. 4,352,919 A (Oct. 5, 1982), E. W. Kluger and C. D. Welch (to Milliken Research Corp.).
35. U.S. Pat. 4,136,044 (Jan. 23, 1979), M. Braid (to Mobil Oil Corp.).
36. W. S. Anderson and H. J. Hyer, *JANNAF Propul. Meet.*, vol. 1, AD-A103 844, CPIA Publ. 340, 1981, 387–398.
37. Jpn. Pat. 56/55,362 (May 15, 1981), (to Teijin Ltd.).
38. U.S. Pat. Appl. 183,707 (Jan. 30, 1981), (to United States National Aeronautics and Space Administration).
39. USSR Pat. 1,035,025 A1 (Aug. 15, 1983), E. B. Smirnova, Z. L. Chilyasova, N. P. Zykova, and L. A. Druganova (to Central Scientific-Research and Design Institute of the Wood Chemical Industry).
40. Ger. Pat. 2,707,875 (Aug. 31, 1978), J. Perner, K. Stork, F. Merger, and K. Oppenlaender (to BASF A.G.).
41. S. Shimizu, Y. Sasaki, and C. Hirai, *Nihon Daigaku Seisankogakubu Hokoku, A*, **15**(1), 47–56 (1982).
42. U.S. Pat. 4,151,211 (Apr. 24, 1979), I. Heckenbleikner and W. P. Enlow (to Borg-Warner Corp.).
43. Ger. Pat. 2,501,285 (July 24, 1975), A Schmidt (to Ciba-Geigy A.G.).
44. Belg. Pat. 885,670 (Feb. 2, 1981), R. Leger, R. Nouguier, J. C. Fayard, and P. Maldonado (to Elf France).
45. Eur. Pat. Appl. EP 46,731 A1 (Mar. 3, 1982), F. Lohse and C. E. Monnier (to Ciba-Geigy A.G.).
46. Jpn. Pat. 63,162,641 A2 (July 6, 1988), G. Watanabe, N. Nakajima, and Y. Ito (to Yokkaichi Chemical Co., Ltd.).
47. Jpn. Pat. 62,223,141 A2 (Oct. 1, 1987), Y. Fujio, Y. Nishi, and T. Nishimoto (to Osaka Soda Co., Ltd.).
48. E. Weber, *J. Org. Chem.* **47**, 3478–3486 (1982).
49. A. B. Padias, H. K. Hall, Jr., D. A. Tomalia, and J. R. McConnell, *J. Org. Chem.* **52**, 5305–5312 (1987).
50. J. E. Vik, *Acta Chem. Scand.* **27**, 239 (1973).
51. T. G. Bonner, E. J. Bourne, and J. Butler, *J. Chem. Soc.*, 301 (1964).
52. J. E. Vik, *Acta Chem. Scand. B* **28**, 325 (1974).
53. P. Werle, E. Busker, and E. Wolf-Heuss, *Liebigs Ann. Chem.* 1082–1087 (1985).
54. D. I. Belkin, *Zh. Prikl. Khim. (Leningrad)* **52**, 237–239 (1979).
55. L. Kovacic-Beck, I. Beck, and F. Anusic, *Nafta (Zagreb)* **34**(3), 131–135 (1983).
56. M. Lichvar, J. Sabados, V. Macho, and L. Komora, *Chem. Prum.* **36**(2), 57–61 (1986).
57. U.S. Pat. 2,612,526 (Sept. 30, 1952), C. W. Gould (to Hercules Powder Co.).
58. Jpn. Pat. 57/139,028 A2 (Aug. 27, 1982), (to Koei Kagaku Kogyo K.K.).
59. U.S. Pat. 3,962,347 (June 8, 1976), K. Herz (to Perstorp AB).
60. Ger. Pat. 2,930,345 (Feb. 19, 1981), P. Werle and G. Pohl (to Degussa).
61. Czech Pat. 183,405 (May 15, 1980), L. Komora and H. Nitoschneiderova.
62. Span. Pat. 467,714 (Oct. 16, 1978), (to Patentes y Novedades S.A.).

63. Eur. Pat. Appl. EP 242,784 A1 (Oct. 28, 1987), H. V. Holmberg and H. E. Larsson (to Perstorp AB).
64. Czech Pat. 220,256 B (Feb. 15, 1986), J. Ziak.
65. Jpn. Pat. 5,808,028 (Jan. 18, 1983), (to Koei Kagaku Kogyo K.K.).
66. Czech Pat. 181,486 (Jan. 15, 1980), M. Lichvar, J. Sabados, J. Vidovenec, and L. Butkovsky.
67. Jpn. Pat. 57/142,929 A2 (Sept. 3, 1982), (to Koei Kagaku Kogyo K.K.).
68. V. V. Pakulin, A. A. Kruglikov, Y. V. Rogachev, and P. E. Gulevich, *Plast. Massy* **3**, 12–13 (1988).
69. *Synthetic Organic Chemicals*, Publication 776, U.S. International Trade Commission.
70. *Technical Bulletin, Pentaerythritol*, Oxyquim S.A.
71. D. S. Wiersma, R. E. Hoyle, and H. Rempis, *Anal. Chem.* **34**, 1533 (1962).
72. R. R. Suchanec, *Anal. Chem.* **37**, 1361 (1965).
73. *Technical Bulletin, Pentaerythrit*, Degussa.
74. *Material Safety Data Sheet C73, Pentaerythritol*, Celanese Canada Inc., 1990.
75. Belg. Pat. 874,241 (June 18, 1979), (to BASF Farben und Fasern A.G.).
76. Jpn. Pat. 55/82,165 (June 20, 1980), (to Nippon Synthetic Chemical Industry Co., Ltd.).
77. U.S. Pat. 4,690,783 A (Sept. 1, 1987), R. W. Johnston, Jr. (to Union Camp Corp.).
78. Czech Pat. 222,510 B (Mar. 15, 1986), K. Hajek and co-workers.
79. Neth. Pat. 77/11852 (May 2, 1979), (to Hercules Inc.).
80. U.S. Pat. 4,229,310 (Oct. 21, 1980), G. Frangatos (to Mobil Oil Corp.).
81. Ger. Pat. 3,328,739 (Feb. 9, 1984), C. J. Dorer and K. Hayashi (to Lubrizol Corp.).
82. Ger. Pat. 1,901,769 (Oct. 9, 1967), H. Thomas and J. Turbet (to Imperial Chemical Industries Ltd.).
83. *U.S. Pharmacopeia: National Formulary XV*, 20th ed., Mack Publishing Co., Easton, Pa., 1980.
84. Eur. Pat. Appl. 17,609 (Oct. 15, 1980), D. Alt, K. D. Hutschgau, A. Schillmoeller, and B. Fischer (to Siemens A.G.).
85. U.S. Pat. 4,762,746 A (Aug. 9, 1988), L. Wesch and E. Weiss (to Odenwald-Chemie GmbH).
86. J. P. Jain, N. K. Saxena, I. Singh, and D. R. Gupta, *Res. Ind.* **30**(1), 20–24 (1985).
87. Ger. Pat. 2,847,628 (May 31, 1979), B. Sallmen, C. A. Sjoegreen, M. O. Maansson, and K. Ogemark (to Perstorp A.B.).
88. U.S. Pat. 4,162,242 (July 24, 1979), R. House (to Chevron Research Co.).
89. Eur. Pat. 219,427 A1 (Apr. 11, 1987), C. D. G. deMezeyrac, R. Fugier, B. Gicquel, and S. Tetard (to Isover Saint-Gobain).
90. Fr. Pat. 2,378,835 (Aug. 25, 1978), (to E. I. du Pont de Nemours & Co., Inc.).
91. Ger. Pat. 3,410,957 A1 (Sept. 26, 1985), K. J. Gardenier and W. Heimbuerger (to Henkel K.-G.a.A.).
92. Belg. Pat. 890,841 A2 (Feb. 15, 1982), S. B. Labelle and J. A. E. Hagquist (to Fuller H.B. Co.).
93. Jpn. Pat. 61,027,987 A2 (Feb. 7, 1986), A. Matsumaya, H. Ozawa, and S. Hirose (to Mitsui Toatsu Chemicals, Inc.).
94. R. Holman, ed., *UV and EB Curing Formulations for Printing Inks, Coatings and Paints*, SITA Technology, London, 1984.
95. C. G. Roffey, *Photopolymerization of Surface Coatings*, John Wiley & Sons, Inc., New York, 1982.
96. Brit. Pat. 896,067 (Aug. 19, 1960), W. R. Whately and G. M. Sheehan (to American Cyanamid Co.).

97. Jpn. Pat. 54/95,688 (July 28, 1979), S. Kondo, A. Matsufuji, and A. Umehara (to Fuji Photo Film Co., Ltd.).
98. Jpn. Pat. 60,237,444 A2 (Nov. 26, 1985), T. Komamura, M. Iwagaki, and T. Masukawa (to Konishiroku Photo Industry Co., Ltd.).
99. Jpn. Pat. 63,115,395 A2 (May 19, 1988), Y. Takeuchi (to Canon K.K.).
100. USSR Pat. 1,310,460 A1 (May 15, 1987), Y. Y. Lukomski, T. V. Mulina, V. V. Vasiliev, and R. V. Kopteva.
101. Jpn. Pat. 61,204,292 A2 (Sept. 10, 1986), S. Anzai, H. Sakaguchi, H. Yamazaki, K. Shiina, and M. Kurodi (to Hitachi, Ltd.).
102. Jpn. Pat. 61,240,627 A2 (Oct. 25, 1986), Y. Kudo, S. Yoshimura, S. Tsuchiya, and T. Kojima (to Matsushita Electric Industrial Co., Ltd.).
103. U.S. Pat. 4,572,864 A (Feb. 25, 1986), D. K. Benson, R. W. Burrows, and Y. D. Shinton (to United States Dept. of Energy).

WILLIAM N. HUNTER
Celanese Canada Inc.