AMYL ALCOHOLS

1. Introduction

Amyl alcohol describes any saturated aliphatic alcohol containing five carbon atoms. This class consists of three pentanols, four substituted butanols, and a disubstituted propanol, ie, eight structural isomers $C_5H_{12}O$: four primary, three secondary, and one tertiary alcohol. In addition, 2-pentanol, 2-methyl-1-butanol, and 3-methyl-2-butanol have chiral centers and hence two enantiomeric forms.

The odd-carbon structure and the extent of branching provide amyl alcohols with unique physical and solubility properties and often offer ideal properties for solvent, surfactant, extraction, gasoline additive, and fragrance applications. Amyl alcohols have been produced by various commercial processes in past years. Today the most important industrial process is low pressure rhodium-catalyzed hydroformylation (oxo process) of butenes.

Mixtures of isomeric amyl alcohols (1-pentanol and 2-methyl-1-butanol) are often preferred because the different degree of branching imparts a more desirable combination of properties; they are also less expensive to produce commercially.

2. Physical Properties

With the exception of neopentyl alcohol (mp 53°C), the amyl alcohols are clear, colorless liquids under atmospheric conditions, with characteristic, slightly pungent and penetrating odors. They have relatively higher boiling points than ketonic or hydrocarbon counterparts and are considered intermediate boiling solvents for coating systems (Table 1) (1–16).

Commercial primary amyl alcohol is a mixture of 1-pentanol and 2-methyl-1-butanol, in a ratio of ca 65 to 35. Typical physical properties of this amyl alcohol mixture are listed in Table 2 (17).

Like the lower alcohols, amyl alcohols are completely miscible with numerous organic solvents and are excellent solvents for nitrocellulose, resin lacquers, higher esters, and various natural and synthetic gums and resins. However, in contrast to the lower alcohols, they are only slightly soluble in water. Only 2-methyl-2-butanol exhibits significant water solubility. As associated liquids, amyl alcohols form azeotropes with water and/or a variety of organic compounds (Table 3).

Figures 1 and 2 show the relationship of viscosity and surface tension with temperature for various amyl alcohols. Curves for lower and higher alcohol homologues are shown for comparison.

The physical characteristics of *tert*-amyl alcohol diverge from the standard trends for the other alcohols; it has a lower boiling point, higher melting point, higher vapor pressure, and low surface tension. Most notably, organic molecules are highly soluble in *tert*-amyl alcohol.

3. Chemical Properties

The amyl alcohols undergo the typical reactions of alcohols which are characterized by cleavage at either the oxygen–hydrogen or carbon–oxygen bonds.

3.1. Dehydration. Dehydration of amyl alcohols is important for the preparation of specialty olefins and where it may produce unwanted by-products under acidic reaction conditions. Olefin formation is especially facile with

Table 1. **The Amyl Alcohols and Some of Their Physical Properties**

Properties	1-Pentanol	2-Pentanol	3-Pentanol	2-Methyl-1-butanol	3-Methyl-1-butanol	2-Methyl-2-butanol	3-Methyl-2-butanol	2,2-Dimethyl-1-propanol
CAS Registry Number	[71-41-0]	[6032-29-7]	[584-02-1]	[137-32-6]	[123-51-3]	[75-85-4]	[598-75-4]	[75-84-3]
common name	*n*-amyl alcohol	*sec*-amyl alcohol			isoamyl alcohol	*tert*-amyl alcohol		neopentyl alcohol
critical temperature, °C	315.35	287.25	286.45	291.85	306.3	272.0	300.85	276.85
critical pressure, kPa[a]	3868.	3710.	3880.	3880.	3880.	3880.	3960.	3880.
critical specific volume, mL/mol	326.5	328.9	325.3	327	327	327	327	327
critical compressibility	0.25810	0.26188	0.27128	0.27009	0.26335	0.27992	0.27133	0.27745
boiling point at pressure, °C								
101.3 kPa[a]	137.8	119.3	115.3	128.7	130.5	102.0	111.5	113.1
40 kPa	111.5	93.8	90.9	103.5	105.6	78.3	87.2	89.0
1.33 kPa	44.6	32.0	27.7	40.2	43.0	21.0	26.0	25.0
vapor pressure[b] kPa[a]	0.218	0.547	0.761	0.274	0.200	1.215	0.810	0.929
melting point, °C	−77.6	−73.2	−69.0	<−70	−117.2	−8.8 −88	forms glass	54.0
heat of vaporization at normal boiling point, kJ/mol[c]	44.83	43.41	42.33	44.75	43.84	40.11	41.10	41.35
ideal gas heat of formation[d], kJ/mol[c]	−298.74	−313.80	−316.73	−302.08	−302.08	−329.70	−314.22	−319.07

liquid density[b], kg/m^3	815.1	809.4	820.3	819.1	810.4	809.6	818.4	851.5[e]
liquid viscosity[b], mPa·s(=cP)	4.06	4.29	6.67	5.11	4.37	4.38	3.51d	2.5[e]
surface tension[b], mN/m(=dyn/cm)	25.5	24.2	24.6	25.1[d]	24.12	22.7	23.0d	14.87[e]
refractive index[d]	1.4080	1.4044	1.4079	1.4086	1.4052	1.4024	1.4075	1.3915
solubility parameter[d] (MJ/m^3)$^{0.5}$[f]	22.576	21.670	21.150	22.274	22.322	20.758	21.607	19.265[e]
solubility in water[b], wt %	1.88	4.84	5.61	3.18	2.69	12.15	6.07	3.74
solubility of water in[b], wt %	9.33	11.68	8.19	8.95	9.45	24.26	11.88	8.23

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[a] To convert kPa to mm Hg, multiply by 7.5.

[b] At 20°C unless otherwise noted.

[c] To convert kJ/mol to cal/mol, multiply by 239.

[d] At 25°C.

[e] At the melting point.

[f] To convert (MJ/m^3) to (cal)$^{0.5}$, divide by 2.045.

Table 2. **Physical Properties of Primary Amyl Alcohol, Mixed isomers**[a]

Property	Value[b]
molecular weight	88.15
boiling point at 101.13 kPa[c], °C	133.2
freezing point, °C	−90[d]
specific gravity 20/20 °C	0.8155
absolute viscosity at 20°C, mPa·s(=cP)	4.3
vapor pressure at 20°C, kPa[c]	0.27
flash point (closed cup), °C	45
solubility at 20°C, by wt %	
in water	1.7
water in	9.2

[a] Ref. 17.

[b] 65/35 blend, ie, a mixture of 1-pentanol and 2-methyl-1-butanol, 65/35 wt %, respectively.

[c] To convert kPa to mm Hg, multiply by 7.5.

[d] Sets to glass below this temperature.

secondary or tertiary amyl alcohols under acidic conditions. The reverse reaction, hydration of olefins, is commonly used for the preparation of alcohols.

An example of a specialty olefin from an amyl alcohol is Phillips Petroleum's process for 3-methyl-1-butene (used in the synthesis of pyrethroids) from the catalytic dehydration of 3-methyl-1-butanol (21,22). The process affords 94% product selectivity and 94% alcohol conversion at 310°C and 276 kPa (40 psig).

Dehydration of 1-pentanol or 2-pentanol to the corresponding olefins has been accomplished, in high purity and yields, by vapor-phase heterogeneous catalyzed processes using a variety of catalysts including neutral gamma–Al_2O_3 catalyst doped with an alkali metal (23), zinc aluminate (24,25), lithiated clays (26), $Ca_3(PO_4)_2$ (27) and montmorillonite clays (28). Dehydration of 2-methyl-1-butanol occurs over zinc aluminate catalyst at 270–370°C to give the expected 2-methyl-1-butene in high selectivites (24). The Al_2O_3 catalyzed process can be optimized to give di-*n*-pentyl ether as the exclusive product (23). Dehydration of 1-pentanol over an alkali metal promoted Al_2O_3 catalyst at 300–350°C

Table 3. **Azeotropic Mixtures of Amyl Alcohols with Water**[a]

	Boiling point of azeotrope, °C[b]	Alcohol in azeotrope, wt %	Wt % alcohol	
			Upper layer	Lower layer
1-pentanol	95.93	43.65	84.29	2.54
2-pentanol	91.7	63.5		
3-pentanol	91.5	65	90.1	5.5
2-methyl-1-butanol	93.8	58.5		
3-methyl-1-butanol	94.82	50.67	84.15	2.96
2-methyl-2-butanol	87.35	72.5		
3-methyl-2-butanol	91.0	67.0		

[a] Refs. (18–20).

[b] At 101.13 kPa = 1 atm.

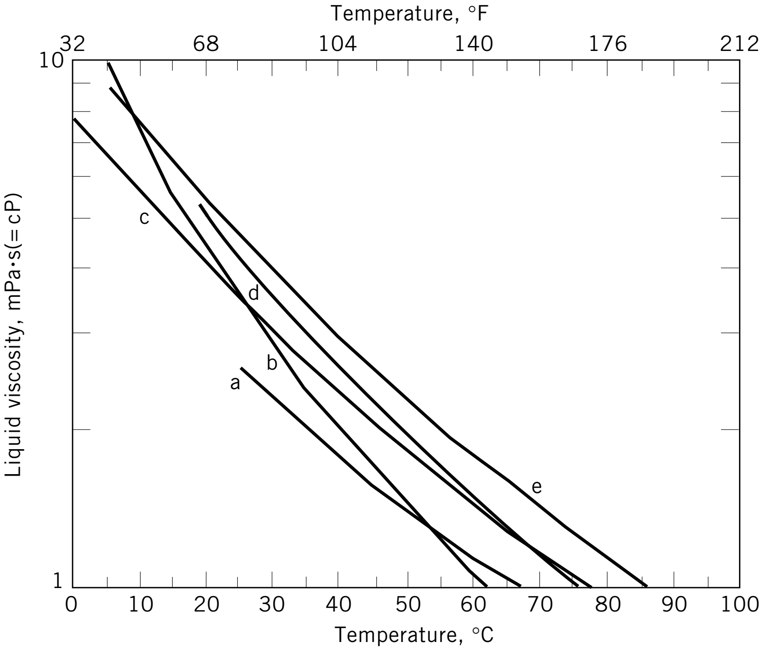


Fig. 1. Viscosities of amyl alcohols compared with 1-butanol and 1-hexanol (15). a, 1-butanol; b, 2-methyl-2-butanol; c, 1-pentanol; d, 2-methyl-1-butanol; e, 1-hexanol.

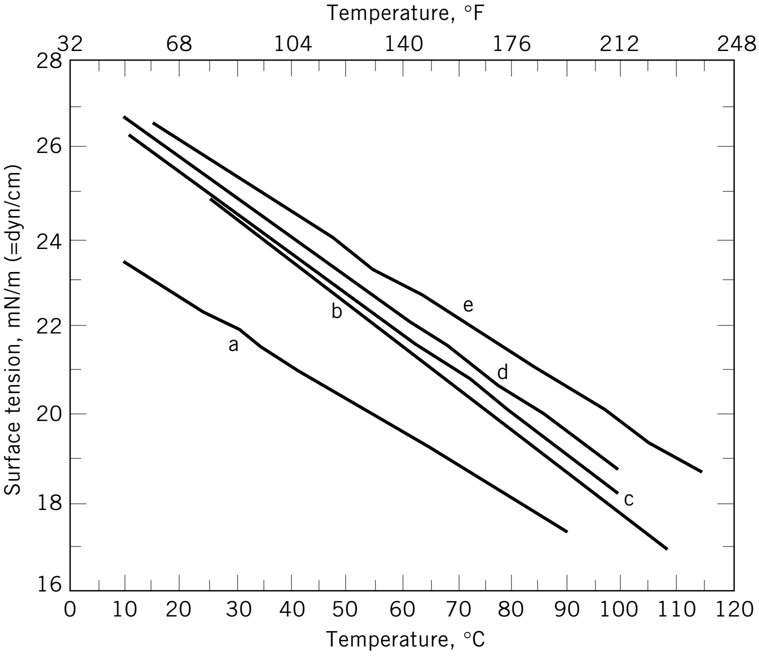


Fig. 2. Surface tension of amyl alcohols compared with 1-butanol and 1-hexanol (15). a, 2-methyl-2-butanol; b, 2-methyl-1-butanol; c, 1-butanol; d, 1-pentanol; e, 1-hexanol.

provides 1-pentene at selectivities of 92% (29,30). Purification produces polymerization grade (99.9% purity) 1-pentene. A flow chart has been shown for a pilot-plant process (29).

Koch Reaction. C-6-neoacids are readily available from amyl alcohols by the Koch reaction. Greater than 95% 2,2-dimethylbutyric acid [595-37-9] was obtained from 2-methyl-1-butene at 304 kPa (3 atm) CO and 35°C for 1 h with cupric oxide and sulfuric acid catalyst (31). Likewise, 2,2-dimethylbutyric acid can be obtained in high yield (75–80%) from 1- or 2-pentanol or neopentyl alcohol from the Koch-Haaf reaction (32,33). *tert*-Amyl alcohol gives a mixture of trimethylacetic acid [75-98-9] (pivalic acid), 2,2-dimethylbutyric acid, C-7 acids, and C-11 acids under similar Koch-Haaf conditions (33).

3.2. Esterification. Extensive commercial use is made of primary amyl acetate, a mixture of 1-pentyl acetate [28-63-7] and 2-methylbutyl acetate [53496-15-4]. Esterifications with acetic acid are generally conducted in the liquid phase in the presence of a strong acid catalyst such as sulfuric acid (34). Increased reaction rates are reported when esterifications are carried out in the presence of heteropoly acids supported on macroreticular cation-exchange resins (35) and zeolite (36) catalysts in a heterogeneous process. Judging from the many patents issued in recent years, there appears to be considerable effort underway to find an appropriate solid catalyst for a reactive distillation esterification process to avoid the product removal difficulties of the conventional process.

Reaction of 1-pentanol with propionic acid provides 1-pentyl propionate [624-54-4], a new coatings solvent for automotive refinish and OEM paints, appliances, and for higher-solids systems (37). The esterification of 1-pentanol with formic acid to 1-pentyl formate [638-49-3] is conducted by concomitant removal of by-product water by azeotropic distillation with diethyl ether (38).

Alkali metal xanthates are prepared in high yield from reaction of amyl alcohols with alkali metal hydroxide and carbon disulfide (39–42). The xanthates are useful as collectors in the flotation of minerals and have minor uses in vulcanization of rubber and as herbicides (39,41).

Zinc dithiophosphates, which serve as antioxidants (qv) and antiwear agents in lubricants, are prepared by reaction of amyl alcohol and phosphorus pentasulfide followed by treatment with zinc sulfate (43).

Esters of *tert*-amyl alcohol can be obtained by acylation of 2-methyl-2-butene in the presence of trifluoromethanesulfonic acid (44). The esters produced, in high yields, from reaction of amyl alcohols with carboxylic anhydrides, are used as intermediates for preparation of pyrylium salts (45, 46) and alkaloids (47). Triazoles prepared by acylation of 3-methyl-1-butanol are useful as herbicides (48).

3.3. Oxidation. Oxidation of the *n*-amyl alcohols produces aldehydes, which after continued oxidation can yield acids. This route to aldehydes has little merit. However, oxidative esterifications with alkali metal hypohalites (eg, calcium chlorite, $Ca(OCl)_2$) (49), bromates (eg, sodium bromate, $NaBrO_3$) (50) and halites (eg, sodium bromite, $NaBrO_2$) (51–53)) have commercial potential. For example, a 90% yield of pentyl pentanoate [2173-56-0] was obtained from treatment of 1-pentanol with bromous acid or its salt in a solvent at pH 7–12 (53); sodium hypochlorite gave 87% yield of 3-methylbutyl isovalerate [659-70-1] from 3-methyl-1-butanol (49). Reaction is believed to involve dehydrogenation of an intermediate hemiacetal which, in turn, is formed from reaction of the first formed aldehyde with starting alcohol. Oxidation of secondary amyl alcohols afford high yields of ketones, eg, 3-pentanol gave 97% yield of diethyl ketone by oxidation with calcium hypochlorite (49).

Other examples of oxidation of amyl alcohols using hydrogen peroxide (54), $RuO_2/NaClO$ (55), $BaMnO_4$ (56), and chromic acid (57, 58) have been described for laboratory synthesis, but have not been utilized commercially.

3.4. Amination. Amyl alcohols can react with ammonia or alkylamines to form primary, secondary, or tertiary-substituted amines. For example, 3-methyl-butylamine [107-85-7] is produced by reductive ammonolysis of 3-methyl-1-butanol over a Ni catalyst at 150°C (59). Some diisoamyl- and triisoamylamines are also formed in this reaction. Good selectivities (88%) of neopentylamine [5813-64-9] are similarly produced by reductive ammonolysis of neopentyl alcohol (60).

Reaction of *tert*-amyl alcohol with urea in the presence of sulfuric acid gives a monoalkylated urea (61,62). Monoalkyl ureas are used to prepare uracil derivatives which are useful as herbicides, fungicides, and plant growth regulators (61).

3.5. Etherification. Ethers of amyl alcohols have been prepared by reaction with benzhydrol (63), activated aromatic halides (64), dehydration-addition reactions (65), addition to olefins (66–71), alkoxylation with olefin oxides (72,73) and displacement reactions involving their alkali metal salts (74–76).

The product benzhydrol pentyl ether [42100-71-0] from etherification of benzhydrol with 1-pentanol is utilized as low odor carrier oils for pressure-sensitive carbonless papers (63) and alkoxylated products are good surfactants (72). The *tert*-amyl functionality imparts pleasant aromas to compounds, eg, amyl substituted bicyclic polymethylated naphthalenones and indanones give fruity amber-like or woody aromas (69), and in acylhexamethylindans they provide a musklike odor (71), useful in perfumes. Ethers of neopentyl alcohol and 4-chlorobenzenethiol (4-thiophenyl neopentyl ether) are intermediates in the synthesis of thioether herbicide and plant growth regulators (64). Alkali *tert*-amyl alcoholates are useful in the preparation of colorfast pigments such as diphenylpyrrolopyroledione (75,76).

3.6. Condensation. The neopentyl trimethylolpropane carbonate [65332-76-5] formed from condensation of the trischloroformate of trimethylolpropane and neopentyl alcohol, is a clear yellow oil, useful as lubricant (77).

Methyl *t*-butyl ketone [1634-04-4] (pinacolone) has been prepared in 74% yield by reaction of *tert*-amyl alcohol with formaldehyde in the presence of strong acid catalyst (78,79).

The Guerbet reaction can be used to obtain higher alcohols; 2-propyl-1-heptanol [10042-59-8] from 1-pentanol condensation and 6-methyl-4-nonanol from 2-pentanol (80–83). Condensations with alkali phenolates as the base, instead of copper catalyst, produce lower amounts of carboxylic acids and require lower reaction temperatures (82,83). The crossed Guerbet reaction of 1-pentanol with methanol in the presence of sodium methoxide catalyst afforded 2-heptanol in selectivities of about 75% (84).

Friedel-Crafts alkylation of benzene with isomeric amyl alcohols proceeds with some rearrangement. For example, both 2- and 3-pentanol gave the identical product mixture (60% 2-phenylpentane, 31% 3-phenylpentane, and 9% *tert*-pentylbenzene) from reaction with benzene in the presence of BF_3 catalyst (85).

Reduction of 1-pentanol to pentane reportedly occurs during condensation of samarium with excess alcohol (86).

3.7. Other Reactions. Primary amyl alcohols can be halogenated to the corresponding chlorides by reaction with hydrogen chloride in hexamethylphosphoramide (87). Neopentyl chloride [753-89-9] is formed without contamination by rearrangement products. A convenient method for preparing *tert*-amyl bromide and iodide involves reaction of *tert*-amyl alcohol with hydrobromic or hydroiodic acid in the presence of Li or Ca halide (88). The metal halides increase the yields (85–95%) and product purity.

A method for the preparation of dipentyl carbonate from reaction of 1-pentanol with CO_2 in the presence of diethyl azodicarboxylate in high yields (81%) has been reported (89).

Neopentyl alcohol is useful for preparation of masked polyol silicate esters, capable of releasing the polyol under moisture conditions, in moisture-curable one-component liquid polyurethane compositions (90).

4. Manufacture

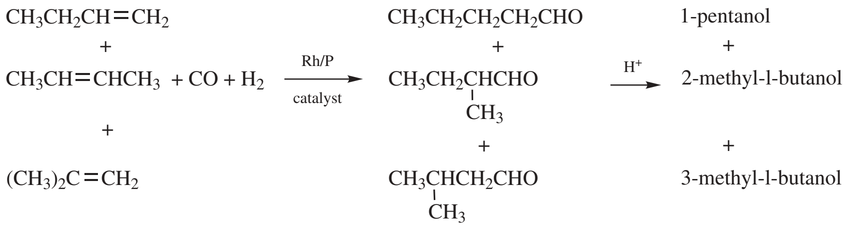
Three significant, commercial processes for the production of amyl alcohols include separation from fusel oils, chlorination of C-5 alkanes with subsequent hydrolysis to produce a mixture of seven of the eight isomers (91), and a low pressure oxo process, or hydroformylation, of C-4 olefins followed by hydrogenation of the resultant C-5 aldehydes.

The oxo process is the principal one in practice today; only minor quantities, mainly in Europe, are obtained from separation from fusel oil. *tert*-Amyl alcohol is produced on a commercial scale in lower volume by hydration of amylenes (92).

4.1. Fusel Oils. The original source of amyl alcohols was from fusel oil which is a by-product of the ethyl alcohol fermentation industry. Refined amyl alcohol from this source, after chemical treatment and distillation, contains about 85% 3-methyl-1-butanol and about 15% 2-methyl-1-butanol, both primary amyl alcohols. Only minor quantities of amyl alcohol are supplied from this source today. A German patent discloses a distillative separation process for recovering 3-methyl-1-butanol from fusel oil (93).

4.2. Chlorination-Hydrolysis Process. The first synthetic production of amyl alcohols was begun during the 1920s by the so-called chlorination-hydrolysis process in which a mixture of amyl chlorides is first produced by the continuous vapor-phase chlorination of a mixture of pentane and isopentane in the absence of light and catalysts. Hydrolysis of the chlorides with aqueous caustic at high temperatures produces a mixture of seven of the eight amyl alcohol isomers; formation of neopentyl alcohol is negligible. In contrast to the fusel oil and the oxo processes, this source provides significant quantities of the three secondary amyl alcohols, especially 2-pentanol. An excellent review with references and a process schematic has been published (91).

4.3. Oxo Process. Because of catalytic advances made since the 1970s in “oxo” chemistry and the comparatively high cost and waste disposal problems associated with the chlorination-hydrolysis process, the oxo process (qv) is now the principal source of amyl alcohols. In the low pressure hydroformylation (oxo) process for the production of amyl alcohols, 1-butene, 2-butene, and 2-methyl-propylene (isobutylene) react with a mixture of carbon monoxide and hydrogen in the presence of a suitable metal catalyst (rhodium) to form an isomeric mixture of aldehydes with one more carbon atom than the olefin. Once made, the 1-pentaldehyde [110-62-3] (*n*-valeraldehyde), 2-methylbutyraldehyde [96-17-3] and 3-methylbutyraldehyde [590-86-3] (isovaleraldehyde) are hydrogenated to the corresponding amyl alcohols.



Prior to 1975, reaction of mixed butenes with syn gas required high temperatures (160–180°C) and high pressures 20–40 MPa (3000–6000 psi), in the presence of a cobalt catalyst system, to produce *n*-valeraldehyde and 2-methylbutyraldehyde. Even after commercialization of the low pressure oxo process in 1975, a practical process was not available for amyl alcohols because of low hydroformylation rates of internal bonds of isomeric butenes (91,94). More recent developments in catalysts have made low pressure oxo process technology commercially viable for production of low cost *n*-valeraldehyde, 2-methylbutyraldehyde, and isovaleraldehyde, and the corresponding alcohols in pure form.

Conventional triorganophosphite ligands, such as triphenylphosphite, form highly active hydroformylation catalysts (95–99); however, they suffer from poor durability because of decomposition. Diorganophosphite-modified rhodium catalysts (94,100,101), have overcome this stability deficiency and provide a low pressure, rhodium catalyzed process for the hydroformylation of low reactivity olefins, thus making lower cost amyl alcohols from butenes readily accessible. The diorganophosphite-modified rhodium catalysts increase hydroformylation rates by more than 100 times and provide selectivities not available with standard phosphine catalysts. For example, hydroformylation of 2-butene with 1,1′-biphenyl-2,2′-diyl 2,6-di-*tert*-butyl-4-methylphenylphosphite ligand (P/Rh ratio of 10:1) achieves a rate of 12.85 mol/(L·h) at 130°C, 0.2 MPa (30 psi) H_2, 0.2 MPa CO, producing a linear:branched C-5 aldehyde molar ratio of 1.13 (102). Hydroformylation of 2-butene provides a higher linear:branched aldehyde ratio (2.30) at 14.50 mol/(L·h). Isobutene produces only 3-methylbutyraldehyde at 1.65 mol/(L·h). Thus, new catalyst technologies have made it possible to increase the ratio of 2-methyl-1-butanol to 1-pentanol from 1- or 2-butene feedstock and provide commercially acceptable routes to 3-methyl-1-butanol at high rates and selectivities (103).

4.4. Hydration of Olefins. Several patents disclose the production of amyl alcohols by hydration of C-5 olefins (92,104–111). The Dow Chemical

Company was the first to come on stream with such a process to produce *tert*-amyl alcohol. In the Dow process (92) *tert*-amyl alcohol is prepared by hydrating 2-methyl butenes in acetone over a cation-exchange resin catalyst distributed through all three reactors of a 3-stage reactor system. A single phase solution containing the reactants and solvent are fed to the first reactor, and the first reactor effluent and additional butene feed is then fed sequentially to the second and third reactors. The effluent from the third reactor is treated with an anion-exchange resin to remove acidic impurities and distilled to recover acetone solvent and remove part of the unreacted hydrocarbon overhead. The bottoms are distilled to recover acetone, unreacted butenes (which are recycled), and product alcohol. Solvent requirements are lowered by introducing additional butene before the second reactor.

4.5. Reduction of Acids. Patents claim catalysts for the hydrogenation of neoacids in the vapor-phase to the neoalcohols in good yields. For example, neopentyl alcohol has been prepared by passing pivalic acid (obtained by the Koch reaction of isobutylene) over a $CuO/ZnO/Al_2O_3$ catalyst at 250°C and 6.9 MPa (70.3 kg/cm^2) in 100% selectivity (112). The neoalcohol was also produced in selectivities of 99% by employing zirconium hydroxide catalysts (113, 114). The rates of the latter process, however, are reportedly low at liquid hourly space velocity (LHSV) of <1 kg/catalyst−h. A catalyst from Re_2O_7 and OsO_4 gave 94% neoalcohol at 100% pivalic acid conversion at 10 MPa (100 atm) hydrogen and 90°C (115). High yields are also obtained by the vapor-phase reduction of pivalic acid [75-98-9] with 2-propanol in the presence of zirconium oxide catalyst (116,117). Reduction with lithium aluminum hydride (118,119) also gives high yields but is less practical for commercial scale production. Production of neopentyl alcohol appears to be commercially viable, but this alcohol seems to be lacking significant large-scale applications.

4.6. Other Methods. As part of a considerable effort during the 1980s to make chemicals, such as acetic acid, ethanol, and ethylene glycol, from C-1 chemistry, some approaches to higher alcohols by either homologation of inexpensive alcohols (such as methanol) with syn gas or from syn gas alone were made. Essentially, this was a search for appropriate catalysts to provide desired conversions and selectivities to selected alcohols. For example, novel $Ru-Mo-Na_2O$ catalysts supported on Al_2O_3 (120) and silica-supported molybdenum catalysts, promoted by KCl, (121) have high activity and good selectivities (up to about 70%) for a mixture of C-1–C-5 primary alcohols from syn gas. High temperatures (250–300°C) and pressures ($10-50$ MPa $= 1450-7250$ psi) are required. A variety of other complex metal catalyst systems have been described such as Cu–Cr–Co–Rh (122), $Cu-Co-Zn-Al_2O_3-K$ (123), $Fe-Cr_2O_3$ (124), Cu–ZnO (125), Cu–U–Al–K (126), Mo–W–Rh–K (127), and the like. Low yields to 1-pentanol are generally obtained. Efforts to homologize methanol to higher alcohols have been much less vigorous. Yields of C-5 alcohols were not much higher than from syn gas alone, but more conventional catalyst compounds of Co, Rh, Ru, and La were employed (128–131). There are several reviews on the subject of C-1 chemistry (132,133).

Recent patents involve the separation of 2-methyl-1-butanol and 3-methyl-1-butanol from 1-pentanol by either extractive distillation or azeotropic. References 134 and 135 are examples.

5. Shipping and Storage

Amyl alcohols are best stored or shipped in either aluminum, lined steel, or stainless steel tanks. Baked phenolic is a suitable lining for steel tanks. Plain steel tanks can also be used for storage or shipping. However, storage of aqueous solutions can cause rusting. Also, the alcohols are sufficiently hygroscopic so that moisture pick-up can cause rusting of plain steel storage tanks. Storage and transfer under dry nitrogen is recommended. Storage and handling facilities should be in compliance with the OSHA “Flammable and Combustible Liquids” regulations (17). Piping and pumps can be made from the same metals as used for storage tanks. The freezing points of amyl alcohols are low and they remain fluid at cold outside temperatures, thus allowing storage facilities above or below ground.

6. Economic Aspects

All eight amyl alcohol isomers are available from fine chemical supply firms in the United States. Five of them, 1-pentanol, 2-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol (*tert*-amyl alcohols) are available in bulk in the United States; in Europe all but neopentyl alcohol are produced. In 2001, 8.4×10^6 t of oxo chemicals were produced. Oxo chemicals are expected to grow at a rate of 1.4% per year through 2007 (136).

7. Specifications

Typical specifications for commercially available amyl alcohols (137) are given in Table 4. The impurities typically present are other monomeric alcohols, dimeric alcohols, acetals, and several miscellaneous substances. The alcohols are substantially free of suspended matter.

8. Health and Safety Factors

The main effects of prolonged exposure to amyl alcohols are irritation to mucous membranes and upper respiratory tract, significant depression of the central nervous system, and narcotic effects from vapor inhalation or oral absorption. All the alcohols are harmful if inhaled or swallowed, appreciably irritating to the eyes and somewhat irritating to uncovered skin on repeated exposure (138, 139). Prolonged exposure causes nausea, coughing, diarrhea, vertigo, drowsiness, headache, and vomiting. Table 5 shows toxicity effects of amyl alcohols from animal studies (139). The toxicity of 3-methyl-2-butanol and 2,2-dimethyl-1-propanol has not been thoroughly investigated.

The C-5 alcohols are more toxic and narcotic than the lower homologues. Toxicity to rats from amyl alcohols decreases in the order: tertiary, secondary, primary. Toxicity of 3-methyl-1-butanol appears to have been studied the

Table 4. **Specifications of Commercial Amyl Alcohols**[a]

	1-Pentanol	2-Methyl-1-butanol	Primary amyl alcohol mixed isomers
purity, wt % min			
1-pentanol	99.0, min	1, max	50–70
2-methyl-1-butanol		98.0, min	
amyl alcohols			98.0 min
3-methyl-1-butanol			0.01, max
2- and 3-methyl-1-butanols	0.5, max		
aldehydes, wt % max[b]		0.20	0.20
total carbonyl, wt %, max[b]	0.05		
unsaturation, wt %, max[c]		0.5	
distillation, °C[d]			
initial, min	135.0	126.0	127.5
dry point, max	139.0	139.0	139.0
acidity, wt %	0.005[e]	0.01[f]	0.01[f]
water, wt %, max	0.2	0.3	0.20
specific gravity (20/20°C)			
min	0.814	0.815	0.812
max	0.818	0.822	0.819
color, Pt-Co	15	15	15

[a] Ref. 137.

[b] Calculated as C-5 aldehyde.

[c] As pentenal.

[d] At 101.3 kPa at 1 atm.

[e] Calculated as valeric acid.

[f] Calculated as acetic acid.

Table 5. **Toxicity of Amyl Alcohols**

	LD_{50} rats[a], mg/kg	LD_{50} rabbits[b], g/kg	LCL_o rats[c], ppm/4 h	Eye injury, rabbits
1-pentanol	2200[d]	3600[d]	14000	20 mg/24 h moderate
2-pentanol	1470[e]			20 mg/24 h moderate
3-pentanol	1870[d]	2520[d]		3 mg open severe
2-methyl-1-butanol	4920[d]	3540[f]		
3-methyl-1-butanol	1300[e]	3212[d]	150[g]	20 mg/24 h moderate
2-methyl-2-butanol	1000			

[a] Ingestion.

[b] Skin penetration.

[c] Inhalation.

[d] No toxic effects noted.

[e] Toxic effects not yet reviewed.

[f] Primary irritation.

[g] Sensory organs, lungs, and respiration irritation.

Table 6. **Flammability Limits of Amyl Alcohols**[a]

Alcohol	Flash point, °C		Flammability limits in air, vol %		Auto ignition temperature, °C
	Open cup	Closed cup	Lower	Upper	
1-pentanol	58	33	1.2	10	300.0
2-pentanol	42	34	1.5	9.7	343.33
3-pentanol	39	41	1.2	9.0	435.0
2-methyl-1-butanol	50	50	1.4	9.0	385
3-methyl-1-butanol	56	43	1.2	9.0	350
2-methyl-2-butanol	24	19	1.2	9.0	437.22
3-methyl-2-butanol	35	39	1.5	9.9	436.85
2,2-dimethyl-1-propanol		37	1.5	9.1	

[a] Refs. (5, 142–150).

most. This alcohol caused a slight increase in cancerous tumors compared to controls in two studies (140,141). The tumors were located primarily in the stomach and liver.

Odor data for the various amyl alcohols is limited. The lowest perceptible limit for 1-pentanol and *tert*-amyl alcohol are 10 and 0.04 ppm, respectively (138). *tert*-Amyl alcohol has a threshold value of 2.3 ppm (and a 100% recognition level of 0.23 ppm); 3-methyl-1-butanol has an odor threshold of 7.0 ppm. The odor of 1-pentanol has been described as sweet and pleasant whereas that of 3-methyl-2-butanol is sour (138).

OSHA PEL TWA for 2-pentanol is 100 ppm (360 mg/m^3); STEL is 125 ppm (450 mg/m^3). NIOSH REL (sec-isoamyl alcohol) TWA is 100 ppm. STEL is 125 ppm (151).

There is no ACGIH standard for 1-pentanol (152).

All of the amyl alcohols are TSCA and EINECS (European Inventory of Existing Commercial Chemical Substances) registered.

The amyl alcohols are readily flammable substances; *tert*-amyl alcohol is the most flammable (closed cup flash point, 19°C). Their vapors can form explosive mixtures with air (Table 6) (5,142–150).

9. Uses

Solvents and coatings are the biggest market for C5 alcohols (136). 1-Pentanol and 2-methyl-1-butanol is used for zinc diamyldithiophosphate lubrication oil additives (136) as important corrosion inhibitors and antiwear additives. Amyl xanthate salts are useful as frothers in the flotation of metal ores because of their low water solubility and miscibility with phenolics and natural oils. Potassium amyl xanthate, a collector in flotation of copper, lead, and zinc ores, is no longer produced in the United States (136).

Another significant application for amyl alcohols is for production of amyl acetates.

As solvents, the amyl alcohols are intermediate between hydrocarbon and the more water-miscible lower alcohol and ketone solvents. For example, they are good solvents and diluents for lacquers, hydrolytic fluids, dispersing agents in textile printing inks, industrial cleaning compounds, natural oils such as linseed and castor, synthetic resins such as alkyds, phenolics, urea–formaldehyde maleics, and adipates, and naturally occurring gums, such as shellac, paraffin waxes, rosin, and manila. In solvent mixtures they dissolve cellulose acetate, nitrocellulose, and cellulosic ethers.

Primary amyl alcohol and its acetate ester are considered important medium-boiling nitrocellulose lacquer coating solvents. This mixture is a latent solvent and coupling agent for nitrocellulose lacquers. In blends, the solvent mixture modifies evaporation rate, lowers viscosities, improves blush resistance, and imparts improved flow and leveling which results in high gloss lacquer coatings.

The principal component of primary amyl alcohol, 1-pentanol, although itself a good solvent, is useful for the preparation of specific chemicals such as pharmaceuticals and other synthetics (154).

Growth applications for amyl alcohols appear to be shifting toward higher boiling esters as plasticizers, perfumes, fragrances, and production of fine chemicals.

tert-Amyl alcohol is employed in formulations for stabilizing 1,1,1-trichloroethane (a replacement for trichloroethylene) which is used for degreasing metals, especially aluminum, copper, zinc, and iron and their alloys (155–158). The *tert*-amyl alcohol in stabilizing formulations allowed only negligible reaction between the 1,1,1-trichloroethane and metal. *tert*-Amyl alcohol is also used for stabilizing 1,1,1-trichloroethane mixtures for rosin flux removal compositions, eg, ionic and nonionic fluxes from circuit boards (159,160) and in stabilizer compositions for 1,1,1-trichloroethane for dry cleaning applications where it is durable against repeated use, without causing corrosion of the dry cleaner metal components and conforms with environmental and health standards enacted by the Occupational Safety and Health Act (161–163). *tert*-Amyl alcohol also has solvent use in the preparation of epoxy-containing novolak resins with low chloride content (164) and in mixtures with surfactants in enhanced petroleum recovery by flooding (165,166) (see PETROLEUM, ENHANCED OIL RECOVERY).

Other applications of amyl alcohols include their use as flavor and fragrance chemicals. Amyl isovalerate and amyl salicylate consume amyl alcohols (136). Isoamyl salicylate is used to a large extent in soap and cosmetic fragrances because of its cost effectiveness (167). Isoamyl alcohol is used as the extracting solvent for purification of wet process phosphoric acid. Total upgrading of 28–54% wet process phosphoric acid is achieved using this alcohol (168,169). *t*-Amyl methyl ether (TAME) is a useful gasoline additive as an octane booster (170,171). Amyl cinnamic aldehyde is an important ester of amyl alcohol (172). 1-Pentanol is used as an alcohol cosurfactant in a variety of applications (173,174). Amyl alcohols are used for the preparation of a variety of herbicides, fungicides, and pesticides. Amyl alcohols are a superior medium, compared to either benzyl alcohols or dichloromethane, for preparation of magnesia suspensions for electrophoretic deposition (175). Isoamyl alcohol is an intermediate in the synthesis of pyrethroids (21,22).

BIBLIOGRAPHY

"Amyl Alcohols" in *ECT* 1st ed., Vol. 1, pp. 844–849, by C. K. Hunt, Sharples Chemicals, Inc., "Amyl Alcohols" in *ECT* 2nd ed., Vol. 2, pp. 374–379, by L. A. Gillette, Pennsalt Chemicals Corporation; in *ECT* 3rd ed., Vol. 2, pp. 570–573, by P. D. Sherman, Jr., Union Carbide Corporation; in *ECT* 4th ed., Vol. 2, pp. 709–728, by Anthony J. Papa, Union Carbide Chemicals and Plastics Company Inc.

CITED PUBLICATIONS

1. Thermodynamics Research Center, *Selected Values of Properties of Chemical Compounds*, Data Project (loose-leaf data sheets), extant, Texas A&M University, College Station, Tex., 1980.
2. R. Wilhoit and B. J. Zwolinski, *J. Phys. Chem. Ref. Data* **2** (Suppl. No. 1) (1973).
3. J. J. Jasper, *J. Phys. Chem. Ref. Data* **1**(4), 841 (1972).
4. A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, *Chem. Rev.* **68**(6), 659 (1968).
5. J. S. Riddick and W. B. Bunger, *Organic Solvents: Physical Properties and Methods of Purification*, 3rd ed., Wiley-Interscience, New York, 1970.
6. J. Timmermans, *Physico-Chemical Constants of Pure Organic Substances*, 2nd ed., 2 vols., Elsevier, New York, 1965.
7. A. L. Lydersen, *Estimation of Critical Properties of Organic Compounds*, Report #3, College Engineering Experiment Station, University of Wisconsin, Madison, Wis., Apr. 1955.
8. B. J. Zwolinski and R. Wilhoit, "Heats of Formation and Heats of Combustion" in D. E. Gray, ed., *American Institute of Physics Handbook*, 3rd ed., McGraw-Hill, New York, 1972, pp. 4, 316, 342.
9. R. F. Fedors, *AIChE J.* **25,** 202 (1979).
10. *CHETAH-The ASTM Chemical Thermodynamic and Energy Release Evaluation Program*, ASTM Data Series Publication DS 51, American Society for Testing Materials, Philadelphia, 1974, original, updated.
11. Yu. V. Efremov, *Russ. J. Phys. Chem.* **40**(6), 667 (1966).
12. G. A. Pope, *Dissertation Abstract International* **33**(04-B), 1587 (1972).
13. S. Sugden, *J. Chem. Soc. Trans. (London)* **125**, 32 (1924).
14. *Physical Property Data*, unpublished, Union Carbide Chemicals and Plastics Corp., Danbury, Conn.
15. G. Sorensen and J. M. W. Arit, *Liquid-Liquid Equilibrium Data Collection, Binary Systems*, DECHEMA Chemistry Data Series, Vol. 5, part 1, Schon & Wetzel GmbH, Frankfurt/Main, Germany, 1979.
16. *TRC Thermodynamic Tables-Non-Hydrocarbons*, (loose-leaf data sheets, extant, 1989, suppl. #62), Thermodynamic Research Center, Texas A&M University System, College Station, Tex., Dec. 31, 1989.
17. *UCAR Alcohols for Coatings Applications, Brochure F-48588*, Solvents and Coatings Materials Division, Union Carbide Chemicals and Plastics Corp., Danbury, Conn., Sept. 1984.
18. T.-H Cho and co-workers, *Kagaku Kogaku Ronbunshu* **10**, 181 (1984), tabulated in Dechema I, 1b Suppl. 2.
19. L. H. Horsley, ed., *Azeotropic Data III, Adv. in Chem. Ser. #116*, American Chemical Society, Washington, D.C., 1973.
20. *Tables of Azeotropic Data*, Union Carbide Chemicals and Plastics Corp., 1957, unpublished.

21. *Chem. Eng. Prog.* **81**, 52–55 (May 1985).
22. *Chem. Eng. News* **63**, 27 (Apr. 22, 1985).
23. W. T. Reichle, *Res. Discl.* **283**, 717 (1987).
24. U.S. Pat. 4,260,845 (Apr. 7, 1981), T. K. Shioyama (to Phillips Petroleum Co.).
25. Brit. Pat. 2,181,070 (Apr. 15, 1987), C. S. John (to Shell International Research Maatschappi j B. V.).
26. Eur. Pat. 284,397 (Sept. 17, 1988), M. P. Atkins, J. Williams, J. A. Ballantine, and J. H. Purnell (to British Petroleum Co.).
27. V. T. Chalkina, S. Ya. Sklyar, S. A. Mannanova, and M. F. Sharnina, *Dokl. Neftekhim. Sekts.—Bashk. Resp. Pravl. Vses. Khim. O-va. im D. I. Mendeleeva*, 65–68 (1976).
28. J. A. Ballantine and co-workers, *J. Mol. Catal.* **26**(1), 37 (1984).
29. A. V. Timofeev and L. Ya. Romanchenko, *Khim. Prom-st (Moscow)*, (6), 333 (1985).
30. T. G. Min'ko and A. V. Timofeev, *Khim. Prom-st (Moscow)* (10), 595 (1986).
31. Jpn. Kokai 49,061,113 (June 13, 1974), Y. Soma and H. Sano (to Agency of Industrial Sciences and Technology).
32. H. Langhals, I. Mergelsberg, and C. Ruechardt, *Tetrahedron Lett.* **22**(25), 2365 (1981).
33. W. Haaf, *Org. Synth.* **5**, 739 (1973).
34. Eur. Pat. 158,499 A2 (Oct. 16, 1985), J. Russell and A. J. Stevenson (to BP Chemicals Ltd.).
35. T. Baba and Y. Ono, *Appl. Catal.* **22**(2), 321 (1986).
36. Z. Chen, *Kexue Tongbao* **30**(5), 616 (1985).
37. *UCAR n-Pentyl Propionate*, Brochure F-60454A, Union Carbide Chemicals and Plastics Corp., Danbury, Conn., May 1987.
38. Ger. Pat. 2,917,087 (Nov. 6, 1980), W. Werner (to Federal Republic of Germany).
39. U.S. Pat. 3,864,374 (Feb. 4, 1975), C-J. Chia, J. E. Currah, and G. R. Lusby (to Canadian Industries Ltd.).
40. J. Sejbl, *Ruby* **31**(5), 163 (1985).
41. Ger. Pat. 2,149,726 (Apr. 6, 1972), G. J. Novak and A. J. Robertson (to American Cynamid Co.).
42. South Afr. Pat. 8,004,227 (Aug. 26, 1981), D. J. Gannon and D. T. F. Fung (to CIL Inc., Canada).
43. A. D. Braazier and J. S. Elliott, *J. Inst. Pet.* **53**(518), 63 (1967).
44. C. Roussel, H. G. Rajoharison, L. Bizzari, and L. Shaimi, *J. Org. Chem.* **53**(3), 683 (1988).
45. Eur. Pat. 96,641 A2 (Dec. 21, 1983), H. G. Rajoharison, C. Roussel, and M. Ader (to Eastman Kodak Co.).
46. H. G. Rajoharison, C. Roussel, and J. Metzger, *J. Chem. Res. Synop.* (7), 186 (1981).
47. R. A. Aitken, J. Gopal, and J. A. Hirst, *J. Chem. Soc. Chem. Commun.* (10), 632 (1988).
48. Jpn. Kokai Tokkyo Koho 63 230,676 (Sept. 27, 1988), T. Shida and co-workers (to Kureha Chemical Industry Co., Ltd.).
49. S. O. Nwaukwa and P. M. Keehn, *Tetrahedron Lett.* **23**(1), 35 (1982).
50. S. Kajigaeshi and co-workers, *Bull. Chem. Soc. Jpn.* **59**(3), 747 (1986).
51. T. Kageyama, Y. Ueno, and M. Okawara, *Synthesis* (10), 815 (1983).
52. T. Kageyama and co-workers, *Chem. Lett.*, **7**, 1097 (1983).
53. Jpn. Kokai Tokkyo Koho 60 123,432 (July 2, 1985) (to Nippon Silica Industries Co., Ltd.).
54. C. M. Ashraf, I. Ahmad, and F. K. N. Lugemwa, *Arab Gulf J. Sci. Res.* **2**(1), 39 (1984).
55. Jpn. Kokai Tokkyo Koho 57 048,931 (Mar. 20, 1982) (to Nippon Zeon Co., Ltd.).
56. H. Firouzabadi and Z. Mostafavipoor, *Bull. Chem. Soc. Jpn.* **56**(3), 914 (1983).
57. J. Lou, *Chem. Ind. (London)* **10**, 312 (1989).

58. S. J. Flatt, G. W. J. Fleet, and B. J. Taylor, *Synthesis* (10), 815 (1979).
59. Jpn. Kokai Tokkyo Koho 63 275,547 (Nov. 14, 1988), L. Fukuya and H. Fukuda (to Daicel Chemicals Industries, Ltd.).
60. Eur. Pat. 22,532 (Jan. 21, 1981), F. Werner and co-workers (to Bayer A.-G.).
61. Hung. Pat. 42,456 (July 28, 1987), J. Kreidl and co-workers (to Richter, Gedeon, Vegyeszeti Gyar Rt.).
62. U.S. Pat. 3,673,249 (June 27, 1972), F. M. Furman (to American Cynamid Co.).
63. D. R. Nutter, *Res. Discl.* **195**, 270 (1980).
64. Ger. Pat. 3,643,851 (June 30, 1988), K. Sasse and co-workers (to Bayer A.-G.).
65. A. M. Habib, A. A. Saafan, A. K. Abou-Seif, and M. A. Salem, *Colloids Surf.* **29**(4), 337 (1988).
66. K. G. Sharonov, A. M. Rozhnov, V. I. Barkov, and R. I. Cherkasova, *Zh. Prikl. Khim. (Leningrad)* **60**(2), 359 (1987).
67. A. M. Habib, M. F. Abd-El-Megeed, A. Saafan, and R. M. Issa, *J. Inclusion Phenom.* **4**(2), 185 (1986).
68. V. Macho, M. Kavala, M. Polievka, M. Okresa, and W. Piecka, *Ropa Uhlie* **24**(7), 397 (1982).
69. Ger. Pat. 2,330,648 (Jan. 10, 1974), J. B. Hall, M. G. J. Beets, L. K. Lala, and W. I. Taylor (to International Flavors and Fragrances, Inc.).
70. U.S. Pat. 3,927,083 (Dec. 16, 1975), J. B. Hall, L. K. Lala, M. G. J. Beets, and W. I. Taylor (to International Flavors and Fragrances, Inc.).
71. Ger. Pat. 2,427,465 (Dec. 19, 1974), H. Miki and H. Hasui (to Mitsui Petrochemical Industries, Ltd.).
72. Rom. Pat. 83,751 (Apr. 30, 1984), A. Vizitiu and R. Manea (to Intreprinderea de Detergenti).
73. J. Chelebicki, *Rocz. Chem.* **49**(1), 207 (1975).
74. Jpn. Kokai Tokkyo Koho 61 010,525 (Jan. 18, 1986), T. Asano, M. Umemoto, and N. Sato (to Mitsui Toatsu Chemicals, Inc.).
75. Eur. Pat. 192,608 A2 (Aug. 27, 1986), W. Surber (to CIBA-GEIGY A.-G.).
76. Eur. Pat. 190,999 A2 (Aug. 13, 1986), F. Baebier (to CIBA-GEIGY A.-G.).
77. Fr. Pat. 2,321,477 (Mar. 18, 1977), D. Boutte and J. P. Senet (to Société Nationale des Poudres et Explosifs).
78. Jpn. Kokai Tokkyo Koho 54 066,613 (May 29, 1979), H. Tanaka, H. Tsuchiya, and S. Kyo (to Kuraray Co., Ltd.).
79. Jpn. Kokai Tokkyo Koho 54 148,711 (Nov. 21, 1979), S. Kyo, H. Tsuchiya, and H. Tanaka (to Kuraray Co., Ltd.).
80. P. L. Burk, R. L. Pruett, and K. S. Campo, *J. Mol. Catal.* **33**(1), 15 (1985).
81. P. L. Burk, R. L. Pruett, and K. S. Campo, *J. Mol. Catal.* **33**(1), 1 (1985).
82. Jpn. Kokai 52,077,002 (June 29, 1977), K. Ota and T. Kito (to Showa).
83. T. Kito, K. Ota, M. Takata, and M. Ariyoshi, *Yuki Gosei Kagaku Kyokai Shi* **36**(4), 331 (1978).
84. J. Sabadie and H. Descotes, *Bull. Soc. Chim. Fr.* **9–10**(2), 253 (1983).
85. A. A. Khalaf and R. M. Roberts, *Rev. Roum. Chim.* **30**(6), 507 (1985).
86. G. B. Sergeev, V. V. Zagorskii, and M. V. Grishechkina, *Metalloorg. Khim.* **1**(5), 1187 (1988).
87. R. Fuchs and L. L. Cole, *Can. J. Chem.* **53**(23), 3620 (1975).
88. H. Masada and Y. Murotani, *Bull. Chem. Soc. Jpn.* **53**(4), 1181 (1980).
89. W. A. Hoffman, III, *J. Org. Chem.* **47**, 5209 (1982).
90. Jpn. Kokai Tokkyo Koho 63 191,820 (Aug. 9, 1988), E. Morita and Y. Komizo (to Auto Chemical Industry Co., Ltd.).
91. Kirkpatrick Chemical Engineering Achievement Award, *Chem. Eng.* **84**, 110 (Dec. 5, 1977).

92. U.S. Pat. 4,182,920 (Jan. 8, 1980), J. H. Giles, J. H. Stultz, and S. W. Jones (to The Dow Chemical Company).
93. Ger. Pat. 255,526 (Apr. 6, 1988), M. Steinbrecker and co-workers (to VEB Leuna-Werke "Walter Ulbricht").
94. *Chem. Eng. News*, 27 (Oct. 10, 1988).
95. B. L. Booth, M. J. Else, R. Fields, and R. N. Hazeldine, *J. Organomet. Chem.* **27**, 119 (1971).
96. Y. Matsui, H. Taniguchi, K. Terada, and M. Irinchijima, *Bull. Jpn. Pet. Inst.* **19**, 68 (1977).
97. U.S. Pat. 3,527,809 (1970), R. L. Pruett and J. A. Smith (to Union Carbide Corp.).
98. P. W. N. M. Van Leeuwen and C. F. Roobeek, *J. Organomet. Chem.* **258**, 343 (1983).
99. U.S. Pat. 4,567,306 (1986), A. J. Dennis, G. E. Harrison, and J. P. Wyber (to Davy McKee (London) Ltd.).
100. U.S. Pat. 4,599,206 (1986), E. Billig and co-workers (to Union Carbide Corp.).
101. U.S. Pat. 4,717,775 (1988), E. Billig and co-workers (to Union Carbide Corp.).
102. U.S. Pat. 4,789,753 (1988), E. Billig and co-workers (to Union Carbide Corp.).
103. U.S. Pat. 4,769,498 (Sept. 6, 1988), E. Billig, A. G. Abatjoglou, and D. R. Bryant (to Union Carbide Corp.).
104. Z. Prokop and K. Setinek, *Collect. Czech. Chem. Commun.* **52**(5), 1272–1279 (1987).
105. Eur. Pat. 127,486 (Dec. 5, 1984), Y. Okumura, S. Kamiyama, H. Furukawa, and K. Kaneko (to Toa Nenryo Kogyo K. K.).
106. U.S. Pat. 3,285,977 (Nov. 15, 1966), A. M. Henke, R. C. Odioso, and B. K. Schmid (to Gulf Research and Development Co.).
107. Ger. Pat. 3,801,275 (July 27, 1989), R. Malessa and B. Schleppinghoff (to EC Erdoelchemic GmbH).
108. Ger. Pat. 3,801,273 (July 27, 1989), R. Malessa, C. Gabel, H. V. Scheef, and M. Lux (to EC Erdoelchemic GmbH).
109. Eur. Pat. 325,144 (July 26, 1989), R. Malessa and B. Schleppinghoff (to EC Erdoelchemic GmbH).
110. Jpn. Kokai 47,039,013 (Dec. 6, 1972), A. Nambu (to Japan Oil Co.).
111. U.S. Pat. 3,285,977 (Nov. 15, 1966), A. M. Henke, R. C. Odioso, and B. K. Schmid (to Gulf Research and Development Co.).
112. Eur. Pat. 180,210 (May 7, 1986), S. A. Butler and J. Stoll (to Air Products and Chemicals, Inc.).
113. Eur. Pat. 285,786 (Oct. 12, 1988), H. Matsushita, M. Shibagaki, and K. Takahashi (to Japan Tobacco Co.).
114. Jpn. Kokai Tokkyo Koho 62 108,832 (May 20, 1987), T. Maki, M. Nakajima, T. Yokoyama, and T. Setoyama (to Mitsubishi Chemical Industries Co., Ltd.).
115. Jpn. Kokai Tokkyo Koho 62 210,056 (Sept. 16, 1987), Y. Kajiwara, I. Y. Inamoto, and T. Yoshiaki (to Kao Corp.).
116. K. Takahashi, M. Shibagaki, H. Kuno, and H. Matsushita, *Chem. Lett.* (7), 1141 (1989).
117. M. Shibagaki, K. Takahashi, and H. Matsushita, *Bull. Chem. Soc. Jpn.* **61**(9), 3283 (1988).
118. A. F. D'Adams and R. H. Kienle, *J. Amer. Chem. Soc.* **77**, 4408 (1955).
119. N. Kornblum and D. C. Iffland, *J. Amer. Chem. Soc.* **77**, 6653 (1955).
120. T. Tatsumi, A. Muramatsu, and H. Tominaga, *Chem. Lett.* **5**, 685 (1984).
121. T. Tatsumi, A. Muramatsu, T. Fukunaga, and H. Tominaga, *Chem. Lett.* **6**, 919 (1986).
122. U.S. Pat. 4,537,909 (Aug. 27, 1985), F. N. Lim and F. Pennella (to Phillips Petroleum Co.).
123. W. X. Pan, R. Cao, and G. L. Griffin, *J. Catal.* **114**(2), 447 (1988).

124. M. Van der Riet, R. G. Copperthwaite, S. F. Demarger, and G. J. Hutchings, *J. Chem. Soc. Chem. Commun.* (10), 687 (1988).
125. D. J. Elliott, *J. Catal.* **111**(2), 445 (1988).
126. U.S. Pat. 4,677,091 (June 30, 1987), T. J. Mazanec and J. G. Frye, Jr., (to Standard Oil Co.).
127. U.S. Pat. 4,670,473 (June 2, 1987), R. H. Walker, D. A. Palmer, D. M. Salvatore, and E. J. Bernier (to Amoco Corp.).
128. Ger. Pat. 3,641,774 (June 30, 1988), W. Hilsebein, E. Supp, W. Friedrichl, and P. Koenig (to Metallgesellschaft A.-G.).
129. Jpn. Kokai Tokkyo Koho 63 190,837 (Aug. 8, 1988), Y. Isogai, A. Uda, K. Tanaka, and M. Hosokawa (to Agency of Industrial Sciences and Technology).
130. U.S. Pat. 4,533,775 (Aug. 6, 1985), J. R. Fox, F. A. Pesa, and B. S. Curatolo (to Standard Oil Co.).
131. U.S. Pat. 4,540,836 (Sept. 10, 1985), D. M. Fenton (to Union Oil Company of California).
132. T. Tatsumi, A. Muramatsu, K. Yokota, and H. Tominaga in D. M. Bibby, C. D. Chang, and R. F. Howe, eds., *Methane Conversion*, Elsevier Science Publishers, Amsterdam, The Netherlands, 1988.
133. Research Association for C1 Chemistry, eds., *Progress in C1 Chemistry in Japan*, Elsevier Science Publishers, Amsterdam, The Netherlands, 1989.
134. U.S. Pat. 6,024,841 (Feb. 15, 2000), L. Berg.
135. U.S. Pat. 5,779,862 (July 14, 1998), L. Berg.
136. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., Nov. 2002.
137. *Product Specifications* (1-6A5-1f, 1-6B5-1.1b, and 1-6E5-1h) Union Carbide Chemicals and Plastics Corp., Danbury, Conn., Jan. 20, 1989.
138. V. K. Rowe, S. B. McCollister, G. D. Clayton, and F. E. Clayton, eds., *Patty's Industrial Hygiene and Toxicology*, 3rd ed., Vol. 2C, Wiley-Interscience, New York, 1982, 2471–4588.
139. D. V. Sweet, ed., *Registry of Toxic Effects of Chemical Substances*, Publication No. 87-114, Vol. 4, National Institute for Occupational Safety and Health, DHHS (NIOSH), Washington, D.C., Apr. 1987.
140. *Amyl Alcohols or Pentanols (C5H12O). Toxicology Card No. 206*, Cahiers de Notes Documentaires, No. 118, 1st quarter, National Institute for Research and Safety, Paris, 1985, 143–146.
141. W. E. T. Gibel and co-workers, *Z. Exp. Chir.* **7**(4), 235 (1974).
142. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Techniques of Chemistry: Organic Solvents*, Vol. 2, 4th ed., John Wiley & Sons, Inc., New York, 1986, p. 887.
143. G. H. Tyron, ed., *Fire Protection Handbook*, 12th ed., National Fire Protection Association, Boston, Mass., 1962.
144. *Fire Protection Guide on Hazardous Materials*, 7th ed., National Fire Protection Association, Boston, Mass., 1978.
145. N. V. Steere, ed., *Handbook of Laboratory Safety*, 2nd ed., CRC Press, Boca Raton, Fla., 1982.
146. N. I. Sax, *Dangerous Properties of Industrial Materials*, 6th ed., Van Nostrand Reinhold Co., Inc., New York, 1984.
147. Yu. N. Shebeko, A. V. Ivanov, and T. M. Dmitrieva, *Sov. Chem. Ind.* **15**(3), 311 (1983).
148. D. P. Danner and T. E. Daubert, *Manual for Prediction Chemical Process Design Data*, AIChE, New York, (extant 1987).
149. N. I. Sax, *Dangerous Properties of Industrial Materials*, 5th ed., Van Nostrand Reinhold Co., Inc., New York, 1979.

150. G. Weiss, ed., *Hazardous Chemical Data Book*, Noyes Data Corp., Park Ridge, N.J., 1980.
151. R. J. Lewis, Sr., *Sax's Dangerous Properties of Industrial Materials*, 10th ed., Vol. 3, John Wiley & Sons, Inc., New York, 2000.
152. C. Bevan in E. Bingham, B. Cohrsson, C. N. Powell, eds., *Patty's Toxicology*, 5th ed., Vol. 6, John Wiley & Sons, Inc., New York, 2001, p. 429.
153. H. Bieber, *Encycl. Chem. Process Des.* **3**, 278 (1977).
154. "Monohydric Alcohols," in I. Mellan, ed., *Source Book of Industrial Solvents*, Vol. 3, Reinhold Publishing Corp., New York, 1959.
155. U.S. Pat. 4,327,232 (Apr. 27, 1982), A. Pryor and N. Ishibe (to The Dow Chemical Company).
156. U.S. Pat. 4,324,928 (Apr. 13, 1982), A. Pryor and N. Ishibe (to The Dow Chemical Company).
157. U.S. Pat. 4,309,301 (Jan. 5, 1982), N. Ishibe and T. G. Metcalf (to The Dow Chemical Company).
158. U.S. Pat. 4,115,461 (Sept. 19, 1978), D. R. Spencer and W. L. Wesley (to The Dow Chemical Company).
159. U.S. Pat. 4,524,011 (June 18, 1985), E. L. Tasset, S. M. Dallessand, and W. F. Richey (to The Dow Chemical Company).
160. Eur. Pat. 108,422 (May 16, 1984), E. L. Tasset, W. F. Richey, and S. M. Dallessandro (to The Dow Chemical Company).
161. U.S. Pat. 3,974,230 (Aug. 10, 1976), W. L. Archer and D. R. Spencer (to The Dow Chemical Company).
162. Jpn. Kokai Tokkyo Koho 54 157,108 (Dec. 11, 1979), T. Mizushiro, T. Kaneko, and Y. Sugawara (to Asahi-Dow, Ltd.).
163. Jpn. Kokai Tokkyo Koho 54 157,107 (Dec. 11, 1979), T. Mizushiro, Y. Sugawara, and T. Kaneko (to Asahi-Dow, Ltd.).
164. U.S. Pat. 4,778,863 (Oct. 18, 1988), C. S. Wang and Z. K. Liao (to The Dow Chemical Company).
165. Ger. Pat. 3,720,330 (Dec. 29, 1988), D. Balzer and H. Lueders (to Huels A.-G.).
166. C. J. Glover, M. C. Puerto, J. M. Maerker, and E. L. Sandvik, *Soc. Pet. Eng. J.* **19**(3), 183 (1979).
167. *Perfumer and Flavorist*, 60, 61 (Nov. 1981).
168. *Eur. Chem. News*, 221 (Aug. 2, 1974).
169. *Phosphorus Potassium*, 10 (Sept.–Oct. 1987).
170. *Chem. Eng. News*, 35, 36 (June 25, 1979).
171. *Hydrocarbon Process.*, 51–521 (Dec. 1985).
172. *Chem. Mark. Rep.*, 65 (Oct. 20, 1975).
173. *Chem. Eng. (N.Y.)* **90**(7), 19 (Apr. 4, 1983).
174. *Chem. Week*, 60 (Nov. 1, 1978).
175. D. U. K. Rao and E. C. Subbarao, *Am. Cer. Soc. Bull.*, 467–469 (Apr. 1979).

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