Kirk-Othmer Encyclopedia of Chemical Technology.

n-PROPYL ALCOHOL

n-Propyl alcohol [71-23-8], 1-propanol, $CH_3CH_2CH_2OH$, mol wt 60.09, is a clear, colorless liquid having a typical alcohol odor; it is miscible in water, ethyl ether, and alcohols. 1-Propanol occurs in nature in fusel oils and forms from fermentation and spoilage of vegetable matter (1).

1. Properties

A number of physical and chemical properties of 1-propanol are listed in Table 1 (2, 3). The chemistry of 1-propanol is typical of low molecular weight primary alcohols (see Alcohols, higher aliphatic). Biologically, 1-propanol is easily degraded by activated sludge and is the easiest alcohol to degrade (4).

2. Manufacture

1-Propanol has been manufactured by hydroformylation of ethylene (qv) (see Oxo process) followed by hydrogenation of propionaldehyde or propanal and as a by-product of vapor-phase oxidation of propane (see Hydrocarbon oxidation). Celanese operated the only commercial vapor-phase oxidation facility at Bishop, Texas. Since this facility was shut down in 1973 (5, 6), hydroformylation or oxo technology has been the principal process for commercial manufacture of 1-propanol in the United States and Europe. Sasol in South Africa makes 1-propanol by Fischer-Tropsch chemistry (7). Some attempts have been made to hydrate propylene in an anti-Markovnikoff fashion to produce 1-propanol (8–10). However, these attempts have not been commercially successful.

2.1. Hydroformylation and Hydrogenation

The production of 1-propanol by hydroformylation or oxo technology is a two-step process in which ethylene is first hydroformylated to produce propanal. The resulting propanal is hydrogenated to 1-propanol (eqs. 1 and 2).

$$CH_2{=}CH_2 + CO + H_2 \xrightarrow[\Delta,\ \text{pressure}]{\text{catalyst}} CH_3CH_2CHO \qquad (1)$$

$$CH_3CH_2CHO + H_2 \xrightarrow[\Delta,\ \text{pressure}]{\text{catalyst}} CH_3CH_2CH_2OH \qquad (2)$$

Propane, 1-propanol, and heavy ends (the last are made by aldol condensation) are minor by-products of the hydroformylation step. A number of transition-metal carbonyls (qv), eg, Co, Fe, Ni, Rh, and Ir, have been

Table 1. Physical and Chemical Properties of 1-Propanol[a]

Property	Value
freezing point, °C	−126.2
boiling point, °C	97.20
vapor pressure, kPa[b]	
at 20°C	1.987
40°C	6.986
60°C	20.292
80°C	50.756
Antoine equation,[c] 2–120°C, t in °C	$\log P_{\mathrm{kPa}} = 6.97257 - 1499.21/(204.64 - t)$
vapor density (air = 1)[d]	2.07
density, at 20°C, g/cm^3	0.80375
Francis equation, −21 to 180°C, t in °C	density $= 0.8813 + (5.448t \times 10^{-4}) - 21.536/(313.09 - t)$
refractive index, $n^{20}{}_{\mathrm{D}}$	1.38556
viscosity, at 20°C, mPa·s(=cP)[d]	2.256
surface tension, at 20°C, mN/m(=dyn/cm)	23.75
critical temperature, °C	263.65
critical pressure, kPa[b]	5169.60
critical density, g/cm^3	0.275
heat capacity, liquid at 25°C, J/(mol·K)[e]	141
heat of vaporization, kJ/mol[e]	
at 25°C	47.53
97.20°C	41.78
heat of combustion, liquid at 25°C, kJ/mol[d,e]	2033
heat of formation, vapor at 25°C, kJ/mol[d,e]	−254.7
flash point, Tag open cup, °C[d]	28.9
autoignition temperature, °C[d]	371.1
explosive limit, in air, vol %[d]	
lower	2.2
upper	14.0
electrical conductivity at 25°C, S(=mho)[d]	2×10^{-8}

[a] Ref. 2, except where noted.

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

[c] To convert log P_{kPa} to log P_{mmHg}, add 0.8751 to the constant.

[d] Ref. 3.

[e] To convert J to cal, divide by 4.184.

used to catalyze the oxo reaction, but cobalt and rhodium are the only economically practical choices. In the United States, Texas Eastman, Union Carbide, and Hoechst Celanese make 1-propanol by oxo technology (11). Texas Eastman, which had used conventional cobalt oxo technology with an $HCo(CO)_4$ catalyst, switched to a phosphine-modified Rh catalyst in 1989 (11) (see Oxo process). In Europe, 1-propanol is made by Hoechst AG and BASF AG (12).

The rhodium–triphenylphosphine catalyst system is generally used instead of cobalt in oxo processes because the former gives higher reaction rates, greater stability, lower operation pressure, and lower by-product production. The use of rhodium carbonyl catalysts is a possible choice for companies that have idle high pressure cobalt facilities. Rhodium carbonyls require high pressure but are more active than cobalt carbonyls and result in less high boiling by-products. In Germany, Hoechst AG (Werk Ruhrchemie) uses rhodium carbonyls to make propanal, which is then hydrogenated to 1-propanol (13) (see High pressure technology).

Simple rhodium carbonyls are ca 100–1000 times more reactive than cobalt carbonyls (14). When triphenylphosphine [603-35-0] is added, the reaction rate increases monotonically until the triphenylphosphine:rhodium mole ratio reaches 20:1 to 50:1 (15). Above this ratio, the rate of reaction decreases.

A substantial amount of research on the rhodium oxo process has been directed toward improving the linear aldehyde selectivity and linear:branched (l:b) aldehyde ratio. Conditions which increase l:b-aldehyde ratios also increase oxo catalyst stability and thus decrease the ligand decomposition. In general, increasing triphenylphosphine concentration or decreasing CO partial pressure leads to higher selectivity to linear aldehyde and increases catalyst stability, but decreases the rate of hydroformylation. Because ethylene can lead neither to internal olefin nor to branched aldehyde, the triphenylphosphine:rhodium ratio that maximizes the rate would seem best for *n*-propyl alcohol production. However, catalyst stability problems dictate operation at higher triphenylphosphine:rhodium ratios. A rhodium-catalyzed, ethylene hydroformylation process operates at 90–120°C, 2.17–3.55 MPa (300–500 psig), 1:1–3:1 H_2:CO, 1–10 m*M* rhodium, and 0.1–0.4 *M* triphenylphosphine. The chemical efficiency to propanal under these conditions is 98–99%. Additionally, there is 0.5–1.0% efficiency to ethane, as well as 0.5–1.0% efficiency to heavy ends. The rhodium can be obtained from almost any source except those that contain halogen. Halogens form complexes that have very low hydroformation activity (16).

Rhodium-catalyzed hydroformylation has been studied extensively (16–29). The most active catalyst source is hydridocarbonyltris(triphenylphosphine)rhodium, $HRhCO[P(C_6H_5)_3]_3$ (30). However, a molecule of triphenylphosphine is presumed to dissociate to form the active species (21, 28). Further dissociation could occur as shown in equation 3.

$$HRhCO[P(C_6H_5)_3]_3 \underset{P(C_6H_5)_3}{\overset{CO}{\rightleftharpoons}} HRh(CO)_2[P(C_6H_5)_3]_2 \underset{+P(C_6H_5)_3}{\overset{-P(C_6H_5)_3}{\rightleftharpoons}} HRh(CO)_2P(C_6H_5)_3 \qquad (3)$$

Catalyst and ligand stability and linear aldehyde formation are favored in catalytic cycles which have more triphenylphosphine bound to Rh, eg, $HRh(CO)_2[P(C_6H_5)_3]_2$. It is probable that the first step in catalyst deactivation and ligand decomposition is phenyl migration from phosphorus to Rh (31, 32). The resulting Rh–phosphide complex can either react with olefin to form alkyldiphenylphosphine (32), or with another Rh complex to form inactive Rh–phosphide clusters (30, 31). Figure 1 illustrates possible pathways. Apparently phenyl migration is inhibited by large excesses of triphenylphosphine, but not by CO; ie, phenyl migration competes better with CO than with triphenylphosphine for coordination sites on Rh.

The technology for hydrogenating the propanal to 1-propanol is well established. Commercially, nickel-based catalysts, eg, Raney nickel or supported nickel, and copper chromium oxide catalysts, are used (33). Vapor-phase or liquid-phase hydrogenation can be carried out. The reactor can be a fixed-bed, slurry-bed, or trickle-bed system (34, 35). Conditions for liquid-phase hydrogenation are 2.17–4.24 MPa (300–600 psig) and 100–170°C. Vapor-phase reactors generally operate below 790 kPa (100 psig) (36). Efficiencies to 1-propanol of $>95\%$ can be expected, and the principal by-products are acetals, ethers, esters, and diols (35). Both CO and triphenylphosphine poison the hydrogenation catalysts and should be removed prior to hydrogenation of propanal.

Figure 2 is a composite flow diagram for the production of 1-propanol by a two-step oxo/hydrogenation process where the oxo catalyst is rhodium– triphenylphosphine (37, 38). The propanal is removed by vapor stripping using excess synthesis gas, $CO + H_2$(15, 38). After condensation, the propanal is sent to a CO-stripping column to remove traces of CO prior to hydrogenation. The crude 1-propanol (after hydrogenation) is purified in a standard two-tower purification system. If $HCo(CO)_4$ or a rhodium carbonyl is the oxo catalyst, the propanal must be removed as a liquid stream because of the higher reactor pressure. Liquid recycle is necessary. Also, provisions for catalyst removal and handling must be installed.

2.2. Sasol Fischer-Tropsch Process

1-Propanol is one of the products from Sasol's Fischer-Tropsch process (7). Coal (qv) is gasified in Lurgi reactors to produce synthesis gas (H_2/CO). After separation from gas liquids and purification, the synthesis gas is fed into the Sasol Synthol plant where it is entrained with a powdered iron-based catalyst within the fluid-bed reactors. The exothermic Fischer-Tropsch reaction produces a mixture of hydrocarbons (qv) and oxygenates.

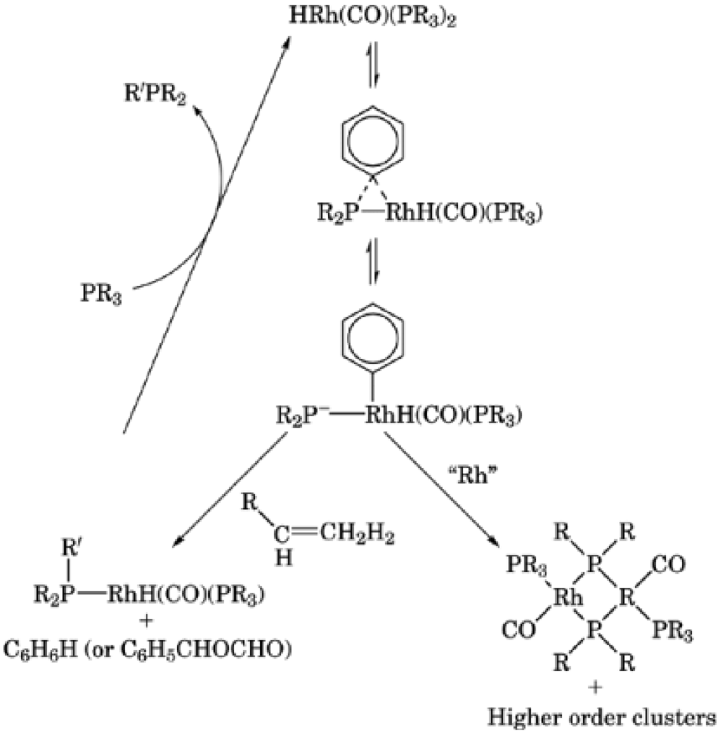

Fig. 1. Pathways for catalyst deactivation and ligand decomposition, where $R=C_6H_5$.

The condensation products from the process consist of hydrocarbon liquids and an aqueous stream that contains a mixture of ketones (qv) and alcohols. The ketones and alcohols are recovered and most of the alcohols are used for the blending of high octane gasoline. Some of the alcohol streams are further purified by distillation to yield pure 1-propanol and ethanol in a multiunit plant, which has a total capacity of 25,000–30,000 t/yr (see Coal conversion processes, gasification).

3. Economic Aspects

There are six 1-propanol producers in the world, ie, Hoechst Celanese, Texas Eastman, and Union Carbide in the United States; BASF AG and Hoechst AG in Western Europe; and Sasol in South Africa. In 1993, worldwide production capacity for 1-propanol was in excess of 180,000 t/yr; actual production was approximately 110,000 t/yr (39). The December 1995 average delivered price for 1-propanol in the United States was $1144/t (40).

1-Propanol economics are sensitive to the raw material costs of ethylene (qv) and the feedstock for synthesis gas, ie, natural gas or liquid petroleum feedstocks (qv). Natural gas-based technology is slightly more economical.

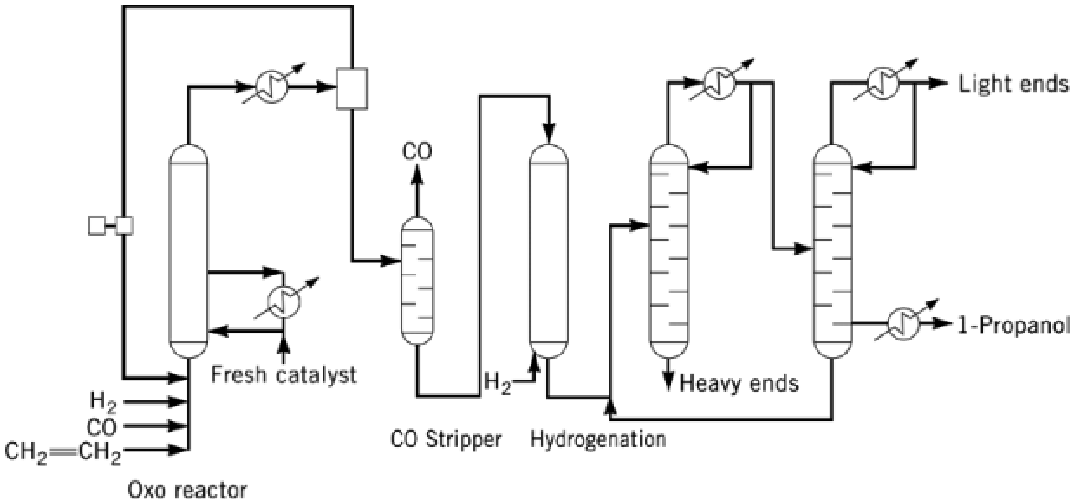

Fig. 2. Oxo/hydrogenation process for 1-propanol.

Table 2. Sales Specifications for 1-Propanol[a]

Specification	Limits[b]
1-propanol, wt %	99.8[c]
water, wt %	0.1
color, Pt–Co units	5
acidity, as acetic acid, wt %	0.003
2-methylpentanal, ppm	10
solubility in water	complete
odor	nonresidual

[a] Ref. 41.
[b] Values given are maximum unless otherwise noted.
[c] Value given is minimum.

4. Analytical and Test Methods, and Purity Specifications

The separation and analysis of 1-propanol are straightforward. Gas chromatography is the principal method employed. Other instrumental techniques, eg, nmr, ir, and classical organic qualitative analysis, are useful. Molecular sieves (qv) have been used to separate 1-propanol from ethanol and methanol. Commercial purification is accomplished by distillation (qv).

1-Propanol is a commodity chemical sold on specification (Table 2). Whereas the specification requires at least 99.8% 1-propanol, purity is generally in excess of 99.9%.

5. Health and Safety Factors

1-Propanol is defined as a flammable liquid. Its flash point is below 38°C. OSHA defines 1-propanol as hazardous according to 29 CFR 1910.1200 for the purposes of communication to employees and employers (42). However, this alcohol is only slightly toxic to animals, as can be seen by the toxicity data given in Table 3 (43). 1-Propanol gives negative results in the Ames test and in the Mouse Lymphoma Forward Mutatation Assay (43–46).

Table 3. 1-Propanol Toxicity[a]

Adminstration method	Value
oral dose, rats, LD_{50}, g/kg	1.9
dermal, rabbits, LD_{50}, g/kg	5.4
inhalation, rats, LC_{50}, ppm	24,000
HCGIH TLV, TWA	200
hazard ratings[b]	
NFPA[c]	1, 3, 0
HMIS[d]	2, 3, 0

[a] Ref. 43.

[b] Numbers are for health, flammability, and reactivity, respectively, with a range of 0 to 4.

[c] National Fire Protection Association.

[d] Hazardous Materials Identification System.

The National Toxicology Program (NTP) and International Agency for Research on Cancer (IARC) do not list 1-propanol as a carcinogen (43).

Eye contact can cause irritation or burns. Repeated skin contact can result in dermatitis. Exposure to excessive vapor concentrations irritates the eyes and respiratory tract. Very high concentrations have a narcotic effect (43).

In the United States, the reportable quantity of 1-propanol for spills under CERCLA "Superfund" is 100 lb/d (45.4 kg/d). However, no reportable quantity is assigned for transport (43). The substance is on the list for atmospheric standards, as defined in 40 CFR 60.489 (47). The intent of these standards is to require all newly constructed, modified, and reconstructed manufacturing units to use the best demonstrated system of continuous emission reduction for equipment leaks of volatile organic compounds (47). 1-Propanol is also on the right-to-know regulations of the states of Connecticut, Florida, Illinois, Louisiana, Massachusetts, New Jersey, Pennsylvania, and Rhode Island (43). 1-Propanol is allowed as a flavoring substance and adjuvants according to 21 CFR 172.515 (48), and is exempted from the requirement of tolerance when used as a solvent or cosolvent in pesticide formulations (49) (see Flavors and spices; Pesticides).

6. Uses

1-Propanol is used mainly as a solvent and as a chemical intermediate. The largest uses are as a specialty solvent in flexographic printing inks (40%), particularly for printing on polyolefin and polyamide film (39). *n*-Propyl acetate [109-60-4] (33%) is the predominant derivative of propanol. The ester is also used as a solvent in flexographic printing inks as well as a solvent in nitrocellulose lacquers, cellulose esters and ethers, waxes, and insecticide formulations. 1-Propanol improves drying rates, reduces foaming, and controls viscosity at constant solids levels in water-based printing inks. It is also used to produce *n*-propylamines that are herbicide intermediates (18%), glycol ethers (12%), and as a ruminant feed supplement (see Feeds and feed additives). 1-Propanol has minor uses as a flavor and fragrance in foods and as a solvent or cosolvent in pesticide formulations. Demand for 1-propanol is expected to grow by 1.8% between 1993 and 1998 (50).

BIBLIOGRAPHY

"*n*-Propyl Alcohol" in *ECT* 1st ed., Vol. 11, pp. 178–182, by M. J. Curry, Celanese Corp. of America; in *ECT* 2nd ed., Vol. 16, pp. 559–564, by J. J. Wocasek, Celanese Chemical Co.; "*n*-Propyl Alcohol" under "Propyl Alcohols" in *ECT* 3rd ed., Vol. 19, pp. 221–227, by J. D. Unruh and L. Spinicelli, Celanese Chemical Co., Inc.

Cited Publications

1. J. A. Monick, *Alcohols, Their Chemistry, Properties and Manufacture*, Van Nostrand Reinhold, New York, 1968, 117–119.
2. R. C. Wilhoit and B. J. Zwolinski, *J. Phys. Chem. Ref. Data 2*, (Suppl. 1), 1–66 (1973).
3. *n-Propanol Product Bulletin*, Hoechst Celanese Chemical Group, Dallas, Tex.
4. J. C. Buzzell, Jr. and co-workers, *Behavior of Organic Chemicals in the Aquatic Environment, Part III—Behavior in Aerobic Treatment Systems (Activated Sludge)*, Association of Manufacturing Chemists, Washington, D.C., 1969, 26–31.
5. *Chemical Products Synopsis*, Mannsville Chemical Products, Mannsville, N.Y., Oct. 1977.
6. *Chem. Mark. Rep.* **3**,15 (Oct. 6, 1976).
7. B. Bryant, Sasolchem Ltd., private communication, June 7, 1995.
8. U.S. Pat. 2,830,091 (Apr. 8, 1958), B. Freedman and F. Marritz (to Sinclair Refining Co.).
9. Ger. Pat. 1,041,938 (Oct. 30, 1958), O. Bankowski and G. Hoffman (to VEB Leuna-Werke "Walter Ulbricht").
10. U.S. Pat. 2,873,290 (Feb. 10, 1959), D. Esmay and C. Johnson (to Standard Oil Co.).
11. *Chemical Economics Handbook*, Stanford Research Institute, Stanford, Calif., Feb. 1995, pp. 682.7000J–682.7000T.
12. *Ibid*, pp. 682.7002M–682.7002P.
13. Personal communication, Mar. 1994.
14. H. Wakamotsu, *Nippon Kagaku Zasshi* **85**, 257 (1964).
15. R. L. Olivier and F. B. Booth, *Hydrocarbon Process.*, 112 (1970).
16. J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Commun.*, 17 (1965).
17. F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Ind. (London)*, 560 (1965).
18. J. A. Osborn, F. H. Jarine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
19. P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem Commun.*, 305 (1967).
20. D. Evans, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 2660 (1968).
21. D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968).
22. M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967).
23. M. C. Baird, C. J. Nyman, and G. Wilkinson, *J. Chem. Soc. A*, 348 (1968).
24. G. Wilkinson, *Bull. Soc. Chim. Fr.* **12**, 5055 (1968).
25. C. K. Brown and G. Wilkinson, *Tetrahedron Lett.* **22**, 1725 (1969).
26. M. Yagupsky, C. K. Brown, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 937 (1970).
27. G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).
28. C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970).
29. Ger. Pat. 1,939,322 (Feb. 12, 1970), G. Wilkinson (to Johnson, Matthey and Co.).
30. W. R. Moser and C. J. Papile, *J. Organometal. Chem.* **41**, 293 (1987).
31. E. Billig and R. L. Pruett, *J. Organometal. Chem.* **192**, C49 (1980); J. D. Jamerson and co-workers, *J. Organometal. Chem.* **193**, C43 (1980).
32. A. G. Abatjoglou and co-workers, *Organometallics* **3**, 923 (1984).
33. H. Adkins, *Reactions of Hydrogen with Organic Compounds over Chromium Oxide and Nickel Catalysts*, University of Wisconsin Press, Madison, 1946.
34. U.S. Pat. 3,491,159 (Jan. 20, 1970), M. Reich and K. Schneider (to Chemische Werke Hüls).
35. Brit. Pat. 1,182,797 (Mar. 4, 1970), M. W. Fewlass and T. M. B. Wilson (to B. P. Chemicals Ltd.).
36. J. J. McKetta, *Encyclopedia of Chemical Processing and Design*, Vol. **5**, Marcel Dekker, Inc., New York, 1977, 393–394.
37. O. A. Hershmann and co-workers, *Ind. Eng. Chem. Prod. Res. Dev.* **8**, 372 (1969).
38. U.S. Pat. 4,247,486 (Jan. 27, 1981), E. A. V. Brewster and R. L. Pruett (to Union Carbide).
39. D. Pearson, personal research, July 1994.
40. *Chem. Mark. Rep.*, 31 (Jan. 1, 1996).

41. *n-Propanol Sales Specifications*, Hoechst Celanese Chemical Group, Dallas, Tex., June 1988.
42. *Code of Federal Regulations*, Title 29, Part 1910.1200, OSHA, Washington, D.C., rev. July 1, 1993.
43. *n-Propanol Material Safety Data Sheet*, Hoechst Celanese Chemical Group, Dallas Tex., Dec. 1994.
44. Celanese Chemical Co., Inc., *Mutagenicity Evaluation of n-Propyl Alcohol in the Ames Salmonella/ Microsome Plate Test*, Litton Bionetics, Inc., Kensington, Md., Mar. 1978.
45. Celanese Chemical Co., Inc., *Mutagenicity Evaluation of n-Propyl Alcohol*, in *The Mouse Lymphoma Forward Mutilation Assay*, Litton Bionetics, Inc., Kensington, Md., Oct. 1978.
46. Celanese Corp., *Range Finding Toxicity Test on n-Propanol*, Industrial Hygiene Foundation of America, Inc., Pittsburgh, Pa., July 1962.
47. *Code of Federal Regulations*, Title 40, Part 60.489, U.S. EPA, Washington, D.C., July 1, 1989.
48. *Code of Federal Regulations*, Title 21, Part 172.5.5, U.S. FDA, Washington D.C., Apr. 1, 1988.
49. Ref. 46, Part 180.1001 (c and e), July 1, 1988.
50. *Chemical Economics Handbook*, Stanford Research Institute, Stanford, Calif., Feb. 1995, pp. 682.7001C–682.7001D.

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