GLYCEROL

Glycerol[56-81-5], propane-1,2,3,-triol, glycerin (USP), a trihydric alcohol, is a clear, water-white, viscous, sweet-tasting hygroscopic liquid at ordinary room temperatures above its melting point. Glycerol was first discovered in 1779 by Scheele, who heated a mixture of litharge and olive oil and extracted it with water. Glycerol occurs naturally in combined form as glycerides in all animal and vegetable fats and oils, and is recovered, as a by-product when these oils are saponified in the process of manufacturing soap, when the fats are split in the production of fatty acids, or when fats are esterified with methanol in the production of methyl esters. Since 1949 it has also been produced commercially by synthesis from propylene [115-07-1]. The latter currently accounts for ca 30% of United States production.

The uses of glycerol number in the thousands, with large amounts going into the manufacture of drugs, cosmetics, toothpastes, urethane foam, synthetic resins, and ester gums. Tobacco processing and foods also consume large amounts either as glycerol or glycerides.

1. Occurrence

Glycerol occurs in combined form in all animal and vegetable fats and oils (see Fats and fatty oils). It is rarely found in the free state in these fats but is usually present as a triglyceride combined with such fatty acids as stearic, oleic, palmitic, and lauric acids, and these are generally mixtures or combinations of glycerides of several fatty acids. Coconut and palm kernel oils containing a high percentage (70–80%) of C-6–C-14 fatty acids yield larger amounts of glycerol than do fats and oils containing mostly C-16 and C-18 fatty acids, such as animal fats, cottonseed, soybean, olive, and palm oil. Glycerol also occurs naturally in all animal and vegetable cells in the form of lipids such as lecithin (qv) and cephalins. These complex fats differ from simple fats in that they invariably contain a phosphoric acid residue in place of one fatty acid residue.

2. Nomenclature

The term *glycerol* applies only to the pure chemical compound 1,2,3-propanetriol, $CH_2OHCHOHCH_2OH$. The term *glycerin* applies to the purified commercial products normally containing $\geq 95\%$ of glycerol. Several grades of glycerin are available commercially. They differ somewhat in their glycerol content and in other characteristics such as color, odor, and trace impurities. The ending -ol in glycerol connotes the presence of hydroxyl groups. The three hydroxyl positions in glycerol are designated 1,2,3-(formerly the designations α, β, and γ were used).

One method of naming the esters of glycerol with organic acids that have simple names is to replace the -ic acid ending by -in, eg, 1-monobutyrin (glycerol 1-butyrate); tributyrin (glycerol tributyrate). The degree of esterification is indicated by the prefixes mono-, di-, and tri-. A mixed triglyceride can be named in three ways, as illustrated for the compound of the formula

$$CH_3(CH_2)_{16}COOCH_2$$
$$CH_3COOCH$$
$$CH_3(CH_2)_{14}COOCH_2$$
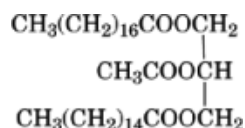
by the names 2-aceto-3-palmito-1-stearin,- 2-aceto-3-stearo-1-palmitin, and 3-palmito-1-stearo-2-acetin. Any one of the three acids can be given the -in termination; if possible, this acid receives the locant 1. The other acids are cited in alphabetical order (regardless of carbon content) and numbered, if there is a choice, to give the lowest possible numbering (see also Carboxylic acids; Esters, organic).

3. Properties

Physical properties of glycerol are shown in Table 1. Glycerol is completely soluble in water and alcohol, slightly soluble in diethyl ether, ethyl acetate, and dioxane, and insoluble in hydrocarbons (1). Glycerol is seldom seen in the crystallized state because of its tendency to supercool and its pronounced freezing point depression when mixed with water. A mixture of 66.7% glycerol, 33.3% water forms a eutectic mixture with a freezing point of $-46.5°C$.

Glycerol, the simplest trihydric alcohol, forms esters, ethers, halides, amines, aldehydes, and such unsaturated compounds as acrolein (qv). As an alcohol, glycerol also has the ability to form salts such as sodium glyceroxide (see also Alcohols, polyhydric).

4. Synthesis

A variety of processes for synthesizing glycerol from propylene are shown in Figure 1. The first glycerol process, put on stream in 1948, followed the discovery that propylene could be chlorinated in high yields to allyl chloride [107-05-1] (see Chlorocarbons and chlorohydrocarbons, allyl chloride). Since allyl chloride could be converted to glycerol by several routes, the synthesis of glycerol from propylene [115-07-1] became possible. Propylene can also be oxidized in high yields to acrolein [107-02-8]. Several routes for conversion of acrolein to glycerol are shown in Figure 1.

In the traditional allyl chloride route, the allyl chloride may be converted into glycerol by two processes. The allyl chloride may be treated with aqueous chlorine, and the resulting mixture of glycerol dichlorohydrins dehydrochlorinated to epichlorohydrin [106-89-8], which is then hydrolyzed to glycerol. In the second process, allyl chloride is hydrolyzed to allyl alcohol [107-18-6] (see Allyl alcohol and monoallyl derivatives). The allyl alcohol is chlorohydrinated with aqueous chlorine solution to yield a mixture of monochlorohydrins which are hydrolyzed to glycerol in 90% yield based on allyl alcohol. The product from either of the above procedures is a dilute aqueous solution containing 5% or less of glycerol. High purity glycerol is obtained in several steps: the crude glycerol is concentrated to ca 80% in multiple-effect evaporators and salt is removed by centrifuging; additional concentration of the product, followed by desalting, yields 98% glycerol; colored substances are removed by solvent extraction; and the product is refined by steam-vacuum distillation (see Chlorohydrins).

Acrolein-based glycerol manufacture via no-chlorine processing proceeds by epoxidation (2) and reduction (Fig. 1), in either order, followed by hydration. The epoxidation to glycidaldehyde [765-34-4] can proceed through treatment of acrolein with aqueous sodium hypochlorite solution (3) or with hydrogen peroxide. If desired, glycidol [556-52-5] can be separated as an intermediate. Alternatively, allyl alcohol from the reduction of acrolein can be hydroxylated with aqueous hydrogen peroxide to yield directly a glycerol solution in 80–90% yield.

Table 1. Physical Properties of Glycerol

Property	Value
mp, °C	18.17
bp, °C	
at 0.53 kPa[a]	14.9
at 1.33 kPa[a]	166.1
at 13.33 kPa[a]	222.4
at 101.3 kPa[a]	290
sp gr, 25/25°C	
in vacuum	1.2617
100% glycerol in air	1.2620
95% glycerol in air	1.2491
n_{D}^{20}	1.47399
vapor pressure, Pa[b]	
at 50°C	0.33
at 100°C	26
at 150°C	573
at 200°C	6100
surface tension at 20°C, mN/m(= dyn/cm)	63.4
viscosity at 20°C, mPa·s(= cP)	1499
heat of vaporization, J/mol[c]	
at 55°C	88.12
at 195°C	76.02
heat of solution to infinite dilution, kJ/mol[c]	5.778
heat of formation, kJ/mol[c]	667.8
thermal conductivity, W/(m·K)	0.28
flash point, °C	
Cleveland open cup	177
Pensky-Martens closed cup	199
fire point, °C	204

[a]To convert kPa to mm Hg, multiply by 7.5.
[b]To convert Pa to mm Hg, multiply by 0.0075.
[c]To convert J to cal, divide by 4.184.

Propylene oxide-based glycerol can be produced by rearrangement of propylene oxide [75-56-9](qv) to allyl alcohol over trilithium phosphate catalyst at 200–250°C (yield 80–85%) (4), followed by any of the appropriate steps shown in Figure 1. The specific route commercially employed is peracetic acid epoxidation of allyl alcohol to glycidol followed by hydrolysis to glycerol (5). The newest international synthesis plants employ this basic scheme.

5. Manufacture

Until 1949 all glycerol was obtained from the glycerides in fats and oils. Currently ca 70% of U.S. production is from natural glycerides. The production of synthetic glycerol peaked in the 1960s and 1970s, when it accounted for 50–60% of the market.

Glycerol from glycerides (natural glycerol) is obtained from three sources: soap manufacture, fatty acid production, and fatty ester production. In soap manufacture, fat is boiled with caustic soda solution and salt. Fats react with the caustic to form soap (qv) and glycerol. The presence of salt causes a separation into two layers: the upper layer is soap and the lower layer, referred to as spent lye, contains glycerol, water, salt, and excess caustic. Continuous saponification (consap) processes for producing soap are now common and produce a
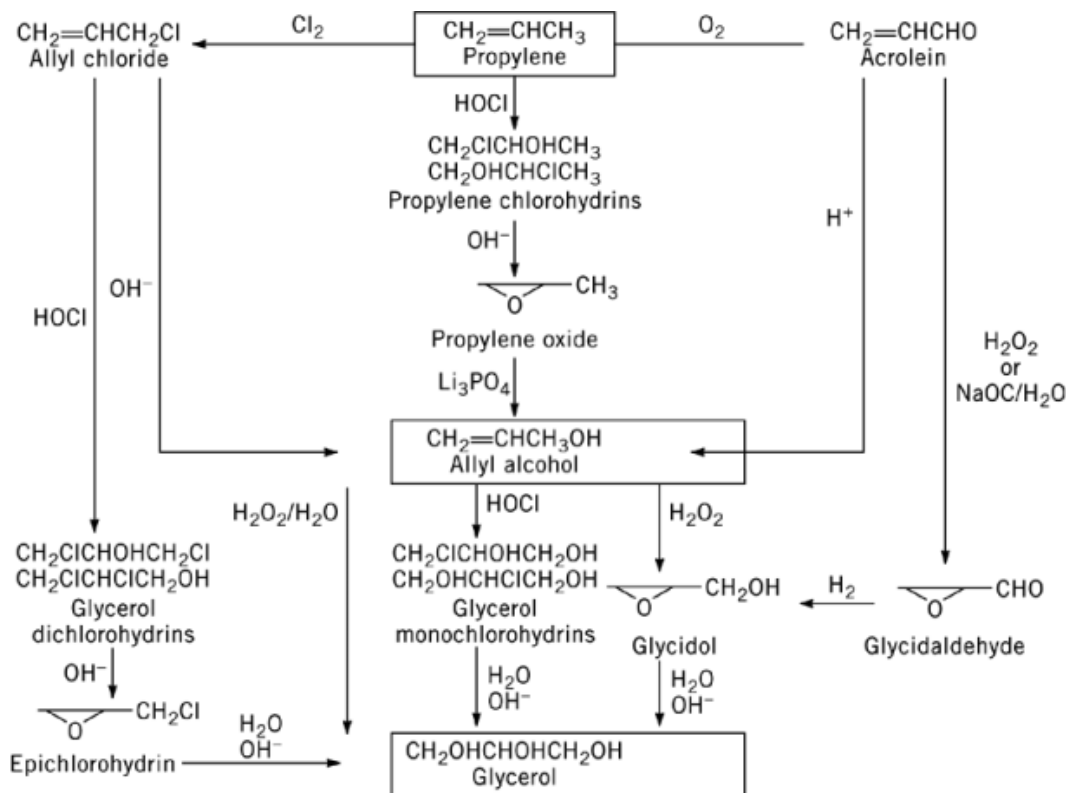
Fig. 1. Routes for the manufacture of glycerol.

spent lye similar to batch or kettle processes. In producing fatty acids, the most common process is continuous, high pressure hydrolysis where a continuous, upward flow of fat in a column flows countercurrent to water at 250–260°C and 5 MPa (720 psi). The fat is split by the water into fatty acids and glycerol. The fatty acids are withdrawn from the top of the column, and the glycerol-containing aqueous phase (called sweet water) falls and is withdrawn from the bottom. Concentration of the sweet water by evaporation results in a product called hydrolysis crude. The fatty acids from splitting are used to make soap, reduced to the corresponding fatty alcohol, or marketed as fatty acids. A third source of natural glycerol is the esterification of fats with alcohol to produce fatty esters. A fat usually reacts with methanol in the presence of an alkali catalyst such as sodium methoxide to produce methyl ester and glycerol, which is separated from the methyl ester by water washing. Acidulation with hydrochloric acid and removal of residual methanol produces a crude glycerol with a few percent salt content. The methyl esters are reduced to the corresponding fatty alcohols, marketed as fatty esters, or used as an emission reducing component of diesel fuels.

5.1. Recovery

The spent lyes resulting from current soapmaking processes generally contain 8–15% glycerol; sweet waters from hydrolysis of fats contain as much as 20% glycerol; crude glycerol from esterification contains 80% or more glycerol. The grade of fat used directly affects the treatment required to produce glycerol of an acceptable commercial quality. The chemicals most commonly used to remove impurities from spent lye and sweet water are hydrochloric acid and caustic soda.

The treatment of spent lye consists of a series of operations designed to remove nearly all of the organic impurities (6, 7). The spent lye commonly is treated with mineral or fatty acids to reduce the content of free caustic and soda ash and to reduce the pH to 4.6–4.8 (8). Sulfates are to be avoided since they are associated with foaming and heat exchanger fouling during subsequent refining. After cooling, the solid soap is skimmed, and an acid and a coagulant are added, followed by filtration. Addition of caustic soda removes the balance of coagulant in solution and adjusts the pH to a point at which the liquor is least corrosive to subsequent process treatment. Spent lyes from modern liquid–liquid countercurrent extraction used with continuous saponification systems require little treatment other than reduction of free alkali by neutralization with hydrochloric acid. The dilute glycerol is now ready for concentration to 80% soap lye crude glycerol.

The sweet water from continuous and batch autoclave processes for splitting fats contains little or no mineral acids and salts and requires very little in the way of purification, as compared to spent lye from kettle soapmaking (9). The sweet water should be processed promptly after splitting to avoid degradation and loss of glycerol by fermentation. Any fatty acids that rise to the top of the sweet water are skimmed. A small amount of alkali is added to precipitate the dissolved fatty acids and neutralize the liquor. The alkaline liquor is then filtered and evaporated to an 88% crude glycerol. Sweet water from modern noncatalytic, continuous hydrolysis may be evaporated to ca 88% without chemical treatment.

Ester crude glycerol is usually of high quality; however, salt residue from the esterification catalyst is typically present at a concentration of one percent or higher. Crude glycerol originating from esterification or splitting of 100% vegetable oils is segregated from other glycerols throughout processing to produce kosher glycerin.

5.2. Concentration

The quality of crude glycerols directly affects the refining operation and glycerin yield. Specifications for crude glycerols usually limit ash content, ie, a measure of salt and mineral residue; matter organic nonglycerol (MONG), which includes fatty acids and esters; trimethylene glycol (TMG), ie, propane-1,3-diol; water; arsenic; and sugars (8).

Dilute glycerol liquors, after purification, are concentrated to crude glycerol by evaporation. This process is carried out in conventional evaporation (qv) under vacuum heated by low pressure steam. In the case of soap–lye glycerol, means are supplied for recovery of the salt that forms as the spent lye is concentrated. Multiple effort evaporators are typically used to conserve energy while concentrating to a glycerol content of 85–90%.

5.3. Refining

The refining of natural glycerol is generally accomplished by distillation, followed by treatment with active carbon. In some cases, refining is accomplished by ion exchange (qv).

5.4. Distillation

In the case of spent-lye crude, the composition is ca 80% glycerol, 7% water, 2% organic residue, and less than 10% ash. Hydrolysis crudes are generally of a better quality than soap–lye crudes with a composition of ca 88% glycerol, <1% ash (little or no salt), and <1.5% organic residue.

Distillation equipment for soap–lye and esterification crude requires salt-resistant metallurgy. The solid salt which results when glycerol is vaporized is removed by filtration or as bottoms from a wiped film evaporator. The Luwa scraped wall evaporator is capable of vaporizing glycerol very rapidly and almost completely, such that a dry, powdery residue is discharged from the base of the unit (8). Distillation of glycerol under atmospheric pressure is not practicable since it polymerizes and decomposes glycerol to some extent at the normal boiling

point of 204°C. A combination of vacuum and steam distillation is used in which the vapors are passed from the still through a series of condensers or a packed fractionation section in the upper section of the still. Relatively pure glycerol is condensed. High vacuum conditions in modern stills minimize glycerol losses due to polymerization and decomposition (see Distillation).

5.5. Bleaching and Deodorizing

The extensive use of glycerol and glycerol derivatives in the food industry (see Food processing) stresses the importance of the removal of both color and odor (also necessary requirements of USP and extra-quality grades). Activated carbon (1–2%) and diatomite (qv) filter aid are added to the glycerol in the bleach tank at 74–79°C, stirred for 1–2 h, and then filtered at the same temperature, which is high enough to ensure easy filtering and yet not so high as to lead to darkening of the glycerol.

5.6. Ion Exchange

Most natural glycerol in the United States is refined by the methods described above. However, several refiners employ or have employed ion-exchange systems. When ionized solids are high, as in soap–lye crude, ion-exclusion treatment can be used to separate the ionized material from the nonionized (mainly glycerol). A granular resin such as Dowex 50WX8 may be used for ion exclusion. For ion exchange, crude or distilled glycerol may be treated with a resin appropriate for the glycerol content and impurities present. Macroreticular resins such as Amberlite 200, 200C, IRA-93, and IRA-90 may be used with undiluted glycerol. However, steam deodorization is often necessary to remove odors imparted by the resin. Ion exchange and ion exclusion are not widely used alternatives to distillation (8).

5.7. Grades

Two grades of crude glycerol are marketed: (*1*) soap–lye crude glycerol obtained by concentration of lyes from kettle or continuous soapmaking processes contains ca 80% glycerol; and (*2*) hydrolysis crude glycerol resulting from hydrolysis of fats contains ca 88–91% glycerol and a small amount of organic salts. Since glycerol from methyl ester production contains salt, it is usually marketed as soap–lye crude.

Several grades of refined glycerol, such as high gravity, dynamite, and USP, are marketed; specifications vary depending on the consumer and the intended use. USP-grade glycerol is water-white, and meets the requirements of the USP (see Fine chemicals). It is classified as GRAS by the FDA, and is suitable for use in foods, pharmaceuticals, and cosmetics, or when the highest quality is demanded or the product is designed for human consumption. It has a minimum specific gravity (25°C/25°C) of 1.249, corresponding to no less than 95% glycerol. Kosher glycerin meets all USP requirements and is produced by synthetically or from 100% vegetable glycerides. The *European Pharmacopoeia* (PH.EUR.) grade is similar to the USP, but the common PH.EUR. grade has a minimum glycerol content of 99.5%. The chemically pure (CP) grade designates a grade of glycerol that is about the same as the USP but with the specifications varying slightly as agreed by buyer and seller. The high gravity grade is a pale-yellow glycerol for industrial use with a minimum specific gravity (25°C/25°C) of 1.2595. The dynamite grade has the same specific gravity but is more yellow (see Explosives and propellants, explosives). All these grades satisfy the federal specifications for glycerol (0-G491B-2).

Table 2. Glycerol Production[a] in the United States, t

Year	Production of crude[b]	Year	Production of crude[b]
1920	19,800	1985	145,500
1940	71,600	1987	139,300
1950	102,300	1988	134,600
1960	136,900	1989	133,200
1970	153,900	1990	133,200
1980	136,577	1991	133,800

[a]100% Glycerol basis.
[b]Synthetic included on a crude basis since June 1949.

Table 3. Glycerol Use,[a] t

Use	1977	1986	1990
alkyd resins	21,300	6,480	2,870
cellophane and meat casings	9,880	3,650	3,340
tobacco	15,900	22,670	21,870
explosives and military use	2,690	930	2,030
drugs, including toothpaste	19,820	24,730	28,330
cosmetics	4,670	6,410	9,170
monoglycerides and foods	13,740	13,480	18,340
urethane foams	13,620	13,730	15,290
miscellaneous	11,710	7,140	6,770
distributor sales	14,520	27,840	35,880
Total	*127,850*	*127,060*	*143,880*

[a]Ref. 10.

6. Economic Aspects

Commercial production and consumption of glycerol has generally been considered a fair barometer of industrial activity, as it enters into such a large number of industrial processes. It generally tends to rise in periods of prosperity and fall in recession times.

Glycerol production in the United States (Table 2) rose from 19,800 metric tons in 1920 to a peak of 166,100 t in 1967 (10). World production of glycerol is ca 600,000 t/yr. Synthetic glycerol accounts for ca 30% of the United States annual production. Widespread consolidation of glycerin refining sites occurred between 1975 and 1992. In North America there were 20 natural and four synthetic sites in 1975. By 1992 there were only 14 natural sites and one synthetic site. During this time natural or glyceride-derived capacity increased by 55,000 t/yr, while synthetic capacity fell by 85,000 t/yr (11). In 1929, the largest single industrial use was as an automotive antifreeze (qv). This use has completely disappeared and been replaced by outlets in food, drug, cosmetics, tobacco processing, and urethane foams (see Urethane polymers). The uses in alkyd resins (qv) (owing to the increase in use of water-based paints) and cellophane (owing to the popularity of other transparent wraps) continue to decrease. The use distribution for the years 1986 and 1990 is compared to that in 1977 in Table 3 (10).

Since 1920, the price of refined glycerol in the United States has varied from a low of $0.22/kg in the early 1930s to a high of nearly $1.95/kg in 1987. In 1992 glycerin prices for USP grade ranged from $1.28 to $1.65/kg. Since glycerol is a by-product of fatty acid, ester, and alcohol production, prices are quite sensitive to changes in oleochemical demand. Glycerol prices also respond to prices for tallow, coconut oil, and petroleum, the feedstocks from which it is prepared.

7. Identification and Analysis

The methods of analysis of the American Oil Chemists' Society (AOCS) are the principal procedures followed in the United States and Canada and are official in commercial transactions. When the material is for human consumption or drug use, it must meet the specifications of the USP (12). Commercial distilled grades of glycerol do not require purification before analysis by the usual methods. The determination of glycerol content by the periodate method (13), which replaced the acetin and dichromate methods previously used, is more accurate and more specific as well as simpler and more rapid.

Glycerol is most easily identified by heating a drop of the sample with ca 1 g powdered potassium bisulfate and noting the very penetrating and irritating odor of the acrolein that is formed. Owing to the toxicity of acrolein, a preferred method is the Cosmetics, Toiletry, and Fragrance Association (CTFA) method GI-1, an ir spectrophotometric method. Glycerol may be identified by the preparation of crystalline derivatives such as glyceryl tribenzoate, mp 71–72°C; glycerol tris(3,5-dinitrobenzoate), mp 190–192°C; or glycerol tris(*p*-nitrobenzoate), mp 188–189°C (14).

The concentration of distilled glycerol is easily determined from its specific gravity (15) by the pycnometer method (16) with a precision of ±0.02%. Determination of the refractive index also is employed (but not as widely) to measure glycerol concentration to ±0.1% (17).

The preferred method of determining water in glycerol is by the Karl Fischer volumetric method (18). Water can also be determined by a special quantitative distillation in which the distilled water is absorbed by anhydrous magnesium perchlorate (19). Other tests such as ash, alkalinity or acidity, sodium chloride, and total organic residue are included in AOCS methods (13, 16, 18).

8. Handling and Storage

Most crude glycerol is shipped to refiners in standard tank cars or tank wagons. Imported crude arrives in bulk, in vessels equipped with tanks for such shipment, or in drums.

Refined glycerol of a CP or USP grade is shipped mainly in bulk in tank cars or tank wagons. These are usually stainless steel-, aluminum-, or lacquer-lined. However, pure glycerol has little corrosive tendency, and may be shipped in standard, unlined steel tank cars, provided they are kept clean and in a rust-free condition. Some producers offer refined glycerol in 4.5-kg (3.8-L or 1-gal) tinned cans and more commonly in 250–259-kg (208-L or 55-gal) drums of a nonreturnable type (ICC-17E). These generally have a phenolic resin lining.

8.1. Storage

For receiving glycerol from standard 30.3-m^3 (8000-gal) tank cars (36.3-t), a storage tank of 38–45-m^3 $((10-12) \times 10^3 - \text{gal})$ capacity should be employed. Preferably it should be of stainless steel (304 or 316), of stainless- or nickel-clad steel, or of aluminum. Certain resin linings such as Lithcote have also been used. Glycerol does not seriously corrode steel tanks at room temperature but gradually absorbed moisture may have an effect. Therefore, tanks should be sealed with an air-breather trap.

8.2. Handling Temperatures

Optimum temperature for pumping is in 37–48°C range. Piping should be stainless steel, aluminum, or galvanized iron. Valves and pumps should be bronze, cast-iron with bronze trim, or stainless steel. A pump of 3.15-L/s (50-gal/min) capacity unloads a tank car of warm glycerol in ca 4 h.

9. Health and Safety Factors

Glycerol, since 1959, is generally recognized as safe (GRAS) as a miscellaneous or general-purpose food additive (qv) under the CFR (20), and it is permitted in certain food packaging (qv) materials.

Oral LD_{50} levels have been determined in the mouse at 470 mg/kg (21) and the guinea pig at 7750 mg/kg (22). Several other studies (23–25) have shown that large quantities of both synthetic and natural glycerol can be administered orally to experimental animals and humans without the appearance of adverse effects. Intravenous administration of solutions containing 5% glycerol to animals and humans has been found to cause no toxic or otherwise undesirable effects (26).

The aquatic toxicity (TLm96) for glycerol is >1000 mg/L (27), which is defined by NIOSH as an insignificant hazard.

10. Uses

Glycerol is used in nearly every industry. The largest single use is in drugs and oral care products including toothpaste, mouthwash, and oral rinses (Table 3). Its use in tobacco processing and urethane foams remains at a fairly even consumption level. Use in foods and cosmetics is growing.

10.1. Foods

Glycerol as a food is easily digested and nontoxic, and its metabolism places it with the carbohydrates, although it is present in combined form in all vegetable and animal fats. In flavoring and coloring products, glycerol acts as a solvent and its viscosity lends body to the product. Raisins saturated with glycerol remain soft when mixed with cereals. It is used as a solvent, a moistening agent, and an ingredient of syrups (qv) as a vehicle. In candies and icings, glycerol retards crystallization of sugar. Glycerol is used as a heat-transfer medium in direct contact with foods in quick freezing, and as a lubricant in machinery used for food processing (qv) and packaging. The polyglycerols and polyglycerol esters have increasing use in foods, particularly in shortenings and margarines.

10.2. Drugs and Cosmetics

In drugs and medicines, glycerol is an ingredient of many tinctures and elixirs, and glycerol of starch is used in jellies and ointments. It is employed in cough medicines and anesthetics (qv), such as glycerol–phenol solutions, for ear treatments, and in bacteriological culture media. Its derivatives are used in tranquilizers (eg, glyceryl guaiacolate [93-14-1]), and nitroglycerin [55-65-0] is a vasodilator in coronary spasm. In cosmetics (qv), glycerol is used in many creams and lotions to keep the skin soft and replace skin moisture. It is widely used in toothpaste to maintain the desired smoothness, viscosity, and lending a shine to the paste (see Dentifrices).

10.3. Tobacco

In processing tobacco, glycerol is an important part of the casing solution sprayed on tobacco before the leaves are shredded and packed. Along with other flavoring agents, it is applied at a rate of ca 2.0 wt % of the tobacco to prevent the leaves from becoming friable and thus crumbling during processing; by remaining in the tobacco, glycerol helps to retain moisture and thus prevents drying out of the tobacco, and influences the burning rate of the tobacco. It is used also in the processing of chewing tobacco to add sweetness and prevent dehydration, and as a plasticizer in cigarette papers.

10.4. Wrapping and Packaging Materials

Meat casings and special types of papers, such as a glassine and greaseproof paper, need plasticizers (qv) to give them pliability and toughness; as such, glycerol is completely compatible with the base materials used, is absorbed by them, and does not crystallize or volatilize appreciably.

10.5. Lubricants

Glycerol can be used as a lubricant in places where an oil would fail. It is recommended for oxygen compressors because it is more resistant to oxidation than mineral oils. It is also used to lubricate pumps and bearings exposed to fluids such as gasoline and benzene, which would dissolve oil-type lubricants. In food, pharmaceutical, and cosmetic manufacture, where there is contact with a lubricant, glycerol may be used to replace oils (see Lubrication and lubricants).

Glycerol is often used as a lubricant because its high viscosity and ability to remain fluid at low temperatures make it valuable without modification. To increase its lubricating power, finely divided graphite may be dispersed in it. Its viscosity may be decreased by addition of water, alcohol, or glycols, and increased by polymerization or mixing with starch; pastes of such compositions may be used in packing pipe joints, in gas lines, or in similar applications (see Packaging materials, industrial products). For use in high pressure gauges and valves, soaps are added to glycerol to increase its viscosity and improve its lubricating ability. A mixture of glycerin and glucose is employed as a nondrying lubricant in the die-pressing of metals. In the textile industry, glycerol is frequently used in connection with so-called textile oils, in spinning, knitting, and weaving operations.

10.6. Urethane Polymers

An important use for glycerol is as the fundamental building block in polyethers for urethane polymers (qv). In this use it is the initiator to which propylene oxide, alone or with ethylene oxide, is added to produce trifunctional polymers which, on reaction with diisocyanates, produce flexible urethane foams. Glycerol-based polyethers (qv) have found some use, too, in rigid urethane foams.

10.7. Gaskets and Cork products

Sheets and gaskets made with ground cork and glue require a plasticizer that has some humectant action in order that they may be pliable and tough. Glycerol is used because it has low vapor pressure, is not readily extractable by oils and greases, is readily absorbed by the cork, and is compatible with glue. With crown sealers and cork stoppers that come into contact with foods, it fulfills the additional requirement of nontoxicity.

10.8. Other Uses

Glycerol is used in cement compounds, caulking compounds, lubricants, and pressure media. It is also used in embalming fluids, masking and shielding compounds, soldering compounds, and compasses; cleaning materials such as soaps, detergents, and wetting agents; emulsifiers and skin protectives used in industry; asphalt (qv); ceramics (qv); photographic products; leather (qv) and wood (qv) treatments; and adhesives (qv).

11. Derivatives

Glycerol derivatives include acetals, amines, esters, and ethers. Of these the esters are the most widely employed. Alkyd resins (qv) are esters of glycerol and phthalic anhydride. Glyceryl trinitrate [55-63-0]

(nitroglycerin) is used in explosives (qv) and as a heart stimulant (see Cardiovascular agents). Included among the esters also are the ester gums (rosin acid ester of glycerol), mono- and diglycerides (glycerol esterified with fatty acids or glycerol transesterified with oils), used as emulsifiers and in shortenings. The salts of glycerophosphoric acid are used medicinally.

Mixtures of glycerol with other substances are often named as if they were derivatives of glycerol; eg, boroglycerides (also called glyceryl borates) are mixtures of boric acid and glycerol. Derivatives, such as acetals, ketals, chlorohydrins, and ethers, can be prepared but are not made commercially, with the exception of polyglycerols.

The polyglycerols, ethers prepared with glycerol itself, have many of the properties of glycerol. Diglycerol, $HOCH_2CHOHCH_2OCH_2CHOHCH_2OH$ [627-82-7], is a viscous liquid ($287 \text{ mm}^2/\text{s}(= \text{cSt})$ at $65.6°C$), about 25 times as viscous as glycerol. The polyglycerols offer greater flexibility and functionality than glycerol. Polyglycerols up to and including triacontaglycerol (30 condensed glycerol molecules) have been prepared commercially; the higher forms are solid. They are soluble in water, alcohol, and other polar solvents. They act as humectants, much like glycerol, but have progressively higher molecular weights and boiling points. Products based on polyglycerols are useful in surface-active agents (see Surfactants), emulsifiers (see Emulsions), plasticizers, adhesives, lubricants, antimicrobial agents, medical specialties and dietetic foods (see Food additives; Sweeteners).

11.1. Esters

The mono- and diesters of glycerol and fatty acids occur naturally in fats that have become partially hydrolyzed. The triglycerides are primary components of naturally occurring fats and fatty oils.

Mono- and diglycerides are made by the reaction of fatty acids or raw or hydrogenated oils, such as cottonseed and coconut, with an excess of glycerol or polyglycerols. Commercial glycerides are mixtures of mono- and diesters, with a small percentage of the triester. They also contain small amounts of free glycerol and free fatty acids. High purity monoglycerides are prepared by molecular or short-path distillation of glyceride mixtures.

The higher fatty acid mono- and diesters are oil-soluble and water-insoluble. They are all edible, except the ricinoleate and the erucinate, and find their greatest use as emulsifiers in foods and in the preparation of baked goods (28) (see Bakery processes and leavening agents). A mixture of mono-, di-, and triglycerides is manufactured in large quantities for use in superglycerinated shortenings. Mono- and diglycerides are important modifying agents in the manufacture of alkyd resins, detergents, and other surface-active agents. The monoglycerides are also used in preparation of cosmetics (qv), pigments (qv), floor waxes (see Polishes), synthetic rubbers (see Rubber chemicals), coatings (qv), textiles (qv) (29), etc.

Tailored triglycerides with unique nutritional properties have grown in importance in recent years. These compounds are produced from glycerol esterification with specific high purity fatty acids. A triglyceride consisting primarily of C-8, C-10, and C-22 fatty acid chains designated "caprenin" has been marketed as a low calorie substitute for cocoa butter (30) (see Fat replacers). By starting with behenic monoglyceride made from glycerol and behenic acid, the shorter caprylic and capric acids can be attached to the behenic monoglyceride to deliver a triglyceride having only one long fatty acid chain (31, 32).

11.2. Acetins

The acetins are the mono-, di-, and triacetates of glycerol that form when glycerol is heated with acetic acid. Physical properties are shown in Table 4; they are all colorless.

Monoacetin (glycerol monoacetate[26446-35-5]), is a thick hygroscopic liquid,and is sold for use in the manufacture of explosives, in tanning, and as a solvent for dyes. Diacetin (glycerol diacetate[25395-31-7]) is a

Table 4. Physical Properties of Acetins

Property	Monoacetin	Diacetin	Triacetin
CAS Registry Number	[26446-35-5]	[25395-31-7]	[102-76-1]
bp, °C			
at 22 kPa[a]	158[b]		
at 101.3 kPa[a]		259	258–259
d_4^{20}, g/cm^3	1.206		1.160
d_4^{16}, g/cm^3		1.184	
solubility			
soluble in	water, ethanol	water, ethanol	ethanol, diethyl ether and other organic solvents
sl sol in	diethyl ether	diethyl ether, benzene	water
insoluble in	benzene	carbon disulfide	

[a]To convert kPa to mm Hg, multiply by 7.5.
[b]At 0.4 kPa,[a] bp = 130°C.

hygroscopic liquid, and is sold in a technical grade for use as a plasticizer and softening agent and as a solvent. Its n_D^{20} is 1.44.

Triacetin, mp = −78°C, has a very slight odor and a bitter taste. Glycerol triacetate[102-76-1] occurs naturally in small quantities in the seed of *Euonymus europaeus*. Most commercial triacetin is USP grade. Its primary use is as a cellulose plasticizer in the manufacture of cigarette filters, and its second largest use is as a component in binders for solid rocket fuels. Smaller amounts are used as a fixative in perfumes, as a plasticizer for cellulose nitrate, in the manufacture of cosmetics, and as a carrier in fungicidal compositions (see Fungicides, agricultural).

BIBLIOGRAPHY

"Glycerol" in *ECT* 1st ed., Vol. 7, pp. 216–229, by N. N. Dalton and J. C. Kern, Association of American Soap & Glycerin Producers, Inc., and C. S. Miner, Jr., The Miner Laboratories; in *ECT* 2nd ed., Vol. 10, pp. 619–631, by J. C. Kern, Glycerin Producers' Association; in *ECT* 3rd ed., Vol. 11, pp. 921–932 by J. C. Kern, Glycerin Producers' Association.

Cited Publications

1. *Physical Properties of Glycerin and Its Solutions*, Glycerin Producers' Association, New York, 1975.
2. G. B. Payne, *J. Am. Chem. Soc.* **80**, 6461 (1958);   **81**, 4901 (1959).
3. C. Schaer, *Helv. Chim. Acta* **41**, 560, 614 (1958);   U.S. Pat. 2,887,498 (May 9, 1959), G. Hearne, D. S. la France, and H. D. Finch (to Shell Development Co.).
4. U.S. Pat. 2,426,264 (Aug. 26, 1947), G. W. Fowler and J. T. Fitzpatrick (to Carbide and Carbon Chemicals Corp.).
5. K. Yamagishi and O. Kageyama, *Hydrocarbon Process.* **55**(12), 139 (1976).
6. T. M. Patrick, Jr., E. T. McBee, and H. B. Haas, *J. Am. Chem. Soc.* **68**, 1009 (1946).
7. W. E. Sanger, *Chem. Met. Eng.* **26**, 1211 (1922).
8. E. Woollatt, *The Manufacture of Soaps, Other Detergents and Glycerin*, John Wiley & Sons, Inc., New York, 1985, 296–357.
9. J. L. Trauth, *Oil Soap* **23**, 137 (1946).
10. *SDA Glycerin and Oleochemicals Statistics Report*, The Soap and Detergent Association, New York, 1992.
11. E. T. Sauer, *World Glycerin Conference*, Paris, Oct. 1992, H. B. International and C. A. Houston and Assoc.
12. *The United States Pharmacopeia XX (USP XX-NF XV)*, The United States Pharmacopeial Convention, Inc., Rockville, Md., 1980.
13. *Official and Tentative Methods*, 3rd ed., American Oil Chemists' Society, Chicago, Ill., 1978, Ea6-51.

14. C. S. Miner and N. N. Dalton, *Glycerol, ACS Monograph 117*, Reinhold Publishing Corp., New York, 1953, 171–175.

15. L. W. Bosart and A. O. Snoddy, *Ind. Eng. Chem.* **19**, 506 (1927).

16. Ref. 13, Ea7-50.

17. L. T. Hoyt, *Ind. Eng. Chem.* **26**, 329 (1934).

18. Ref. 13, Ea8-58.

19. C. P. Spaeth and G. F. Hutchinson, *Ind. Eng. Chem. Anal. Ed.* **8**, 28 (1936).

20. *Code of Federal Regulations*, Title 21, Sect. 182.1320, Washington, D.C., 1993.

21. H. F. Smyth, J. Seaton, and L. Fischer, *J. Ind. Hyg. Toxicol.* **23**, 259 (1941).

22. R. C. Anderson, P. N. Harris, and K. K. Chen, *J. Am. Pharm. Assoc. Sci. Ed.* **39**, 583 (1950).

23. V. Johnson, A. J. Carlson, and A. Johnson, *Am. J. Physiol.* **103**, 517 (1933).

24. C. H. Hine, H. H. Anderson, H. D. Moon, M. K. Dunlap, and M. S. Morse, *Arch. Ind. Hyg. Occup. Med.* **7**, 282 (1953).

25. W. Deichman, *Ind. Med. Ind. Hyg. Sec.* **9**(4), 60 (1940).

26. H. A. Sloviter, *J. Clin. Inv.* **37**, 619 (1958).

27. W. Hann and P. A. Jensen, *Water Quality Characteristics of Hazardous Materials*, Texas A&M University, College Station, 1974, p. 4.

28. N. H. Nash and V. K. Babayan, *Food Process. (Chicago)* **24**(11), 2 (1963);   *Baker's Dig.* **38**(9), 46 (1963).

29. A. E. Parolla and C. Z. Draves, *Am. Dyestuff Rep.* **46**, 761 (Oct. 21, 1957);   **47**, 643 (Sept. 22, 1958).

30. *Caprenin*, U.S. FDA GRAS Petition 1G0373, U.S. Food and Drug Administration, Washington, D.C., 1990.

31. U.S. Pat. 5,142,071 (Aug. 25, 1992), B. W. Kluesener, G. K. Stipp, and D. K. Yang (to Procter & Gamble).

32. U.S. Pat. 5,142,072 (Aug. 25, 1992), G. K. Stipp and B. W. Kluesener (to Procter & Gamble).

LOWEN R. MORRISON
Procter & Gamble

Related Articles

Distillation; Fats and fatty oils; Alcohols, polyhydric; Dentifrices