

## BENZOIC ACID

### 1. Introduction

Benzoic acid [65-85-0],  $C_6H_5COOH$ , the simplest member of the aromatic carboxylic acid family, was first described in 1618 by a French physician, but it was not until 1832 that its structure was determined by Wöhler and Liebig. In the nineteenth century benzoic acid was used extensively as a medicinal substance and was prepared from gum benzoin. Benzoic acid was first produced synthetically by the hydrolysis of benzotrichloride. Various other processes such as the nitric acid oxidation of toluene were used until the 1930s when the decarboxylation of phthalic acid became the dominant commercial process. During World War II in Germany the batchwise liquid-phase air oxidation of toluene became an important process. In the United States, all other processes have been completely phased out and virtually all benzoic acid is manufactured by the continuous liquid-phase air oxidation of toluene. In the late 1950s and the early 1960s both Dow Chemical and Snia Viscosa constructed facilities for liquid-phase toluene oxidation because of large requirements for benzoic acid in the production of phenol and caprolactam. Benzoic acid, its salts, and esters are very useful and find application in medicinals, food and industrial preservatives, cosmetics, resins, plasticizers, dyestuffs, and fibers.

### 2. Occurrence

Benzoic acid in the free state, or in the form of simple derivatives such as salts, esters, and amides, is widely distributed in nature. Gum benzoin (from *styrax benzoin*) may contain as much as 20% benzoic acid in the free state or in combinations easily broken up by heating. Acaroid resin (from *Xanthorrhoea haslilis*) contains from 4.5 to 7%. Smaller amounts of the free acid are found in natural products including the scent glands of the beaver, the bark of the black cherry tree, cranberries, prunes, ripe cloves, and oil of anise seed. Peru and Tolu balsams contain benzyl benzoate; the latter contains free benzoic acid as well. The urine of herbivorous animals contains a small proportion of the glycine derivative of benzoic acid, hippuric acid [495-69-2], ( $C_6H_5CONHCH_2COOH$ ). So-called natural benzoic acid is not known to be available as an item of commerce.

### 3. Properties

Selected physical properties of benzoic acid are given in Table 1, solubilities in water in Table 2, solubilities in various organic solvents in Table 3, and vapor pressures in Table 4. In its chemical behavior benzoic acid shows few exceptional properties; the reactions of the carboxyl group are normal, and ring substitutions take place as would be predicted.

Table 1. **Physical Properties of Benzoic Acid**

molecular formula	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>
mp, °C	122.4
bp, at 101.3 kPa, <sup>a</sup> °C	249.2
density	
solid, $d_4^{24}$	1.316
liquid, $d_4^{180}$	1.029
refractive index, $n_D^b$ , liquid	1.504
viscosity at 130°C, mPa·s (= cP)	1.26
surface tension at 130°C, mN/m (= dyn/cm)	31
specific heat, J/g <sup>c</sup>	
solid	1.1966
liquid	1.774
heat of fusion, J/g <sup>c</sup>	147
heat of combustion, kJ/mol <sup>c,d</sup>	3227
heat of formation at 26.16°C, kJ/mol <sup>c</sup> , solid <sup>e</sup>	−385
heat of vaporization, <sup>f</sup> at 140°C, J/g <sup>c</sup>	534
at 249°C, J/g <sup>c</sup>	425
dissociation constant, $K_a$ , at 25°C	$6.339 \times 10^{-5}$
flash point, °C	121–131
autoignition temperature, °C, in air	573
pH of saturated aqueous solution at 25°C	2.8

<sup>a</sup> To convert kPa to atm, divide by 101.3.<sup>b</sup> At 131.9°C.<sup>c</sup> To convert J to cal, divide by 4.184.<sup>d</sup> Refs. (1,2).<sup>e</sup> Ref. 3.<sup>f</sup> Ref. 4.Table 2. **Solubilities in Water**

Temperature, °C	g/100 g <sup>a</sup>	Temperature, °C	g/100 g <sup>a</sup>
0	0.17	50	0.85
10	0.21	60	1.20
20	0.29	70	1.77
25	0.34	80	2.75
30	0.42	90	4.55
40	0.60	95	6.80

<sup>a</sup> Grams benzoic acid per 100 g water.Table 3. **Solubilities in Nonaqueous Solvents at 25°C**

Solvent	g/100 g <sup>a</sup>	Solvent	g/100 g <sup>a</sup>
acetone	55.6	ethyl ether	40.8
benzene	12.2	hexane, 17°C	0.9
carbon tetrachloride	4.1	methanol, 23°C	71.5
chloroform	15.0	toluene	10.6
ethanol (abs)	58.4		

<sup>a</sup> Grams benzoic acid per 100 g solvent.

Table 4. Vapor Pressure of Benzoic Acid<sup>a</sup>

Temperature, °C	Pressure, kPa <sup>b</sup>	Temperature, °C	Pressure, kPa <sup>b</sup>
96.0	0.13	172.8	8.0
119.5	0.67	186.2	13.3
132.1	1.33	205.8	26.6
146.7	2.66	227.0	53.3
162.6	5.32	249.2	101.3

<sup>a</sup> Ref. 5.<sup>b</sup> To convert kPa to mm Hg, multiply by 7.5.

## 4. Manufacture

Benzoic acid is almost exclusively manufactured by the cobalt catalyzed liquid-phase air oxidation of toluene [108-88-3]. Large-scale plants have been built for benzoic acid to be used as an intermediate in the production of phenol (by Dow Chemical) and in the production of caprolactam (by Snia Viscosa) (6–11). The basic process usually consists of a large reaction vessel in which air is bubbled through pressurized hot liquid toluene containing a soluble cobalt catalyst as well as the reaction products, a system to recover hydrocarbons from the reactor vent gases, and a purification system for the benzoic acid product.

**4.1. Reaction.** Typical liquid-phase toluene oxidizer reaction conditions may be as follows:

reactor pressure	200–700 kPa (~2–7 atm)
reactor temperature	136–160°C
cobalt catalyst concentration	25–1000 ppm
reactor benzoic acid concentration	10–60 wt%

A number of different cobalt salts have been used in the oxidation of toluene, the most common being cobalt acetate [71-48-7], cobalt naphthenate, and cobalt octoate [1588-79-0]. Manganese has also been suggested as a cocatalyst. There is some indication that manganese adversely affects the reactor equilibrium such that the coproduction of benzaldehyde [100-52-7] suffers. Those benzoic acid producers who also produce benzaldehyde do not use manganese in their systems.

Catalysts other than the above cobalt salts have been considered. Several patents suggest that cobalt bromide gives improved yields and faster reaction rates (12–16). The bromide salts are, however, very corrosive and require that expensive materials of construction, such as Hastalloy C or titanium, be used in the reaction system.

**4.2. Purification.** Small amounts of reaction by-products are produced during the liquid-phase oxidation of toluene. These by-products include acetic and formic acids, benzene, benzaldehyde, benzyl alcohol, aliphatic benzyl esters such as benzyl formate and benzyl acetate, biphenyl, 2-, 3-, and 4-methylbiphenyls, and phthalic acid. Of these only benzaldehyde and benzene [71-43-2] are currently separated commercially.

The recovery and purification of benzoic acid from a liquid-phase toluene oxidizer may involve distillation alone or it may involve a combination of distillation followed by extraction and crystallization.

In either case, the initial distillation involves separating toluene and any material lower boiling than benzoic acid and recycling those low boilers to the toluene oxidizer. The benzoic acid and higher boiling fractions are then distilled and/or subjected to an extraction and crystallization process to produce the desired product.

The toluene-to-phenol production plants have a significant advantage regarding cost in producing benzoic acid. These plants produce an industrial-grade benzoic acid by distillation, and that industrial-grade product then serves as the feedstock to the phenol plant as well as to the technical and USP/FCC production facilities. Utilizing distillation or extraction and crystallization, these plants reject undesirable impurities, such as the methyl biphenyls, into the phenol reactors in dilute concentrations with benzoic acid. These impurities are actually beneficial to the phenol plant, assisting in the removal of reaction tars. Stand-alone benzoic acid producers are forced to spend large amounts of capital and/or suffer significant unit ratio penalties to produce a similar product.

In addition to the presence of organic trace impurities, the color and color stability of the benzoic acid are often important to customers. Various techniques are utilized to improve color and color stability. Most if not all of these are considered trade secrets.

The USP/FCC grade of benzoic acid is usually produced by crystallization from solution or from the melt. Toluene, water, and methanol have all been used as solvents and each is capable of producing a high quality benzoic acid product.

**4.3. Hydrocarbon Recovery.** Toluene is typically recovered from the oxidizer vent gases through the use of refrigeration followed by activated carbon adsorption. Thermal oxidation is then employed to remove carbon monoxide and the remaining traces of hydrocarbons.

The vapor-phase oxidation of toluene to produce benzoic acid and benzaldehyde has been tried utilizing several different catalysts, but yields are low and the process cannot compete with the liquid-phase process (see BENZALDEHYDE). Other processes for the production of benzoic acid are presently of little commercial importance.

## 5. Economic Aspects

The growth of demand for benzoic acid is expected to increase at a rate of between 1 and 2%/year (17). Glycol dibenzoate plasticizers have been growing at close to 10% annually for the past several years, in part due to environmental and product labeling concerns with regard to phthalate plasticizers (qv). The growth of the diet soft drink market has increased the demand for sodium and potassium benzoates (17). All of the benzoic acid producers in the United States employ the liquid-phase toluene air oxidation process. As toluene becomes more important in the gasoline pool as an octane booster, the benzoic acid producers have to compete with gasoline marketers for the available toluene. If the

attractiveness of toluene as an octane booster continues, the cost of producing benzoic acid will most likely increase. The North American producers of benzoic acid and their estimated production capacities (17) are as follows:

Producer	Capacity (mt/year)
Noveon—Kalama, Kalama, Wash.	100,000
Velsicol Chemical, Chattanooga, Tenn.	~30,000

The bulk of this benzoic acid production capacity is consumed internally by these producers. Noveon—Kalama converts over one-half of its production to phenol. A large portion of Velsicol's benzoic acid production is utilized in the manufacture of glycol dibenzoate plasticizer esters.

## 6. Specifications, Analysis, Packaging, and Shipment

Benzoic acid is available as technical grade as well as grades meeting the specifications of the *United States Pharmacopeia (USP)* (18), the *Food Chemicals Codex (FCC)* (19), or the *British Pharmacopeia (BP)* (20). Typical specifications are listed in Table 5. Analytical methods required for testing to meet the specifications listed in regulatory texts are described in those texts.

Trace impurities typically present in technical grade benzoic acid include methyl diphenyls and phthalic acid. Gas chromatography (gc) and high pressure liquid chromatography (hplc) are useful for determining the concentrations of those impurities.

Technical grade benzoic acid is available in molten as well as solid forms (called flakes or chips). USP/FCC grade is available in solid form, either as crystals or powder. The solid forms of technical grade is usually packaged in 25-kg polylined bags and also in a flexible intermediate bulk container (FIBC), each FIBC containing from 500 to 1000 kg of product. USP/FCC grade is usually packaged in polylined fiber drums, each containing 100 lb (45.5 kg).

Molten technical benzoic acid may be transported in type 316 stainless steel tank cars, usually 76 m<sup>3</sup> (20,000 gal) of product, or in ~5000 gal (19 m<sup>3</sup>) 316 stainless steel tank trucks.

## 7. Health and Safety Aspects

Benzoic acid's toxicity is rated as moderate based upon its LD<sub>50</sub> (oral-rat) of 2530 mg/kg. Healthy individuals may tolerate small doses (<0.5 g of benzoates per day) mixed with food without ill effects. Large doses, up to 4 g of sodium benzoate per day, have mainly digestive effects such as gastric pain, nausea, and vomiting. A 67-kg man reportedly ingested single doses of 50 g without ill effects, although the mean lethal dose in dogs and cats is 2.5 g/kg (21).

In the early 1900s, several food inspection decisions regarding the use of benzoic acid and sodium benzoate were issued, the latter based upon human feeding studies. As a result of these decisions, since 1909 sodium benzoate and

Table 5. **Specifications for Benzoic Acid**

Item	Technical	USP	FCC	BP/EP <sup>a</sup>
identification assay	passes test 99.5%, min	passes test nlt 99.5% and nmt 100.5% of C <sub>7</sub> H <sub>6</sub> O, on anhydrous basis	passes test nlt 99.5% and nmt 100.5% of C <sub>7</sub> H <sub>6</sub> O, on anhydrous basis	passes test contains nlt 99.0% and nmt 100.5% of benzenecarboxylic acid
appearance	white flakes			
chlorinated compounds	none			
odor	characteristic			
halogenated compounds and halides				passes test (300 ppm, max)
heavy metals (as pb)		nmt 10 ppm	nmt 10 ppm	10 ppm, max
readily carbonizable substances		passes test	passes test	
readily oxidizable substances		passes test	passes test	
residue on ignition		nmt 0.05%	nmt 0.05%	
solidification point			between 121 and 123°C	
congealing range		between 121 and 123°C		
melting point				121–124°C
water		nmt 0.7%	nmt 0.7%	
appearance of solution				passes test
carbonisable substances				passes test
oxidisable substances				passes test
sulphated ash				nmt 0.1%

<sup>a</sup> The specifications for benzoic acid contained in the monographs of the British and European Pharmacopeias have been harmonized.

benzoic acid have been allowed to be added to foods at concentrations not to exceed 0.1% (22). A hazard analysis of benzoic acid and a detailed reference on the toxicity of benzoic acid are available (23,24). Manufacturer's product and information bulletins provide an excellent source for information regarding the safety and handling of benzoic acid.

The principal safety concern in handling molten benzoic acid is its elevated temperature. Thermal burns may result from improper handling of the molten product (25,26).

## 8. Uses

Although the main uses for benzoic acid are as a chemical raw material, it also has numerous direct uses. Benzoic acid is used in substantial quantities to improve the properties of various alkyd resin coating formulations, where it tends to improve gloss, adhesion, hardness, and chemical resistance. Benzoic acid terminates chain propagation in alkyd resins (qv) and promotes crystallinity in the final product.

Benzoic acid is also used as a down-hole drilling mud additive where it functions as a temporary plugging agent in subterranean formations. Since this is a secondary oil recovery application, this use is heavily dependent on the price of crude oil.

In medicine, the internal uses of benzoic acid are relatively unimportant. Its principal medicinal use is external; it is used in dermatology as an antiseptic stimulant and irritant. Combined with salicylic acid [69-72-7], benzoic acid is employed in the treatment of ringworm of the scalp and other skin diseases (Whitfield's ointment).

The largest use for benzoic acid is as a chemical raw material in the production of phenol, caprolactam, glycol dibenzoate esters, and sodium and/or potassium benzoate.

**8.1. Phenol.** In the early 1960s The Dow Chemical Company built three phenol (qv) plants utilizing benzoic acid as the feedstock (6,27). Dow is no longer involved with these plants. Two of the original three are currently operating and another came on line in Japan in 1991. In this process, benzoic acid is air-oxidized to phenol [108-95-2] in a liquid-phase reaction utilizing copper and magnesium catalysts according to the following:

The hydroxyl group of the resulting phenol is situated immediately adjacent to where the carboxyl group was previously located. This same liquid-phase copper oxidation process chemistry has been suggested for the production of cresols by the oxidation of toluic acids. *m*-Cresol would be formed by the oxidation of either ortho or para toluic acids; a mixture of *o*- and *p*-cresols would be produced from *m*-toluic acid (6). A process involving the vapor-phase catalytic oxidation of benzoic acid to phenol has been proposed, but no plants have ever been built utilizing this technology (27).

**8.2. Caprolactam.** At the same time that Dow was constructing toluene to phenol plants, Snia Viscosa (28–30) introduced two processes for the manufacture of caprolactam (qv) from benzoic acid. The earlier process produced ammonium sulfate as a by-product, but the latter process did not. In either process benzoic acid is hydrogenated to cyclohexanecarboxylic acid [98-89-5], which then reacts with nitrosylsulfuric acid to form caprolactam [105-60-2].

**8.3. Glycol Dibenzoates.** The benzoate esters of several glycols are another large use for benzoic acid. These high boiling, chemically stable esters find application as plasticizers in the manufacture of floor coverings, vinyl extrusions, plastisols, adhesives, and coatings. The most common types of resins modified with glycol dibenzoates are poly(vinyl acetate) and poly(vinyl chloride). A wide variety of glycol esters have been prepared and evaluated as plasticizers (qv).

The bulk of the commercial production consists of the dibenzoate esters of diethylene and dipropylene glycol. (These products are mixtures of glycol mono- and dibenzoate esters, containing from 5 to 13% monobenzoate.) The largest volume product is a 50:50 wt blend of those two. The glycol dibenzoates are fast-fusing plasticizers that compete favorably with butyl benzyl phthalate. The properties of these two esters are shown in Table 6 (31). Propylene glycol dibenzoate [19224-26-1] and polyethylene glycol 200 dibenzoate also have applications in certain areas. Dipropylene glycol dibenzoate and diethylene glycol dibenzoate both have FDA approval for use in adhesive and food packaging applications (21 CFR 175.105; 21 CFR 176.170/180)

Table 6. Physical Properties of Selected Glycol Dibenzoates

Property	Dipropylene glycol dibenzoate	Diethylene glycol dibenzoate
CAS Registry Number	[27138-31-4]	[120-55-8]
molecular formula	C <sub>20</sub> H <sub>22</sub> O <sub>5</sub>	C <sub>18</sub> H <sub>18</sub> O <sub>5</sub>
mol wt	342	314
specific gravity, 25°C	1.129	1.178
freezing point, °C	−30	28
bp at 0.7 kPa <sup>a</sup> , °C	232	240
refractive index, 25°C	1.5282	1.5424
flash point, tcc, °C	>149	>149
viscosity, 20°C, mPa·s (= cP)	170	70

<sup>a</sup> To convert kPa to mm Hg, multiply by 7.5.

**8.4. Sodium and Potassium Benzoate.** These salts are available in grades meeting the specifications of the *National Formulary* (18), the *Food Chemicals Codex* (19), and the *British Pharmacopeia* (20) (Table 7). Sodium benzoate [532-32-1] is produced by the neutralization of benzoic acid with caustic soda and/or soda ash. The resulting solution is then treated to remove trace impurities as well as color bodies and then dried in steam heated double drum dryers. The product removed from the dryers is light and fluffy and in order to reduce

Table 7. Specifications for Sodium and Potassium Benzoate

Item	NF/FCC	Sodium Benzoate <sup>a</sup> BP/EP	Potassium Benzoate <sup>a</sup> FCC
identification	passes tests	passes test	passes tests
assay	nlt 99.0% and nmt 100.5% of C <sub>7</sub> H <sub>5</sub> NaO <sub>2</sub> , calculated on the anhydrous basis	contains nlt 99.0% and nmt the equivalent of 100.5% of sodium benzenecarboxylate, calculated with reference to the dried substance	nlt 99.0% and nmt 100.5% of C <sub>7</sub> H <sub>5</sub> NaO <sub>2</sub> , calculated on the anhydrous basis
alkalinity (as NaOH)	nmt 0.04%	passes test	
alkalinity (as KOH)		passes test	nmt 0.06%
acidity (as benzoic acid)			
heavy metals	nmt 10 mg/kg	10 ppm, max	nmt 10 mg/kg
water	nmt 1.5%		nmt 1.5%
organic volatile impurities (USP)	passes test		
appearance of solution		passes test	
ionized chlorine		200 ppm, max	
total chlorine		300 ppm, max	
loss on drying		nmt 2.0%	

<sup>a</sup> Not more than = nmt.

Not less than = nlt.



shipping and storage space the sodium benzoate is normally compacted. It is then milled and classified into two product forms; dense granular and dense powder. Sodium Benzoate is also available in extruded form. This form has the advantage of being almost totally “dust free”. It also dissolves more quickly than the dense granular form in both water and antifreeze.

Potassium benzoate [582-25-2] is produced by neutralizing benzoic acid with caustic potash. The resulting solution is processed in a fashion nearly identical to that of sodium benzoate. Potassium benzoate is usually available in the dense granular form.

Sodium and potassium benzoate are employed in a wide range of preservative applications because they provide an effective combination of antimicrobial action, low cost, and safety. Although sodium and potassium benzoate are the preservatives offered in the marketplace, the actual active ingredient being sold is free (ie, undissociated) benzoic acid. The benzoate ion has essentially no antimicrobial properties. Since it is the undissociated benzoic acid that provides the antimicrobial action, sodium benzoate and potassium benzoate are recommended for use in application areas where the pH is at 4.5 or lower (Table 8).

Benzoic acid is supplied to this market in the form of salts because the benzoate salts have a high solubility in water and aqueous stock solutions of up to 35% can easily be prepared. In addition, it is easier, and therefore cheaper, to purify sodium and potassium benzoate than to produce the USP/FCC grade of benzoic acid.

Sodium and potassium benzoate are substances that may be added directly to human food and are affirmed as GRAS (33–35). Benzoic acid and sodium and potassium benzoate are now used as preservatives in such foods as sauces, pickles, cider, fruit juices, wine coolers, syrups and concentrates, mincemeat and other acidic pie fillings, margarine, egg powder, fish (as a brine dip component), bottled carbonated beverages, and fruit preserves, jams, and jellies. The popularity of diet soft drinks has led to increased demand for both benzoate salts.

Nonfood preservative applications of sodium and potassium benzoate are found in pharmaceutical and cosmetic preparations, such as toothpastes and powders, tobacco, pastes and glue, as well as starch and latex (36,37).

The use of the potassium salt of benzoic acid as a soft drink preservative originally resulted from concerns regarding sodium intake and its possible relationship to high blood pressure. Later it was determined that in combination with aspartame, potassium benzoate had positive taste attributes.

Sodium benzoate also has application as a corrosion inhibitor. It is incorporated into paper wrapping materials for the prevention of rust or corrosion in the production of such diverse items as razor blades, engine parts, bearings, etc. It is

**Table 8. Undissociated (Free) Benzoic Acid vs pH**

pH	Free Benzoic acid (%)	pH	Free Benzoic acid (%)
2.5	98.0	4.5	32.9
3	93.9	5	13.4
3.5	83.0	5.5	4.7
4	60.8	6	1.5
4.19	50.0	6.5	0.15

also used in the automotive industry as a corrosion inhibitor in engine cooling systems (at ~1.5%). Unlike in its application as a preservative where free benzoic acid is required to provide antimicrobial action, it appears to be the benzoate ion that provides the corrosion protection.

Sodium benzoate is also employed as a nucleating agent for polypropylene plastics, where it imparts strength and reduces processing times.

## 9. Benzoic Acid Derivatives

*Benzoyl chloride*, [98-88-4],  $\text{C}_6\text{H}_5\text{COCl}$ , mp,  $-1^\circ\text{C}$ ; bp,  $197.2^\circ\text{C}$  at 101.3 kPa;  $d_4^{25}$ , 1.2070;  $n_D^{20}$ , 1.55369. Benzoyl chloride is a colorless liquid that fumes upon exposure to the atmosphere, has a sharp odor, and in vapor form is a strong lachrimator. It is decomposed by water and alcohol, and is miscible with ether, benzene, carbon disulfide, and oils. Benzoyl chloride may be prepared in several ways, including the partial hydrolysis of benzotrichloride, the chlorination of benzaldehyde, and from benzoic acid and phosphorus pentachloride. The most common method is the reaction of benzoic acid and benzotrichloride [98-07-7]. Since benzoic acid may be easily obtained from benzotrichloride, the latter is used as the sole raw material for large-scale production of benzoyl chloride.

Benzoyl chloride is an important benzoylating agent. In this use the benzoyl radical is introduced into alcohols, phenols, amines, and other compounds through the Friedel-Crafts reaction and the Schotten-Baumann reaction. Other significant uses are in the production of benzoyl peroxide [94-36-0], benzophenone [119-61-9], and in derivatives employed in the fields of dyes, resins, perfumes, pharmaceuticals, and as polymerization catalysts.

*Benzoic anhydride*, [93-97-0]  $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$ , mp,  $42^\circ\text{C}$ ; bp,  $360^\circ\text{C}$  at 101.3 kPa;  $d_4^{15}$ , 1.1989;  $n_D^{15}$ , 1.157665. Almost insoluble in water, benzoic anhydride is soluble in most common solvents. A number of methods for the preparation of benzoic anhydride are reported (38). Probably the best is the reaction of benzoyl chloride and benzoic acid (39).

Benzoic anhydride is not manufactured on a large scale. Its primary use is as a benzoylating agent in the manufacture of pharmaceuticals and chemical intermediates.

## 10. Benzoic Acid Salts

*Ammonium benzoate* [1863-63-41],  $\text{C}_6\text{H}_5\text{COONH}_4$ , mp,  $198^\circ\text{C}$ . This is a dull white powder which gradually loses ammonia on exposure to air. Its aqueous solution, it is slightly acidic. Ammonium benzoate has been suggested as a component in certain rubber formulations (40) and as a preservative in paints and glues.

*Sodium benzoate* [532-32-1],  $\text{C}_6\text{H}_5\text{COONa}$ , is highly soluble in water (61.2 g dissolve in 100 g of water at  $25^\circ\text{C}$ ) and somewhat soluble in ethyl alcohol, glycerol, and methanol. A 25% aqueous solution of sodium benzoate exhibits a pH of 7.5–8.

*Lithium Benzoate* [553-54-8],  $\text{LiC}_7\text{H}_5\text{O}_2$ , soluble in water. Used in medicines and to improve the mechanical properties and transparency of polypropylene.

*Potassium Benzoate* [582-25-2],  $\text{C}_6\text{H}_5\text{COOK}$ , is even more soluble in water than sodium benzoate (73.6 g dissolve in 100 g of water at 25°C). A 25% aqueous solution of potassium benzoate exhibits a pH of 8–8.5.

## 11. Benzoic Acid Esters

*Benzyl benzoate* [120-51-4],  $\text{C}_6\text{H}_5\text{COOCH}_2\text{C}_6\text{H}_5$ , mp, 21°C,  $d_4^{25}$ , 1.118; bp, 323–324°C at 101.3 kPa;  $n_D^{21}$ , 1.5681. This compound is a colorless, oily liquid with a faint, pleasant aromatic odor and a sharp, burning taste. It occurs naturally in Peru and Tolu balsams, is sparingly volatile with steam, and is insoluble in water. Benzyl benzoate is prepared commercially by the direct esterification of benzoic acid and benzyl alcohol or by reaction of benzyl chloride and sodium benzoate. The pleasant odor of benzyl benzoate, like other benzoic esters, has long been utilized in the perfume industry, where it is employed as a solvent for synthetic musks and as a fixative. It has also been used in confectionery and chewing gum flavors.

Benzyl benzoate has been used as an insect repellent in formulations for repelling mosquitoes, chiggers, ticks, and fleas, and in the control of livestock insects. Benzyl benzoate was used in the Vietnam War to eradicate and repel certain ticks and mites. It has also found some usage in medicine, cosmetics, and as a plasticizer.

*Butyl benzoate* [136-60-7],  $\text{C}_6\text{H}_5\text{COOC}_4\text{H}_9$ , mp, –22°C; bp, 250°C at 101.3 kPa. This ester is a thick, oily liquid that has found usage as a dye carrier for polyester fibers.

*Ethyl benzoate* [93-89-0],  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$ , mp, –35°C; bp, 212°C at 101.3 kPa;  $d_4^{20}$ , 0.8788. Used in synthetic ylang–ylang oil, ethyl benzoate is similar in odor to methyl benzoate but is reportedly smoother.

*n-Hexyl benzoate* [6789-88-4],  $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_{13}$ , bp, 272°C at 103.9 kPa. This compound is used in perfumery as a fixative and has a melonlike odor.

*Methyl benzoate* [93-58-3],  $\text{C}_6\text{H}_5\text{COOCH}_3$ , bp, 198–200°C at 101.3 kPa;  $d_4^{15}$ , 1.094;  $n_D^{15}$ , 1.5205. Insoluble in water, this is a colorless, transparent liquid solidifying at about 15°C. Methyl benzoate is prepared by the direct esterification of benzoic acid and methanol. It is used in the fragrance industry and in the production of other benzoate esters (via transesterification). A technical-grade methyl benzoate is available as a by-product in the manufacture of dimethyl terephthalate [120-61-6].

*Phenyl benzoate* [93-99-2],  $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$ , mp, 70–71°C; bp, 314°C at 101.3 kPa. This compound has been suggested as an antioxidant (qv) for certain high temperature lubricants (41). Phenyl benzoate exists as a nonisolated intermediate in the production of phenol from benzoic acid.

*Alkyl (C12-15) Benzoate* [68411-27-8],  $\text{C}_{20}\text{H}_{32}\text{O}_2$  (av), bp, 300°C at 101.3 kPa. A widely used emollient for personal care and cosmetic products. Ester of benzoic acid and mixed C12–15 alcohols.

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