AMMONIUM COMPOUNDS

1. Introduction

There are a considerable number of stable crystalline salts of the ammonium ion [14798-03-9], NH_4^+. Several are of commercial importance because of large scale consumption in fertilizer and industrial markets. The ammonium ion is about the same size as the potassium and rubidium ions, so these salts are often isomorphous and have similar solubility in water. Compounds in which the ammonium ion is combined with a large, uninegative anion are usually the most stable. Ammonium salts containing a small, highly charged anion generally dissociate easily into ammonia (qv) and the free acid (1). At about 300°C most simple ammonium salts volatilize with dissociation, for example

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

Exceptions are salts of oxidizing anions, which decompose with oxidation of the ammonium ion to nitrous oxide [10024-97-2], N_2O, or nitrogen, N_2.

A number of simple, standard methods have been developed for the analysis of ammonium compounds, several of which have been adapted to automated or instrumental methods. Ammonium content is most easily determined by adding excess sodium hydroxide to a solution of the salt. Liberated ammonia is then distilled into standard sulfuric acid and the excess acid titrated. Other methods include colorimetry (2) and the use of a specific ion electrode (3).

Covered in detail in this article are the quaternary ammonium compounds. Covered elsewhere are: ammonium borates [12007-89-5], $NH_4B_5O_8$, (see BORON COMPOUNDS); ammonium chromate [7788-98-9], $NH_4Cr_2O_4$, and ammonium dichromate [7789-09-5], $NH_4Cr_2O_7$, (see CHROMIUM COMPOUNDS); ammonium cyanide [12211-52-8], NH_4CN, (see CYANIDES); ammonium glutamate [20806-32-0], $NH_4C_5H_8NO_4$, (see AMINO ACIDS); ammonium hydroxide [1336-21-6], NH_4OH, (see AMMONIA); ammonium molybdate [13106-76-8], $(NH_4)_2\ MoO_4$, (see MOLYBDENUM COMPOUNDS); ammonium oxalate [1113-38-8], $(NH_4)_2C_2O_4$, (see OXALIC ACID); ammonium phosphate dibasic [7783-28-0], $(NH_4)_2HPO_4$, and ammonium phosphate monobasic [7722-76-1], $(NH_4)H_2PO_4$, (see PHOSPHORIC ACID AND THE PHOSPHATES); ammonium sulfamate [7773-06-0], $NH_4SO_3NH_2$, (see SULFAMIC ACID AND SULFAMATES); and ammonium thiosulfate [7783-18-8], $(NH_4)_2S_2O_3$ (see THIOSULFATES).

2. Ammonium Acetates

Both normal or neutral ammonium acetate [631-61-8], $NH_4C_2H_3O_2$, and the acid salt are known. The normal salt results from exact neutralization of acetic acid using ammonia; the acid salt is composed of the neutral salt and acetic acid.

The normal salt, CH_3COONH_4, is a white, deliquescent, crystalline solid, formula wt 77.08, having a specific gravity of 1.073. It is quite soluble in water or ethanol: 148 g dissolve in 100 g of water at 4°C. The salt's solubility in water increases only slightly as temperature increases up to about 25°C. The specific gravity of aqueous neutral ammonium acetate ranges from 1.022 to 1.092 as solution concentration increases from 10 to 50 wt % (4). The normal salt melts at 114°C, but decomposes before reaching its boiling point.

Ammonium acetate solutions formed by neutralizing acetic acid using ammonium hydroxide are essentially neutral. Thus, these solutions are suitable for standardization of electrodes, and for use as titration standards. Solutions must be used while fresh, however, as they become acidic on standing.

Isolation of dry, normal ammonium acetate, prepared by neutralizing acetic acid with anhydrous ammonia or ammonium carbonate, is difficult because of ammonia loss during evaporation of water. Consequently, commercial grades of ammonium acetate are often mixtures of the neutral and acid salts, or are supplied as ammonium acetate solution [8013-61-4].

The acidic double salt of ammonium acetate and acetic acid [25007-86-7], $CH_3COONH_4 \cdot CH_3COOH$, is made by dissolving the neutral salt in hot acetic acid or by distilling the neutral salt. During distillation the acid salt is formed as a heavy oil that solidifies on cooling. It crystallizes as long, deliquescent needles that melt at 66°C. Acid ammonium acetate is readily soluble in both water and alcohol.

Ammonium acetate has limited commercial uses. It serves as an analytical reagent, and in the production of foam rubber and vinyl plastics; it is also used as a diaphoretic and diuretic in pharmaceutical applications. The salt has some importance as a mordant in textile dyeing. In a hot dye bath, gradual volatilization of ammonia from the ammonium acetate causes the dye solution to become progressively more acidic. This increase in acidity enhances the color and permanence of the dyeing process. Ammonium acetate is a poison by intravenous route. When heated to decomposition, it emits toxic fumes (5).

3. Ammonium Carbonates

The earliest mention of an ammonium carbonate, salt of hartshorn, appears in English manuscripts of the 14th century. As the name implies, the material was obtained by dry distillation of animal waste such as horn, leather, and hooves. Although many salts have been described in the literature for the ternary $NH_3{-}CO_2{-}H_2O$ system, most, except for ammonium bicarbonate [1066-33-7], NH_4HCO_3, ammonium carbonate [506-87-6], $(NH_4)_2CO_3$, and ammonium carbamate [1111-78-0], $NH_4CO_2NH_2$, are mixtures (6,7).

3.1. Ammonium Bicarbonate. Ammonium bicarbonate, also known as ammonium hydrogen carbonate or ammonium acid carbonate, is easily formed. However, it decomposes below its melting point, dissociating into ammonia, carbon dioxide, and water. If this process is carefully controlled, these compounds condense to reform ammonium bicarbonate. The vapor pressures of dry ammonium bicarbonate are shown below (8). (To convert kPa to mm Hg, multiply by 7.5.)

Temperature, °C	Vapor Pressure, kPa	Temperature, °C	Vapor Pressure, kPa
25.4	7.85	50.0	52.65
34.2	16.26	55.8	82.11
40.7	26.79	59.3	108.64
45.0	37.06		

Ammonium bicarbonate, sp gr 1.586, formula wt 79.06, is the only compound in the NH_3–CO_2–H_2O system that dissolves in water without decomposition. Solubility in 100 g of H_2O ranges from 11.9 g at 0°C to 59.2 g/100 g of H_2O at 60°C (9). The heat of formation from gaseous ammonia and carbon dioxide and liquid water is 126.5 kJ/mol (30.2 kcal/mol). Ammonium bicarbonate is manufactured by passing carbon dioxide gas countercurrently through a descending stream of aqua ammonia. The reaction is normally carried out in a packed tower or absorption column. Because the reaction is exothermic, cooling the lower portion of the tower is advisable. Concentration of the solution is monitored by determining specific gravity. When the solution is sufficiently saturated, crystallization of ammonium bicarbonate occurs. The crystals are separated from the mother liquor by filtration or centrifugation and washing, and are dried using 50°C air.

Ammonium bicarbonate is produced as both food and standard grade and the available products are normally very pure. Although purification is possible by sublimation at low temperatures, it is more economical to prepare the desired product directly by using ammonia and carbon dioxide of high purity.

When heated, ammonium bicarbonate decomposes to ammonia, water, and carbon dioxide, leaving no solid residue. This property explains its use as a leavening agent for certain baked goods (see BAKERY PROCESSES AND LEAVENING AGENTS). At about 150°C, 1 kg yields 1.3 m^3 (46.2 ft^3) of STP gas. Ammonium bicarbonate is also used in pharmaceuticals (qv), in production of ammonium salts, and in formulation of fire-extinguishing agents (qv). It is effective in scale removal, for example, in heat-exchanger tubes by dissolving thin layers of calcium sulfate.

$$CaSO_4 + 2\,NH_4HCO_3 \longrightarrow CaCO_3 + (NH_4)_2SO_4 + CO_2 + H_2O$$

For thicker layers of scale, alternate treatments using dilute hydrochloric acid appear desirable (10). Its DOT number is NA9081. Ammonium bicarbonate is poisonous by intravenous route. When heated to accomposition, it emits toxic fumes (5).

3.2. Ammonium Carbonate.

Normal ammonium carbonate, mp 43°C, formula wt 96.09, is a crystalline solid. The commercial product may be produced by passing carbon dioxide into an absorption column containing aqueous ammonia solution and causing distillation. Vapors containing ammonia, carbon dioxide, and water condense to give a solid mass of crystals. Ammonium carbonate is the principal ingredient of smelling salts because of its characteristic strong ammonia odor. It is also used for other medicinal purposes and as a leavening agent.

Ammonium carbonate is poisonous by subcutaneous and intravenous routes. When heated to decomposition, it emits toxic fumes (5).

4. Ammonium Citrate

Diammonium citrate [3012-65-5], $(NH_4)_2C_6H_6O_7$, mol wt 226.19, is soluble in an equal weight of water, but is only slightly soluble in ethanol. The pH of a 0.1 *M* solution is 4.3. It is made by neutralization of citric acid with ammonia; the crystalline or granular product is used as a chemical reagent and pharmaceutically as a diuretic.

5. Ammonium Halides

Ammonium chloride [12125-02-9], NH_4Cl, ammonium bromide [12124-97-9], NH_4Br, ammonium fluoride [12125-01-8] and ammonium iodide [12027-06-4], NH_4I, are crystalline, ionic compounds of formula wts 53.49, 97.94, and 144.94, respectively. Their densities d_4^{20} systematically follow the increase in formula weight: 1.53, 2.40, and 2.52. All three exist in two crystal modifications (12): the chloride, bromide, and iodide have the CsCl structure below temperatures of 184.5, 137.8, and −17.6°C, respectively; each reversibly transforms to the NaCl structure at higher temperatures.

Ammonium fluoride is a white, deliquescent, crystalline salt. It tends to lose ammonia gas to revert to the more stable ammonium bifluoride. Its solubility in water is 45.3 g/100 g of H_2O at 25°C and its heat of formation is −466.9 kJ/mol (−116 kcal/mol). Ammonium fluoride is available principally as a laboratory reagent. If it is needed in large quantities, one mole of aqueous ammonia can be mixed with one mole of the more readily available ammonium bifluoride (11).

The solubility of the ammonium halides in water also increases with increasing formula weight. For ammonium chloride, the integral heat of solution to saturation is 15.7 kJ/mol (3.75 kcal/mol); at saturation, the differential heat of solution is 15.2 kJ/mol (3.63 kcal/mol). The solubility of three salts is given in Table 1 (8).

All ammonium halides exhibit high vapor pressures at elevated temperatures, and thus, sublime readily. The vapor formed on sublimation consists not of discrete ammonium halide molecules, but is composed primarily of equal volumes of ammonia and hydrogen halide. The vapor densities are essentially half that expected for the vaporous ammonium halides. Vapor pressures at various temperatures are given in Table 2 (13). Latent heats of sublimation, assuming complete dissociation of vapors and including heats of dissociation are 165.7, 184.1, and 176.6 kJ/mol (39.6, 44.0, and 42.2 kcal/mol), for NH_4Cl, NH_4Br, and NH_4I, respectively.

The heat of formation of ammonium chloride from the elements is 317 kJ/mol (75.8 kcal/mol); it is 175 kJ/mol (41.9 kcal/mol) from gaseous ammonia and gaseous hydrogen chloride. The heat of formation of ammonium bromide from the elements, bromine in the liquid form, is 273 kJ/mol (65.3 kcal/mol); for ammonium iodide, the corresponding heat of formation is 206 kJ/mol (49.3 kcal/mol). Iodine is in the solid state.

Aqueous solutions of ammonium halides, like the other ammonium salts of strong acids, are acidic; on storage and exposure these solutions tend to become more acidic through ammonia loss. They also have a pronounced tendency to

Table 1. **Solubilities of Ammonium Halides**

Temperature, °C	Solubility, g/100 g water			Temperature, °C	Solubility, g/100 g water		
	NH_4Cl	NH_4Br	NH_4I		NH_4Cl	NH_4Br	NH_4I
0	29.4	60.6	154.2	60	55.3	107.8	208.9
20	37.2	75.5	172.3	80	65.6	126.0	228.8
40	45.8	91.1	190.5	100	77.3	145.6	250.3

Table 2. **Vapor Pressures of Ammonium Halides**

	Vapor pressure, kPa[a]		
Temperature, °C	NH_4Cl	NH_4Br	NH_4I
250	6.5		
280	17.9		
300	33.5	7.3	
320	60.9	13.3	
338	101.1		
360		41.2	31.3
380		73.4	54.1
395		101.1	
400		115.4	89.8
405			101.1

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

attack ferrous and other metal surfaces, especially those of copper and copper alloys.

5.1. Ammonium Chloride.

Manufacture. The history of ammonium chloride manufacture is linked to the birth of the soda and synthetic ammonia industries. Consequently this halide has always been a by-product in great supply. Production by direct reaction of ammonia and hydrochloric acid is simple but usually economically unattractive; a process based on metathesis or double decomposition is generally preferred.

Several commercial grades are available: fine crystals of 99 to 100% purity, large crystals, pressed lumps, rods, and granular material.

Double-Decomposition Methods. Double-decomposition processes all involve the reaction of sodium chloride, the cheapest chlorine source, with an ammonium salt. The latter may be supplied directly, or generated *in situ* by the reaction of ammonia and a supplementary ingredient. Ammonium chloride and a sodium salt are formed. The sodium salt is typically less soluble and is separated at higher temperatures; ammonium chloride is recovered from the filtrate by cooling.

Ammonia-Soda Process. Ammonium chloride is made as a by-product of the classic Solvay process, used to manufacture sodium carbonate (qv) (14,15). The method involves reaction of ammonia, carbon dioxide, and sodium chloride in water

$$NH_3 + CO_2 + NaCl + H_2O \longrightarrow NaHCO_3 + NH_4Cl$$

Sodium bicarbonate precipitates from solution and is recovered by filtration. Ammonium chloride is then crystallized from the filtrate, separated, washed, and dried. The exact proportion of ammonium chloride recovered depends on the relative demands for sodium carbonate and ammonium chloride. If economic conditions require, part of the ammonia can be recovered and returned to the brine-ammoniation step by distillation of the ammonium chloride solution in the presence of lime. The spent calcium chloride liquor, a final product in manufacture of sodium carbonate by the ammonia–soda process, can also be used to obtain ammonium chloride. This liquor is treated with ammonia and carbon dioxide

$$CaCl_2 + 2\,NH_3 + CO_2 + H_2O \longrightarrow CaCO_3 + 2\,NH_4Cl$$

Calcium carbonate is removed by filtration leaving an ammonium chloride solution.

Ammonium Sulfate–Sodium Chloride Process. Ammonium sulfate, a readily available by-product, has been much used to make ammonium chloride by a double decomposition reaction with sodium chloride.

$$(NH_4)_2SO_4 + 2\,NaCl \longrightarrow Na_2SO_4 + 2\,NH_4Cl$$

The ammonium sulfate and sodium chloride are simultaneously dissolved, preferably in a heel of ammonium chloride solution. The sodium chloride is typically in excess of about 5%. The pasty mixture is kept hot and agitated vigorously. When the mixture is separated by vacuum filtration, the filter and all connections are heated to avoid crust formation. The crystalline sodium sulfate is washed to remove essentially all of the ammonium chloride and the washings recycled to the process. The ammonium chloride filtrate is transferred to acid resistant crystallizing pans, concentrated, and cooled to effect crystallization. The crystalline NH_4Cl is washed with water to remove sulfate and dried to yield a product of high purity. No attempt is made to recover ammonium chloride remaining in solution. The mother liquor remaining after crystallization is reused as a heel.

Ammonium Sulfite–Sodium Chloride Process. Ammonium chloride has been produced by the reaction of ammonium sulfite [10196-04-0], NH_4SO_3, and sodium chloride in a large Canadian plant (16). Ammonium sulfite is never actually isolated, rather ammonia and sulfur dioxide react in water with sodium chloride.

$$2\,NaCl + SO_2 + 2\,NH_3 + H_2O \longrightarrow Na_2SO_3 + 2\,NH_4Cl$$

This process is only practical when the raw materials are readily available and of high purity.

The sodium sulfite precipitates first and is removed by centrifugation, washed with water, and dried. The mother liquor containing ammonium chloride is sent to crystallizing tanks and the salt thus formed is washed and dried, giving a product said to analyze well over 99%.

Direct Neutralization. Because of the availability of by-product ammonium salts, the double decomposition routes are usually more favorable economically for ammonium chloride manufacture. However, where surplus hydrogen chloride is available, the direct neutralization process has been used (17)

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl \qquad \Delta H = -175.7\ \text{kJ/mol}\ (-42\ \text{kcal/mol})$$

The reaction is very exothermic and the heat generated is used to evaporate a large part of the water present when aqueous hydrochloric acid is used. Batch or continuous crystallization is then employed to recover the ammonium chloride.

A Brazilian company had reported producing ammonium chloride from hydrogen chloride gas (18). Hydrogen chloride is mixed with air and introduced into a saturated ammonium chloride suspension at 80°C. Excess ammonia is added to a conical section of the saturator to maintain a pH of 8. The ammonium chloride is recovered from the suspension by thickening in a hydroclone, followed by centrifugation and drying. Mother liquor and the water used to scrub waste gases, are returned to the saturator.

Uses. Ammonium chloride is used as a nitrogen source for fertilization of rice, wheat, and other crops in Japan, China, India, and Southeast Asia. Japan is a large producer, much of which is as by-product.

Ammonium chloride has a number of industrial uses, most importantly in the manufacture of dry-cell batteries, where it serves as an electrolyte. It is also used to make quarrying explosives, as a hardener for formaldehyde-based adhesives, as a flame suppressant, and in etching solutions in the manufacture of printed circuit boards. Other applications include use as a component of fluxes in zinc and tin plating, and for electrolytic refining of zinc.

Technical grade ammonium chloride is widely available as the crystalline salt; technical rods and granules are also available. Its DOT number is NA9085.

5.2. Ammonium Bifluoride.

Properties. Ammonium bifluoride, NH_4HF_2, is a colorless, orthorhombic crystal (19). The compound is odorless; however, less than 1% excess HF can cause an acid odor. The salt has no tendency to form hydrates yet is hygroscopic if the ambient humidity is over 50%. A number of chemical and physical properties are listed in Table 3.

Ammonium bifluoride dissolves in aqueous solutions to yield the acidic bifluoride ion; the pH of a 5% solution is 3.5. In most cases, NH_4HF_2 solutions react readily with surface oxide coatings on metals; thus NH_4HF_2 is used in

Table 3. **Properties of Ammonium Bifluoride, NH_4HF_2**

Property	Value	Reference
melting point, °C	126.1	20
boiling point, °C	239.5	20
index of refraction, n_D	1.390	20
solubility at 25°C, wt %		
water	41.5	20
90% ethanol	1.73	20
specific gravity	1.50	20
standard heat of formation, kJ/mol[a]	−798.3	21
heat of fusion, kJ/mol[a]	19.1	21
heat of vaporization, kJ/mol[a]	65.3	21
heat of solution, kJ/mol[a]	20.3	21
heat of dissociation,[b] kJ/mol[a]	141.4	21
heat capacity, C_p, J/(mol·K)[a] at 25°C	106.7	21
vapor pressure,[c] $\log P_{\mathrm{Pa}} = a - bT^{-1}$		
153–207°C	$a = 11.72, b = 3370$	22
207–245°C	$a = 9.38, b = 2245$	22

[a] To convert kJ to kcal, divide by 4.184.

[b] $NH_4HF_2 \longrightarrow NH_3 + 2\,HF$.

[c] To convert Pa to mm Hg, multiply by 7.5×10^{-3}.

pickling solutions (see METAL SURFACE TREATMENTS). Many plastics, such as polyethylene, polypropylene, unplasticized PVC, and carbon brick, are resistant to attack by ammonium bifluoride.

Manufacture. Anhydrous ammonium bifluoride containing 0.1% H_2O and 93% NH_4HF_2 can be made by dehydrating ammonium fluoride solutions and by thermally decomposing the dry crystals (23). Commercial ammonium bifluoride, which usually contains 1% NH_4F, is made by gas-phase reaction of one mole of anhydrous ammonia and two moles of anhydrous hydrogen fluoride (24); the melt that forms is flaked on a cooled drum.

Production of bifluoride from fluoride by-products from the phosphate industry (25) has had little if any commercial significance.

Health and Safety Factors. Ammonium bifluoride, like all soluble fluorides, is toxic if taken internally. When heated to decomposition, it emits very toxic fumes (5). Hydrofluoric acid burns may occur if the material comes in contact with moist skin. Ammonium bifluoride solutions should be thoroughly washed from the skin with mildly alkaline soap as soon as possible; however, if contact has been prolonged, the affected areas should be soaked with 0.13% solution of Zephiran chloride, or 0.2% Hyamine 1622 or calcium gluconate, the treatment recommended for hydrofluoric acid burns. If any of these solutions come in contact with the eyes, they should be washed with water for at least 10 min and a physician should be consulted.

Uses. Ammonium bifluoride solubilizes silica and silicates by forming ammonium fluorosilicate [16919-19-0], $(NH_4)_2SiF_6$. Inhibited 15% hydrochloric acid containing about 2% ammonium bifluoride has been used to acidize oil wells in siliceous rocks to regenerate oil flow (26) (see PETROLEUM). Ammonium fluoride solution is made on-site near the well bore from ammonium bifluoride and ammonia mixed with methyl formate to prevent rapid consumption of most of the HF (27). The use of ammonium bifluoride is important in locations where dissolved silicates foul boiler tubes with scale that cannot be removed using usual cleaning aids (28). Ammonium bifluoride is also used as an etching agent for silicon wafers.

Rapid frosting of glass is accomplished in a concentrated solution of ammonium bifluoride and hydrofluoric acid with nucleating agents that assure uniform frosts (29). A single dip in an aqueous solution of NH_4HF_2, HF, and sorbitol at $<20°C$ for less than 60 s produces the low specular-reflecting finish on television face plates and on (qv) for picture framing (30). Treating glass, eg, often badly weathered window panes, with 2–5% solutions of ammonium bifluoride results in a polishing effect. Glass ampuls for parenteral solutions (31) and optical lenses (32) are best cleaned of adhering particulate matter in dilute ammonium bifluoride solutions.

Ammonium bifluoride is used as a sour or neutralizer for alkalies in commercial laundries and textile plants. Treatment also removes iron stain by forming colorless ammonium iron fluorides that are readily rinsed from the fabric (33).

Ammonium fluorides react with many metal oxides or carbonates at elevated temperatures to form double fluorides; eg,

$$2\,NH_4HF_2 + BeO \xrightarrow{-H_2O} (NH_4)_2BeF_4 \xrightarrow{\Delta} BeF_2 + 2\,NH_3 + 2\,HF$$

The double fluorides decompose at even higher temperatures to form the metal fluoride and volatile NH_3 and HF. This reaction produces pure salts less likely to be contaminated with oxyfluorides. Beryllium fluoride [7787-49-7], from which beryllium metal is made, is produced this way (34) (see BERYLLIUM AND BERYLLIUM ALLOYS). In pickling of stainless steel and titanium, NH_4HF_2 is used with high concentrations of nitric acid to avoid hydrogen embrittlement. Ammonium bifluoride is used in acid dips for steel (qv) prior to phosphating and galvanizing, and for activation of metals before nickel plating (35,36). Ammonium bifluoride also is used in aluminum anodizing formulations. Ammonium bifluoride is used in treatments to provide corrosion resistance on magnesium and its alloys (37). Such treatment provides an excellent base for painting and good abrasion resistance, heat resistance, and protection from atmospheric corrosion. A minor use for ammonium bifluoride is in the preservation of wood (qv) (38).

5.3. Ammonium Bromide and Iodide.

Manufacture. Ammonium bromide and Ammonium iodide are manufactured either by the reaction of ammonia with the corresponding hydrohalic acid or, more economically, by the reaction of ammonia with elemental bromine or iodine. In the latter reaction, an excess of ammonia must be used.

$$8\,NH_3 + 3\,Br_2 \longrightarrow 6\,NH_4Br + N_2$$

For ammonium bromide, another method involving reaction of an aqueous bromine solution and iron filings has been used. The solution of ferrous and ferric bromide thus formed then reacts with ammonia to precipitate hydrated oxides of iron. Ammonium bromide can be recovered by crystallization from the concentrated liquor.

Uses. Ammonium bromide is available as a dry technical grade or as 38 to 45% solutions. It is used to manufacture chemical intermediates, and in photographic chemicals; it also has some flame retardant applications.

Ammonium iodide has limited use in photographic and pharmaceutical preparations.

6. Ammonium Nitrate

Ammonium nitrate [6484-52-2], NH_4NO_3, formula wt 80.04, is the most commercially important ammonium compound both in terms of production volume and usage. It is the principal component of most industrial explosives and nonmilitary blasting compositions; however, it is used primarily as a nitrogen fertilizer. Ammonium nitrate does not occur in nature because it is very soluble. It was first described in 1659 by the German scientist Glauber, who prepared it by reaction of ammonium carbonate and nitric acid. He called it nitrium flammans because its yellow flame (from traces of sodium) was different from that of potassium nitrate.

Ammonium nitrate fertilizer incorporates nitrogen in both of the forms taken up by crops: ammonia and nitrate ion. Fertilizers (qv) containing only ammoniacal nitrogen are often less effective, as many important crops tend to take up nitrogen mainly in the nitrate form and the ammonium ions must be transformed into nitrate by soil organisms before the nitrogen is readily available. This transformation is slow in cool, temperate zone soils. Thus, ammonium nitrate is a preferred source of fertilizer nitrogen in some countries.

One general disadvantage of nitrogen fertilizers, and ammonium nitrate in particular, is that the nitrate ion is more prone to leach through the soil profile and enter the groundwater. The presence of nitrate in groundwater became an important environmental issue in the 1980s (see GROUNDWATER MONITORING). Efforts by farmers to address this problem have focused on improved management techniques, such as multiple or delayed applications, accurate and efficient placement, and the use of cover crops to take up residual nitrogen and reduce erosion. Controlling the dissolution and release of ammonium nitrate into the soil by use of rosin-coated fertilizer (39) has also been suggested.

6.1. Physical and Chemical Properties. Ammonium nitrate is a white, crystalline salt, $d_4^{20} = 1.725$, that is highly soluble in water, as shown in Table 4 (8). Although it is very hygroscopic, it does not form hydrates. This hygroscopic nature complicates its usage in explosives, and until about 1940, was a serious impediment to its extensive use in fertilizers. The solid salt picks up water from air when the vapor pressure of water exceeds the vapor pressure of a saturated aqueous ammonium nitrate solution (see Table 5).

The boiling point of ammonium nitrate–water solutions, given in Table 6, indicates the temperatures required for removing water (40).

Solid ammonium nitrate occurs in five different crystalline forms (41) (Table 7) detectable by time–temperature cooling curves. Because all phase

Table 4. **Solubility of Ammonium Nitrate**

	Solubility of NH_4NO_3, g/100 g			Solubility of NH_4NO_3, g/100 g	
Temperature, °C	Water	Soln	Temperature, °C	Water	Soln
0	118	54.2	60	410	80.4
10	150	60.0	70	499	83.3
20	187	65.2	80	576	85.2
30	232	69.9	90	740	88.1
40	297	74.8	100	843	89.4
50	346	77.6			

Table 5. **Vapor Pressure of Ammonium Nitrate Solutions**

	Vapor pressure, kPa[a]	
Temperature, °C	Water	Saturated NH_4NO_3 soln
10	1.2	0.85
20	2.3	1.5
30	4.2	2.5
40	7.4	3.9

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

Table 6. **Boiling Point of Ammonium Nitrate Solutions**

NH_4NO_3, wt %	Bp, °C	NH_4NO_3, wt %	Bp, °C	NH_4NO_3, wt %	Bp, °C
10	101	60	113.5	94	165
20	102.5	70	119.5	95	170
30	104	80	128.5	96	182
40	107.5	85	136	98	203
50	109.5	90	157	99	222

changes involve either shrinkage or expansion of the crystals, there can be a considerable effect on the physical condition of the solid material. This is particularly true of the 32.3°C transition point which is so close to normal storage temperature during hot weather.

The specific heat of solid β-phase ammonium nitrate is 1.70 J/g (0.406 cal/g) between 0 and 31°C; the specific heats of aqueous NH_4NO_3 solutions are shown in Table 8 (9,42). The coefficient of expansion is 0.000920 at 0°C, 0.000982 at 20°C, and 0.001113 at 100°C; the heat of formation from the elements is 364 kJ/mol (87.1 kcal/mol).

Ammonium nitrate has a negative heat of solution in water, and can therefore be used to prepare freezing mixtures. Dissolution of ammonium nitrate in anhydrous ammonia, however, is accompanied by heat evolution. In dilute solution the heat of neutralization of nitric acid using ammonia is 51.8 kJ/mol (12.4 kcal/mol).

Decomposition and Detonation Hazard. Ammonium nitrate is considered a very stable salt, even though ammonium salts of strong acids generally lose ammonia and become slightly acidic on storage. For ammonium nitrate, endothermic dissociation from lowering pH occurs above 169°C.

$$NH_4NO_3 \longrightarrow HNO_3 + NH_3 \qquad \Delta H = 175 \text{ kJ/mol (41.8 kcal/mol)}$$

Table 7. **Crystalline Forms of Ammonium Nitrate**

Designation	Temperature range, °C	Crystal system
α	<−18	tetragonal
β	−18 – 32.1	rhombic
γ	32.1–84.2	rhombic
δ	84.2–125.2	tetragonal
ε	125.2–169.6	cubic

Table 8. **Specific Heats of Aqueous Solutions of Ammonium Nitrate at 100°C**

NH_4NO_3, wt %	Specific heat, J/g[a]	NH_4NO_3, wt %	Specific heat, J/g
10	3.9	70	2.4
30	3.4	90	1.9
50	2.9		

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

When the salt is heated to temperatures from 200 to 230°C, exothermic decomposition occurs (4,43). The reaction is rapid, but it can be controlled, and it is the basis for the commercial preparation of nitrous oxide [10024-97-2].

$$NH_4NO_3 \longrightarrow N_2O + 2\,H_2O \qquad \Delta H = -37 \text{ kJ/mol } (-8.8 \text{ kcal/mol})$$

Above 230°C, exothermic elimination of N_2 and NO_2 begin.

$$4\,NH_4NO_3 \longrightarrow 3\,N_2 + 2\,NO_2 + 8\,H_2O \qquad \Delta H = -102 \text{ kJ/mol } (-24.4 \text{ kcal/mol})$$

The final violent exothermic reaction occurs with great rapidity when ammonium nitrate detonates.

$$2\,NH_4NO_3 \longrightarrow 2\,N_2 + 4\,H_2O + O_2 \qquad \Delta H = -118.5 \text{ kJ/mol } (-28.3 \text{ kcal/mol})$$

Ammonium nitrate is normally classified as an oxidizing agent. The pure salt is not classed as an explosive because it is difficult to detonate. Spark, flame, or friction do not cause detonation, and ammonium nitrate is relatively insensitive to shock. However, a variety of substances, such as chloride and oil, are known to sensitize the material, so manufacturers strive to eliminate such substances from their processes.

When used in blasting, ammonium nitrate is mixed with fuel oil and sometimes sensitizers such as powdered aluminum. Lower density ammonium nitrate is preferred for explosive formulation, because it absorbs the oil more effectively. When detonated,these mixtures have an explosive power of 40 to 50% that of TNT (see EXPLOSIVES).

6.2. Manufacture. Historically, ammonium nitrate was manufactured by a double decomposition method using sodium nitrate and either ammonium sulfate or ammonium chloride. Modern commercial processes, however, rely almost exclusively on the neutralization of nitric acid (qv), produced from ammonia through catalyzed oxidation, with ammonia. Manufacturers commonly use onsite ammonia although some ammonium nitrate is made from purchased ammonia. Solid product used as fertilizer has been the predominant form produced. However, sale of ammonium nitrate as a component in urea–ammonium nitrate liquid fertilizer has grown to where about half the ammonium nitrate produced is actually marketed as a solution.

Three steps are essential to ammonium nitrate manufacture: neutralization of nitric acid with ammonia to produce a concentrated solution; evaporation to give a melt; and processing by prilling or granulation to give the commercial solid product.

Neutralization. The reaction of ammonia and nitric acid is highly exothermic and the heat released evaporates water, most commonly concentrating the reaction mixture to 83–87% ammonium nitrate. Both reactants are also volatile at the resulting temperatures, thus close control of reactor conditions is necessary to prevent loss of material. Strict temperature regulation in the entire reactor, normally achieved by regulating the addition of feeds and by removal of heat, is particularly important. The heat removed can be recovered for acid preheating, ammonia evaporation, or evaporation of additional water. To avoid localized overheating, reactors are also designed for excellent mixing and utilize automatic pH control.

Neutralizers can be of three designs, depending on the temperature in the reactor zone. They may operate under, exactly at, or above the atmospheric boiling point of the contained ammonium nitrate solution.

Vacuum flash processes, which operate under the atmospheric boiling point of the solution, include the Uhde–I.G. Farbenindustrie process and the closely related Kestner process (44). In these, ammonia, nitric acid, and recirculated ammonium nitrate solution are fed into the neutralizer. Hot solution overflows to an intermediate tank and then to a flash evaporator kept at 18–20 kPa (0.18–0.2 atm) absolute pressure. Partial evaporation of water at this point cools and concentrates the solution, part of which is routed to evaporation. The rest is circulated to the neutralizer.

The ICI process is an example of neutralization at atmospheric pressure. Nitric acid feed is preheated by part of the vapors produced in the neutralizer and is then split into two streams. Recycled, undersized product is dissolved in one stream, conditioning material in the other. The recombined streams are added to a two stage neutralizer along with ammonia and recirculated solution to give 87 to 89% ammonium nitrate feed for evaporation. The C&I–Girdler-Cominco process is similar in principle; the Pintsch-Bamag (45) process uses a two-stage neutralizer without recirculation.

The Fauser process (46), which operates above atmospheric pressure, was an early attempt to fully utilize the heat of neutralization. The neutralizing zone of the enclosed reactor operates at 500–600 kPa (5 to 6 atm). Reactants enter at the bottom of this chamber and hot ammonium nitrate streams upward, where it is discharged continuously into an outer vessel operated at atmospheric pressure. The arriving solution loses part of its water; subsequently most is recirculated through the outer vessel to the lower neutralizing space, while part is removed for further processing. Ammonia and nitric acid feed streams are preheated by partial utilization of the steam from the outer vessel.

The Stamicarbon (44) and Kaltenbach high concentration processes are designed to use the evaporated water vapor produced by pressure neutralization to heat the evaporator used for concentration. The Kaltenbach neutralizer operates at 350 kPa (3.5 bar) and 175°C, and produces steam used to concentrate the solution to 95% in a vacuum evaporator. A recent variation uses a final atmospheric evaporator to produce a 99.7% melt (44).

Other processes, including the Société Belge de l'Azote and Union Chimique Belge (44) are designed to achieve even higher heat recovery which is inherently possible through use of pressure neutralization.

Concentration. Evaporation procedures depend on the concentration of the solution produced during neutralization and the water content required for the subsequent production of solid product. Neutralizer solutions can contain as little as 2% and as much as 25% water; feeds to drum granulators can contain 5% water, prill towers 0.3 to 0.5% water.

Since about 1965, efficient vacuum evaporators have been used in most plants. Second stage evaporators, where the ammonium nitrate is concentrated to more than 99%, are designed to retain only a small volume of melt, have short residence times, and are protected from overheating and contamination by sensitizers. Falling film units are especially suited for this application.

Solid Finished Product. The final step in ammonium nitrate fertilizer manufacture is the production of a uniformly sized, abrasion and crush-resistant, and free-flowing solid possessing good storage properties. Besides being hygroscopic, ammonium nitrate is subject to degradation, or "sugaring", which occurs during storage as temperatures fluctuate across the 32.1°C crystal phase change. Most manufacturers seek to overcome this latter problem by adding a stabilizing agent to the melt.

Graining, flaking, and spraying have all been used to make solid ammonium nitrate particles. Most plants have adopted various prilling or granulation processes. Crystallized ammonium nitrate has been produced occasionally in small quantities for use in specialty explosives. The Tennessee Valley Authority developed and operated a vacuum crystallization process (47), but the comparatively small crystals were not well received as a fertilizer. The process was subsequently modified to pan granulation (48).

Prilling Process. Prilling is the formation of a rounded, granular solid by allowing molten droplets to fall through a fluid cooling medium. Prilling of ammonium nitrate involves spraying the concentrated (96% or 99 + %) solution into the top of a large tower. The descending droplets are cooled by an upward flow of air, solidifying into spherical prills that are collected at the bottom. The process yields particles that vary in size depending on the residual moisture of solution, air temperature, and flow rate.

The 96–97% ammonium nitrate solutions are sprayed into towers 33 to 60 m high to produce low density 770 kg/m^3 (48 lbs/ft^3) prills favored for use in ammonium nitrate–fuel oil blasting agents. A drying step is required after prilling. This porous product promotes propagation of detonation and allows for a higher fuel oil loading.

The 99.7–99.8% solutions are sprayed into towers only 20 to 30 m high (49) to give high density 860 kg/m^3 (54 lbs/ft^3) prills preferred by the fertilizer industry. These prills, which require cooling but no drying, are sometimes coated using 2.5–3% of activated clay or diatomaceous earth, although some producers add chemical additives to the melt, giving a product needing no surface conditioner.

Granulation Processes. In the early 1970s, production of large-particle ammonium nitrate using the spheroidizer granulation process was adopted by several manufacturers. This process, developed by Cominco, Ltd. (Canada) and the C&I–Girdler Corporation, is an adaptation of one used for production of other fertilizers (50). Ammonium nitrate is layered in onion-skin fashion on small seed particles by spraying a 99 + % solution on a dense cascading curtain of granules. This process is carried out in a 3.5–4.5 m diameter by 14–18 m rotating drum having specially designed flights.

The well-rounded particles produced are screened and cooled, giving granules having a moisture content of about 0.1%; they do not require a conditioner. These granules also have a higher crushing strength than prills, and are less subject to breakdown in storage and handling. The process is used by several ammonium nitrate producers in the United States; most calcium ammonium nitrate [39368-85-9] and ammonium nitrate sulfate

[12436-94-1] producers outside of the United States also use this granulation technique.

A fluid bed granulation process developed by Nederlandse Stikstof Maatschappij (NSM) is also available (51). The granules grow from single seed particles. These are fed to a baffled, rectangular vessel, where they are fluidized by a flow of preheated air. A 97% ammonium nitrate solution is sprayed upward into this bed of particles, continuously coating them. Efficient air contact during the 15 min residence time allows evaporation of water as the particles grow in size. The largest granules finally settle and flow from the bottom of the vessel. Pollution control is effected by a wet scrubber and presents few problems.

Blungers and classic drum granulator equipment have also been adapted to the production of granular ammonium nitrate. In the Norsk Hydro Fertilizer, Ltd. process a 92–95% solution is sprayed onto a bed of recycled fines inside a drum granulator (52). Granulator temperatures are held between 85 and 100°C; a small amount of ammonia is also fed to the rolling bed. Material discharged from the granulator is dried either by indirectly heated air or by a gas-fired burner.

Granulation processes offer a number of important advantages. The most significant are decreased pollution problems and the ability to produce granules of almost any reasonable size allowing close size matching with granular ammonium phosphates and potassium chloride in the preparation of NPK fertilizers (48).

6.3. Quality of Product. Ammonium nitrate, commonly made from pure synthetic raw materials, is itself of high purity. If the product is intended for use in explosives, it should be at least 99% ammonium nitrate and contain no more than 0.15% water. It should contain only small amounts of water-insoluble and ether-soluble material, sulfates and chlorides, and should not contain nitrites. The solid product ought to be free from alkalinity, but be only slightly acidic.

If the product is to be used in the manufacture of nitrous oxide, an anesthetic gas, a purity of not less than 99.5% is required. The salt must be almost completely free of contaminating organic matter, iron, sulfate, and chloride.

6.4. Health and Safety Factors. Ammonium nitrate can be considered a safe material if treated and handled properly. Potential hazards include those associated with fire, decomposition accompanied by generation of toxic fumes, and explosion. It is also an allergien (5).

Although ammonium nitrate does not itself burn, it is a strong oxidizer capable of supporting the combustion of numerous substances when heated. It can support and intensify a fire even when air is excluded. Fires involving ammonium nitrate also present a toxic hazard from the release of nitrogen oxides, even though the solid itself is generally considered not to be toxic.

Pure ammonium nitrate is a relatively insensitive explosive material, requiring high initiation energy, but when detonated it can have about 70% of the disruptive strength of nitroglycerine. In 1947, after vigorous fires, two explosions occurred on freighters loaded with heavy paper containers of fertilizer grade ammonium nitrate. These explosions resulted in the proposal of precautions for the handling and transportation of ammonium nitrate (53). Thus, ammonium nitrate must be considered a high explosive under the following three conditions: bolstering by a high velocity explosive, confinement at elevated temperatures, and presence of oxidizable materials.

6.5. Economic Aspects and Uses. Before World War II most ammonium nitrate was used as an ingredient in high explosives. Subsequently its use as a fertilizer grew rapidly, absorbing about 90% of production in 1975. Ammonium nitrate lost its position as fertilizer to urea. Consumption peaked at 18×10^6 t in 1988 and declined by 12% to 16×10^6 t in 1998. Consumption declined because of changes in agricultural subsidy policies. In 1998, Western Europe, the United States, and the former USSR accounted for 75% of world production in 1998. Marginal growth at a rate of 0.3% is expected. Some of the growth is expected in the former USSR (54).

The DOT label required is OXY; the United Nations number is UN 1842.

Most ammonium nitrate manufactured for the explosives market is used in blasting agents prepared by adding a fuel component, such as diesel oil, to the prilled product. Ammonium nitrate can be hardened for use in explosives (55). Much is consumed in coal mining; the remaining explosive markets are metal mining, nonmetal mining, quarrying, and highway construction.

A small but important use of ammonium nitrate is in the production of nitrous oxide. The gas is generated by controlled heating of ammonium nitrate above 200°C. Nitrous oxide is used primarily as an anesthetic and as an aerosol propellant for food products (see ANESTHETICS; AEROSOLS).

7. Ammonium Nitrate Limestone

Many plants outside of North America prill or granulate a mixture of ammonium nitrate and calcium carbonate. Production of this mixture, often called calcium ammonium nitrate, essentially removes any explosion hazard. In many cases calcium nitrate recovered from acidulation of phosphate rock (see PHOSPHORIC ACID AND THE PHOSPHATES) is reacted with ammonia and carbon dioxide to give a calcium carbonate–ammonium nitrate mixture containing 21 to 26% nitrogen (45).

8. Ammonium Nitrite

Ammonium nitrite [13446-48-5], NH_4NO_2, a compound of questionable stability, can be prepared by reaction of barium nitrite and aqueous ammonium sulfate. After removal of the precipitated barium sulfate by filtration, the ammonium nitrite can be recovered from solution. The salt is a powerful oxidizer and there is a severe explosion hazard when shocked or exposed to heat (60–70°C). When heated to decomposition, it emits toxic fumes (5).

9. Ammonium Sulfate

Ammonium sulfate [7783-20-2], $(NH_4)_2SO_4$, is a white, soluble, crystalline salt having a formula wt of 132.14. The crystals have a rhombic structure; d_4^{20} is 1.769. An important factor in the crystallization of ammonium sulfate is the sensitivity of its crystal habit and size to the presence of other components in the crystallizing solution. If heated in a closed system ammonium sulfate melts at 513 ± 2°C (14); if heated in an open system, the salt begins to decompose at 100°C, giving ammonia and ammonium bisulfate [7803-63-6], NH_4HSO_4, which melts at 146.9°C. Above 300°C, decomposition becomes more extensive giving sulfur dioxide, sulfur trioxide, water, and nitrogen, in addition to ammonia.

The solubility of ammonium sulfate in 100 g of water is 70.6 g at 0°C and 103.8 g at 100°C. It is insoluble in ethanol and acetone, does not form hydrates, and deliquesces at only about 80% relative humidity. The integral heat of solution of ammonium sulfate to saturation in water is 6.57 kJ/mol (1.57 kcal/mol) at 30°C; at saturation at the same temperature, the differential heat of solution is 6.07 kJ/mol (1.45 kcal/mol).

9.1. Manufacture. Ammonium sulfate is produced from the direct neutralization of sulfuric acid with ammonia; the heat of reaction is sufficient to evaporate all water if the concentration of the acid is 70% or higher.

$$2\,NH_3(g) + H_2SO_4(aq) \longrightarrow (NH_4)_2SO_4(s) \qquad \Delta H = -274 \text{ kJ/mol } (-65.5 \text{ kcal/mol})$$

Ammonium sulfate is also recovered as a by-product in large amounts during the coking of coal, nickel refining, and organic monomer synthesis, particularly during production of caprolactam (qv). About four metric tons of ammonium sulfate are produced per ton of caprolactam which is an intermediate in the production of nylon.

Some companies have used the Merseburg process to manufacture ammonium sulfate from gypsum, but the process is only economically attractive where sulfur is unavailable or very expensive (56), and is thus not used in the United States. Ammonium carbonate, formed by the reaction of ammonia and carbon dioxide in an aqueous medium, reacts with suspended, finely ground gypsum. Insoluble calcium carbonate and an ammonium sulfate solution are formed.

$$(NH_4)_2CO_3 + CaSO_4{\cdot}2H_2O \longrightarrow (NH_4)_2SO_4 + CaCO_3 + 2\,H_2O$$

After removal of the calcium carbonate, the sulfate is recovered by evaporation and crystallization.

Some sulfuric acid producers use ammoniacal solutions to scrub tail gases from stacks in order to conform to federal and state regulations on sulfur dioxide emissions; ammonium sulfate is recovered as a product. Several similar scrubbing processes for removal of sulfur dioxide from electric power plant stack gas have been studied (57). However, such scrubbing operations could generate huge tonnages of ammonium sulfate, flooding local markets because long-distance shipment of the product is generally uneconomical.

9.2. Economic Aspects and Uses. Almost all ammonium sulfate is used as a fertilizer; for this purpose it is valued both for its nitrogen content and for its readily available sulfur content. In North America ammonium sulfate is largely recovered from caprolactam production.

Ammonium sulfate is a good fertilizer for rice, citrus, and vines, and can be especially useful for some sulfur-deficient or high pH soils. Nonfertilizer uses include food processing, fire control, tanning, and cattle feed.

In general, industrialized nations account for world production. World production in 1999 was 3.5×10^6 t. In 1999, Western Europe, the United States, and the former USSR accounted for 44% of world capacity and 49% world production. Southeast Asia was the largest consumer in 1999 and accounted for 19% of consumption (58).

9.3. Health and Safety Factors.

Ammonium sulfate is moderately toxic by several routes. Effects of human ingestion are hypermotility, diarrhea, nausea or vomiting. Reactions with sodium hypochlorite gives the unstable explosive nitrogen trichloride. When heated to decomposition, it emits very toxic fumes (5).

10. Ammonium Sulfides

Ammonia combines with hydrogen sulfide, sulfur, or both, to form various ammonium sulfides and polysulfides. Generally these materials are somewhat unstable, tending to change in composition on standing. Ammonium sulfides are used by the textile industry.

10.1. Ammonium Sulfide.

Ammonium sulfide [12135-76-1], $(NH_4)_2S$, can be produced by the reaction of hydrogen sulfide with excess ammonia

$$2\,NH_3 + H_2S \longrightarrow (NH_4)_2S$$

Solid ammonium sulfide decomposes to ammonia and ammonium hydrosulfide at about −18°C; consequently it is normally marketed as a 40–44% aqueous solution.

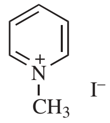
10.2. Ammonium Hydrosulfide.

The reaction of equimolar amounts of ammonia and hydrogen sulfide results in the formation of ammonium hydrosulfide [12124-99-1], NH_4HS, which is also produced by the loss of ammonia from ammonium sulfide. The hydrosulfide is very soluble in water, liquid ammonia, liquid hydrogen sulfide, and alcohol. Solid ammonium hydrosulfide has a high vapor pressure, 99.7 kPa (748 mm Hg) at 32.1°C, and sublimes easily at ordinary temperatures. Vapors from the hydrosulfide, composed of ammonia and hydrogen sulfide, are very toxic.

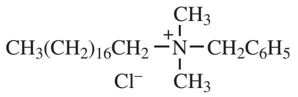
11. Quaternary Ammonium Compounds

There are a vast number of quaternary ammonium compounds or quaternaries (59,60). Many are naturally occurring and have been found to be crucial in biochemical reactions necessary for sustaining life. A wide range of quaternaries are also produced synthetically and are commercially available. Over 344,000 metric tons of quaternary ammonium compounds are produced annually in the United States. The economic value is estimated at $810 MM (61). These have many diverse applications. Most are eventually formulated and make their way to the marketplace to be sold in consumer products. Applications range from cosmetics (qv) to hair preparations (qv) to clothes softeners, sanitizers for eating utensils, and asphalt emulsions.

Most quatemary ammonium compounds have the general formula $R_4N^+ X^-$ and are a type of cationic organic nitrogen compound. The nitrogen atom, covalently bonded to four organic groups, bears a positive charge that is balanced by a negative counterion. Heterocyclics, in which the nitrogen is bonded to two carbon atoms by single bonds and to one carbon by a double bond, are also considered quaternary ammonium compounds. The R group may either be equivalent or correspond to two to four distinctly different moieties. These groups may be any type of hydrocarbon: saturated, unsaturated, aromatic, aliphatic, branched chain, or normal chain. They may also contain additional functionality and heteroatoms. Examples include methylpyridinium iodide [930-73-4] (59), benzyldimethyloctadecylammonium chloride [122-19-0] (61), and di(hydrogenated tallow)alkyldimethylammonium chloride [61789-80-8] (62), where $R{=}C_{14}{-}C_{18}$.

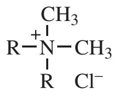


(**1**)



$CH_3(CH_2)_{16}CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{+}{N}}}-CH_2C_6H_5 \quad Cl^-$

(**2**)



$R-\overset{\overset{CH_3}{|}}{\underset{\underset{R}{|}}{\overset{+}{N}}}-CH_3 \quad Cl^-$

(**3**)

11.1. Nomenclature. Quaternary ammonium compounds are usually named as the substituted ammonium salt. The anion is listed last (62). Substituent names can be either common (stearyl) or IUPAC (octadecyl). If the long chain in the compound is from a natural mixture, the chain is named after that mixture, eg, tallowalkyl. Prefixes such as di- and tri- are used if an alkyl group is repeated. Complex compounds usually have the substituents listed in alphabetical order. Some common quaternary ammonium compounds and their applications in patent literature are listed in Table 9.

11.2. Physical Properties. Most quaternary compounds are solid materials that have indefinite melting points and decompose on heating. Physical properties are determined by the chemical structure of the quaternary ammonium compound as well as any additives such as solvents. The simplest quaternary ammonium compound, tetramethylammonium chloride [75-57-0], is very soluble in water (211) insoluble in nonpolar solvents. As the molecular weight of the quaternary compound increases, solubility in polar solvents decreases and solubility in nonpolar solvents increases (212–214). For example, trimethyloctadecylammonium chloride [112-03-8] is soluble in water up to 27%, whereas dimethyldioctadecylammonium chloride [107-64-2] has virtually no solubility in water. Appropriately formulated, however, this latter compound can be dispersed in water at relatively high (~15%) levels.

The ability to form aqueous dispersions is a property that gives many quaternary compounds useful applications. Placement of polar groups, eg, hydroxy or ethyl ether, in the quaternary structure can increase solubility in polar solvents.

Higher order aliphatic quaternary compounds, where one of the alkyl groups contains ~10 carbon atoms, exhibit surface-active properties (215,216). These compounds compose a subclass of a more general class of compounds known as cationic surfactants (qv). These have physical properties such as substantivity and aggregation in polar media (217) that give rise to many practical

Table 9. **Selected Quaternary Ammonium Compounds and Their Applications**

Quaternary	CAS Registry Number	Industry	Application and function	Comments	References
many compounds claimed, as an example: polypropoxylated (6) choline chloride		agricultural	surfactant	key component in glyphosphate composition	63–66
tetrabutylammonium hydroxide	[2052-49-5]	chemical	phase-transfer catalyst	used as a catalyst for the production of gem-dichloro compounds	67
alkyltrimethyl or dialkydimethyl type quaternaries, as an example dicocoalkyldimethylammonium chloride	[61789-77-3]	chemical	emulsifier	emulsifier for silanes useful as masonry water repellents	68
many compounds claimed, as an example: dicocoalkyldimethylammonium chloride	[61789-77-3]	chemical	complex agent	complexed with anionic dyes to produce a formulation free of inorganic salts	69,70
many perfluoroalkyl quaternary ammonium compounds claimed, as an example: di(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)dimethylammonium chloride		chemical	phase-transfer catalyst	a family of novel quaternaries useful as phase-transfer catalysts especially in basic media	71
many diquaternary ammonium compounds claimed, as an example: 1,3-bis(dipentylethylammonium)propane dibromide		chemical	catalysts	catalyst for the interfacial polymerization polycarbonate preparation	72
many compounds claimed, as an example: tridecylmethylammonium chloride	[5137-56-4]	chemical	component in catalyst	key component in a catalyst composition containing a zirconium compound	73
di(hydrogenated tallowalkyl)dimethyl ammonium chloride and others	[61789-80-8]	chemical	nonvolatile compositions	compositions containing vegetable oils as diluents useful in organoclays	74

many compounds claimed, as an example: diallyldimethylammonium chloride	[7398-69-8]	chemical	antimicrobial	antibacterials for polymer latexes and resins	75–77
benzyltrimethylammonium chloride and others	[56-93-9]	defense	surfactant	component in a formulation to neutralize chemical and biological warfare agents	78,79
many compounds claimed, as an example: benzyldimethyl[2-(3,5-di-*tert*-butyl 4-hyroxybenzoyloxy)ethyl]ammonium *m*-nitrobenzenesulfonate		electronics	charge control agent	component in toner compositions	80–84
benzylacetyldimethylammonium chloride		electronics	dispersant	component in electrostatic liquid developer formulation useful in color copying	85
mixtures of quaternary ammonium hydroxides and halides		electronics	dissolution agent	components in positive photoresist formulation to improve the dissolution selectivity between exposed and unexposed portion of photoresist	86
polyquaternary ammonium compounds		electronics	binder	key component in information storage layer of electronic recording medium	87
many compounds claimed, as example: methyltrioctylammonium chloride and tridecylmethylammonium chloride	[5137-55-3] and [5137-56-4]	electronics	surfactant	component in blocking layer of an electrographic photosensitive material	88
mixtures of quaternary ammonium hydroxides and carbonates, as an example: tetramethyl ammonium hydroxide and tetramethylammonium hydrogen carbonate	[75-59-2]	electronics	surfactant/ buffering agent	components in a developing solution for producing printed circuit boards	89

Table 9 (*Continued*)

Quaternary	CAS Registry Number	Industry	Application and function	Comments	References
As an example: tetrabutylammonium tetrafluoroborate	[429-42-5]	electronics	charge control agent	additive for the preparation of phase change inks with increased specific conductance	90
many compounds claimed, as an example: tetradecyltrimethylammonium bromide	[1119-97-7]	electronics	biocides	biocides for color reversal photographic film and photographic reversal bath	91–93
tetramethylammonium hydroxide	[75-59-2]	electronics	surface active agent	in formulation for polishing semiconductor wafers	94
quaternary ammonium hydroxide		electronics	surfactant	key component in removing agent formulation for producing semiconductor integrated circuits	95
quaternary ammonium hydroxide		electronics	surfactant	components in cleaning formulations for semiconductor devices	96,97
quaternary ammonium hydroxide		electronics	surfactant	component in cleaning composition for removing plasma etching residues	98
tetraalkylammonium halide		food	antimicrobial	compositions for removal and prevention of microbial contamination	99,100
many compounds claimed		household	antimicrobial	disenfecting component in cleaning composition	101–109
hexadecylpyridinium chloride	[123-03-5]	household	antimicrobial	antimicrobial is dispersed throughout plastic toothbrush	110

dimethyldialkylquaternary ammonium		household	antimicrobial	claimed synergy when used in combination with water soluble anionic surfactant	111
pentamethyltallowalkyl-1,3-propanediammonium chloride	[68607-29-4]	household	antimicrobial	used in a composition for deodorizing footware	112
hexadecyltrimethylammonium chloride	[112-02-7]	household	surfactant	component in vicoselastic thickening system for opening drains	113
ethoxylated quaternary ammonium compounds		household	surfactant	used in a formulation to remove road-film	114,115
trialkylammoniumacetylpyrrolidone chloride		household	bleach activator	in a detergent or cleaning formulation	116
ester based quaternary ammonium compounds		household	fabric Softening	for the preparation of rinse cycle fabric softening formulations	117–136
amidoamine and branched quaternary ammonium compounds		household	fabric softening	for the preparation of rinse cycle fabric softening formulations	137,138
ester based quaternary ammonium compounds		household	antistatic	for use in dryer-activated fabric conditioning and antistatic compositions	139–144
alkoxylated quaternary ammonium compounds		household	detergents	for improved performance in detergent formulations such as optimum grease and soil removal, enhancement of bleach efficacy, and better cold temperature performance	145–153
many compounds claimed, as an example: hexadecyltrimethylammonium bromide	[57-09-0]	household	antimicrobial	for use in liquid laundry detergent composition	154,155
ester based quaternary ammonium compounds		household	fabric softening	for use in liquid detergent formulations that soften fabric	155–158

Table 9 (*Continued*)

Quaternary	CAS Registry Number	Industry	Application and function	Comments	References
2-hydroxyethyltrialkyl ammonium halide		mining	complexing agent for gold anions	quat is adsorbed onto porous polymer resin and forms ion pairs with gold anions	159
quaternary ammonium salts and mixtures		mining	froth flotation	recovery of petalite free of feldspar	160
many compounds claimed, as an example: didecyldimethylammonium chloride	[7173-51-5]	other	antimicrobial	active component in antimicrobial formulations	161–164
pyridinium halides such as decylpyridinium bromide		other	anticorrosion	functions as corrosion inhibitor to protect metal surfaces from acid	165,166
polyquaternary ammonium		other	superabsorbent	cationic copolymer with improved water absorbing properties	167
unsaturated quaternary ammonium compounds		other	surfactant	component in a photocurable antifogging composition for glass	168
polyquaternary ammonium		other	pesticide	to control the infestation of snails in aqueous systems	169
2-ethylhexylhydrogenated-*t*-allowalkyl-dimethyl ammonium methosulfate	[308074-31-9]	organoclay	modify smectite-type clay	organoclay product containing branched chain quaternary ammonium compounds	170
alkyl quaternary ammonium salt		organoclay	modify mineral clay	organoclay composition comprising a mineral clay treated with an alkyl quaternary ammonium salt	171
ester based quaternary ammonium compounds		organoclay	modify smectite-type clay	organoclays useful for non-aqueous systems like paints, inks and coatings	172

preferred is dimethyldi(hydrogenated tallowalkyl)ammonium chloride	[61789-80-8]	organoclay	modify smectite-type clay	organoclays useful for nanocomposites and rheological additives	173
many compounds claimed, as an example: octadecyltrimethylammonium chloride	[112-03-8]	paper	active in paper softening composition	key component to prepare tissue with a soothing feeling	174
many compounds claimed, as an example: dimethyldi(hydrogenated tallowalkylalkyl)ammonium methosulfate	[61789-81-9]	paper	component in tissue paper web	acts as an antimigration material for emollient lotion	175
ester based quaternary ammonium compounds		paper	softening	for the manufacture of soft absorbent paper products such as paper towels, facial tissue and toilet tissue	176–180
polyquaternary ammonium		personal care	thickeners and dispersants	quaternary ammonium copolymers useful in cosmetic compositions	181,182
many compounds claimed, as an example: *N*-methyl-*N*,*N*-bis(2-($C_{16/18}$-acyloxy)ethyl)-*N*-hydroxyethylammonium methosulfate	[57905-74-3]	personal care	conditioning shampoo	conditioning component	183–188
as an example: 1,2-ditallowalkyloxy-3-trimethylammoniumpropane chloride		personal care	hair conditioner	active ingredient in formulation	189,190
unsaturated quaternary ammonium compounds		personal care	delivery agent	used in a formulation to deliver the active component to the hair or skin	191,192
polyquaternary ammonium		personal care	antimicrobial	used as a disinfectant for ophthalmic compositions	193
as an example: dimethyldi(hydrogenated tallowalkyl)ammonium chloride	[61789-80-8]	petroleum	drilling fluids	drilling fluid compositions having special rheological properties	194,195
quaternary ammonium hydroxides		petroleum	key component of a process	method for scavenging mercaptans in hydrocarbon fluid	196,197

Table 9 (*Continued*)

Quaternary	CAS Registry Number	Industry	Application and function	Comments	References
dicocoalkyldimethylammonium chloride	[61789-77-3]	petroleum	oil spill recovery	oil spill redediation agent containing organoclay and waste paper	198
eg, tetrabutylammonium bromide	[1643-19-2]	petroleum	phase-transfer catalyst	method of removing contaminants from petroleum distillates and contaminants from used oils	199–201
ester based quaternary ammonium compounds		petroleum	surfactant	used in a composition for enhanced recovery of crude oils	202
chloromethyl(8-hexadecenyl)dimethylammonium chloride		pharmaceutical	antitumorous	active component in composition	203
cationic lipids		pharmaceutical	receptor	improved cell targeting ability for the delivery of molecules into cells	204
polyquaternary ammonium		pharmaceutical		used to lower cholesterol levels	205
hydrogenatedtallowalkyltrimethyl ammonium chloride	[61788-78-1]	remediation	component in an organoclay	organoclay adsorbs dissolved heavy metals including lead and radiactive contaminants from aqueous solutions	206
many compounds claimed, as an example: benzyltrimethylammonium chloride	[56-93-9]	remediation	component in an organoclay	removal of aromatic petroleum-based contaminants from water	207
trimethylbetahydroxyethyl ammonium hydroxide and others	[123-41-1]	rubber	accelerator	for vulcanization of rubber with non-toxic material	208
dialkyldimethyl quaterary ammonium compounds		wood	biocides	biocidal component in a formulation to waterproof and preserve wood	209,210

applications. The aqueous phase behavior (218) and adsorption at interfaces (219) of cationic surfactants has been discussed. In some cases the ammonium compounds are referred to as inverse soaps because the charge on the organic portion of the molecule is cationic rather than anionic.

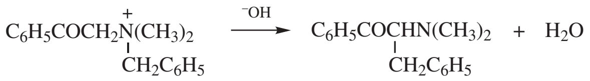
11.3. Chemical Properties. Reactions of quaternaries can be categorized into three types (220): Hofmann eliminations, displacements, and rearrangements. Thermal decomposition of a quaternary ammonium hydroxide to an alkene, tertiary amine, and water is known as the Hofmann elimination (eq. 1a) (221). This reaction has not been used extensively to prepare olefins. Some cyclic olefins, however, are best prepared this way (222). Exhaustive methylation, followed by elimination, is known as the Hofmann degradation and is important in the structural determination of unknown amines, especially for alkaloids (qv) (223).

$$CH_3CH_2CH_2\overset{+}{N}(CH_3)_3 + {}^{-}OH \xrightarrow{\text{elimination}} CH_3CH_2{=}CH_2 + N(CH_3)_3 + H_2O \qquad (1a)$$

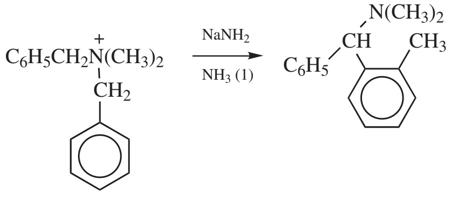
$$CH_3CH_2CH_2\overset{+}{N}(CH_3)_3 + {}^{-}OH \xrightarrow{\text{displacement}} CH_3CH_2CH_2N(CH_3)_2 + CH_3OH \qquad (1b)$$

Displacement of a tertiary amine from a quaternary (eq. 1b) involves the attack of a nucleophile on the α-carbon of a quaternary and usually competes with the Hofmann elimination (224). The counterion greatly influences the course of this reaction. For example, the reaction of propyltrimethylammonium ion with hydroxide ion yields 19% methanol and 81% propylene, whereas the reaction with phenoxide ion yields 65% methoxybenzene and 15% propylene (225).

The Stevens rearrangement (eq. 2) is a base-promoted 1,2-migration of an alkyl group from a quaternary nitrogen to carbon (226,227). The Sommelet-Hauser rearrangement (eq. 3) is a base-promoted 1,2-migration of a benzyl group to the ortho position of that benzyl group (228,229).

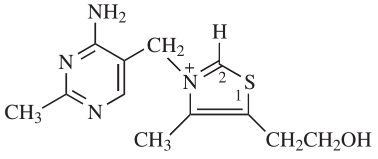


$$C_6H_5COCH_2\overset{+}{N}(CH_3)_2(CH_2C_6H_5) \xrightarrow{{}^{-}OH} C_6H_5COCH(CH_2C_6H_5)N(CH_3)_2 + H_2O \qquad (2)$$

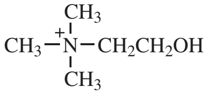


(3)

11.4. Naturally Occurring Quaternaries. Naturally occurring quaternary ammonium compounds have been reviewed (230). Many types of aliphatic, heterocyclic, and aromatic derived quaternary ammonium compounds are produced both in plants and invertebrates. Examples include thiamine (vitamin B_1) (231) (see VITAMINS); choline (qv) [62-49-7] (4); and acetylcholine (64). These have numerous biochemical functions. Several quaternaries are precursors for active metabolites.

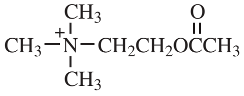


(**4**)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}-CH_2CH_2OH$$

(**5**)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}-CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$$

(**6**)

Thiamine (231) functions as a coenzyme in several enzymatic reactions in which an aldehyde group is transferred from a donor to a receptor molecule. The thiazole ring is the focus of this chemistry. Thiamine also serves as a coenzyme in the pyruvate dehydrogenase and α-ketoglutarate dehydrogenase reactions. These take place in the main pathway of oxidation of carbohydrates (qv) in cells.

Choline functions in fat metabolism and transmethylation reactions. Acetylcholine functions as a neurotransmitter in certain portions of the nervous system. Acetycholine is released by a stimulated nerve cell into the synapse and binds to the receptor site on the next nerve cell, causing propagation of the nerve impulse.

Biochemically, most quaternary ammonium compounds function as receptor-specific mediators. Because of their hydrophilic nature, small molecule quaternaries cannot penetrate the alkyl region of bilayer membranes and must activate receptors located at the cell surface. Quaternary ammonium compounds also function biochemically as messengers, which are generated at the inner surface of a plasma membrane or in a cytoplasm in response to a signal. They may also be transferred through the membrane by an active transport system.

General types of physiological functions attributed to quaternary ammonium compounds are curare action, muscarinic–nicotinic action, and ganglia blocking action. The active substance of curare is a quaternary that can produce muscular paralysis without affecting the central nervous system or the heart. Muscarinic action is the stimulation of smooth-muscle tissue. Nicotinic action is primary transient stimulation and secondary persistent depression of sympathetic and parasympathetic ganglia.

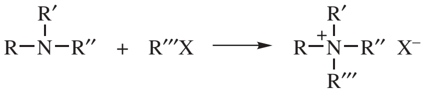
11.5. Synthesis and Manufacture. A wide variety of methods are available for the preparation of quaternary ammonium compounds (232–234). Significantly fewer can be used on a commercial scale. A summary of the most commonly used commercial methods is given herein.

Quaternary ammonium compounds are usually prepared by reaction of a tertiary amine and an alkylating agent (eq. 4). The most widely used alkylating

Table 10. **Typical Alkylating Agents for the Preparation of Quaternaries**

Alkylating Agent	Chemical Formula	CAS Registry Number	Final Quaternary
methyl chloride	CH_3Cl	[74-87-3]	$R_3N^+CH_3\ \ Cl^-$
dimethyl sulfate	$(CH_3)_2SO_4$	[77-78-1]	$R_3N^+CH_3\ \ CH_3SO_4$
diethyl sulfate	$(CH_3CH_2)_2SO_4$	[64-67-5]	$R_3N^+CH_3\ \ CH_3CH_2SO_4$
benzyl chloride	$C_6H_5CH_2Cl$	[100-44-7]	$R_3N^+CH_2C_6H_5\ \ Cl^-$

agents are listed in Table 10. Some of these alkylating reagents pose significant health concerns and require special handling techniques. Alkylation reactions are usually run at moderate (60–100°C) temperatures. When methyl chloride is used, the reactions are often performed under moderate [415–790 kPa (60–115 psi)] pressures.



$$\mathrm{R{-}\overset{R'}{\underset{}{N}}{-}R''} + \mathrm{R'''X} \longrightarrow \mathrm{R{-}\overset{R'}{\underset{R'''}{\overset{+}{N}}}{-}R''}\ \mathrm{X^-} \tag{4}$$

Equation 4 can be classified as S_N2, ie, substitution nucleophilic bimolecular (235). The rate of the reaction is influenced by several parameters: basicity of the amine, steric effects, reactivity of the alkylating agent, and solvent polarity. The reaction is often carried out in a polar solvent, eg, isopropyl alcohol, which may increase the rate of reaction and make handling of the product easier.

Primary and secondary amines are usually converted to tertiary amines using formaldehyde and hydrogen in the presence of a catalyst (eqs. 5 and 6). This process, known as reductive alkylation (236), and is attractive commercially. The desired amines are produced in high yields and without significant by-product formation. Quaternization by reaction of an appropriate alkylating reagent then follows.

$$\mathrm{RNH_2 + 2\ CH_2O \xrightarrow[H_2/catalyst]{} RN(CH_3)_2} \tag{5}$$

$$\mathrm{R_2NH + CH_2O \xrightarrow[H_2/catalyst]{} R_2NCH_3} \tag{6}$$

Dialkyldimethyl and alkyltrimethyl quaternaries can be prepared directly from secondary and primary amines as shown in eqs. 7 and 8, respectively. This process, known as exhaustive alkylation, is usually not the method of choice on a commercial scale. This technique requires the continuous addition of basic material over the course of the reaction to prevent the formation of amine salts (237–238). Furthermore, products such as inorganic salt and water must be removed from the quaternary. The salt represents a significant disposal problem.

$$\mathrm{R_2NH + 2\,CH_3Cl + NaOH \rightarrow R_2N^+(CH_3)_2 + NaCl + H_2O} \tag{7}$$

$$\mathrm{RNH_2 + 3\,CH_3Cl + 2\,NaOH \rightarrow RN^+(CH_3)_3 + 2\,NaCl + 2\,H_2O} \tag{8}$$

Synthesis and Manufacture of Amines. The chemical and business segments of amines (qv) and quaternaries are so closely linked that it is difficult to consider these separately. The majority of commercially produced amines originate from three amine raw materials: natural fats and oils, α-olefins, and fatty alcohols. Most large commercial manufacturers of quaternary ammonium compounds are fully back-integrated to at least one of these three sources of amines. The amines are then used to produce a wide array of commercially available quaternary ammonium compounds. Some individual quaternary ammonium compounds can be produced by more than one synthetic route.

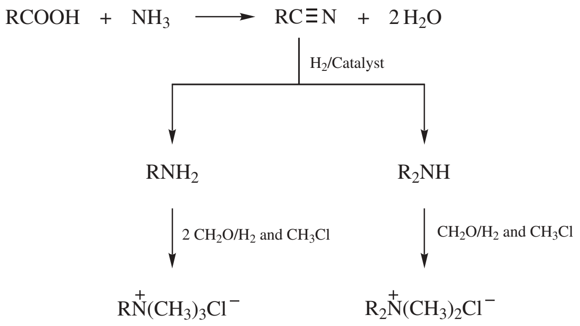


Fig. 1. Quaternaries from fatty nitriles where R is a fatty alkyl group.

Nitrile Intermediates. Most quaternary ammonium compounds are produced from fatty nitriles (qv), which are in turn made from a natural fat or oil-derived fatty acid and ammonia (qv) (Fig. 1) (see FATS AND FATTY OILS) (239). The nitriles are then reduced to the amines. A variety of reducing agents may be used (240). Catalytic hydrogenation over a metal catalyst is the method most often used on a commercial scale (241). Formation of secondary and tertiary amine side-products can be hindered by the addition of acetic anhydride (242) or excess ammonia (243). In some cases secondary amines are the desired products.

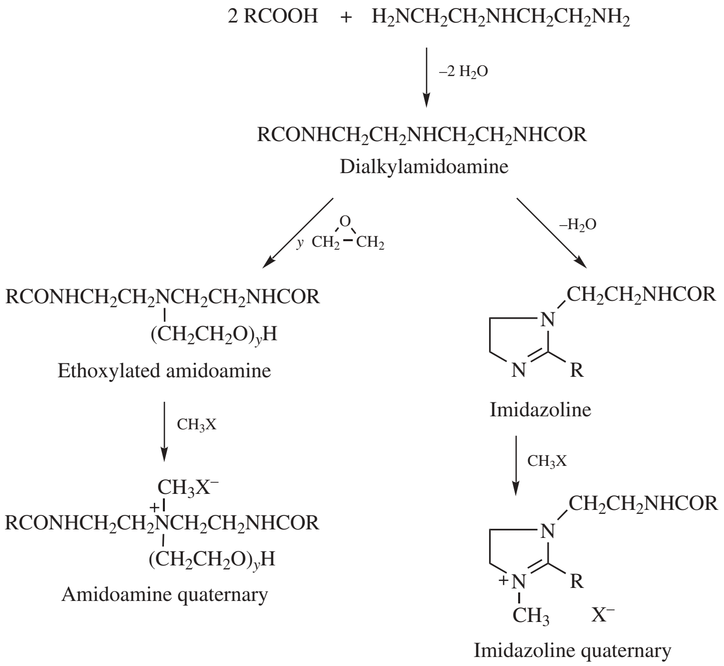


Fig. 2. Quaternaries from amidoamines and imidazolines where R is a fatty alkyl group.

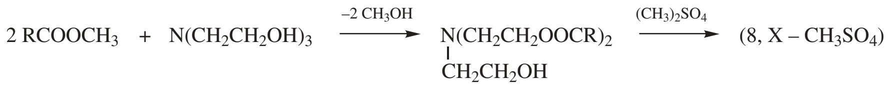
Fats, Oils, or Fatty Acids. The primary products produced directly from fats, oils, or fatty acids without a nitrile intermediate are the quaternized amidoamines, imidazolines, and ethoxylated derivatives (Fig. 2). Reaction of fatty acids or tallow with various polyamines produces the intermediate dialkylamidoamine. By controlling reaction conditions, dehydration can be continued until the imidazoline is produced. Quaternaries are produced from both amidoamines and imidazolines by reaction with methyl chloride or dimethyl sulfate. The amidoamines can also react with ethylene oxide (qv) to produce ethoxylated amidoamines that are then quaternized.

These compounds and their derivatives can be manufactured using relatively simple equipment compared to that required for the fatty nitrile derivatives. Cyclization of amidoamines to imidazolines requires higher reaction temperatures and reduced pressures. Prices of imidazolines are therefore high.

Olefins and Fatty Alcohols. Alkylbenzyldimethylammonium (ABDM) quaternaries are usually prepared from α-olefin or fatty alcohol precursors. Manufacturers that start from the fatty alcohol usually prefer to prepare the intermediate alkyldimethylamine directly by using dimethylamine and a catalyst rather than from fatty alkyl chloride. Small volumes of dialkyldimethyl and alkyltrimethyl quaternaries in the $C_8{-}C_{10}$ range are also manufactured from these precursors (Fig. 3).

Quaternized Esteramines. Esterquaternary ammonium compounds or esterquats can be formulated into products that have good shelf stability (244). Many examples of this type of molecule have been developed (see Fig. 4).

Quaternized esteramines are usually derived from fat or fatty acid that reacts with an alcoholamine to give an intermediate esteramine. The esteramines are then quaternized. A typical reaction scheme for the preparation of a diester quaternary is shown in equation 9 (246), where R is a fatty alkyl group. Reaction occurs at 75–115°C in the presence of sodium methoxide catalyst. Free fatty acids (254) and glycerides (255) can be used in place of the fatty acid methylester.



$$2\,RCOOCH_3 + N(CH_2CH_2OH)_3 \xrightarrow{-2\,CH_3OH} \underset{\displaystyle CH_2CH_2OH}{N(CH_2CH_2OOCR)_2} \xrightarrow{(CH_3)_2SO_4} (8,\ X - CH_3SO_4) \qquad (9)$$

11.6. Economic Aspects.

A summary of list prices and suppliers for selected quaternaries is given in Table 11. Other commercial products include

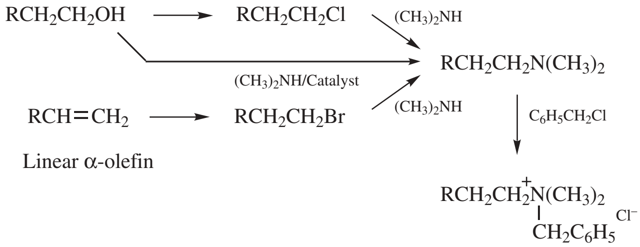


Fig. 3. Quaternaries from α-olefins of fatty alcohols where R is a fatty alkyl group. The product is alkylbenzyldimethyl quaternary.

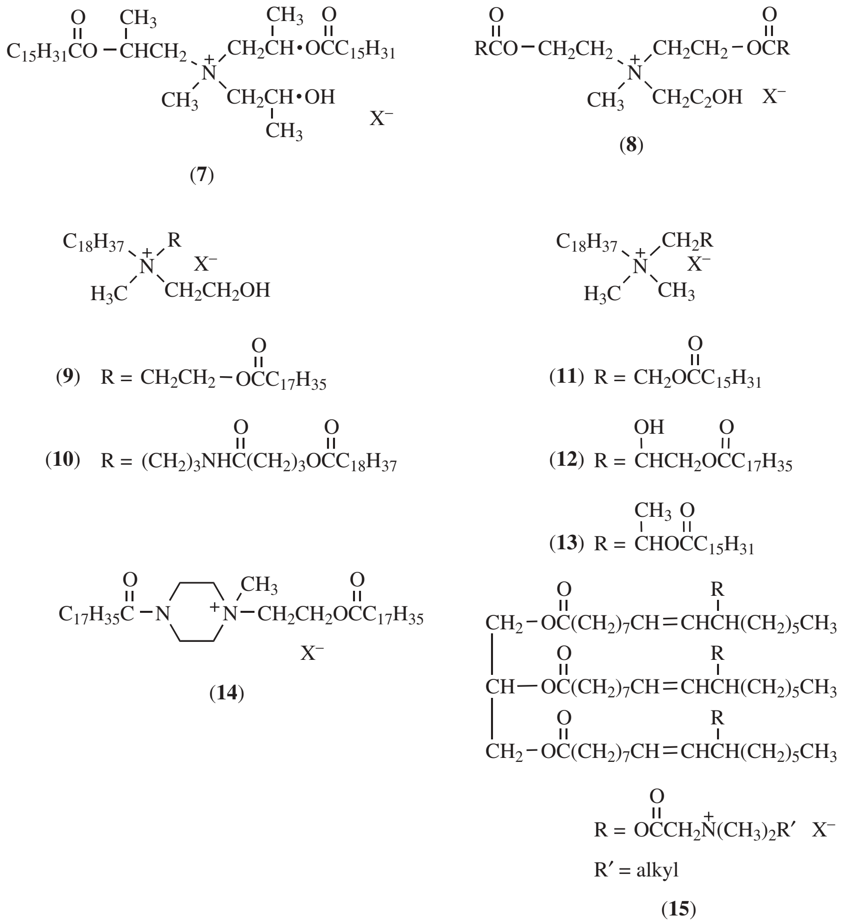


Fig. 4. Quaternary esteramines: (**7**) (245); (**8**) (244,246); (**9**) (247,248); (**10**) (249); (**11**) (250); (**12**) (251); (**13**) (196); (**14**) (252); and (**15**) (253).

diallyldimethylammonium chloride [7398-69-8], produced by Ciba Specialty Chemicals; di(hydrogenated tallow)alkyldimethylammonium methosulfate [61789-81-9], produced by Akzo Nobel; and tetrabutylammonium bromide [1643-19-2], produced by Cognis Corp., RSA Corp and Sachem Inc. The leading producers of phase-transfer quaternaries are Eastman Kodak Company, Hexcel Corporation, RSA, Chemical Dynamics Corporation, Lindan Chemicals, Henkel Corporation, and Akzo Nobel. From 2,300 to 11,300 metric tons of quaternaries were used as phase-transfer catalysts during 1991 (257). The principal producers of perfluorinated quaternaries are Ciba, 3M Specialty Chemicals, and E. I. du Pont de Nemours & Company, Inc.

The leading U.S. manufacturers in terms of volumes of fatty nitrogen derivatives are Akzo Nobel and Goldschmidt-Degussa. The combined annual production of these two companies accounts for ~80% of the fatty nitrogen products manufactured in the United States. The remaining production is divided

Table 11. **1998 Prices and Suppliers of Selected Quaternaries and Tertiary Amine Precursors**[a]

Material	CAS Registry Number	Percent active as supplied	$/kg	Manufacturer[b]
methyl bis(tallowamido ethyl)-2-tallow imidazolinium methosulfate	[68122-86-1]	75	1.76	A, Cr, G, S
methyl bis(tallowalkylamidoethyl)-2-hydroxyethylammonim methosulfate	[68410-69-5]	90	1.76	Cr, L, S
di(hydrogenated tallow)-alkyldimethyl ammonium chloride	[61789-80-8]	80	2.29	A, G, R
tallowalkyl diamine	[61791-55-7]	100	2.67	A, C, T
(hydrogenated tallow)alkyl amine	[61788-45-2]	100	2.45	A, C, G
(hydrogenated tallow)alkyl amine, distilled	[61788-45-2]	100	2.98	A
methyldi(hydrogenated tallow)alkyl amine	[61788-63-4]	100	2.27	A, C, G
cocoalkylamine	[61788-46-3]	100	3.48	A, C, Cl, G
alkyl(C12-C16)dimethyl amine	[61788-93-0]	100	2.65	A, C, L
alkyl(C12-C16)benzyldimethyl ammonium chloride	[61789-71-7]	50	2.98	A, Al, L, M, R, S

[a] Ref. 256.

[b] Manufacturer: A = Akzo Nobel Chemicals Inc; Al = Alfachem; C = Atofina North America; Cl = Clar-Clariant Corp; Cr = Croda Inc; G = Goldschmidt-Degussa Chemical Group; L = Lonza Inc; M = Mason Chemical Co; R = Rhodia; T = Tomah Products Inc.

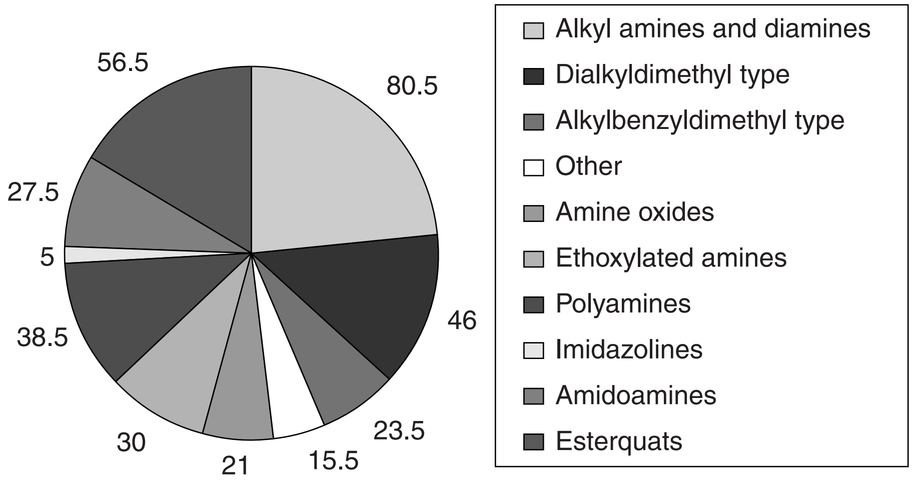


Fig. 5. North American consumption of quaternaries by product type (1997 total is 344 M metric tons).

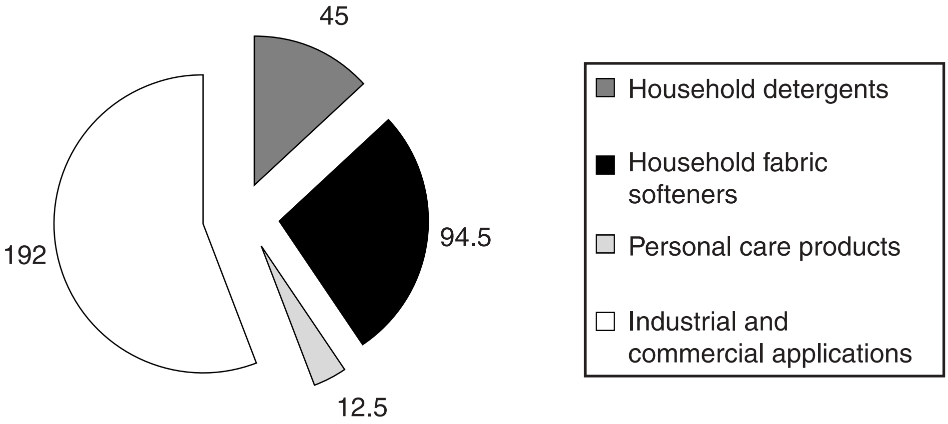


Fig. 6. North American consumption by market (1997 total is 344 M metric tons).

among smaller-volume producers. Nearly all fatty nitrile plants require considerable technological expertise and capital investment to operate.

Figure 5 shows the consumption of quaternaries in North America during 1997 as a function of product type. Alkyl amines and diamines accounted for 80,000 metric tons during 1997. The next largest volume type of quaternary ammonium compound was esterquats accounting for over 56,000 metric tons. The single largest market for quaternary ammonium compounds is as fabric softeners. Both household and industrial type formulations are produced, the household market is larger. In 1997 the household market accounted for over 94,000 metric tons of quaternaries in the United States (258). Consumption of these products is increasing at an annual rate of ~2–3%. The hair care market consumed over 12,000 metric tons of quaternary ammonium compounds in 1997 (259). The annual consumption for organoclays is estimated at 18,000 metric tons (260).

Figure 6 shows the consumption of quaternaries in North America during 1997 as a function of market segment. Industrial and commercial applications is made up of several market segments including I&I cleaning, agricultural emulsions, textiles, oilfield, mining, and asphalt.

11.7. Analytical Methods. There are no universally accepted wet analytical methods for the characterization of quaternary ammonium compounds. The American Oil Chemists' Society (AOCS) has established, however, a number of applicable tests (261). These include sampling, color, moisture, amine value, ash, iodine value, average molecular weight, pH, and flash point.

Numerous "wet chemical" methods have been developed for the determination of the activity of quaternary ammonium samples (262–264). First is the partition titration in immiscible solvent systems, usually chloroform and water, using an anionic surfactant such as sodium lauryl sulfate [151-21-3] and an anionic dye indicator (265). This process, essentially a microtitration, is often referred to as the Epton titration (266,267). The end point requires considerable practice to detect. Second is the direct titration of the long-chain cation with sodium tetraphenylboron [143-66-8] using an anionic indicator (268). This macro method is convenient and relatively simple to perform. Third is the titration of the halide anion (Volhardt type) or perchloric acid titration in acetic anhydride (269). The fourth category includes colorimetric methods using anionic dyes or indicators and partition solvent systems. These partition/colorimetric analytical methods, which have found widespread use in environmental analysis, have long been used for determining small amounts of quaternary ammonium compounds (270). Although they are not specific, these methods do indicate the presence of long-chain cationics that have at least one chain composed of eight or more carbon atoms. The use of electrodes to determine the end point of the activity titration is becoming more popular in the industry (271). The change is prompted by several factors. Among them are a trend toward minimizing the use of chlorinated solvents required for many partition-based methods and the increased use of the esterquat molecule, which does not give a sharp visual endpoint. Both platinum sheet and platinum bulb electrodes are used. Ion specific electrodes offer a high degree of specificity but have the drawback of being sensitive to potential interferences (272). Where relatively pure compounds are used, ion specific electrodes have begun to gain acceptance (273,274).

The chain length composition of quaternaries can be determined by gas-chromatography (qv) (275). Because of low volatility, quaternaries cannot be chromatographed directly, but only as their breakdown products. Quaternary ammonium salts can be analyzed by injecting them directly dimethylsilicone based capillary columns. In most cases, long-chain monoalkyl quaternaries break down to form two sets of peaks: short-chain alkyl halides and the long-chain tertiary amines. Long-chain dialkyl quaternaries elute on the basis of total carbon atoms present in the resulting methyldialkyl tertiary amine.

Mass spectral analysis of quaternary ammonium compounds can be achieved by fast-atom bombardment (fab) ms (276,277). This technique relies on bombarding a solution of the molecule, usually in glycerol [56-81-5] or *m*-nitrobenzyl alcohol [619-25-0], with argon and detecting the parent cation plus a proton (MH^+). A more recent technique has been reported (278), in which information on the structure of the quaternary compounds is obtained indirectly through cluster-ion formation detected via liquid secondary ion mass spectrometry (lsims) experiments.

Liquid chromatography has been widely applied for analysis of quaternaries. Modified reverse-phase columns can provide chain length information, whereas normal-phase chromatography results in groupings of alkyl distributions. Quaternary ammonium compounds can be separated into their mono-, di-, and trialkyl components on a normal-phase silica or alumina column using a conductivity detector (279). Solvent systems generally include tetrahydrofuran, methanol, and acetic acid. Because the conductivity detector is only sensitive to ionic species, solvents and nonionic components of the sample are not seen by the detector. Alternative columns are amino, modified silica, or cation exchange. Evaporative laser light scattering detectors (elsd) have also been utilized for the nonvolatile, nonultraviolet-absorbing quaternaries (286).

Nuclear magnetic resonance (nmr) spectroscopy is useful for determining quaternary structure. The ^{15}N nmr can distinguish between quaternary ammonium compounds and amines, whether primary, secondary, or tertiary, as well as provide information about the molecular structure around the nitrogen atom.

The ^{13}C nmr can distinguish among oleic, tallow, and hydrogenated tallow sources (281). In addition to information on chemical structure, nmr is useful for understanding the physical chemistry of cationic surfactants in solution. For example, pulsed field gradient self-diffusion nmr experiments have shown that water permeates readily through vesicle membranes in dispersions of dialkyl quaternary ammonium compounds (282).

11.8. Health and Safety Factors. Acute oral toxicity data (albino rats) show most structures to have an LD_{50} in the range of 100–5000 mg kg (283). Many quaternaries are considered to be moderately to severely irritating to the skin and eyes.

Some quaternary ammonium compounds are potent germicides (212, 284,285), toxic in small (mg L range) quantities to a wide range of microorganisms. Bactericidal, algicidal, and fungicidal properties are exhibited. Ten-minute-contact kills of bacteria are typically produced by quaternaries in concentration ranges of 50–333 mg L (286). Toxicity of quaternary ammonium salts to aquatic organisms is measured in standard laboratory toxicity tests with aqueous medium containing the test chemical (287).

Acute toxicity at low (1 mg L) levels has been reported in invertebrates, snails, and fish (288,289). In plant systems, growth inhibition of green algae and great duckweed occurs at 3–5 mg L (290).

Over the last decade, considerable advances have been made in understanding the metabolic pathway of quaternary ammonium compounds. The general metabolic pathway of several quaternary ammonium materials is given in Figure 7. All research to date shows the main pathway is cleavage of the calkyl-N bonds to produce smaller molecular weight amines and alkanals. The alkanals are degraded by β-oxidation. The amines are readily degraded by microorganisms. The results obtained with ester quats are consistent (64–66).

Numerous internationally recognized standardized methods are available for assessing the biodegradation of chemicals under aerobic conditions. There are three testing method levels: ready biodegradeability, inherent biodegradeability, and simulation of biological treatment systems.

Ready biodegradeability tests are used primarily for regulatory purposes. These include the Closed Bottle test, MITI I test, and the Sturm test. All these tests are usually performed within a 28-day period. A biodegradation percentage of $>60\%$ is interpreted as complete. The biodegradation of surfactants in these tests has been reviewed extensively (67,68). The biodegradation classification of some selected quaternaries in given in Table 12.

There are three standard test methods to assess inherent biodegradeability. These are the MITI II test, Zahn-Wellens and SCAS test. Sludge (CAS) and Semi-Continuous Activated Sludge (SCAS) tests are used to simulate behavior of materials in biological treatment systems. The CAS test is believed to give realistic results similar to full-scale treatment. Results obtained in the CAS and SCAS tests with cationic surfactants are summarized in Table 13. These studies show extensive removal.

A dynamic equilibrium exists between quaternary ammonium species in the aqueous phase and those existing as a soild after absorption. Thus, only the fraction in the aqueous phase is "available" at any given time to be biodegraded. Bioavailability is defined as that fraction of material that is readily

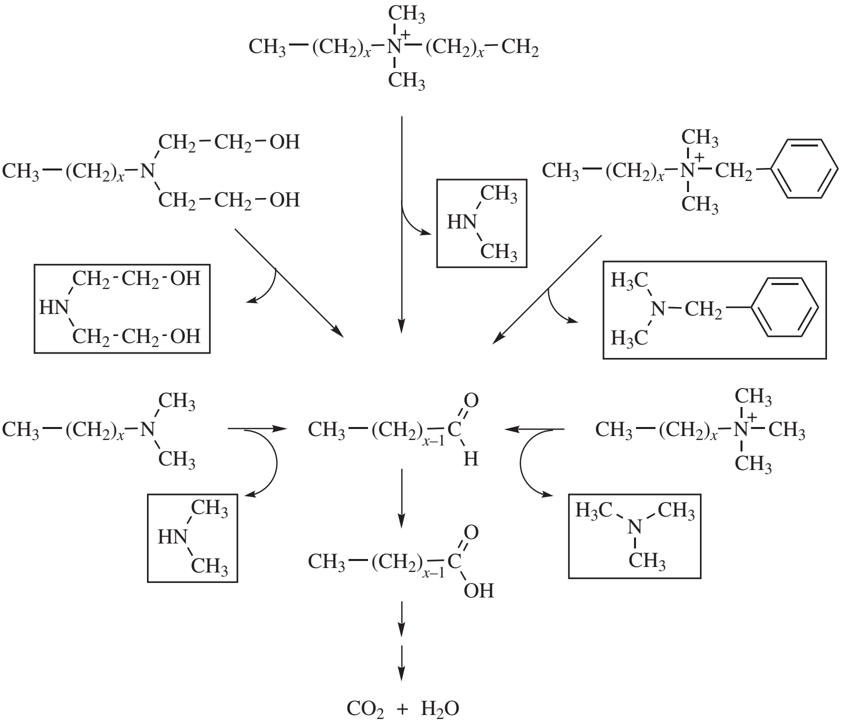


Fig. 7. General metabolic pathway of quaternary ammonium compounds.

accessible to microbial degradation. Recently a method was developed to test the hypothesis that water-insoluble dialkyldimethylammonium salts are available to microorganisms when desorbed. The method consists of a flow-through system comprising a storage vessel with aerated river water, a pump, a column with a quaternary ammonium salt adsorbed on silica gel, and a collecting vessel. Aerated river water was pumped through the column packed with particles of silica gel with adsorbed quaternary compounds. Biodegradation of dicocodimethylammonium chloride was evident from the marked decline in the quaternary ammonium salt concentration in the effluent after a few days (71). The concept of bioavability helps to explain earlier observations for dicocodimethylammonium chloride obtained during prolonged Closed Bottle testing (70).

Most uses of quaternary ammonium compounds can be expected to lead to these compounds' eventual release into wastewater treatment systems except for those used in drilling muds. Useful properties of the quaternaries as germicides can make these compounds potentially toxic to sewer treatment systems. It appears, however, that quaternary ammonium compounds are rapidly degraded in the environment and strongly sorbed by a wide variety of materials. Quaternaries appear to bind anionic compounds and thus are effectively removed from wastewater by producing stable, lower toxicity compounds (291). Under normal circumstances these compounds are unlikely to pose a significant risk to microorganisms in wastewater treatment systems (292). Microbial populations acclimate readily to low levels of quaternary compounds and biodegrade them.

Table 12. **Biodegradation Data for Selected Quaternaries**

Cationic compound	CAS Registry Number	Classification	Percent and degraded time	Reference
octyltrimethylammonium chloride		readily	$>$ 70% in 10 days	100
octadecyltrimethylammonium chloride	[112-03-8]	readily	60%[a] in 10 days	AN unpubl
didecyldimethylammonium chloride	[7173-51-5]	readily	$>$ 70% in 28 days	AN unpubl
didodecyldimethylammonium chloride	[3401-14-9]	readily	$>$ 60%[a]	AN unpubl
polyoxyethylene(15)-cocoalkymethyl-ammonium chloride	[61791-10-4]	inherently	30% in 28 days	62
polyoxyethylene(15)-cocoalkyl amine	[61791-14-8]	inherently		79
bis(2-hydroxyethyl)octadecyl amine	[10213-78-2]	readily	$>$ 70% in 28 days	78,79
alkylbenzyldimethylammonium salts		readily	$>$ 60% in 10 days	100,101
benzyldecyldimethylammonium chloride	[965-32-2]	readily	$>$ 60% in 6 days	100,101
primary fatty amines C8–C18		readily	$>$ 60% in 12 days	70
alkyldimethylamines C12–C18		readily	$>$ 60%	70,76
di-(tallowalkyl)ester of di-2-hydroxyethyldimethylammonium chloride		readily	80% in 28 days	80
N-methyl-*N*,*N*-bis(2-$C_{16/18}$-acyloxy)ethyl)-*N*-(2-hydroxyethyl ammonium methosulfate)	[157905-74-3]	readily		102
di-(hydrogenated tallowalkyl)ester of 2,3-dihydroxypropyltrimethylammonium chloride		readily	85%	22

[a] Test conducted with humic acid present.

Environmental toxicity and stability of these compounds have been described (292,293).

Newer classes of quaternaries, eg, esters (294) and betaine esters (295), have been developed. These materials are more readily biodegraded. The mechanisms of antimicrobial activity and hydrolysis of these compounds have

Table 13. **Removal/Biodegradation of Cationic Surfactants in Continuous Flow Activated Sludge (CAS) and Semicontinuous Activated Sludge (SCAS) Treatment Systems**

Test compound	CAS Registry Number	Test	Removal (%)	Reference
hexadecyltrimethylammonium bromide	[57-09-0]	CAS	91–98	109
hexadecyltrimethylammonium bromide	[57-09-0]	CAS	98–99	110
hexadecyltrimethylammonium bromide	[57-09-0]	CAS	100	111
octadecyltrimethylammonium chloride	[112-03-8]	SCAS	98	107
didecyldimethylammonium chloride	[7173-51-5]	CAS	95	109
dioctadecyldimethylammonium chloride	[107-64-2]	CAS	95	109
dioctadecyldimethylammonium chloride	[107-64-2]	CAS	91–93	112
benzyldodecyldimethylammonium chloride	[7281-04-1]	CAS	96	109
tetradecylbenzyldimethylammonium chloride	[139-08-2]	CAS	>70	113
cocobenzyldimethylammonium chloride	[61789-71-7]	CAS	94	114
di-(tallow fatty acid) ester of di-2-hydroxyethyldimethyammonium chloride		CAS	>99	80
N-methyl-*N*,*N*-bis(2-($C_{16/18}$-acyloxy)ethyl)-*N*-hydroxyethylammonium methosulfate	[157905-74-3]	CAS	>90	102
ditallow ester of 2,3-dihydroxypropane-trimethylammonium chloride		CAS	>99	81

been studied (295). Applications as surface disinfectants, antimicrobials, and *in vitro* microbiocidals have also been reported. Examples of ester-type quaternaries are shown in Figure 4.

11.9. Uses. Uses of quaternary ammonium compounds range from surfactants to germicides and encompass a number of diverse industries (see Table 9).

Fabric Softening. The use of quaternary surfactants as fabric softeners and static control agents can be broken down into three main household product types: rinse cycle softeners; tumble dryer sheets; and detergents containing softeners, also known as softergents. Rinse cycle softeners are aqueous dispersions of quaternary ammonium compounds designed to be added to the wash during the last rinse cycle (191,195,197,203). Original products contained from 3–8% quaternary ammonium compound, typically di(hydrogenated tallow)alkyldimethylammonium chloride [61789-80-8] (DHTDMAC). During the 1980s and early 1990s, rinse cycle softeners went through significant changes as the active concentration of the dispersions was increased to reduce packaging and solid waste. Refills were introduced that had cationic activity of 16–27%. These products are meant to be added to a regular-strength softener bottle [typically 64 oz (0.9 kg)] and diluted. As of 1995, the latest innovation was the ultrafabric softener. This product, also formulated to contain from 16–27% cationic activity, is designed to be used without dilution. The actual dosage to the washer was decreased to approximately one fluid ounce (29 mL) from the older standard of 3–4-fluid oz (87–116 mL). Although DHTDMAC is a widely employed softener, the use of imidazoline and amidoamine quaternaries has increased because these latter are easier to formulate into high active systems. The combination of DHTDMAC, imidazoline, and amidoamine is used to maximize softening performance and facilitate handling and formulation.

In 1991, the European fabric softener market took a sharp turn. Producers in Germany, the Netherlands, and later in Austria and Switzerland voluntarily gave up the use of DHTDMAC (290) because of pressure from local environmental authorities, who gave an environmentally hazardous classification to DHTDMAC. A number of esterquats were developed as candidates to become successors to DHTDMAC (see Fig. 8). The ester group facilitates biodegradation. The esterquat is now the molecule of choice in North America as well, accounting for well over the half the volume of cationic surfactants used in this market segment. Figure 8 shows consumption of fabric softening actives by type for 1997.

Tumble dryer sheets contain a quaternary ammonium compound formulation applied to a nonwoven sheet typically made of polyester or rayon (190,192) (see Nonwoven fabrics). These sheets are added with wet clothes to the tumble dryer. Although these products afford some softening to the clothes, their greatest strength is in preventing static charge buildup on clothes during the drying cycle and during wear. A nonionic surfactant, such as an ethoxylated alcohol or fatty acid, is typically used in combination with the quaternary ammonium compound. The nonionics are known as release agents (qv) or distribution agents. More efficient transfer of the quaternary from the substrate to the drying fabric can be obtained.

Detergents containing softeners are also produced (194) (see Detergency). These softergents are made from complex formulas in order to accomplish both detergency and softening during the wash cycle. These formulations typically

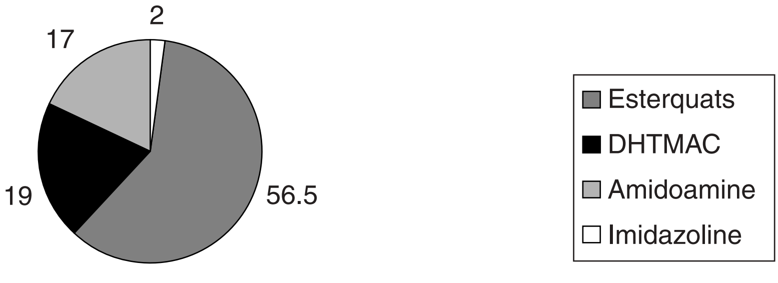


Fig. 8. Fabric softening consumption of cationics by type (1997 total is 94.5 M metric tons).

contain quaternary ammonium compounds mixed with other materials such as clays (qv) for softening, in conjunction with the typical nonionic and anionic cleaning surfactant. The consumer benefits of quaternaries are fabric softening, antistatic properties, ease of ironing, and reduction in energy required for drying.

Hair Care. Quaternary ammonium compounds are the active ingredients in hair conditioners (88–97,297). Quaternaries are highly substantive to human hair because the hair fiber has anionic binding sites at normal pH ranges. Surface analysis by X-ray photoelectron spectroscopy (XPS) has shown specific 1:1 (ionic) interaction between cationic alkyl quaternary surfactant molecules and the anionic sulfonate groups present on the hair surface (298). The use of quaternaries as hair conditioners can be broken down into creme rinses and shampoo conditioners.

Creme rinses are applied to the hair after washing. Frequently used quaternaries in creme rinses are dodecyltrimethylammonium chloride [112-00-5], dimethyloctadecyl(pentaethoxy)ammonium chloride, benzyldimethyloctadecylammonium chloride [122-19-0], and dimethyldioctadecylammonium chloride [107-64-2] (89–92,94).

Conditioning shampoos are formulations that contain anionic surfactants for cleaning hair and cationic surfactants for conditioning (97,259,297). The quaternary ammonium compounds most often used are either trihexadecylmethylammonium chloride [71060-72-5], ethoxylated quaternaries, or one of the polymeric quaternaries. The polymeric quaternaries have either a natural or a synthetic backbone and numerous quaternary side functions. The polymer may offer an advantage by showing a high degree of affinity to the human hair surface and providing better compatibility with the other ingredients of conditioner shampoos (299).

Regardless of how the conditioner is applied or what the structure of the quaternary is, benefits provided to conditioned hair include the reduction of combing forces, increased luster, and improved antistatic properties.

Germicides. The third largest market for quaternaries is sanitation (300). Generally, quaternaries offer several advantages over other classes of sanitizing chemicals, such as phenols, organohalides, and organomercurials, in that quaternaries are less irritating, low in odor, and have relatively long activity (301). The first use of quaternaries in the food industry occurred in the dairy industry for the sanitization of processing equipment. Quaternaries find use as disinfectants and sanitizers in hospitals, building maintenance, and food processing (qv) (302–310); in secondary oil recovery for drilling fluids (152–156); and in cooling water applications (see DISINFECTANTS AND ANTISEPTICS; PETROLEUM). Quaternaries have also received extensive attention for use as a general medicinal antiseptics (161) and in the pharmaceutical area as skin disinfectants and surgical antiseptics (162). In addition, quaternaries have been used in the treatment of eczema and other dermatological disorders as well as in contraceptive formulations (see CONTRACEPTIVES) (163) and ocular solutions for contact lenses (qv) (164).

Alkylbenzyldimethyl quaternaries (ABDM) are used as disinfectants (107) and preservatives. The most effective alkyl chain length for these compounds is between 10 and 18 carbon atoms. Alkyltrimethyl types, alkyldimethylbenzyl types, and didodecyldimethylammonium chloride [3401-74-9] exhibit excellent germicidal activity (302–310). Dialkyldimethyl types are effective against anaerobic bacteria such as those found in oil wells (152–156). One of the most effective and widely used biocides is didecyldimethylammonium chloride [7173-57-5].

Organoclays. Another large market for quaternary ammonium salts is the manufacture of organoclays, ie, organomodified clays (260). Clay particles are silicate minerals that have charged surfaces and that attract cations or anions electrostatically. Organoclays are produced by ion-exchange (qv) reaction between the quaternary ammonium salt and the surface of the clay particles (137,138,174,311). The quaternary ammonium salt displaces the adsorbed cations, usually sodium or potassium, producing an organomodified clay. The new modified clay exhibits different behavior from that of the initial clay. Most importantly, it is preferentially wet by organic liquids and not by water.

The main use of these clays is to control, or adjust, viscosity in nonaqueous systems. Organoclays can be dispersed in nonaqueous fluids to modify the viscosity of the fluid so that the fluid exhibits non-Newtonian thixotropic behavior. Important segments of this area are drilling fluids, greases (137,138), lubricants, and oil-based paints. Quaternaries used to produce organoclays are dimethyldi(hydrogenated tallow)alkylammonium chloride [61789-80-8], dimethyl(hydrogenated tallow)alkylbenzylammonium chloride [61789-72-8], and methyldi(hydrogenated tallow)alkylbenzylammonium chloride [68391-01-5].

Miscellaneous Uses. *Phase-Transfer Catalysts.* Many quaternaries have been used as phase-transfer catalysts (PTC). A PTC increases the rate of reaction between reactants in different solvent phases. Usually, water is one phase and a water-immiscible organic solvent is the other. An extensive amount has been published on the subject of PTC (257). Both the industrial applications in commercial manufacturing processes (312) and their synthesis (313) have been reviewed. Common quaternaries employed as phase-transfer agents include benzyltriethylammonium chloride [56-37-1], tetrabutylammonium bromide [1643-19-2], tributylmethylammonium chloride [56375-79-2], and hexadecylpyridinium chloride [123-03-5].

Polyamine-Based Quaternaries. Another important class of quaternaries are the polyamine based or polyquats. Generally, polyamine-based quaternaries have been used in the same applications as their monomeric counterparts (314). Discussions, including the use of polymeric quaternaries in laundry formulations (315) and in the petroleum industry as damage control agents (316), have been published.

Perfluorinated Quaternaries. Perfluorinated quaternaries are another important, but smaller, class of quaternary ammonium compounds. In general, these are similar to their hydrocarbon counterparts but have at least one of the hydrocarbon chains replaced with a perfluoroalkyl group. These compounds are generally much more expensive than hydrocarbon-based quaternaries, so they must offer a significant performance advantage if they are to be used. Production volumes of perfluorinated quaternary ammonium compounds are significantly smaller than those of other classes. Many of these quaternaries have proprietary chemical structures. They are used in water-based coating applications to promote leveling, spreading, wetting, and flow control.

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CHARLES W. WESTON
Freeport Research and Engineering Company
JOHN R. PAPCUN
Atotech
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Akzo Nobel Chemicals, Inc.