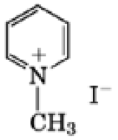
Kirk-Othmer Encyclopedia of Chemical Technology.

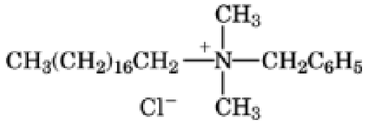
QUATERNARY AMMONIUM COMPOUNDS

There are a vast number of quaternary ammonium compounds or quaternaries (1). 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 204,000 metric tons of quaternary ammonium compounds are produced annually in the United States (2). 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 quaternary 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] (**1**); benzyldimethyloctadecylammonium chloride [122-19-0] (**2**); and di(hydrogenated tallow)alkyldimethylammonium chloride [61789-80-8] (**3**), where $R = C_{14} - C_{18}$.

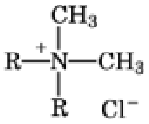


(1)



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

(2)



$$\begin{array}{c} CH_3 \\ | \\ R-\overset{+}{N}-CH_3 \\ | \\ R \quad Cl^- \end{array}$$

(**3**)

1. Nomenclature

Quaternary ammonium compounds are usually named as the substituted ammonium salt. The anion is listed last (3). 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 1.

Table 1. Selected Quaternary Ammonium Compounds and Their Applications

Compound	CAS Registry Number	Application and function	Comments	Reference
		Agricultural chemicals		
cetyltrimethylammonium chloride	[112-02-7]	phase-transfer catalyst	used in production of furfuryl alcohol	4
dodecyltrimethylammonium bromide	[1119-94-4]	phase-transfer catalyst	used in production of furfuryl alcohol	4
dicocoalkyldimethylammonium chloride	[61789-77-3]	surfactant, flocculating agent	for herbicidal compositions	(5–8)
soyaalkyltrimethylammonium chloride	[61790-41-8]	surfactant, flocculating agent	for herbicidal compositions	(5–8)
2-chloroethyltrimethylammonium chloride	[999-81-5]	surfactant	used in formulations for plant growth regulation	(9–11)
trimethyloctadecylammonium chloride	[112-03-8]	surfactant	used in formulations for plant growth regulation	(9–11)
dimethyldioctadecylammonium chloride	[107-64-2]	surfactant, flocculating agent	for sugar liquor purification	12
dihexadecyldimethylammonium chlorides		surfactant, flocculating agents	for sugar liquor purification	12
short-chain alkyl quaternaries		fungicides, mold inhibitors	for protection of seeds and agricultural products	(13, 14)
imidazoline-type quaternaries		fungicides, mold inhibitors	for protection of seeds and agricultural products	(13, 14)
		Chemical industry		
benzylcetyldimethylammoniumchloride	[122-18-9]	defoaming agent	used in the precipitation of $NaCO_3$ precursor crystals such as $NaHCO_3$	15
trimethyloctadecylammonium chloride	[112-03-8]	surfactant	for decolorization and purification of halogenated silane	16
C_{10}–C_{18}-ethoxylated quaternaries		surfactants	for coating polystyrene beads in the manufacture of lightweight concrete	17
dibenzyldimethylammonium chloride	[100-94-7]	directing agent	used in the preparation of cyrstalline silicate catalysts	(18–20)

Table 1. ***Continued***

Compound	CAS Registry Number	Application and function	Comments	Reference
DL-3-cyano-2-hydroxypropyltrimethylammonium hydroxide		optically active counterion	for production of optically active L-carnitine (vitamin B_T) for pharmaceuticals	21
many compounds claimed[a]		antistatic	for antistatic materials containing polyethylene glycol and poly-(vinyl chloride)	22
		Coatings and paints		
dodecyltrimethylammonium chloride	[112-00-5]	leveling agent	enhances the leveling activity of fluorochemical coatings	23
ethoxylated quaternaries		surfactants	stabilizes epoxy–polyamide coatings and imparts sag resistance	(24, 25)
dialkyldiethoxylated quaternaries		foaming agents	for textile coating formulations	(26–28)
trialkyl (C_8–C_{10}) methyl-ammonium chlorides		surfactants	solubilizes hexavalent chromium compounds in paints	29
cocoalkylmethyldiethoxylated quaternaries		cations	for the preparation of organo-modified clays for paint thickeners	30
		Cosmetics		
dodecyltrimethylammonium chloride	[112-00-5]	combing aids, conditioners, creme rinses, antistatic	for hair conditioning formulations, creme rinses, and shampoos	(31–39)
quaternary ammonium-substituted sterol derivatives		surfactants	in cosmetic formulations	40
dimethyl and trimethyl alkyl quaternaries		emulsifiers	produces water-in-oil emulsions	41
quaternary ammonium derivatives of lanolinic acid		surfactants	produces high solids, clear costme-tic formulations	42
		Detergents		
dicocoalkyldimethylammonium chloride	[61787-77-3]	surfactant	for liquid crystal detergent composition for cold-temperature cleaning	43
dialkyldiethoxylatedammonium chlorides		surfactants	for formulations removing road film from transportation vehicles	44
didodecyldimethylammonium chloride	[3401-74-9]	surfactant	removes iron sulfate from metal surfaces and acid cleaning compositions	(45–47)
octadecyltrimethylammonium chloride	[112-03-8]	surfactant	removes iron sulfate from metal surfaces and acid cleaning compositions	(45–47)
ditallowalkyldimethylammonium chloride	[68783-78-8]	surfactant	for improved perfume deposition on hard surfaces	48
alkylbenzyldimethyl quaternaries		biocides	for liquid disinfectant laundry detergent composition	49
many compounds claimed[b]		processing aids	incorporates positively charged nitrogen atom into spray-dried nonionic detergents to reduce autoxidation	50
many compounds claimed[c]		surfactants	for hard-surface cleaning formulations	(51, 52)
		Electronics		

Table 1. ***Continued***

Compound	CAS Registry Number	Application and function	Comments	Reference
dodecyltrimethylammonium chloride	[112-00-5]	etching solution, leveling agent	eliminates nonuniformities in etch rates as a result of variations in mass transport conditions	53
hexadecyltrimethylammonium chloride	[112-02-7]	etching solution, leveling agent	eliminates nonuniformities in etch rates as a result of variations in mass transport conditions	53
octadecyltrimethylammonium chloride	[112-03-8]	etching solution, leveling agent	eliminates nonuniformities in etch rates as a result of variations in mass transport conditions	53
hydroxyethyltrimethylammonium hydroxide	[123-41-1]	remover solution	for manufacture of semiconductor devices	54
		Mining and flotation		
hydroxy-propoxylated quaternaries		surfactants	purifies calcium carbonate ore by removing silicate impurities through reverse flotation	(55, 56)
dialkyldimethyl quaternaries		surfactants	purify calcium carbonate ore by removing silicate impurities through reverse flotation	(55, 56)
didodecyldimethylammonium chloride	[3401-74-9]	flocculent	recovery of precious metals by froth flotation	(57–62)
		Paper manufacture		
di(hydrogenated tallow)-alkyldimethylammonium chloride	[61789-80-8]	softener	gives improved absorbency and softness to paper towels and tissues	(63–66)
(3-chloro-2-hydroxypropyl)-trimethylammonium chloride	[3327-22-8]	surfactant	stabilizes pulp bleaching formulations	(67–69)
cetyltrimethylammonium chloride	[112-02-7]	flocculent	precipitates lignins and lignin derivatives from pulp mill waste waters	70
		Petroleum		
dicocoalkyldimethylammonium chloride	[61789-77-3]	counterion	used to prepare thiomolybdates for antifriction additives in oils and greases	(71–73)
tallowalkyltrimethyl quaternaries		suspending agents	stabilize coal-oil slurries	(74–78)
imidazoline-type quaternaries		suspending agents	stabilize coal-oil slurries	(74–78)
ethoxylated quaternaries		suspending agents	stabilize coal-oil slurries	(74–78)
dioctadecyldimethylammonium chloride	[107-64-2]	organo-modified clays	used in polyolefin-based greases	(79, 80)
diethoxylatedtallowmethyl quaternaries		dispersants	stabilizes drilling fluids and minimizes solids disintegration in down-hole fluids	81
tetraethoxylated quaternaries		corrosion inhibitors, demulsifiers	crude-oil refining	82
benzyldodecyldimethylammonium hydroxide	[10328-35-5]	surfactant	used in catalyst preparation for the oxidation of mercaptans in sour petroleum distillates	(83–89)
dibenzyldimethylammonium sulfocyanate		suspending agent	for sludge recovery in storage vessels	90
alkylbenzyldimethylammonium chlorides		complexing agents	for regeneration of used oils	91

Table 1. ***Continued***

Compound	CAS Registry Number	Application and function	Comments	Reference
trimethyloctadecylammonium hydroxide	[15461-40-2]	catalyst	for removing elemental sulfur from refined petroleum products	(92, 93)
many compounds claimed[d]		biocides	for drilling fluids, enhanced oil recovery, and hydraulic fluid compositions	(94, 97)
		Pharmaceuticals and dermopharmacy		
quaternary ammonium salicylates		microbiocides	as bactericidal and keratolytic agents in the treatment of dermatoses	(98, 99)
quaternary ammonium retinoates		microbiocides	as bactericidal and keratolytic agents in the treatment of dermatoses	(98, 99)
benzyloctadecyldimethyl-ammonium chloride	[122-19-0]	germicide	in contraceptive formulations	100
dodecyldimethyl (2-phenoxyethyl)-ammonium bromide	[538-71-6]	antimicrobial	in aqueous ocular solutions for contact lenses	101
phosphate-type quaternaries		cleaners and disinfectants	formulated for preoperative skin scrubs, treatment for poison ivy and other skin disorders	(102, 103)
imidazoline-type quaternaries		cleaners and disinfectants	formulated for preoperative skin scrubs, treatment for poison ivy and other skin disorders	(102, 103)
		Photographic industry		
disoyaalkyldimethylammonium ethosulfate		antistatic agent	added to developer rolls to increase productivity	104
didodecyldimethylammonium chloride	[3401-74-9]	cationic activator	in recovery solution for a silver salt photographic plate in offset printing	105
alkynyl-substituted heterocyclic quaternaries		emulsifiers	for silver halide photographic materials	(106–108)
		Polymer industry		
dialkyldiethoxylated quaternaries		antistatics	for producing expandable styrene polymer particles having antistatic and antilumping properties	(109–113)
didodecyldimethylammonium molybdates		smoke retardants	as additives for vinyl chloride polymer compositions	114
dialkyldimethylammonium chlorides		organoclays	as thixotropic agents in thermoset resins containing unsaturated polyesters	115
		Textile manufacture		
dodecyltrimethyl quaternaries		dye bath additives	for dyeing jute backing of multi-level nylon carpet; dyeing assistants for polyamide fibers	(116, 117)
imidazoline-type quaternaries		dye bath additives	for dyeing jute backing of multi-level nylon carpet; dyeing assistants for polyamide fibers	(116, 117)
ethoxylated quaternaries		antistatics	for woven and nonwoven fibers from natural and synthetic sources	(118–120)
ditallowalkyldimethylammonium chloride	[68783-78-8]	germicide	as disinfecting cleaning intensifier for dry cleaning	121
dodecyltrimethylammonium chloride	[112-00-5]	emulsifier	as cationic emulsifier for fluoro-carbon finishes	122

Table 1. ***Continued***

Compound	CAS Registry Number	Application and function	Comments	Reference
		Other industries		
dicocoalkyldimethylammonium chloride	[61789-77-3]	surfactant in automotive services	a key ingredient in protective polish formulations	(123–125)
hexadecyltrimethylammonium hydroxide	[505-86-2]	surfactant in analytical chemistry	mobile-phase modifier for chromatographic determination of ions by reverse-phase liquid chromatography	126
di(hydrogenated tallow)alkyldi-methylammonium chloride (DHTDMAC)	[61789-80-8]	household fabric softening, antistatic agent	for fabric softener compositions at the industrial and consumer level; rinse additive and impregnated substance compo-sition for tumble dryers	(127–144)
distearyldimethylammonium methosulfate	[3843-16-1]	positive-charge carrier, charge control agent in electro-photographic imaging	as a charge control agent in electrographic toner and developer compositions	(145–150)
didodecyldimethylammonium chloride	[3401-74-9]	house biocide, fungicide, algicide, and germicide	cleaning and disinfecting formulations	(151–159)
cetyltrimethylammonium bromide	[57-09-0]	biocide for wastewater treatment	for disinfectant in wastewater treatment	160
many compounds claimed[e]		organoclays for wastewater	for removal of aromatic contaminants, such as benzene from water and air	161
many compounds claimed[f]		coupling agents for rubber	for incorporation of carbon black into natural rubber compositions	162

[a] (3-Dodecylamidopropyl)trimethylammonium methylsulfate [10595-49-0] is an example.
[b] Trimethyltallowalkylammonium chloride [8030-78-2] is an example.
[c] Benzyldimethyl-2-hydroxydodecylammonium isononanoate is an example.
[d] Alkylbenzyldimethylammonium chlorides are an example.
[e] Tetramethylammonium chloride [75-57-0] is an example.
[f] Ditallowalkyldimethylammonium chloride [68783-78-8] is an example.

2. Properties

2.1. Physical Properties

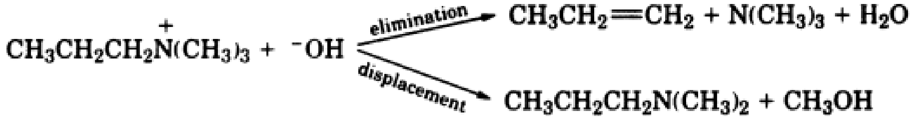
Most quaternary compounds are solid materials that have indefinite melting points and decompose on heating. Physical properties are determined by the chemical structure of the quaternary ammonium compound as well as any additives such as solvents. The simplest quaternary ammonium compound, tetramethylammonium chloride [75-57-0], is very soluble in water (163) and insoluble in nonpolar solvents. As the molecular weight of the quaternary compound increases, solubility in polar solvents decreases and solubility in nonpolar solvents increases (164–166). 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 ($\sim$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 (167). 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 (168) that give rise to many practical applications. 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.

2.2. Chemical Properties

Reactions of quaternaries can be categorized into three types (169): Hoffman eliminations, displacements, and rearrangements. Thermal decomposition of a quaternary ammonium hydroxide to an alkene, tertiary amine, and water is known as the Hoffman elimination (eq. **1a**) (170). This reaction has not been used extensively to prepare olefins. Some cyclic olefins, however, are best prepared this way (171). Exhaustive methylation, followed by elimination, is known as the Hoffman degradation and is important in the structural determination of unknown amines, especially for alkaloids (qv) (172).

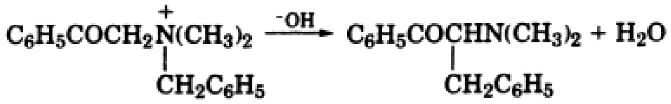


$$CH_3CH_2CH_2\overset{+}{N}(CH_3)_3 + {}^{-}OH \xrightarrow{\text{elimination}} CH_3CH_2{=}CH_2 + N(CH_3)_3 + H_2O \qquad (1a)$$

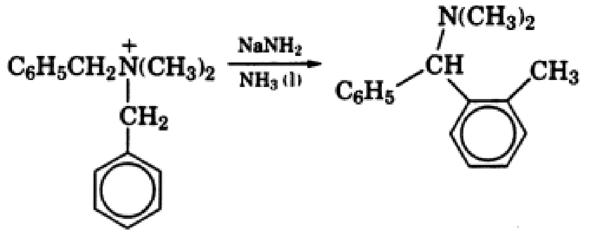
$$CH_3CH_2CH_2\overset{+}{N}(CH_3)_3 + {}^{-}OH \xrightarrow{\text{displacement}} CH_3CH_2CH_2N(CH_3)_2 + CH_3OH \qquad (1b)$$

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 Hoffman elimination (173). 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 (174).

The Stevens rearrangement (eq. **2**) is a base-promoted 1,2-migration of an alkyl group from a quaternary nitrogen to carbon (175, 176). 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 (177, 178).



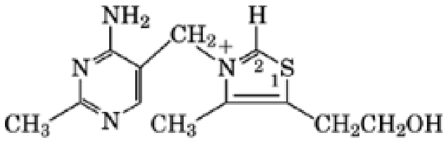
$$C_6H_5COCH_2\underset{CH_2C_6H_5}{\overset{+}{N}}(CH_3)_2 \xrightarrow{{}^{-}OH} C_6H_5CO\underset{CH_2C_6H_5}{C}HN(CH_3)_2 + H_2O \qquad (2)$$



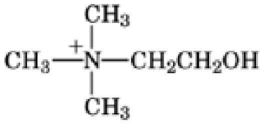
(3)

3. Naturally Occurring Quaternaries

Naturally occurring quaternary ammonium compounds have been reviewed (179). Many types of aliphatic, heterocyclic, and aromatic derived quaternary ammonium compounds are produced both in plants and invertebrates. Examples include thiamine (vitamin B_1) (**4**) (see Vitamins); choline(qv) [62-49-7] (**5**); and acetylcholine (**6**). These have numerous biochemical functions. Several quaternaries are precursors for active metabolites.

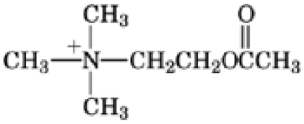


(**4**)



$CH_3-\overset{+}{N}(CH_3)_2-CH_2CH_2OH$

(**5**)



$CH_3-\overset{+}{N}(CH_3)_2-CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$

(**6**)

Thiamine (**4**) 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. Acetylcholine 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.

4. Analytical Test 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 (180). These include sampling, color, moisture, amine value, ash, iodine value, average molecular weight, pH, and flash point.

Determination of the activity of quaternary samples falls into four categories (181, 182). 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 (183). This process, essentially a microtitration, is often referred to as the Epton titration (184, 185). 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 (186). This is a macro method that is convenient and relatively simple to perform. Third is the titration of the halide anion (Volhardt type) or perchloric acid titration in acetic anhydride (187). 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. 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 chain length composition of quaternaries can be determined by gas chromatography (qv) (188). 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 onto Apiezon grease columns treated with potassium hydroxide. 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 (189, 190). 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 (191), 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 (192). 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 (193).

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 (194).

5. Toxicology and Environmental Fate

Some quaternary ammonium compounds are potent germicides (164, 195, 196), 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 (197). Acute toxicity at low (1 mg/L) levels has been reported in invertebrates, snails, and fish (198, 199). In plant systems, growth inhibition of green algae and great duckweed occurs at 3–5 mg/L (200). Acute oral

Table 2. Biodegradation Data[a] for Quaternaries[b]

Chloride compound	CAS Registry Number	Concentration of actives, mg/L	Quantity biodegraded in 48 h, %
trimethyltallowalkylammonium	[8030-78-2]	5	95.3
trimethylsoyaalkylammonium	[61790-41-8]	5	94.1
cocoalkyltrimethylammonium	[61789-18-2]	5	82.0
di(hydrogenated tallow)alkyl-dimethylammonium	[61789-80-8]	7.5	79.0
dodecyltrimethylammonium	[112-00-5]	5	98.3
trimethyloctadecylammonium	[112-03-8]	5	98.4
hexadecyltrimethylammonium	[112-02-7]	5	81.9
dicocoalkyldimethylammonium	[61789-77-3]	5	80.3
benzyldi(hydrogenated tallow)-alkylmethylammonium	[61789-73-9]	7.5	79.0

[a] Ref. 204.

[b] Aerated, acclimated cultures from raw city sewage.

toxicity data (albino rats) show most structures to have an LD_{50} in the range of 100–5000 mg/kg (201). Many quaternaries are considered to be moderately to severely irritating to the skin and eyes.

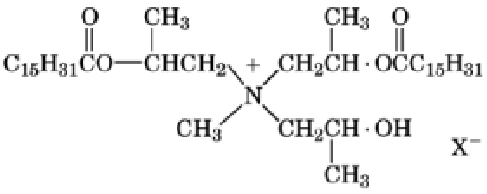
Most uses of quaternary ammonium compounds can be expected to lead to these compounds' eventual release into wastewater treatment systems except for those used in drilling muds. Useful properties of the quaternaries as germicides can make these compounds potentially toxic to sewer treatment systems. It appears, however, that quaternary ammonium compounds are rapidly degraded in the environment and strongly sorbed by a wide variety of materials. Under normal circumstances these compounds are unlikely to pose a significant risk to microorganisms in wastewater treatment systems (202). Microbial populations acclimate readily to low levels of quaternary compounds and biodegrade them. Environmental toxicity and stability of these compounds have been described (202, 203). Biodegradation data for some common quaternaries are given in Table 2.

There are two reasons why the concentration of quaternaries is believed to remain at a low level in sewage treatment systems. First, quaternaries appear to bind anionic compounds and thus are effectively removed from wastewater by producing stable, lower toxicity compounds (205). Anionic compounds are present in sewer systems at significantly higher concentrations than are cations (202). Second, the nature of how most quaternaries are used ensures that their concentrations in wastewater treatment systems are always relatively low but steady. Consumer products such as fabric softeners, hair conditioners, and disinfectants contain only a small amount of quaternary compounds. This material is then diluted with large volumes of water during use.

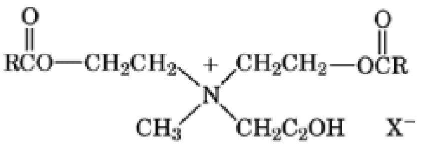
The threat of accidental misuse of quaternary ammonium compounds coupled with potential harmful effects to sensitive species of fish and invertebrates has prompted some concern. Industry has responded with an effort to replace the questionable compounds with those of a more environmentally friendly nature. Newer classes of quaternaries, eg, esters (206) and betaine esters (207), have been developed. These materials are more readily biodegraded. The mechanisms of antimicrobial activity and hydrolysis of these compounds have been studied (207). Applications as surface disinfectants, antimicrobials, and *in vitro* microbiocidals have also been reported. Examples of ester-type quaternaries are shown in Figure 1.

6. Synthesis and Manufacture of Quaternaries

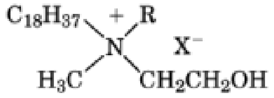
A wide variety of methods are available for the preparation of quaternary ammonium compounds (218–220). Significantly fewer can be used on a commercial scale. A summary of the most commonly used commercial methods is given herein.

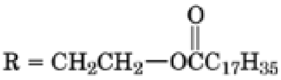


(7)



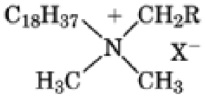
(8)



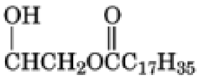


(9) $R = CH_2CH_2{-}O\overset{\overset{O}{\|}}{C}C_{17}H_{35}$

(10) $R = (CH_2)_3NH\overset{\overset{O}{\|}}{C}(CH_2)_3O\overset{\overset{O}{\|}}{C}C_{18}H_{37}$

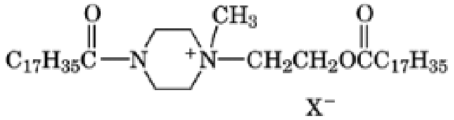


(11) $R = CH_2O\overset{\overset{O}{\|}}{C}C_{15}H_{31}$

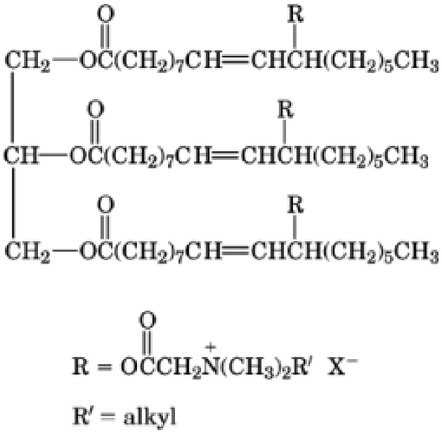


(12) $R = \underset{}{\overset{\overset{OH}{|}}{C}}HCH_2O\overset{\overset{O}{\|}}{C}C_{17}H_{35}$

(13) $R = \overset{\overset{CH_3}{|}}{C}HO\overset{\overset{O}{\|}}{C}C_{15}H_{31}$



(14)



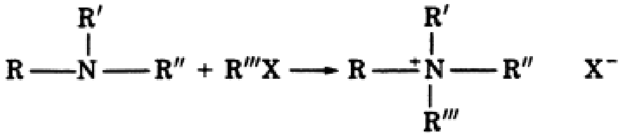
(15)

Fig. 1. Quaternary esteramines: (**7**) (208); (**8**) (209, 210); (**9**) (211, 212); (**10**) (213); (**11**) (214); (**12**) (215); (**13**) (136); (**14**) (216); and (**15**) (217).

Quaternary ammonium compounds are usually prepared by reaction of a tertiary amine and an alkylating agent (eq. **4**). The most widely used alkylating agents are listed in Table 3. 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.

Table 3. Typical Alkylating Agents for Preparation of Quaternaries

Alkylating agent	CAS Registry Number	Chemical formula	Quaternary using R_3N	
methyl chloride	[74-87-3]	CH_3Cl	$R_3N^+CH_3$	Cl^-
dimethyl sulfate	[77-78-1]	$(CH_3)_2SO_4$	$R_3N^+CH_3$	$CH_3SO_4^-$
diethyl sulfate	[64-67-5]	$(CH_3CH_2)_2SO_4$	$R_3N^+CH_2CH_3$	$CH_3CH_2SO^-{}_4$
benzyl chloride	[100-44-7]	$C_6H_5CH_2Cl$	$R_3N^+CH_2C_6H_5$	Cl^-



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

Equation **4** can be classified as S_N2, ie, substitution nucleophilic bimolecular (221). 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, isopropanol, 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 (222), 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.

$$RNH_2 + 2\ CH_2O \longrightarrow_{H_2/\text{catalyst}} RN(CH_3)_2 \tag{5}$$

$$R_2NH + CH_2O \longrightarrow_{H_2/\text{catalyst}} R_2NCH_3 \tag{6}$$

Dialkyldimethyl and alkyltrimethyl quaternaries can be prepared directly from secondary and primary amines as shown in equations 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 (223, 224). Furthermore, products such as inorganic salt and water must be removed from the quaternary. The salt represents a significant disposal problem.

$$R_2NH + 2\ CH_3Cl + NaOH \longrightarrow R_2^+N\,(CH_3)_2\ Cl^- + NaCl + H_2O \tag{7}$$

$$RNH_2 + 3\ CH_3Cl + 2\ NaOH \longrightarrow R\overset{+}{N}(CH_3)_3Cl^- + 2\ NaCl + 2\ H_2O \tag{8}$$

6.1. 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.

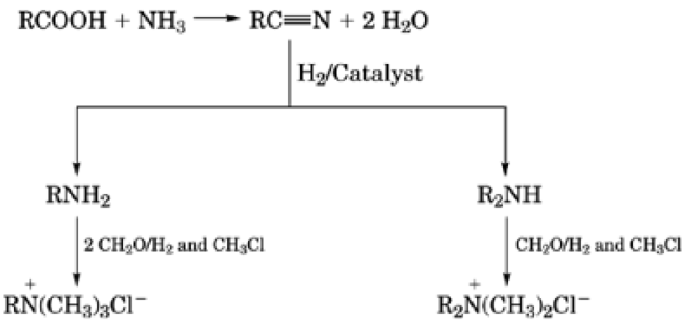


Fig. 2. Quaternaries from fatty nitriles where R is a fatty alkyl group.

6.1.1. 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. 2) (see Fats and fatty oils) (225). The nitriles are then reduced to the amines. A variety of reducing agents may be used (226). Catalytic hydrogenation over a metal catalyst is the method most often used on a commercial scale (227). Formation of secondary and tertiary amine side-products can be hindered by the addition of acetic anhydride (228) or excess ammonia (229). In some cases secondary amines are the desired products.

6.1.2. 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. 3). 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 which 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.

6.1.3. 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. 4).

6.2. Quaternized Esteramines

Esterquaternary ammonium compounds or esterquats can be formulated into products that have good shelf stability (209). Many examples of this type of molecule have been developed (see Fig. 1).

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 4 (210), where R is a fatty alkyl group. Reaction

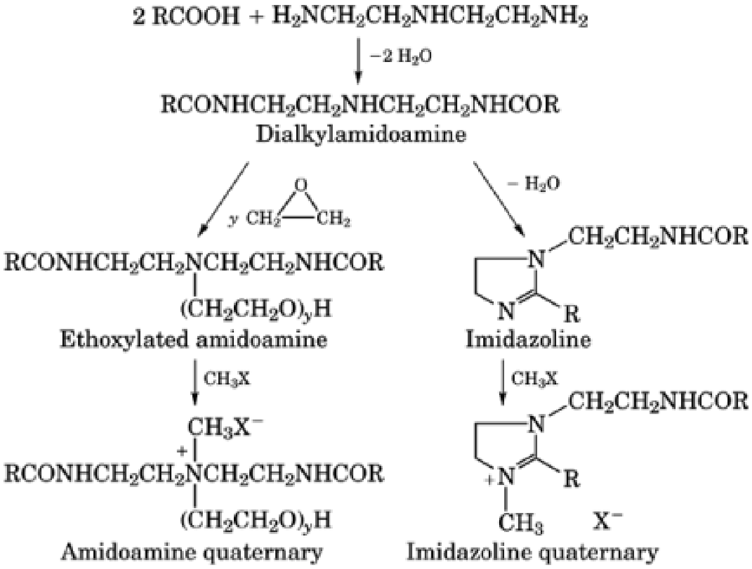


Fig. 3. Quaternaries from amidoamines and imidazolines where R is a fatty alkyl group.

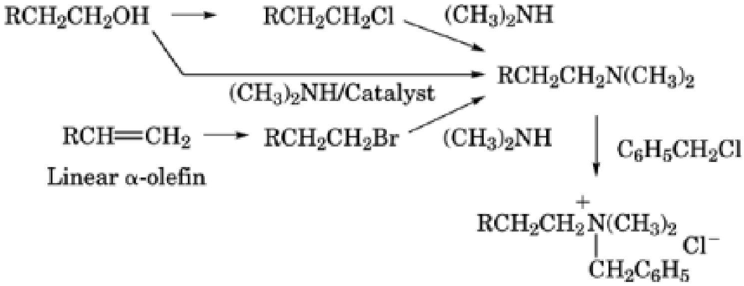


Fig. 4. Quaternaries from α-olefins of fatty alcohols where R is a fatty alkyl group. The product is alkylbenzyldimethyl quaternary.

occurs at 75–115°C in the presence of sodium methoxide catalyst. Free fatty acids (230) and glycerides (231) can be used in place of the fatty acid methylester.

7. Economic Aspects

A summary of the U.S. economic perspective, approximate production volumes, average retail prices, and leading producers is given in Table 4. Other commercial products include diallyldimethylammonium chloride [7398-69-8], produced by CPS Chemical Company; di(hydrogenated tallow)alkyldimethylammonium methosulfate [61789-81-9], produced by Akzo Nobel and High Point Chemical Corporation; and tetrabutylammonium bromide [1643-19-2], produced by Zeeland Chemical. 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 (233). 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 Witco. The combined annual production of these two companies accounts for about 80% of the fatty nitrogen products manufactured in the United States. The remaining production is divided among smaller-volume producers. Nearly all fatty nitrile plants require considerable technological expertise and capital investment to operate. The largest-volume product types in the 1990s are di(hydrogenated tallow)alkyldimethylammonium (DHT) quaternaries, which are sold as the chloride or methyl sulfate salts (234). The principal U.S. producers of imidazoline quaternaries are Akzo Nobel, Witco, Croda, and Lonza.

The single largest market for quaternary ammonium compounds is as fabric softeners. In 1993 this market accounted for over 50,000 metric tons of quaternaries in the United States (235). Consumption of these products is increasing at an annual rate of about 2–3%. The hair care market consumed over 9000 metric tons of quaternary ammonium compounds in 1992 (236). The annual consumption for organoclays is estimated at 12,700 metric tons (237). Esterquats have begun to gain market share in Western Europe and growth is expected to continue.

8. Uses

Uses of quaternary ammonium compounds range from surfactants to germicides and encompass a number of diverse industries (see Table 1).

8.1. 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 (131, 135, 137, 143). 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 ounces (0.9 kg)) and diluted. As of 1995, the latest innovation was the ultra-fabric 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 ounces (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 (238) 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. 1). The ester group facilitates biodegradation.

Tumble dryer sheets contain a quaternary ammonium compound formulation applied to a nonwoven sheet typically made of polyester or rayon (130, 132) (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,

Table 4. 1993 U.S. Economic Aspects of Quaternaries[a]

Compound	CAS Registry Number	Production, t	Sales, t	Sales, $\$ \times 10^3$	Average retail price, \$/kg	Manufacturer[b]
benzyldimethyloctadecylammonium chloride	[122-19-0]	826	698	1,696	2.43	Cr, GC, L, P, RP, W
benzyltrimethylammonium chloride	[56-93-9]	1,732	1,132	1,971	1.74	HPC, RSA, Sy, W
benzylcocoalkyldimethylammonium chloride	[61789-71-7]	467	480	1,350	2.81	A, En, Ex, Gr, HP, J, W
assorted benzyldimethylalkylammonium chlorides		8,580	4,348	18,236	4.19	HL, L, P, St, Sy
benzyldimethyltallowalkylammonium chloride	[61789-75-1]	138	140	439	3.13	B, En, W
dicocoalkyldimethylammonium chloride	[61789-77-3]	2,118	1,985	5,090	2.56	A, Ex, J, W
dodecyltrimethyl-ammonium chloride	[112-00-5]		239	702	2.93	A, J, L
hexadecyltrimethylammonium chloride	[112-02-7]	1,420	1,093	2,949	2.70	A, L, W
di(hydrogenated tallow)alkyldimethylammonium chloride	[61789-80-8]	24,009				A, En, W
oxygen-containing quaternaries (excluding amides)		2,431	1,624	4,524	2.79	Et, Ex, HC, K, L, SC
quaternary ammonium compounds with amide linkages		2,702	2,473	4,134	1.67	A, Ex, HPC, HD, I, L
quaternary ammonium compounds (cyclic) not containing oxygen		817	536	1,865	3.48	A, L
trimethyloctadecyl-ammonium chloride	[112-03-8]	27	26	91	3.48	A, Ex, W
trimethyltallowalkylammonium chloride	[8030-78-2]	1,101	931	2,821	3.03	A, En, J, W

[a] Ref. 232.

[b] Manufacturer: A = Akzo Nobel Chemicals Inc.; B = Boehme Filatex., Inc.; CPS = CPS Chemical Co., Inc.; Cr = Croda, Inc.; En = Enenco, Inc.; Et = Ethox Chemicals, Inc.; Ex = Exxon Chemical Americas; GC = Gillette Chemical Co.; Gr = Gresco, Mfg., Inc.; HP = Hart Products Corp.; HC = Henkel Corp.; HPC = High Point Chemical Corp.; HD = Hilton Davis Chemical Corp.; HL = Huntington Laboratories, Inc.; I = Inolex Chemical Co.; J = Jetco Chemicals, Inc.; K = Karlshamms; L = Lonza, Inc.; P = PPG Industries, Inc.; RSA = RSA Corp.; RP = Rhocirc; ne – Poulenc, Inc.; SC = Sandoz Chemicals Corp.; St = Stepan Co.; Sy = Sybron Chemicals, Inc.; W = Witco Corp.; and Z = Zeeland Chemical, Inc.

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 (134) (see Detergency). These softergents are made from complex formulas in order to accomplish both detergency and softening during the wash cycle. These formulations typically 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.

8.2. Hair Care

Quaternary ammonium compounds are the active ingredients in hair conditioners (31–39, 239). Quaternaries are highly substantive to human hair because the hair fiber has anionic binding sites at normal pH ranges. 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] (31–34, 36).

Conditioning shampoos are formulations that contain anionic surfactants for cleaning hair and cationic surfactants for conditioning (39, 236, 239). 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 (240).

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.

8.3. Germicides

The third largest market for quaternaries is sanitation (241). 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 (242). 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) (151–159); in secondary oil recovery for drilling fluids (94–97); and in cooling water applications (see Disinfectants and antiseptics; Petroleum). Quaternaries have also received extensive attention for use as a general medicinal antiseptics (102) and in the pharmaceutical area as skin disinfectants and surgical antiseptics (103). In addition, quaternaries have been used in the treatment of eczema and other dermatological disorders as well as in contraceptive formulations (see Contraceptives) (104) and ocular solutions for contact lenses (qv) (105).

Alkylbenzyldimethyl quaternaries (ABDM) are used as disinfectants (49) 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 (151–159). Dialkyldimethyl types are effective against anaerobic bacteria such as those found in oil wells (94–97). One of the most effective and widely used biocides is didecyldimethylammonium chloride [7173-57-5].

8.4. Organoclays

Another large market for quaternary ammonium salts is the manufacture of organoclays, ie, organo-modified clays (237). Clay particles are silicate minerals that have charged surfaces and which 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 (79, 80, 115, 161). The quaternary ammonium salt displaces the adsorbed cations, usually sodium or potassium, producing an organo-modified 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 (79, 80), lubricants, and oil-based paints. The most used commercial products in this area 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].

8.5. Miscellaneous Uses

8.5.1. Phase-Transfer Catalysts

Many quaternaries have been used as phase-transfer catalysts. A phase-transfer catalyst (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 phase-transfer catalysts (233). Both the industrial applications in commercial manufacturing processes (243) and their synthesis (244) 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].

8.5.2. 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 (245). Discussions, including the use of polymeric quaternaries in laundry formulations (246) and in the petroleum industry as damage control agents (247), have been published.

8.5.3. 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.

BIBLIOGRAPHY

"Quaternary Ammonium Compounds" in *ECT* 2nd ed., Vol. 19, pp. 859–865, by R. A. Reck, Armour Industrial Chemical Co.; in *ECT* 3rd ed., Vol. 19, pp. 521–531, by R. A. Reck, Armak Co.

Cited Publications

1. E. Jungermann, ed., *Cationic Surfactants*, Marcel Dekker, Inc., New York, 1969, Chapts. 2–5.
2. *Chemical Economics Handbook*, SRI International, Menlo Park, Calif., 1990, p. 583.8200G; Supplemental data, May 1994, 107–108.
3. J. Fletcher, O. Dermer, and R. Fox, *Nomenclature of Organic Compounds*, ACS, Washington, D.C., 1974, 189–195.
4. U.S. Pat. 5,008,410 (Apr. 16, 1991), K. Tashiro and K. Tanaka (to Sumitomo Chemical Co., Ltd.).
5. Ger. Pat. 2,506,834 (Aug. 21, 1975), R. Ford and T. Tadros (to Imperial Chemical Industries Ltd.).
6. U.S. Pat. 5,078,781 (Jan. 7, 1992), C. Finch (to Imperial Chemical Industries Ltd.).
7. Ger. Pat. 2,304,204 (Aug. 2, 1973), N. Drewe, R. Parker, and T. Tadros (to Imperial Chemical Industries Ltd.).
8. Ger. Pat. 2,352,334 (May 9, 1974), F. Hauxwell, H. Murton, and R. Brain (to Imperial Chemical Industries Ltd.).
9. U.S. Pat. 2,844,466 (July 22, 1958), A. Rogers and co-workers (to Armour and Co.).
10. U.S. Pat. 3,506,433 (Apr. 14, 1970), W. Abramitis and R. A. Reck (to Armour and Co.).
11. U.S. Pat. 4,765,823 (Aug. 23, 1988), K. Lurssen (to Bayer AG).
12. U.S. Pat. 3,698,951 (Oct. 17, 1972), M. Bennett (to Tate and Lyle Ltd.).
13. U.S. Pat. 5,017,612 (May 21, 1987), J. Nayfa (to J. Nayfa).
14. U.S. Pat. 2,740,744 (Apr. 3, 1956), W. Aoramitis and co-workers (to Armour and Co.).
15. U.S. Pat. 3,725,014 (Apr. 3, 1973), R. Poncha and co-workers (to Allied Chemical Corp.).
16. U.S. Pat. 5,210,250 (Aug. 27, 1992), I. Watanuki and co-workers (to Shin-Etsu Chemical Co.).
17. U.S. Pat. 4,398,958 (Aug. 16, 1983), R. Hodson and co-workers (to Cempol Sales Ltd.).
18. U.S. Pat. 4,636,373 (Aug. 30, 1987), M. Rubin (to Mobil Oil Corp.).
19. U.S. Pat. 4,640,829 (Aug. 30, 1987), M. Rubin (to Mobil Oil Corp.).
20. U.S. Pat. 4,642,226 (Mar. 29, 1985), R. Calvert and co-workers (to Mobil Oil Corp.).
21. U.S. Pat. 5,191,085 (Mar. 2, 1993), H. Jakob and co-workers (to Degussa AG).
22. U.S. Pat. 4,661,547 (Apr. 28, 1987), M. Harada, K. Tsukanoto, and E. Tomohiro (to Nippon Rubber Co., Ltd.).
23. U.S. Pat. 4,064,067 (Dec. 20, 1977), A. Lore (to E. I. du Pont de Nemours & Co., Inc.).
24. U.S. Pat. 4,771,088 (Jan. 15, 1987), A. Pekarkik (to Glidden Co.).
25. U.S. Pat. 4,840,980 (Feb. 29, 1988), A. Pekarkik (to Glidden Co.).
26. U.S. Pat. 4,208,485 (June 17, 1980), R. Nahta (to GAF Corp.).
27. U.S. Pat. 4,230,746 (Oct. 28, 1980), R. Nahta (to GAF Corp.).
28. U.S. Pat. 4,198,316 (Apr. 15, 1980), R. Nahta (to GAF Corp.).
29. U.S. Pat. 4,226,624 (Oct. 7, 1980), J. Ohr (to U.S. Navy).
30. U.S. Pat. 4,677,158 (Nov. 12, 1985), S. Tso and co-workers (to ted Catalysts Inc.).
31. U.S. Pat. 5,019,376 (May 28, 1991), H. Vick (to S. C. Johnson & Son, Inc.).
32. U.S. Pat. 4,818,523 (Apr. 4, 1989), J. Clarke and co-workers (to Colgate-Palmolive Co.).
33. U.S. Pat. 4,886,660 (Dec. 12, 1989), A. Patel and co-workers (to Colgate-Palmolive Co.).
34. U.S. Pat. 4,144,326 (Mar. 13, 1979), O. Luedicke and F. Gichia (to American Cyanamide Co.).
35. U.S. Pat. 5,034,219 (July 23, 1991), V. Deshpande and J. Walts (to Sterling Drug Inc.).
36. U.S. Pat. 4,719,104 (Jan. 12, 1988), C. Patel (to Helene Curtis, Inc.).
37. U.S. Pat. 3,980,091 (Sept. 14, 1976), G. Dasher and co-workers (to Alberto Culver Co.).
38. U.S. Pat. 4,919,846 (Apr. 24, 1990), Y. Nakama and co-workers (to Shiseido Co., Ltd.).
39. U.S. Pat. 3,577,528 (May 4, 1971), E. McDonough (to Zotos International).
40. U.S. Pat. 5,004,737 (Apr. 2, 1991), Y. Kim and B. Ha (to Pacific Chemical Co. Ltd.).
41. U.S. Pat. 5,015,469 (May 14, 1991), T. Yoneyama and co-workers (to Shiseido Co., Ltd.).
42. U.S. Pat. 4,069,347 (Jan. 17, 1978), J. McCarthy and co-workers (to Emery Industries, Inc.).
43. U.S. Pat. 5,035,826 (Sept. 22, 1991), P. Dorbut, M. Mondin, and G. Broze (to Colgate-Palmolive Co.).
44. U.S. Pat. 4,284,435 (Aug. 18, 1981), D. Fox (to S. C. Johnson & Son, Inc.).
45. U.S. Pat. 3,969,281 (July 13, 1976), T. Sharp (to T. Sharp.).
46. U.S. Pat. 4,011,097 (Mar. 8, 1977), T. Sharp (to T. Sharp.).
47. U.S. Pat. 4,541,945 (Sept. 17, 1985), J. Anderson and S. Seiglle (to Amchem Products).
48. U.S. Pat. 4,636,330 (Jan. 13, 1987), J. Melville (to Lever Brothers Co.).
49. U.S. Pat. 4,576,729 (Mar. 18, 1986), L. Paszek and B. Gebbia (to Sterling Drug, Inc.).

50. U.S. Pat. 4,126,586 (Nov. 21, 1978), M. Curtis, R. Davies, and J. Galvin (to Lever Brothers Co.).
51. U.S. Pat. 4,814,108 (Mar. 21, 1989), J. Geke and H. Rutzen (to Henkel Kommanditgesellschaft auf Aktien).
52. U.S. Pat. 4,678,605 (July 7, 1987), J. Geke and S. Seiglle (to Henkel Kommanditgesellshaft auf Aktien).
53. U.S. Pat. 5,127,991 (July 7, 1992), S. Lai and C. Smith (to AT&T Bell Laboratories).
54. U.S. Pat. 5,185,235 (Mar. 30, 1990), H. Sato, K. Tazawa, and T. Aoyama (to Tokyo Ohka Kogyo Co., Ltd.).
55. U.S. Pat. 4,892,649 (Jan. 9, 1990), J. Mehaffey and T. Newman (to Akzo America Inc.).
56. U.S. Pat. 4,995,965 (Feb. 26, 1991), J. Mehaffey and T. Newman (to Akzo American Inc.).
57. U.S. Pat. 3,976,565 (Aug. 24, 1976), V. Petrovich (to V. Petrovich).
58. U.S. Pat. 4,098,686 (July 4, 1978), V. Petrovich (to V. Petrovich).
59. U.S. Pat. 4,225,428 (Sept. 30, 1980), V. Petrovich (to V. Petrovich).
60. U.S. Pat. 3,979,207 (Sept. 7, 1976), J. MacGregor (to Mattey Rustenburg Refiners).
61. U.S. Pat. 4,306,081 (Dec. 15, 1981), G. Rich (to Albee Laboratories, Inc.).
62. U.S. Pat. 4,289,530 (Sept. 15, 1981), G. Rich (to Albee Laboratories, Inc.).
63. U.S. Pat. 4,351,699 (Sept. 28, 1982), T. Osborn (to Procter & Gamble Co.).
64. U.S. Pat. 4,441,962 (Apr. 10, 1984), T. Osborn (to Procter and Gamble Co.).
65. U.S. Pat. 5,240,562 (Aug. 31, 1993), D. Phan and P. Trokhan (to Procter & Gamble Co.).
66. U.S. Pat. 3,916,058 (Oct. 28, 1975), P. Vossos (to Nalco Chemical Co.).
67. U.S. Pat. 4,119,486 (Oct. 10, 1978), R. Eckert (to Westvaco Corp.).
68. U.S. Pat. 5,013,404 (May 7, 1991), S. Christiansen, T. Littleton, and R. Patton (to Dow Chemical Co.).
69. U.S. Pat. 5,145,558 (Sept. 8, 1992), S. Christiansen, T. Littleton, and R. Patton (to Dow Chemical Co.).
70. U.S. Pat. 4,134,786 (Jan. 16, 1979), J. Fletcher and M. Humphrey (to J. Fletcher and M. Humphrey).
71. U.S. Pat. 4,343,746 (Aug. 10, 1982), J. Anglin, Y. Ryu, and G. Singerman (to Gulf Research & Development Co.).
72. U.S. Pat. 4,400,282 (Aug. 23, 1983), J. Anglin, Y. Ryu, and G. Singerman (to Gulf Research & Development Co.).
73. U.S. Pat. 4,343,747 (Aug. 10, 1982), J. Anglin, Y. Ryu, and G. Singerman (to Gulf Research & Development Co.).
74. U.S. Pat. 4,364,742 (Dec. 21, 1982), K. Knitter and J. Villa (to Diamond Shamrock Corp.).
75. U.S. Pat. 4,364,741 (Dec. 21, 1982), J. Villa (to Diamond Shamrock Corp.).
76. U.S. Pat. 4,398,918 (Aug. 16, 1983), T. Newman (to Akzona Inc.).
77. U.S. Pat. 4,478,602 (Oct. 23, 1984), E. Kelley, W. Herzberg, and J. Sinka (to Diamond Shamrock Chemicals Co.).
78. U.S. Pat. 4,575,381 (Mar. 11, 1986), R. Corbeels and S. Vasconcellos (to Texaco Inc.).
79. U.S. Pat. 4,317,737 (Mar. 2, 1982), A. Oswald, G. Harting, and H. Barnum (to Exxon Research and Engineering Co.).
80. U.S. Pat. 4,365,030 (Dec. 21, 1982), A. Oswald and H. Barnum (to Exxon Research & Engineering Co.).
81. U.S. Pat. 4,828,724 (May 9, 1989), C. Davidson (to Shell Oil Co.).
82. U.S. Pat. 3,974,220 (Aug. 10, 1976), L. Heiss and M. Hille (to chst AG).
83. U.S. Pat. 4,206,079 (June 3, 1980), R. Frame (to UOP Inc.).
84. U.S. Pat. 4,260,479 (Apr. 7, 1981), R. Frame (to UOP Inc.).
85. U.S. Pat. 4,290,913 (Sept. 22, 1981), R. Frame (to UOP Inc.).
86. U.S. Pat. 4,295,993 (Oct. 20, 1981), D. Carlson (to UOP Inc.).
87. U.S. Pat. 4,354,926 (Oct. 19, 1982), D. Carlson (to UOP Inc.).
88. U.S. Pat. 4,337,141 (June 19, 1982), R. Frame (to UOP Inc.).
89. U.S. Pat. 4,124,493 (Nov. 7, 1978), R. Frame (to UOP Inc.).
90. U.S. Pat. 4,474,622 (Oct. 2, 1984), M. A. Forster (to ablisments Somalor-Ferrari Somafer SA).
91. U.S. Pat. 4,376,040 (Mar. 8, 1993), G. Sader (to G. Sader).
92. U.S. Pat. 5,200,062 (Apr. 6, 1993), M.-A. Poirier and J. Gilbert (to Exxon Research and Engineering Co.).
93. U.S. Pat. 4,514,286 (Apr. 30, 1985), S. Wang, G. Roof, and B. Porlier (to Nalco Chemical Co.).
94. U.S. Pat. 4,427,435 (Jan. 24, 1984), J. Lorenz and R. Grade (to a-Geigy Corp.).
95. U.S. Pat. 4,470,918 (Apr. 19, 1984), B. Mosier (to Global Marine, Inc.).
96. U.S. Pat. 4,560,761 (Dec. 24, 1985), E. Fields and M. Winzenburg (to Standard Oil Co.).
97. U.S. Pat. 4,526,986 (July 2, 1985), E. Fields and M. Winzenburg (to Standard Oil Co.).
98. U.S. Pat. 4,857,525 (Aug. 15, 1989), M. Philippe and co-workers (to L'Oreal).
99. U.S. Pat. 5,001,156 (Mar. 19, 1991), M. Philippe and co-workers (to L'Oreal).
100. U.S. Pat. 4,321,277 (Mar. 23, 1982), V. Saurino (to Research Lab Products, Inc.).
101. U.S. Pat. 5,165,918 (Jan. 5, 1990), B. Heyl, L. Winterton, and F. P. Tsao (to a-Geigy Corp.).

102. U.S. Pat. 5,244,666 (Sept. 14, 1993), J. Murley (to Consolidated Chemical, Inc.).
103. U.S. Pat. 4,941,989 (July 17, 1990), D. Kramer and P. Snow (to Ridgely Products Co., Inc.).
104. U.S. Pat. 5,132,050 (July 21, 1992), R. Baker and J. Thompson (to Lexmark International, Inc.).
105. U.S. Pat. 4,965,168 (Oct. 23, 1990), H. Yoshida, T. Kamada, and O. Kainuma (to Nikken Chemical Laboratory Co., Ltd.).
106. U.S. Pat. 5,035,993 (July 30, 1991), S. Hirano, A. Murai, and S. Suzuki (to i Photo Film Co., Ltd.).
107. U.S. Pat. 4,828,973 (May 9, 1989), S. Hirano, A. Murai, and S. Suzuki (to i Photo Film Co., Ltd.).
108. U.S. Pat. 4,471,044 (Sept. 11, 1984), R. Parton, W. Gaugh, and K. Wiegers (to Eastman Kodak Co.).
109. U.S. Pat. 4,628,068 (Dec. 9, 1986), H. Kesling and J. Harris (to Atlantic Richfield Co.).
110. U.S. Pat. 4,603,149 (July 29, 1986), H. Kesling and J. Harris (to Atlantic Richfield Co.).
111. U.S. Pat. 4,599,366 (July 8, 1986), H. Kesling and J. Harris (to Atlantic Richfield Co.).
112. U.S. Pat. 4,622,345 (Nov. 11, 1986), H. Kesling and J. Harris (to Atlantic Richfield Co.).
113. U.S. Pat. 5,110,835 (May 5, 1992), M. Walter, K.-H. Wassmer, and M. Lorenz (to BASF AG).
114. U.S. Pat. 4,410,462 (Oct. 18, 1983), W. Kroenke (to B. F. Goodrich Co.).
115. U.S. Pat. 3,974,125 (Aug. 10, 1976), A. Oswald and H. Barnum (to Exxon Research and Engineering Co.).
116. U.S. Pat. 3,981,679 (Sep. 21, 1976), N. Christie and J. Karnilaw (to Diamond Shamrock Corp.).
117. U.S. Pat. 4,441,884 (Apr. 10, 1984), H.-P. Baumann and U. Mosimann (to Sandoz Ltd.).
118. U.S. Pat. 4,104,175 (Aug. 1, 1978), M. Martinsson and K. Hellsten (to Modokemi Aktiebolag).
119. U.S. Pat. 3,972,855 (Aug. 3, 1976), M. Martinsson and K. Hellsten (to Modokemi Aktiebolag).
120. U.S. Pat. 4,104,443 (Aug. 1, 1978), (to J. P. Stevens & Co., Inc.).
121. U.S. Pat. 4,406,809 (Sept. 27, 1983), K. Hasenclever (to Chemische Fabrik Kreussler & Co., GmbH).
122. U.S. Pat. 4,416,787 (Nov. 22, 1983), R. Marshall, W. Archie, and K. Dardoufas (to Allied Corp.).
123. U.S. Pat. 3,756,835 (Sept. 4, 1973), R. Betty and H. Nemeth (to Akzona Inc.).
124. U.S. Pat. 3,497,365 (Feb. 24, 1970), J. Roselle and W. Wagner (to Armour Industrial Chemicals, Co.).
125. U.S. Pat. 3,551,168 (Dec. 29, 1970), J. Roselle and W. Wagner (to Armour Industrial Chemicals, Co.).
126. U.S. Pat. 5,167,827 (Jan. 8, 1992), B. Glatz (to Hewlett-Packard Co.).
127. U.S. Pat. 3,625,891 (Dec. 7, 1991), M. Walden, W. Springs, and A. Mariahazey-Westchester (to Armour Industrial Chemical Co.).
128. U.S. Pat. 3,505,221 (Apr. 7, 1970), M. Walden, Northbrook, and A. Mariahazey-Westchester (to Armour Industrial Chemical Co.).
129. U.S. Pat. 3,573,091 (Mar. 30, 1971), M. Walden, Northbrook, and A. Mariahazey-Westchester (to Armour and Co.).
130. U.S. Pat. 4,096,071 (June 20, 1978), A. Murphy (to Procter & Gamble Co.).
131. U.S. Pat. 4,203,852 (May 20, 1980), J. Johnson and W. Chirash (to Colgate-Palmolive Co.).
132. U.S. Pat. 4,255,484 (Mar. 10, 1981), F. Stevens (to A. E. Staley Manufacturing Co.).
133. U.S. Pat. 4,772,404 (Sept. 20, 1988), D. Fox, M. Sullivan, and A. Cuomo (to Lever Brothers Co.).
134. U.S. Pat. 4,806,260 (Feb. 21, 1989), G. Broze and D. Bastin (to Colgate-Palmolive Co.).
135. U.S. Pat. 4,844,822 (July 6, 1987), P. Fox and B. Felthouse (to Dial Corp.).
136. U.S. Pat. 4,808,321 (Feb. 28, 1989), D. Walley (to Procter and Gamble Co.).
137. U.S. Pat. 4,895,667 (Jan. 23, 1990), P. Fox and B. Felthouse (to Dial Corp.).
138. U.S. Pat. 4,970,008 (Nov. 13, 1990), T. Kandathil (to T. Kandathil).
139. U.S. Pat. 4,948,520 (Aug. 14, 1990), H. Sasaki (to Lion Corp.).
140. U.S. Pat. 4,986,922 (Jan. 22, 1991), S. Snow and L. Madore (to Dow Corning Corp.).
141. U.S. Pat. 5,132,425 (July 21, 1992), K. Sotoya, U. Nishimoto, and H. Abe (to Kao Corp.).
142. U.S. Pat. 5,151,223 (Sept. 29, 1992), H. Maaser (to Colgate-Palmolive Co.).
143. U.S. Pat. 5,259,964 (Nov. 9, 1993), N. Chavez and I. Oliveros (to Colgate-Palmolive Co.).
144. U.S. Pat. 5,221,794 (June 22, 1993), J. Ackerman, M. Miller, and D. Whittlinger (to Sherex Chemical Co., Inc.).
145. U.S. Pat. 4,256,824 (Mar. 17, 1981), C. Lu (to Xerox Corp.).
146. U.S. Pat. 4,323,634 (Apr. 6, 1982), T. Jadwin (to Eastman Kodak Co.).
147. U.S. Pat. 4,604,338 (Aug. 5, 1986), R. Gruber, R. Yourd, and R. Koch (to Xerox Corp.).
148. U.S. Pat. 4,560,635 (Dec. 24, 1985), T. Hoffend and A. Barbetta (to Xerox Corp.).
149. U.S. Pat. 3,985,663 (Oct. 12, 1976), C. Lu and R. Parent (to Xerox Corp.).
150. U.S. Pat. 4,059,444 (Nov. 22, 1977), C. Lu and R. Parent (to Xerox Corp.).

151. U.S. Pat. 3,970,755 (July 20, 1976), E. Gazzard and M. Singer (to Imperial Chemical Industries Ltd.).
152. U.S. Pat. 4,272,395 (June 9, 1981), R. Wright (to Lever Brothers Co.).
153. U.S. Pat. 4,444,790 (Apr. 24, 1984), H. Green, A. Petrocci, and Z. Dudzinski (to Millmaster Onyx Group, Inc.).
154. U.S. Pat. 4,868,217 (Sept. 19, 1989), S. Araki and co-workers (to Eisai Co., Ltd. Kao Corp.).
155. U.S. Pat. 4,800,235 (Jan. 24, 1989), T. La Marre and C. Martin (to Nalco Chemical Co.).
156. U.S. Pat. 4,847,089 (July 11, 1989), D. Kramer and P. Snow (to D. N. Kramer).
157. U.S. Pat. 4,941,989 (July 17, 1990), D. Kramer and P. Snow (to Ridgely Products Co., Inc.).
158. U.S. Pat. 4,983,635 (Jan. 8, 1991), H. Martin (to M. Howard).
159. U.S. Pat. 5,049,383 (Sept. 17, 1991), (to Hoechst AG).
160. U.S. Pat. 4,615,807 (Oct. 7, 1986), F. Haines and D. Forte (to United States Environmental Resources, Corp.).
161. U.S. Pat. 5,286,109 (Dec. 7, 1993), S. Boyd (to S. Boyd).
162. U.S. Pat. 4,602,052 (July 22, 1986), K. Weber and D. Oberlin (to Amoco Corp.).
163. *CRC Handbook of Chemistry and Physics*, 61st ed., CRC Press, Inc., Boca Raton, Fla., 1981, p. C-586.
164. R. Shelton and co-workers, *J. Am. Chem. Soc.* **66**, 753 (1946).
165. R. Reck, H. Harwood, and A. Ralston, *J. Org. Chem.* **12**, 517 (1947).
166. A. Ralston and co-workers, *J. Org. Chem.* **13**, 186 (1948).
167. Ref. 1, Chapts. 7 and 8.
168. Ref. 1, Chapts. 9, 10, and 11.
169. E. White and D. Woodcock, in Patai, ed., *The Chemistry of the Amino Group*, Wiley-Interscience, New York, 1968, 409–416.
170. A. Hofmann, *Ann. Chem.* **78**, 253 (1851); H. Hofman, *Ann. Chem.* **79**, 11 (1851).
171. J. March, *Advanced Organic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1985, 906–908.
172. A. Cope and E. Trumbull, *Org. Reactions*, **11**, 317 (1960).
173. J. Baumgarten, *J. Chem. Ed.* **45**, 122 (1968).
174. W. Hawart and C. Ingold, *J. Chem. Soc.*, 997 (1927).
175. T. Stevens and co-workers, *J. Chem. Soc.*, 3193 (1928); G. Wittig, R. Mangold, and G. Felletschin, *Ann. Chem.* **560**, 117 (1948).
176. T. Stevens, *J. Chem. Soc.* (2), 2107 (1930); R. Johnson and T. Stevens, *J. Chem. Soc.* (4), 4487 (1955).
177. M. Sommelet, *Compt. Rend.* **205**, 56 (1937); S. Kantor and C. Hauser, *J. Am. Chem. Soc.* **73**, 4122 (1951); C. Hauser and D. Van Eenam, *J. Am. Chem. Soc.* **79**, 5513 (1957); W. Beard and C. Hauser, *J. Am. Chem. Soc.* **25**, 334 (1961).
178. H. Zimmerman, in de Mayo, ed., *Molecular Rearrangements*, Vol. **1**, John Wiley & Sons, Inc., New York, 1963, p. 387.
179. U. Anthoni and co-workers, *Comp. Biochem. Physiol.* **99B**, 1–18 (1991).
180. *Official Methods and Recommended Practices of American Oil Chemists' Society*, 4th ed., American Oil Chemists Society, Champaign, Ill., 1990, pp. S 4c-64 and Section T; L. Metcalfe, *J. Am. Oil Chem. Soc.* **61**, 363 (1984).
181. Ref. 1, Chapt. 13.
182. M. Rosen and H. Goldsmith, *Systematic Analysis of Surface Active Agents*, Interscience, New York, 1960.
183. D. Herring, *Laboratory Practice*, **II**, 113 (1962).
184. S. Epton, *Nature* **160**, 795 (1947).
185. S. Epton, *Trans. Faraday Soc.* **44**, 226 (1948).
186. Ref. 182, p. 455.
187. Ref. 182, p. 445.
188. Ref. 1, p. 430.
189. M. Bambagiottialberti and co-workers, *Rapid Commun. Mass Spectrom.* **8**, 439 (1994).
190. A. Tyler, L. Romo, and R. Cody, *Int. J. Mass. Spectrom. Ion Process.* **122**, 25 (1992).
191. D. Fisher and co-workers, *Rapid Commun. Mass Spectrom.* **8**, 65 (1994).
192. V. Wee and J. Kennedy, *Anal. Chem.* **54**, 1631 (1982).

193. G. Szajer, in G. Szajer, *Analyses of Fats, Oils and Lipoproteins*, American Oil Chemists Society, Champaign, Ill., 1991, Chapt. 18; T. Schmitt, *ibid.*, Chapt. 19.
194. F. Mozayeni, in J. Cross and E. Singer, eds., *Cationic Surfactants*, Marcel Dekker, Inc., New York, 1994, Chapt. 11.
195. R. Shelton and co-workers, *J. Am. Chem. Soc.* **66**, 755 (1946).
196. *Ibid.*, p. 757.
197. W. Sexton, *Chemical Constitution and Biological Activity*, Van Nostrand, Princeton, N.J., 1963.
198. A. Vallejo-Freire, *Science*, **114**, 470 (1954).
199. K. Biesinger and co-workers, *J. Water Pollut. Control Fed.* **48**, 183 (1976).
200. J. Walker and S. Evans, *Marine Pollut. Bull.* **9**, 136 (1978).
201. Technical data, *Toxicity*, Akzo Nobel Chemicals Inc., Dobbs Ferry, N.Y., Apr. 1995.
202. R. Boethling, *Water Res.*, **18**, 1061 (1984); L. Huber, *J. Am. Oil Chem. Soc.* **61**, 377 (1984).
203. J. Cooper, *Ecotoxicity Environ. Safety*, **16**, 65 (1988).
204. Technical data, Akzo Nobel Chemical Inc., Dobbs Ferry, N.Y., Apr. 1995.
205. U.S. Pat. 4,204,954 (May 27, 1980), J. Jacob (to Chemed Corp.) for a patented procedure to remove quaternaries from wastewater.
206. W. Ruback, *Chem. Today*, 15 (May/June 1994).
207. L. Edebo and co-workers, *Ind. Appl. Surfactants*, **III**, 184 (1992).
208. U.S. Pat. 4,787,491 (Dec. 6, 1988), N. Chang and D. Walley (to Procter & Gamble Co.).
209. U.S. Pat. 4,767,547 (Aug. 30, 1988), T. Straathof and A. Konig (to Procter & Gamble Co.).
210. U.S. Pat. 3,915,867 (Oct. 28, 1975), H. Kang and R. Peterson, and E. Knaggs (to Stepan Chemical Co.).
211. U.S. Pat. 4,339,391 (July 13, 1982), E. Hoffmann and co-workers (to Hoechst AG).
212. U.S. Pat. 4,963,274 (Oct. 16, 1990), W. Ruback and co-workers (to Hüls AG).
213. R. Lagerman and co-workers, *J. Am. Oil Chem. Soc.* **71**, 97 (1994).
214. U.S. Pat. 5,066,414 (Nov. 19, 1991), N. Chang (to Procter & Gamble Co.).
215. U.S. Pat. 4,840,738 (June 20, 1981), F. Hardy and D. Walley (to Procter & Gamble Co.).
216. U.S. Pat. 5,128,473 (July 7, 1992), F. Friedli and M. Watts (to Sherex Chemical Co.).
217. U.S. Pat. 4,857,310 (Aug. 15, 1989), A. Baydar (to Gillette Co.).
218. B. Challis and A. Butler, in Ref. 169, 290–300.
219. M. Gibson, in Ref. 169, 44–55.
220. Ref. 171, p. 364.
221. C. Ingold, *Structure and Mechanism in Organic Chemistry*, Bell, London, 1953, Chapt. 7; A. Streitwieser, *Chem. Rev.* **56**, 571 (1956).
222. W. Emerson, *Organic Reactions*, Vol. **IV**, John Wiley & Sons, Inc., New York, 1948, Chapt. 3.
223. H. Sommer and L. Jackson, *J. Org. Chem.* **35**, 1558 (1970).
224. H. Sommer, H. Lipp, and L. Jackson, *J. Org. Chem.* **36**, 824 (1971).
225. S. Billenstein and G. Blaschke, *J. Am. Oil Chem. Soc.* **61**, 353 (1984).
226. R. Schroter, in Houben-Weyl, ed., *Methoden der Organischen Chemie*, Vol. **XIII**, 4th ed., George Thieme Verlag, Stuttgart, Germany, 1957, Chapt. 4; M. Rabinovitz, in Z. V. C. Rappoport, *The Chemistry of the Cyano Group*, Wiley-Interscience, New York, 1970, 307–340; C. De Bellefon and P. Fouilloux, *Catal. Rev.-Sci. Eng.* **36**, 459 (1994).
227. P. Rylander, *Catalytic Hydrogenation Over Platinum Metals*, Academic Press, Inc., New York, 1967, 203–226.
228. F. Gould, G. Johnson, and A. Ferris, *J. Org. Chem.* **25**, 1658 (1960).
229. M. Freifelder, *J. Am. Chem. Soc.* **82**, 2386 (1960).
230. U.S. Pat. 4,830,771 (May 16, 1989), W. Ruback and J. Schut (to Hüls AG).
231. Can. Pat. 1,312,619 (Jan. 12, 1993), M. Hofinger and co-workers (to Hoechst AG).
232. *Synthetic Organic Chemicals*, U.S. International Trade Commission, Washington, D.C., 1994.
233. C. Starks, *Ind. Appl. Surfactants II*, **77**, 165 (1990); C. Starks, ed., *Phase-Transfer Catalysis: New Chemistry, Catalysts and Applications*, American Chemical Society, Washington, D.C., 1987; E. Dehmlov, *Phase-Transfer Catalysis*, Verlag Chemie, Deerfield Beach, Fla., 1983; M. Halpern, *Phase-Transfer Catalysis* in *Ullman's Encyclopedia of Industrial Chemistry*, Vol. **A19**, VCH V6, New York, 1991; M. Halpern, *Phase-Transfer Catalysis Commun.* **1**, 1 (1995).
234. *Specialty Surfactants Worldwide* in *Specialty Chemicals*, SRI International, Menlo Park, Calif., 1989, 81–94.
235. Ref. 2, p. 657.5000yz; W. Evans, *Chem. Ind.* **27**, 893 (1969); R. Puchta, *J. Am. Oil Chem. Soc.* **61**, 367 (1984).
236. *Cosmetic Chemicals*, in *Specialty Chemicals*, SRI International, Menlo Park, Calif., 1992, p. 73.

237. Technical data, Akzo Nobel Chemicals Inc., Dobbs Ferry, N.Y., Apr. 1995; for a review, see W. Mardis, *J. Am. Oil Chem. Soc.* **61**, 382 (1984).
238. H. Berenbold, *Inform*, **5**, 82 (1994).
239. E. Spiess, *Perfumerie Kusmetik*, **72**, 370 (1991); M. Jurczyk, D. Berger, and D. Damaso, *Cosmetics Toiletries* **106**, 63 (1991).
240. C. Reich and C. Robbins, *J. Soc. Cosmet. Chem.* **44**, 263 (1993).
241. P. D'Arcy and E. Taylor, *J. Pharm. Pharmacol.* **14**, 193 (1962); P. Schaeufele, *J. Am. Oil Chem. Soc.* **61**, 387 (1984).
242. Ref. 1, Chapt. 14.
243. H. Freedman, *Pure Appl. Chem.* **58**, 857 (1986).
244. J. D'Souza and N. Sridhar, *J. Sci. Ind. Res.* **42**, 564 (1983).
245. J. Salamone and W. Rice, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., John Wiley & Sons, Inc., New York, 1988.
246. R. McConnell, *Soap, Cosmetics, Chem. Special.*, 37 (Apr. 1989).
247. J. K. Borchardt, *Proceedings of the Symposium on Advances in Oil Field Chemistry*, Toronto, Canada, June 5–11, 1988.

MAURICE DERY
Akzo Nobel Chemicals Inc.