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ALUMINUM CARBOXYLATES

Aluminum salts of carboxylic acids, aluminum carboxylates, may occur as aluminum tricarboxylates (normal aluminum carboxylates), $Al(OOCR)_3$; monohydroxy (monobasic) aluminum dicarboxylates, $(RCOO)_2Al(OH)$; and dihydroxy (dibasic) aluminum monocarboxylates, $RCOOAl(OH)_2$. Aluminum carboxylates are used in three general areas: textiles, gelling, and pharmaceuticals. Derivatives of low molecular weight carboxylic acids have been mainly associated with textile applications; those of fatty carboxylic acids are associated with gelling salts; and more complex carboxylates find applications in pharmaceuticals.

The development of new aluminum carboxylates is evident in the literature. However, sales volume has decreased or the number of suppliers has been concentrated to such an extent that the U.S. International Trade Commission now reports data only for aluminum tristearate (867 t at $1.34/kg) (1). The aluminum carboxylates of most commercial interest according to the trade literature (2, 3) are given in Table 1.

1. Aluminum Salts of Low Molecular Weight Carboxylic Acids

Monobasic aluminum acetate (eg, aluminum subacetate), aluminum formoacetate, normal aluminum formate, and basic aluminum formate have found widespread use as mordants in dyeing, in the formulation of waterproofing compositions for textiles, and for dermatological treatment.

Monobasic aluminum acetate, $HOAl(OOCCH_3)_2$, the most commercially significant of the low molecular weight salts, is available as a fine white powder stabilized with boric acid It is soluble in water and insoluble in most organic solvents (4). Although it has been prepared from aluminum chloride hexahydrate and sodium acetate (5), the commercial method involves the reaction of metallic aluminum and aqueous acetic acid containing a small amount of boric acid stabilizer. Mercury chloride can be used as a catalyst (6). The resulting solution is filtered and spray dried. The energetics of the aluminum soap formation seems to be dominated by the chemistry of the carboxyl and solvated metal ions. Controlled decomposition of a variety of aluminum carboxylates has been carried out at different rates in different atmospheres. Hydroxyl stoichiometry can be controlled by water content to make $Al(OH)_n(OOCCH_3)_{3-n}$ (7–9).

The greatest industrial consumption of monobasic aluminum acetate has been as a solution in the preparation of red color lakes for the dyeing of cotton. Formation of a water-resistant coating on fabrics, paper, leather, or other materials is also an important application. In this process, for example, cloth is dipped into a solution of water-soluble soap, then into the aluminum salt solution, forming an insoluble, water-resistant aluminum soap coating on the fiber surfaces (10).

$$NaOOCR\,(aq) + AlX_3\,(aq) \longrightarrow Al\,(OOCR)_n\,(OH)_{(3-n)}\,(s) + NaX\,(aq) \quad \text{where} n = 2, 3$$

Freshly prepared aluminum subacetate is also used to cross-link acid-hydrolyzed, collagen-derived protein. This procedure is useful in the food, pharmaceutical, and photographic industries (11).

Table 1. Commercially Important Aluminum Carboxylates

Name	CAS Registry Number	Empirical formula	Mol wt	Mp,°C
monobasic aluminum formate	[51575-25-8]	$C_2H_3AlO_5$	134.02	
normal aluminum formate	[7360-53-4]	$C_3H_3AlO_6$	162.03	
monobasic aluminum acetate	[142-03-0]	$C_4H_7AlO_5$	162.08	54
normal aluminum acetate	[139-12-8]	$C_6H_9AlO_6$	204.09	
dihydroxyaluminum aminoacetate	[13682-92-3]	$C_2H_6AlNO_4$	135.06	
dihydroxyaluminum aminoacetate hydrate	[41354-58-7]	$C_2H_6AlNO_4{\cdot}xH_2O$		
aluminum octanoate	[30745-55-2]	$C_{16}H_{31}AlO_5$	474.4	
aluminum 2-ethylhexanoate	[6028-57-5]	$C_{16}H_{31}AlO_5$	474.4	
aluminum monostearate	[7047-84-9]	$C_{18}H_{37}AlO_4$	344.5	155
aluminum distearate	[300-92-5]	$C_{36}H_{71}AlO_5$	610.9	145
aluminum tristearate	[637-12-7]	$C_{54}H_{108}AlO_6$	877.4	115

Monobasic aluminum acetate is dispensed as a 7% aqueous solution for the topical treatment of certain dermatological conditions, where a combination of detergent, antiseptic, astringent, and heat-dispersant effects are needed (12). The solution, diluted with 20–40 parts water, is applied topically to the skin and mucous membranes as a wet dressing (13). Burrow's solution, prepared from aluminum subacetate solution by the addition of a specific amount of acetic acid, is also used as a topical wet dressing. Standards of purity and concentration have been established for both pharmaceutical aluminum acetate solutions (13). Each 100 mL of aluminum subacetate solution yields 2.30–2.60 g of aluminum oxide and 5.43–6.13 g of acetic acid upon hydrolysis. For the Burow's solution, each 100 mL yields 1.20–1.45 g of aluminum oxide and 4.25–5.12 g of acetic acid. Both solutions may be stabilized to hydrolysis by the addition of boric acid in amounts not to exceed 0.9% and 0.6% for the subacetate and Burow's solutions, respectively (13).

Aluminum diacetate is used as a nucleating agent with crystalline polypropylene to improve the efficiency of reproducing lightweight printing plates having high dimensional stability and superior printing characteristics (14). It is also used as an esterification catalyst: 2,6-naphthalenedicarboxylic acid and methanol are converted to the dimethyl ester (82.5%) in one hour at 220°C (15). Dibasic aluminum monoacetate [7360-44-3], $(HO)_2Al(OOCCH_3)$, is an essential feature in formaldehyde-free durable press finishing by the glyoxal-glycol process. It is a heat stabilizer acting to suppress tendering and yellowing during curing (16).

Production of both monobasic aluminum diformate, $(HO)Al(OOCH)_2$, and monobasic aluminum formoacetate, $(HO)Al(OOCH)(OOCCH_3)$, has declined. One reason could be the ready substitution of inexpensive aluminum formate solution (17–19) for solid aluminum acetate in formoacetate in most of the common commercial applications. Monobasic aluminum formoacetate, mol wt 148.05, mp 350°C, is a fine crystalline powder, prepared from aluminum metal. It is used for fabric water repellency and in the tanning of collagen tape for surgical sutures (10).

Aluminum triformate [7360-53-4], commercially available as a white crystalline powder, appears amorphous under the microscope. Its solubility in cold water is very low, rising to nearly 25% in boiling water (pH 3.2). It remains in solution in a highly saturated state. Infared analysis of solid aluminum triformate suggests that both oxygen atoms of the formate ion are coordinated to the aluminum, giving a coordination number of six (20). Aluminum chloride, isopropoxide, or hydrate reacts with 98% formic acid (21, 22) to yield a mixture of aluminum formates plus their hydrates in a highly supersaturated solution. When excess formic acid is added, the triformate crystallizes after standing for a day (23). Aluminum formate is formulated as $Al(OOCH)_3{\cdot}HCOOH$ (24). Aluminum triformate trihydrate can be made from $AlCl_3$ and sodium formate or from formic acid plus freshly prepared $Al(OH)_3$. At 100°C this product is hydrolyzed to the monobasic formate.

Decomposition to the monobasic formate also occurs at $\leq 290^{\circ}C$, going then to alumina at 350°C (25), as shown

$$Al(OOCH)_3 \cdot 3H_2O \xrightarrow{} {}_{100-290^{\circ}C}\ (HO)Al(OOCH)_2 \cdot xH_2O \xrightarrow{} {}_{290-350^{\circ}C}\ Al_2O_3$$

Most commercial aluminum formate is monobasic aluminum diformate because of the difficulties involved in triformate preparation. The main application is in textile waterproofing. Aluminum formate reacts with casein to form a water-soluble complex, which can emulsify paraffin and certain other waxes. Fabrics immersed in these emulsions are rendered water repellent (26–28).

2. Aluminum Salts of Higher Molecular Weight Fatty Acids

This group of aluminum carboxylates is characterized mainly by its ability to gel vegetable oils and hydrocarbons. Again, monocarboxylate, dicarboxylate, and tricarboxylate salts are important. The chemical, physical, and biological properties of the various types of aluminum stearates have been reviewed (29). Other products include aluminum palmitate and aluminum 2-ethylhexanoate (30).

Dihydroxyaluminum monostearate, $(HO)_2Al(OOC(CH_2)_{16}CH_3)$, is a fine white to yellowish-white powder with a faint characteristic odor and low toxicity. This salt melts at 155°C and is insoluble in water, alcohol, and ether (31). It is prepared by treating an aqueous solution of chlorodihydroxyaluminum with a solution of sodium stearate (32). USP dihydroxyaluminum stearate assays between 14.5 and 16.5% alumina (31), partly because it contains a mixture of stearate and palmitate.

Aluminum monostearate has been used in the pharmaceutical industry as a gelling agent for penicillin G procaine (31), as a virus vaccine adjuvant (32), in long-lasting depot-injectable formulations (33), and for prolonged somatotropin release to enhance lactation in dairy cattle (34). It is also used with adrenocorticotrophic hormone (ACTH) peptides for injection (35), for acid release (36), and for dispersion of suppository ingredients (37, 38). Aluminum monostearate has been used in the preparation of synthetic greases (39), in water-repellent formulations (40), for fiber lubrication with improved dye receptivity for polyolefins (41), to improve melt and heat resistance of polyesters (42), and as an aqueous-based spray-on mold-release agent for urethane-bound particle board (43).

Monohydroxyaluminum distearate, $(HO)Al(OOC(CH_2)_{16}CH_3)_2$, used to be the largest selling aluminum carboxylate (1). Although still sold, the product is no longer listed in the U.S. International Trade Commission Report (1) because of low volume or confidentiality constraints because of too few suppliers. Aluminum distearate is a white powder that is insoluble in water, alcohol, and ether. A key property is its ability to gel vegetable oils and hydrocarbons. Aluminum distearate is prepared by the reaction of aqueous sodium stearate with aqueous aluminum sulfate or chloride at pH 7.3. Aluminum monostearate is formed if the sodium stearate solution is held at pH 9.5 (44).

Gels made from aluminum distearate (and some other carboxylate analogues) have more body than those made from other metals; the aluminum gels also show marked thixotropic properties. Aluminum distearate has been used in cosmetics formulas (45–47) (see Cosmetics) (48, 49), as a thickener in grease (50–52), as a gasoline additive for combustion efficiency (53) or gelation (54), as a coating additive (55–57) and a polymer additive to enhance dyeability and weatherability (58), as a salt-bridge-type cross-linker (59), and as a mold-release agent (60).

Aluminum tristearate, $Al(OOC(CH_2)_{16}CH_3)_3$, is available as a hard, white, technical-grade solid. It is insoluble in water, alcohol, and ether, forming gels with vegetable oils and hydrocarbons (61). High quality aluminum tristearate is made by reaction of aluminum isopropoxide [551-31-7] and stearic acid in anhydrous pyridine; the product precipitates as a pyridine complex. Infrared analysis indicates that no hydroxyl remains after the pyridine is removed under vacuum (62). Applications for aluminum tristearate include cosmetic gels

Table 2. Aluminum Carboxylates Used as Pharmaceuticals

Name	CAS Registry Number	Empirical formula	Mol wt
monohydroxyaluminum glycinate	[13682-92-3]	$C_2H_6AlNO_4$	135.06
monohydroxyaluminum acetylsalicylate	[23413-80-1]	$C_{18}H_{15}AlO_9$	402.3
monohydroxyaluminum ibuprofen	[61054-06-6]	$C_{26}H_{35}AlO_5$	454.5
dihydroxyaluminum ibuprofen	[63649-76-3]	$C_{13}H_{19}AlO_4$	266.3
monohydroxyaluminum fenoprofen	[58348-96-2]	$C_{20}H_{27}AlO_7$	526.5
dihydroxyaluminum fenoprofen	[58348-95-1]	$C_{15}H_{15}AlO_5$	302.3
aluminum flufenamate	[16449-54-0]	$C_{42}H_{27}AlF_9N_3O_6$	867.6

(45), pharmaceutical additives (63, 64), polymer additives (65, 66), grease additives (67, 68), toner adjuvants (69), antifoam agents (70), rocket-fuel and explosives additives (71, 72), and waterproofing agents (40, 72).

Other aluminum fatty carboxylates have been used to a lesser degree. Hydroxyaluminum dilaurate is used in agricultural feed to optimize digestion (73) and as a liquid petroleum grease thickener (74). Aluminum palmitate [14236-50-1], $C_{32}H_{63}AlO_5$, is used as a gelling agent in rocket propellents and in ointment bases for polyolefin dyeing (65, 75). Aluminum (stearate/myristate) has been used as an acid catalyst scavenger during polypropylene manufacture (76), whereas aluminum "octoate" (aluminum 2-ethylhexanoate) [6028-57-5], has been used as a gasoline gellant (77, 78).

3. Aluminum Salts of More Complex Carboxylic Acids

The aluminum salts of drugs are significant for two principal reasons: reduction of drug acidity in the stomach lining and reduction of undesirable flavor. Examples are the aluminum salts of glycine, acetylsalicylic acid, ibuprofen, flurbiprofen, fenoprofen, flufenamic acid, oxaprozin, and a variety of aminobenzoic acid Some of these compounds are listed in Table 2.

Dihydroxyaluminum aminoacetate (aluminum glycinate), a white, odorless powder with a faintly sweet taste, is insoluble in water and organic solvents. It is made by the reaction of aluminum isopropoxide with glycine, $HOOCCH_2NH_2$, in aqueous solution (79) or by reaction of aluminum chloride in methanol with aqueous sodium glycinate (80). Upon drying, moisture loss of the hydrated product cannot exceed 14.5% (81). Aluminum oxide assay yields 35.5–38.5%. Because dihydroxyaluminum aminoacetate gives a pH of 6.5–7.5 when suspended in water (81), it provides prompt buffering in the biologically ideal pH range, affording consistent neutralization. This action minimizes pain and promotes healing (see Gastrointestinal agents). It is thus useful for treatment of gastritis and hyperacidity (82).

Aluminum acetylsalicylate is a tasteless, nonbasic, stable, alternative therapeutic salt to aspirin (83). Also called aluminum aspirin, it is an insoluble white to off-white powder prepared by reaction of aluminum isopropoxide with sodium acetylsalicylate in an organic solvent. The product precipitates from the reaction mixture (83). Standards require that aluminum aspirin contain not less than the equivalent of 80% aspirin, corresponding to 90% purity on an anhydrous basis. The aluminum oxide assay must be 12–17% (81).

Analgesic and antipyretic ibuprofen, 2-(*p*-isobutylphenyl)propionic acid , is converted to its monohydroxyaluminum salt by converting the acid to its sodium salt using dilute caustic, followed by concurrent addition of equimolar amounts of aluminum nitrate and sodium bicarbonate (84). This salt can also be prepared by reaction of aluminum chloride with the sodium salt of ibuprofen at 18°C and pH 7.1–7.3 (85). The dibasic aluminum salt must be made under different conditions (86). The monobasic aluminum salt has a more pleasant taste than either the parent acid or the more basic salt (84). The aluminum salts are useful for preventing scar tissue (3) and in the treatment of *Herpes simplex* I and II infections (87). Aspirin, acetaminophen, and phenacetin behave

synergistically with ibuprofen aluminum salts with respect to anti-inflammatory and analgesic response (88, 89).

Fenoprofen, 2-(3-phenoxyphenyl)propionic acid, is made into its monohydroxyaluminum or dihydroxyaluminum salt by reaction of the sodium salt of the acid with aluminum nitrate or chloride under pH control (90, 91). The aluminum salt, which is hydrolyzed in the stomach, is more palatable for arthritis treatment (92, 93).

Aluminum flufenamate, tris-[2-(3-trifluoromethylphenyl)aminobenzoate]aluminum, is a safer and more effective analgesic than aspirin (94). The dihydroxyaluminum flufenamate is made by reaction of flufenamic acid with aqueous caustic, followed by addition of aluminum chloride with stirring at 42°C for 15 min to give 99% yield (95). Both forms are less irritating and less toxic than the parent acid or aspirin (94, 95).

The anti-inflammatory agent Oxaprozin, 2-(4,5-diphenyl-2-oxazole)propionic acid monoaluminum and dihydroxyaluminum salts, is made by reaction of the sodium salt with aluminum sulfate under controlled conditions (96). Again, the aluminum salts of many carboxylic acid based drugs are less irritating, ulcerous, and/or toxic, and have a more pleasant taste than their parent acids.

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