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Chemical Products Synopsis

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CHLOROACETIC ACID

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FOCUS.....US demand for chloroacetic acid peaked at 111 million pounds in [illegible]. By 1988, US consumption of chloroacetic acid, also known as monochloroacetic acid (MCAA), declined to about 65 MM pounds per year. MCAA is a raw material for the phenoxy herbicide 2,4-dichlorophenoxyacetic acid (2,4-D). Consumption for herbicides peaked in the late 1960's. In addition to a high level of domestic consumption, the military required large quantities for the defoliant "Agent Orange", a mixture of 2,4-D and 2,4,5-T. Military demand for 2,4-D stopped at the end of the Vietnam War. Civilian consumption also declined. There was some replacement of chlorinated phenoxies by other herbicides. In addition, environmental concerns contributed to reduced use of these herbicide types. Current annual consumption of chloroacetic acid for 2,4-D production is probably 7 MM pounds. The US government 1983 PIK (payment-in-kind) program compensated farmers for taking land out of production, causing an overall decline in demand for agricultural chemicals. However, consumption of 2,4-D was reportedly not reduced as much as other herbicides because it was often used on fallow land to keep weeds down. Some farmers prefer 2,4-D over competitive weed killers because of comparatively low price. The herbicide 2,4-D is still claimed to be the best all-around broadleaf weed killer for wheat. Chloroacetic acid was once used as a raw material for 2,4,5-T. However, this herbicide is no longer produced. In 1979, the EPA cancelled most registrations for 2,4,5-T owing to environmental objections. Dow shut down and dismantled its 2,4,5-T unit at Midland, MI. In addition, Vertac stopped production at Jacksonville, AR. Monsanto makes chloroacetanilide (for example, Lasso™) and chloroacetamide herbicides. These can be made from chloroacetic acid. However, trade sources indicate that Monsanto uses chloroacetyl chloride, rather than chloroacetic acid, as a starting material.

Chloroacetic acid is a raw material for carboxymethylcellulose (CMC). Estimated annual consumption of MCAA for CMC manufacture increased at an average annual rate of 2% from about 24 MM pounds in 1960 to 35 MM pounds in 1975. Since 1975, estimated consumption of MCAA used to make CMC has fluctuated between 34 and 39 MM pounds.

OUTLOOK.....Trade sources predict that the EPA will eventually cancel all remaining 2,4,5-T registrations. There is, however, no equally effective product for some applications. The best available herbicide substitute for 2,4,5-T is 2,4-D. A complete ban on 2,4,5-T should therefore provide additional 2,4-D sales. Growth in other 2,4-D uses is also expected over the next few years. The use of chloroacetic acid as a raw material for CMC should increase at about 2% per year. Over 20% of the carboxymethylcellulose produced is used as a drilling mud additive in oil production. Drilling mud applications stagnated in mid-1983, but have since been increasing. Textile uses for CMC should grow at 4% annually during the 1985-89 period. Consumption of chloroacetic acid for other uses, including dyes, pharmaceuticals, personal care products, and food additives, is expected to grow at about 3% per year. Overall, chloroacetic acid demand should increase by 5% in 1984 as the economic recovery continues. Thereafter, annual growth should average about 3%.

PRICING.....The list price for MCAA has been 56 cents per pound since 1982. Import values in the 1980-83 period ranged from 34 to 37 cents per pound (foreign port) compared to US list prices in the same period of 40 to 56 cents per pound. Although some imports were purchased directly by consumers, a large proportion is believed to have been resold at prices closer to list. Chloroacetic acid prices should rise with increasing costs of raw materials and energy for foreign and domestic producers.

AVERAGE PRICE RANGE–CHLOROACETIC ACID (MONO)

Cents Per Pound–High Purity–Flake–99%–Drums–Carloads–FOB

	1960	1965	1970	1975	1980	1981	1982	1983	1984	1985	1987	1989
Trade List	19	19	21	40	50	52½	56	56	56	58	62	66

Prices for 1970 were listed on a freight equalized basis. Before April 1983, prices were listed for "technical, 98%" material.

SUPPLY AND DEMAND.....Millions of Pounds.....Estimated.....Domestic US

	1960	1965	1970	1975	1980	1981	1982	1983	1984	1985	1987	1989
Capacity	66	68	79	70	102	102	102	122	138			
Production	53	71	55	48	27	29	23	40				
Imports	11	17	26	25	38	37	30	19				
Demand	64	88	81	73	65	66	53	59	62	64	68	72

Production was reported by the International Trade Commission through 1969, but has not been reported since (except in 1979, but the value was low because a major producer did not report). Therefore, demand and production figures for the years after 1965 are estimates. Exports are not reported separately by the government, but trade sources report that they are small.

AVAILABILITY.....US merchant market sales of chloroacetic acid are estimated at about 20-30 MM pounds. Currently, American Hoechst is the only merchant market supplier of chloroacetic acid. American Hoechst, until starting US production in 1983, resold imported material. Dow's chloroacetic acid production is now thought to be quite small. In the past, Dow probably used chloroacetic acid as a raw material for both chloroacetyl chloride and 2,4-D. It is now probable that Dow can produce chloroacetyl chloride by a different process. It is possible that Dow now produces chloroacetic acid by hydrolysis of chloroacetyl chloride for use in 2,4-D production. Hercules produces chloroacetic acid captively for carboxymethylcellulose.

Chloroacetic acid imports rose from 11 MM pounds in 1960 to 30–38 MM pounds in 1980-82. In 1982 and 1983, more than two-thirds of the imports came from Germany. Imports dropped in 1983, reflecting the startup of Hoechst's new 40 MM pound plant at Baton Rouge, LA. Availability of chloroacetic acid should be excellent. If American Hoechst's plant were to encounter operating difficulties, MCAA would be available from several foreign sources.

PRODUCERS AND CAPACITIES–CHLOROACETIC ACID–1984–MILLIONS OF POUNDS

PRODUCER	LOCATION	1984 CAPACITY
American Hoechst	Baton Rouge, LA	40
Dow Chemical	Midland, MI	30
Hercules	Hopewell, VA	60
Pfizer	Groton, CT	2
Vertac	Jacksonville, AR	6
	TOTAL	138

Based on published data and trade estimates. American Hoechst started production in early 1983. Buckeye Cellulose (Procter & Gamble) shut down a 4 MM pounds per year plant at Memphis, TN in late 1983, stopping carboxymethylcellulose production as well.

END USES.....Chloroacetic acid, monochloroacetic acid or MCAA, is a light-colored solid melting at 62° C., supplied as flakes, molten, or in 80% aqueous solution. The major application for MCAA is the manufacture of carboxymethylcellulose (CMC). Sodium chloroacetate reacts with alkali cellulose (made by soaking cellulose in 18% sodium hydroxide) to produce sodium carboxymethylcellulose. The degree of substitution of the active hydrogen atoms in the cellulose molecule governs the properties of the carboxymethylcellulose. Commercial grades range from 13% to 40% in degree of substitution. CMC is a water-soluble polymer with many applications. It is used in oil well drilling muds as a thickener and suspension agent. As a textile warp size, it competes with polyvinyl alcohol and starch. As an additive to frozen desserts, notably ice cream, it suppresses ice crystal growth and gives the product a smooth texture. It also improves the texture of cake icings, salad dressings, and beverages, and acts as a thickener and stabilizer. CMC is used as a pharmaceutical additive in ointments. lotions, and syrups as a stabilizer and viscosity modifier. It is used as a pulp additive in paper manufacture to promote dry strength.

Monochloroacetic acid is also an important intermediate for the manufacture of crop protection agents. MCAA and 2,4-dichlorophenol react in aqueous sodium hydroxide to form 2,4-dichlorophenoxy acetic acid (2,4-D). 2,4-D is a preferred herbicide on wheat and is used on home lawns as well as pastures and grazing lands. Chloroacetic acid also reacts with 2,4,5-trichlorophenol to form 2,4,5-trichlorophenoxy acetic acid (2,4,5-T). In making 2,4,5-T, small amounts of dioxin may be co-produced. The high toxicity of dioxin has led to environmental objections to the use of 2,4,5-T type herbicides.

Chloroacetic acid is a raw material for some important dyes. The synthesis of Vat Blue 1 (indigo) begins with phenylglycine formed by the condensation of aniline with chloroacetic acid. The synthesis of Vat Red 41 (thioindigo) starts with the reaction of thiosalicylic acid with chloroacetic acid.

Chloroacetic acid reacts with alkali cyanides to form cyanoacetic acid. Hydrolysis of cyanoacetic acid produces malonic acid; alcoholysis produces malonic esters. Barbiturates are produced by condensing urea or thiourea with disubstituted malonic esters. Chloroacetic acid reacts with sodium hydrosulfide to form thioglycolic acid. Ammonium thioglycolate is used in permanent hair waving preparations. Thioglycolic acid is also used as a raw material for polyvinyl chloride stabilizers. Pfizer reports production of chloroacetic acid to the International Trade Commission, and is believed to make caffeine from this raw material.

Substituted chloroacetanilide and chloroacetamide herbicides are produced by reacting either chloroacetic acid or chloroacetyl chloride with 2,4-dichlorophenol. Monsanto, the largest producer of these herbicides, starts with chloroacetyl chloride and, therefore, does not require chloroacetic acid. Ciba-Geigy may use chloracetic acid as a starting material for metolachlor (Dual TM).

Chattem Chemical produces glycine, aminoacetic acid, from chloroacetic acid and ammonia. WR Grace also produces glycine, but trade sources indicate that Grace uses technology not requiring chloroacetic acid.

END USE PATTERN–1983 ESTIMATE

DERIVATIVE	PERCENT
Carboxymethylcellulose	58
2,4-Dichlorophenoxy Acetic Acid	12
Miscellaneous	30

MANUFACTURING.....Hercules, American Hoechst, and Vertac are believed to produce chloroacetic acid by direct chlorination of acetic acid. Dry chlorine gas is sparged into liquid glacial acetic acid in the presence of catalytic quantities of sulfur or red phosphorus. The hydrogen chloride gas evolved is recovered as hydrochloric acid by water scrubbing. Crude crystals of chloroacetic acid, formed by cooling the reactor contents, are purified by solvent recrystallization to remove co-product dichloroacetic acid as well as unreacted acetic acid.

Chloroacetic acid can also be produced by the hydrolysis of chloroacetyl chloride. Dow can probably produce chloroacetic acid by this process. Dow is believed to make chloroacetyl chloride by the oxidation of vinylidene chloride. Dow separately produces vinylidene chloride monomer for polymer production or sale to the merchant market.

ENVIRONMENTAL.....Chloroacetic acid is a corrosive, hazardous chemical. It is a severe irritant to the eyes and respiratory tract. A systemic poison, it is highly toxic by ingestion and skin absorption. It causes persistent burns. Human fatality has resulted from contact over 10% of the body surface. The threshold limit value for chloroacetic acid, 8-hour time-weighted average, is 0.13 ppm.

When heated to decomposition, chloroacetic acid releases highly toxic fumes of phosgene and hydrogen chloride.