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COLLABORATIVE REPORT

EDTA

Tree with light-colored foliage suffers from iron ▶ deficiency; soil treament with sodium ferric EDTA gives dark-colored foliage (right)

ETHYLENEDIAMINETETRAACETIC ACID (EDTA), [(ethylenedinitrilo)tetraacetic acid] something more than a specialty but not quite yet a commodity, has attracted a number of producers, large and small. Among them, Geigy Chemical is a recognized leader. Geigy has acquired this status despite trade predictions that a basic position in EDTA raw materials, especially ethylenediamine and cyanide, is necessary to survive in an increasingly competitive market.

Lacking a preferred position on raw materials, the company has stressed and capitalized on process and marketing know-how. Today, Geigy claims to offer the most extensive line of EDTA derivatives and related products in the field.

Geigy got into the EDTA business when it bought Alrose Chemical in Cranston, R. I., in 1949. Alrose had been selling EDTA since 1947. After an abortive effort at a joint venture with Bersworth Laboratories, Alrose obtained a licence to make EDTA under General Aniline's patents (*4*). For Alrose, EDTA was a convenient way to diversify its textile chemical business. It was a product with a ready market in the textile trade, yet offered potential in new fields.

Although EDTA wasn't the reason Geigy bought Alrose (Geigy wanted Alrose's other textile chemicals), they recognized EDTA's potentials. Geigy built a new plant to replace the jerry-built unit which Alrose had used for EDTA.

By 1954, with demand promising to soon outstrip production capacity, Geigy began to overhaul its process and made plans to move EDTA production to McIntosh, Ala., where they already had units to make DDT and other agricultural chemicals. The McIntosh EDTA unit went on stream in 1958. Since then, it has already undergone one expansion and is ready for another one.

European Beginning

The history of EDTA goes back to the early thirties. Ferdinand Munz of I. G. Farbenindustrie is generally credited with inventing the product and with being the first to appreciate the compound's valuable metal chelating or sequestering properties. He had been investigating amino acids in textile processing and, apparently, tested routinely the reaction products of ammonia and chloracetic acid. This led to nitrilotriacetic acid and then to EDTA.

General Dyestuffs Corp. began to import the sodium salts of EDTA into the United States as early as 1936 and, in 1940, started making the material in this country. Frederick Bersworth, a pioneer in EDTA chemistry and then a special student at Clark University, also synthesized EDTA independently as early as 1931.

The original route to EDTA, using chloracetic acid and ethylenediamine, was relatively simple. Yields are satisfactory but the crude tetrasodium salt solution obtained contains by-product sodium chloride. This process, though used in Europe, has never been used in the U. S.

A second process (*6*, *7*) developed by I. G. Farbenindustrie was a two-step cyanomethylation. Ethylenediamine, formaldehyde, and sodium cyanide are reacted in aqueous solution to yield water-insoluble ethylenediamine tetraacetonitrile. This can be isolated readily in excellent yield and high purity, then may be converted to EDTA by acid or, preferably, alkaline hydrolysis. Yield via the hydrolysis route is practically quantitative. Ammonia is boiled off and the resulting crude solution is of high quality, containing only insignificant amounts of organic and inorganic impurities.

Bersworth, meanwhile, was developing his famous one-step cyanomethylation reaction and applied for a patent (*1*) on it in 1941. By-passing ethylenediaminetetraacetonitrile, the process yields a crude solution of tetrasodium EDTA directly. Compared to the two-step reaction, the process allows much lower plant investment and labor costs. Hence, it is an important industrial reaction today. One drawback to it, however, is that an excess of formaldehyde and cyanide are needed and, as a result, product purification is more of a problem. Still another modification of the cyanomethylation route to EDTA substitutes glycolonitrile for cyanide and formaldehyde.

Two other EDTA syntheses have been developed. Although they are commercially feasible, they have never been used industrially. One involves the catalytic oxidation of tetrahydroxyethylethylenediamine (*2*). The other is a reaction of ethylene dichloride and disodium iminodiacetate (*5*).

Alrose originally adopted the two-step cyanomethylation reaction, principally because of the excellent product quality. With reasonable selling prices, they could tolerate the higher costs of the process. But, as selling price dropped, the advantages of a single-step cyanomethylation reaction could not be

Ethylenediaminetetraacetic Acid

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overlooked. Potentially cheap hydrogen cyanide became a key to a process which could meet competition. Geigy began research on a liquid hydrogen cyanide route to EDTA in 1952 and obtained this patent (*3*) in 1958.

Working with hydrogen cyanide, however, can be dangerous and the Alrose plant at Cranston edged on a residential district. So Geigy switched EDTA operations to McIntosh, which was "out in the woods" and where there was plenty of room.

Geigy's Operation

Geigy's process, like the Bersworth synthesis, is a one-step cyanomethylation process, but it uses hydrogen cyanide instead of sodium cyanide. The advantage is obvious: it costs less. However, hydrogen cyanide is much trickier to handle.

Geigy's process, as described in its patent, sounds simple enough: A stabilized formaldehyde–hydrogen cyanide solution is prepared by adding 119 parts of hydrogen cyanide to 340 parts of 37% formaldehyde at pH 1. This, in turn, is added to a solution of 60 parts ethylenediamine and 197 parts sodium hydroxide in 497 parts water at 100° to 105° C. When the reaction is complete, the solution contains 380 parts of tetrasodium ethylenediamine tetraacetate (Na_4EDTA). Behind these simple steps, however, lies a lot of process "know-how" which is necessary to assure product quality.

Major raw materials (with the exception of hydrogen cyanide which gets special storage and handling attention, see box, right) are stored in 15,000-gallon tanks at some distance from the

Hydrogen Cyanide . . . Handle with Care

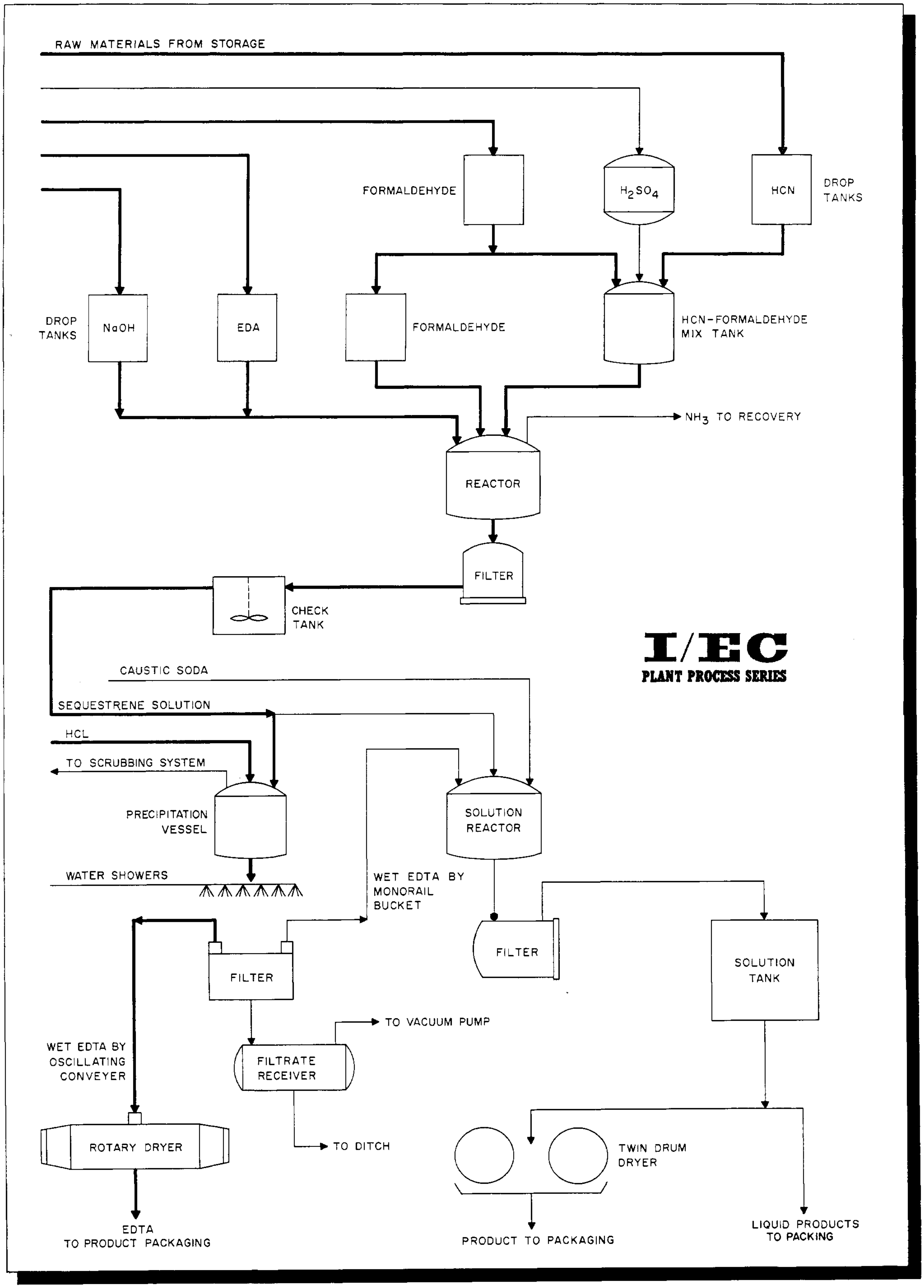
Before an employee is accepted for the EDTA plant, he must be able to detect 2 to 5 p.p.m. hydrogen cyanide by smell. But so far, no one has had to sniff and then run for his life. Though hydrogen cyanide is highly toxic, it is safe to work with if proper precautions are taken. And Geigy's hydrogen cyanide storage and handling systems are designed for safety. Du Pont, from whom Geigy gets its hydrogen cyanide, helped design the storage unit and, in fact, had to approve the unit before it delivered the first tankcar of HCN.

The hydrogen cyanide storage tank is an 8000-gallon insulated steel vessel equipped with a sulfuric acid pot from which sulfuric acid can be added. Hydrogen cyanide must be kept acidic and daily checks are made to see that minimum acidity is 0.03% sulfuric acid. Alkaline materials, such as ammonia, soda ash, and caustic, induce decomposition, which may become violent as well as release the deadly hydrogen cyanide to the atmosphere.

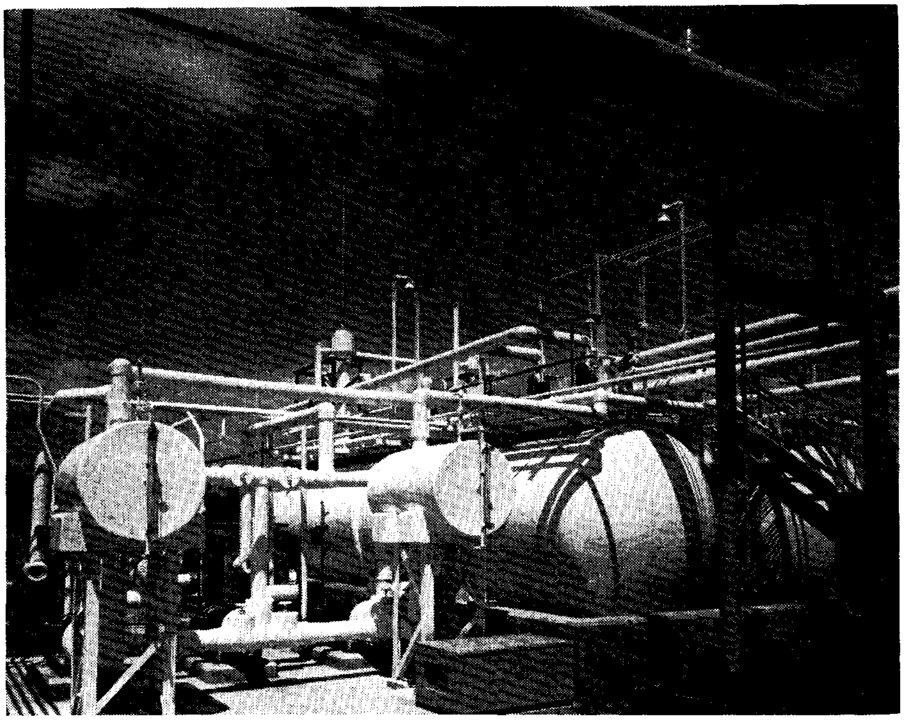
Hydrogen cyanide storage is equipped with an hydrogen cyanide liquid chiller. This is cooled with methanol rather than brine to ensure that no alkaline chemicals leak into the system. In the EDTA plant, both the hydrogen cyanide drop tank and the vent condenser of the formaldehyde-hydrogen cyanide mix tank are also cooled with methanol. Hydrogen cyanide in storage is kept between 0° and 5° C. An automatic alarm sounds if the temperature rises to 15° C. Abnormal temperature rise or brown discoloration are signs of hydrogen cyanide decomposition.

Piping is arranged so that no hydrogen cyanide can be trapped in the lines. There is also an automatic indicator on the storage tank which sounds if the hydrogen cyanide volume gets within 1000 gallons of the 8000-gallon capacity.

The entire hydrogen cyanide system is laid out in duplicate so that the material can be safely handled in case any part of one system fails. An emergency generator also serves the hydrogen cyanide area in case of power failure. A final cardinal rule at Geigy: No one enters the hydrogen cyanide storage area by himself or works with hydrogen cyanide alone.



Flowsheet for the manufacture of ethylenediaminetetraacetic acid, Geigy Chemical Corp., McIntosh, Ala.



Hydrogen cyanide storage tanks. Small tanks on left are storage tanks for cold methanol in hydrogen cyanide liquid chillers

EDTA unit for safety. These tanks feed to 3000-gallon intermediate storage tanks which are closer to the reaction vessels for convenience. Formaldehyde in storage is kept above 90° F. to retard polymerization.

Ethylenediamine and 50% caustic soda are metered directly into the stainless steel reactor. Process water from 350-foot wells, although relatively free of hardness and iron, nevertheless passes through a treating unit before it enters the reactor. Water does two things:

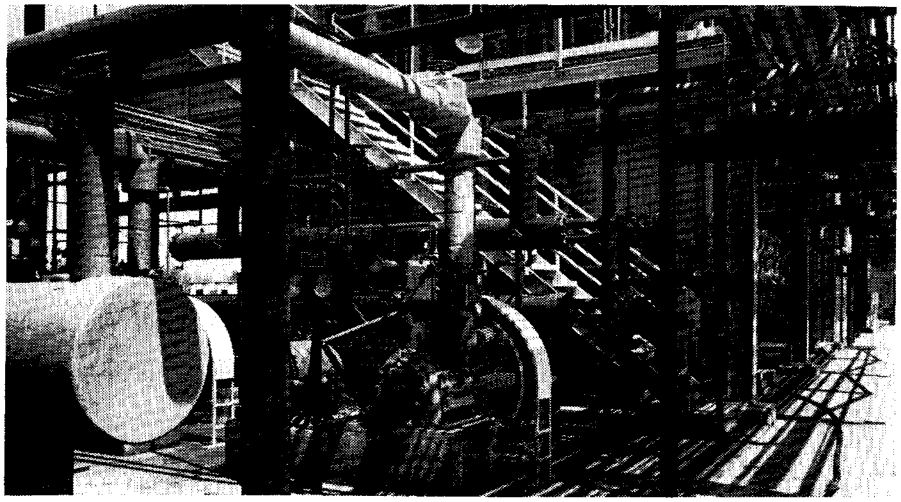
- It ensures complete solution of ethylenediamine and caustic; without it a two-phase system results.
- It prevents Na_4EDTA from crystallizing during the reaction.

Formaldehyde and hydrogen cyanide are premixed in a glass-lined tank; the formaldehyde goes in first. When it is cooled to 0 to 5° C., sulfuric acid is added to pH 1. Low temperature prevents the low-boiling hydrogen cyanide from volatilizing and low pH prevents formaldehyde and hydrogen cyanide from reacting. If pH were left at 3.5 or higher, a dangerous, uncontrollable reaction would occur when the hydrogen cyanide was added. These conditions, low pH and low temperature, hasten the formation of paraformaldehyde, which is harmful to equipment. But the hydrogen cyanide–formaldehyde mixture is in the tank for such a short time that this is no problem. When all other materials are in the reactor, the hydrogen cyanide–formaldehyde solution is slowly added (about 3 gallons per minute) with reaction temperature at 100° to 105° C.

Geigy heats and agitates the reaction solution until no by-product ammonia can be detected. At this point the reaction is complete. If there is a trace of cyanide in the product, dilute (10%)

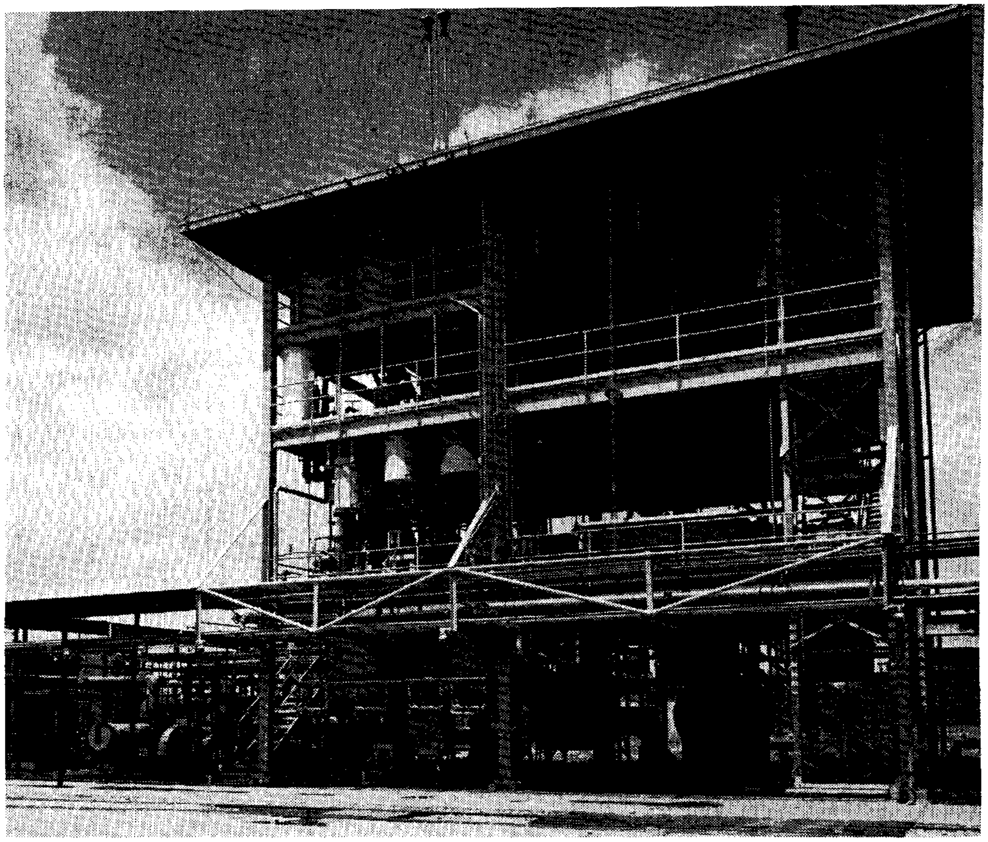
Various amines can be substituted for ethylenediamine as a starting material or EDTA can be further reacted to give a host of different complexing agents and metal chelates. Here are some:

Tetrapotassium ethylenediamine tetraacetate solution
Disodium ethylenediamine tetraacetate dihydrate
Trisodium ethylenediamine tetraacetate trihydrate
Trisodium ethylenediamine tetraacetate monohydrate
Tetrasodium ethylenediamine tetraacetate dihydrate
Tetrasodium ethylenediamine tetraacetate solution
Sodium ferric EDTA
Dihydrogen ferrous EDTA
Disodium calcium EDTA
Disodium magnesium EDTA
Disodium cobaltous EDTA
Disodium manganous EDTA
Disodium cupric EDTA
Disodium zinc EDTA
Disodium nickel EDTA
Purified disodium calcium EDTA
Recrystallized disodium EDTA dihydrate
Analytical grade disodium EDTA dihydrate
Ethylenediamine di(*o*-hydroxyphenylacetic acid)
Sodium dihydroxyethyl glycine
Hydroxyethyl ethylenediaminetriacetic acid
Diethylenetriamine pentaacetic acid
1,2-Diaminocyclohexane tetraacetic acid
Disodium iminodiacetate solution
Sodium sarcosine
Nitrilotriacetic acid



▶

This refrigeration unit provides the brine which cools the hydrogen cyanide–formaldehyde mix tank. The brine also cools methanol which, in turn, is coolant for hydrogen cyanide systems



Geigy's EDTA unit shows the reaction vessels and drop tanks

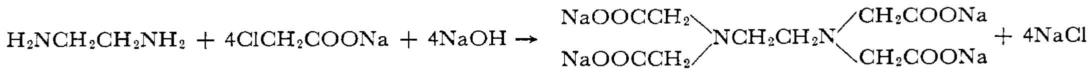
formaldehyde is added and the solution heated to convert cyanide to hydroxyacetic acid. Geigy tests for cyanide with picric acid, tolerates no cyanide in the product. Traces of formaldehyde are also destroyed.

Hydrogen peroxide is added to produce a water-white stock solution. If necessary, Geigy adds water to bring the solution's equivalent EDTA content to between 32 and 34%. The product is then cooled, passed through clarifying filters, and held in a check tank until quality control reports are complete. Plant controls include activity and solids content, pH and specific gravity, appearance, color, and trace impurities.

By-product ammonia is recovered and used as feedstock in other agricultural chemical units at McIntosh.

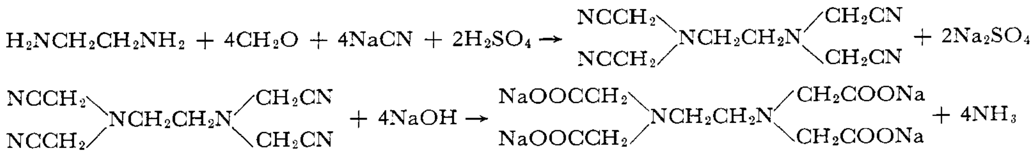
The Na_4EDTA solution, called Sequestrene Solution (Geigy trademark), has a final equivalent EDTA content of 30 to 32%. It is the starting point for many other Geigy sequestering and chelating agents. Or, with its EDTA content standardized at 29.5 to 30%, it is sold under the trade name Sequestrene 30A.

Many Routes to EDTA



$$\mathrm{H_2NCH_2CH_2NH_2 + 4ClCH_2COONa + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 4NaCl}$$

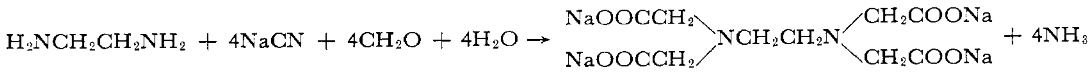
Ethylenediamine and Chloracetic Acid



$$\mathrm{H_2NCH_2CH_2NH_2 + 4CH_2O + 4NaCN + 2H_2SO_4 \rightarrow \begin{matrix}NCCH_2\\NCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2CN\\CH_2CN\end{matrix} + 2Na_2SO_4}$$

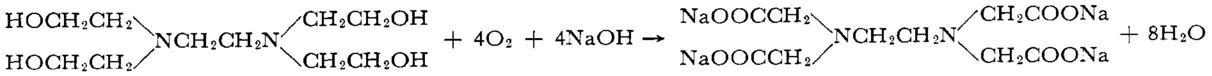
$$\mathrm{\begin{matrix}NCCH_2\\NCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2CN\\CH_2CN\end{matrix} + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 4NH_3}$$

Two-Step Cyanomethylation



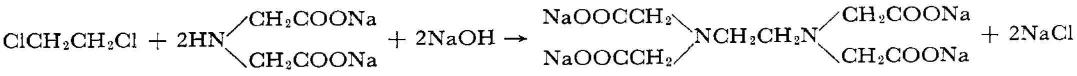
$$\mathrm{H_2NCH_2CH_2NH_2 + 4NaCN + 4CH_2O + 4H_2O \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 4NH_3}$$

Bersworth's One-Step Cyanomethylation



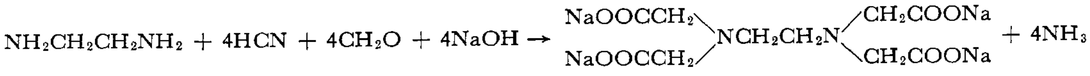
$$\mathrm{\begin{matrix}HOCH_2CH_2\\HOCH_2CH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix} + 4O_2 + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 8H_2O}$$

Catalytic Oxidation of Tetrahydroxyethylethylenediamine



$$\mathrm{ClCH_2CH_2Cl + 2HN\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 2NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 2NaCl}$$

Ethylene Dichloride and Disodium Iminodiacetate



$$\mathrm{NH_2CH_2CH_2NH_2 + 4HCN + 4CH_2O + 4NaOH \rightarrow \begin{matrix}NaOOCCH_2\\NaOOCCH_2\end{matrix}\!\!>\!NCH_2CH_2N\!<\!\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix} + 4NH_3}$$

Geigy's One-Step Cyanomethylation

The Acid

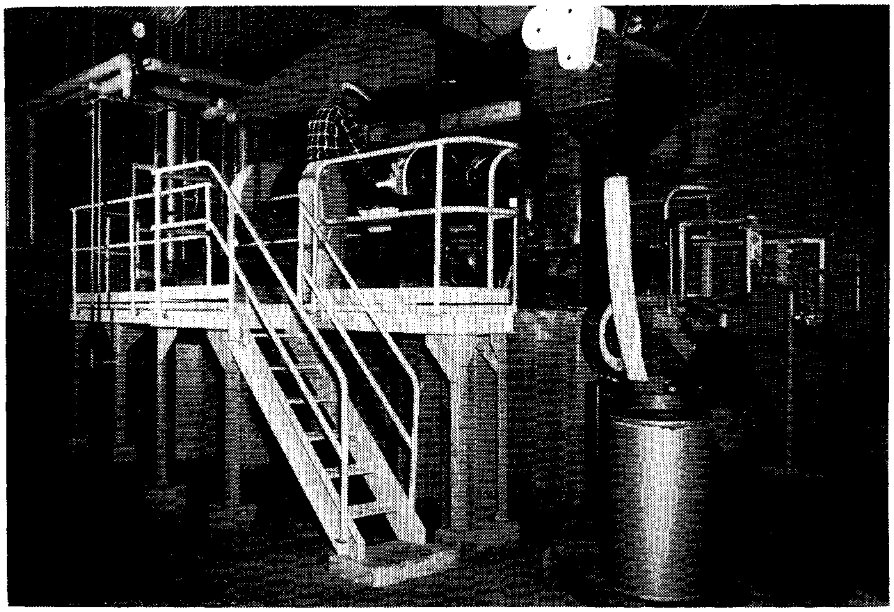
EDTA itself is made by reacting Na$_4$EDTA with hydrochloric acid. The Na$_4$EDTA stock solution is pumped into a rubber-lined, steel precipitation vessel. Hydrochloric acid is added slowly to pH 1.8 to 2.0 to precipitate the insoluble free acid.

The reaction solution flows by gravity to rubber-lined filter boxes fitted with acid resistant, porous stone filter beds and overhead showers which wash the filter cake until the effluent is chloride-free. Geigy takes great care in the precipitation step to get just the right crystal habit so that the product washes readily in the filters.

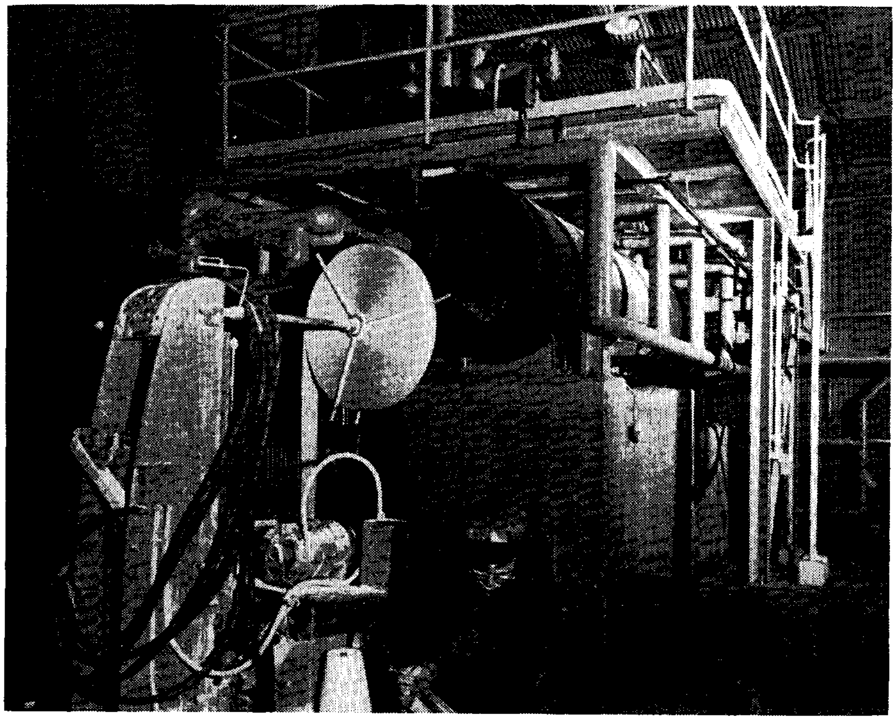
After the EDTA wet cake is sucked as dry as possible, it goes by oscillating conveyer to a rotary dryer and, then, to a drum filler. Or the wet EDTA can be shovelled into a bucket suspended from a monorail which carries it to reaction vessels for further processing.

The McIntosh plant produces disodium, trisodium, and tetrasodium salts from the EDTA acid filter cake. Most metal chelates are also made from the acid. Recrystallized grades for pharmaceutical, food, and reagent uses are still made at Cranston, R. I., from wet acid shipped there from McIntosh.

Other chemicals which Geigy's EDTA plant cyanomethylates are diethylenetriamine, aminoethylethanolamine, diethanolamine, ammonia, and methylamine. Aside from the chelating agents which Geigy obtains from this reaction, they also produce disodium iminodiacetate, sodium sarcosine, and sodium glycine for use as intermediates in the manufacture of *N*-acyl amino acid surfactants. Thus, the company has spread its risks and hedged against the uncertainties of a single-product plant.



Twin drum dryer yields solid products from liquid solutions



This is the rotary dryer used for EDTA and other solid EDTA products

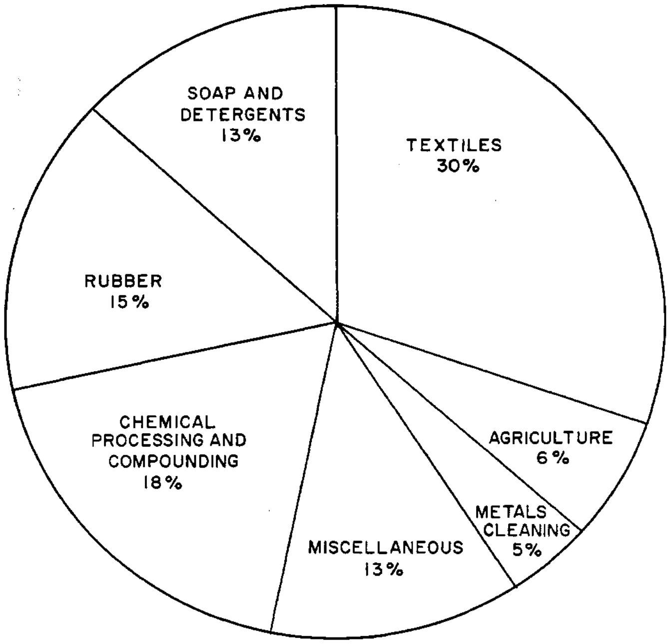
Hazy Market Picture

The EDTA market presents a picture of ever-changing patterns and sharp contrasts. Nor was its development predictable and smooth. EDTA made its mark first in textile processing, where it is used to "complex" foreign metal ions on the cloth or in the dye bath. These impurities would otherwise react with the dyestuff and ruin the color. Today the textile industry still remains the largest single outlet for chelating agents, accounting for 30 to 45% of total production, depending upon who does the estimating.

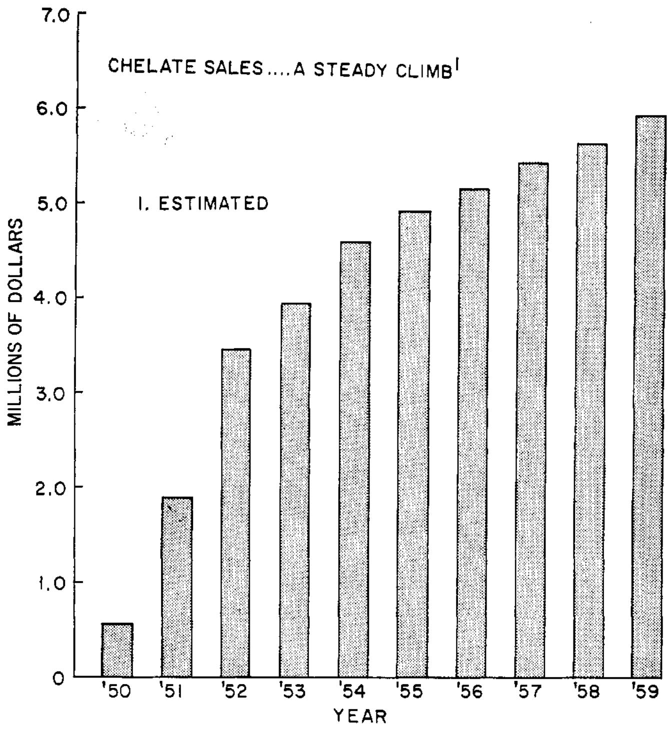
Clarification of liquid soap shampoos (dissolving lime soap) was another early use for EDTA, but as synthetic surfactants replaced soap, the market here for EDTA dwindled. However, it began to show up before long in synthetic-based shampoos to prevent discoloration by traces of iron.

Large amounts of EDTA were used with 2,4-D weed killer to prevent precipitation of 2,4-D by hard water upon dilution. Then cheaper and equally effective citric acid squeezed it out. Meanwhile, EDTA found applications in photographic developers, cold rubber polymerization, toilet soap, and metal descaling. Most of these uses are described as sequestration or metal deactivation.

EDTA eventually became a valuable processing tool while EDTA metal chelates proved to be highly regarded products in their own right. In 1952, for instance, it was discovered that iron EDTA would correct iron deficiency in Florida tree and field crops. EDTA



The chelate market is changing all the time. Here's about the way it looks now



Chelate sales show a steady climb

also became important in ion exchange processes, such as the purification of streptomycin and separation of high purity rare earths. For awhile, rare-earth separation loomed as a top market for EDTA but the ever-changing nuclear development program, increased use of solvent extraction, and new EDTA recovery systems whittled down this market too.

EDTA producers are eying hopefully a number of possible new applications for their product. Among them:

Agriculture. EDTA is still limited mainly to the acid soil of Florida, but ethylenediamine di(*o*-hydroxyphenyl acetic acid) (Geigy's Chel 138) looks good on western alkaline soil after a season of commercial use.

Electroplating. Restrictions on cyanide disposal are encouraging efforts to work out practical EDTA plating procedures, but commercial use of EDTA plating baths is still small.

Mineral Separations. EDTA is being used in beryllium purification as well as in "bound-to-grow" rare-earth separations. But large scale beneficial use is still in the future.

Food Additives. Use of EDTA in trace quantities in food products as a stabilizer and preservative is one of the industry's great potential outlets, but it must await clearance by the Food and Drug Administration.

Sales Up, Prices Down

Sales in 1959 were expected to exceed $6 million. By comparison, in 1950 the total was less than $500,000. As surely and as steadily as sales have climbed, prices have dropped. In 1948, Na_4EDTA solution sold for $1.00 per pound (EDTA basis), but today tank car shipments are available at $0.45 per pound, delivered. EDTA acid has similarly dropped from $1.30 to $0.70 per pound in 10 years.

What brought on these lower prices? For one thing, bigger and more efficient production in response to increased demand. A downward trend in raw material prices helped; and finally, competition.

In 1948, there were only three producers. By the mid fifties, there were more than three dozen producers according to some trade estimates. In the past, the small fellow has found Na_4EDTA solution a tempting attraction. Because the product could be made by almost anybody with some second-hand equipment, many found it expedient to jump into the business when the market was favorable, jump back out when it was not. But, as profit was squeezed out of the product, only the firms with a real stake in EDTA held on.

Major producers of chelates today are Geigy, Dow (which bought Bersworth Chemical in 1954), Refined Products (purchased by Johnson and Johnson last year), General Aniline, and Glyco. Victor's A. R. Maas division is the only West Coast manufacturer. American Cyanamid, sole producer with captive cyanide, has been in the business for a few years but makes only Na_4EDTA liquid. Hampshire Chemical has been an aggressive newcomer.

No one knows with certainty the combined capacity of this group. One market researcher says 75 million pounds per year; another doubts that it is anywhere near that much, but adds that it isn't too difficult to expand a properly designed plant. In any event, there is plenty of capacity among current producers to handle foreseeable demand for the next few years.

Geigy continues to emphasize, and is still researching, exotic chelating agents and high purity products. This field offers more elbow room than the relatively simple liquid products. And these specialty chelates are difficult, if not impossible, for the fly-by-night operator to make.

Competition in the chelate business promises to get rougher and some people may not want to bother with it. Geigy, however, plans to stay in.

Acknowledgment

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