I/EC
STAFF-INDUSTRY
COLLABORATIVE REPORT

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Sorbitol

Sorbitol has become a good item for Merck since it entered the business in 1956. Demands for the polyol keep rising 5 to 10% a year and Merck figures this pace will continue for the next few years. Established outlets such as vitamin C synthesis, pharmaceutical preparations, and surface active agent manufacture should keep the sorbitol market moving ahead. In the past decade these products have brought about a fivefold increase in sorbitol output. Production of all forms should reach 50 million pounds this year—up 5 million pounds over 1959. For contrast, output hovered in the 10 million-pound range in the late 1940's.

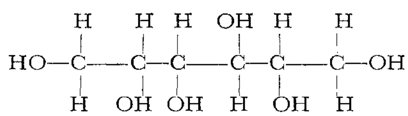
Domestic capacity is about 90 million pounds today and one third of this is geared for captive use. Atlas Powder and Merck make it for commercial as well as internal use; Chas. Pfizer and Hoffmann-La Roche make sorbitol for captive use only.

Some Critical Points to Watch While Making Sorbitol

- Catalyst activity
- Hydrogen dispersion
- Optimum pressure and temperatures
- Elimination of catalyst poisons and trace impurities
- Maintenance of all necessary safety practices inherent in high pressure use of hydrogen
- Cleanliness
- Complete quality control of raw materials and finished products

Sorbitol, a Polyol

Sorbitol is a hexahydric alcohol with a straight chain of six carbon atoms and six hydroxyl groups. The molecular weight is 182.1.



As a pure solid, sorbitol is a white, odorless, crystalline material. It has a negative heat of solution, hence produces a cooling effect when tasted. Also, sorbitol is two third's as sweet as sugar.

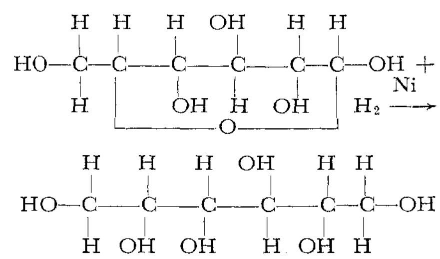
Sorbitol is readily soluble in water but only slightly soluble in methanol and ethanol. It is virtually insoluble in the common organic solvents. And, it is inert to dilute acids and alkalies.

Sorbitol is found in many natural products such as seaweed, tobacco, edible fruits, and plants. Sorb berries and mountain ash berries are particularly rich sources of the polyol. It was first isolated in 1872 by the French chemist, Joseph Boussingault. However, natural materials are not a good commercial source. It can be made by the reduction of several sugars such as D-glucose, D-fructose, L-gulose, or D-mannose.

Atlas Powder was the first to make sorbitol commercially. Its interest stems back to manufacture of mannitol for use in explosives. In the mannitol process, Atlas got sorbitol as a by-product. But in time the tail began to wag the dog so Atlas started to develop a sorbitol process based on electrolysis of glucose. The firm began to make it on a pilot plant scale in the early 1930's and in 1937 began commercial production. Atlas had the commercial market to itself until 1956, when Merck decided to enter the field using a process based on catalytic hydrogenation of dextrose at its Cherokee plant in Danville, Pa. Merck's move was a natural for the firm because it had large captive needs for sorbitol in vitamin C production and other pharmaceutical uses. A second reason was to broaden Merck's position in the industrial chemical field.

Sorbitol by Catalytic Hydrogenation

Merck makes sorbitol by pressure hydrogenation of dextrose solution using a Raney nickel catalyst. It is a batch process and the reaction is as follows:



D-Sorbitol

Here Are the Key Steps in Merck's Sorbitol Process

- Make a deionized dextrose solution
- Generate and store hydrogen
- Prepare an active nickel catalyst
- React hydrogen with dextrose to make sorbitol
- Filter and purify the sorbitol solution

Dextrose is bought (as the monohydrate) on contract from several supply sources. The contract specifies a commercial (edible) grade which is 99.5% dextrose on a dry basis.

The monohydrate is delivered to Danville in conventional railroad hopper cars and transferred pneumatically to a glass-lined storage silo with a capacity of 4600 cubic feet. The silo is equipped with a cyclone separator and bag filter.

For conversion to sorbitol, the dextrose is again conveyed pneumatically to a solution make-up tank in the plant processing area. This tank has an 8000-gallon capacity. A 50% dextrose solution is made using warm water from the plant's steam condensate system. The mixture is circulated in the make-up tank until the dextrose dissolves completely.

The final solution has small amounts of inorganic salts which could poison the catalyst during hydrogenation, so these are removed by passing the solution through a cationic-anionic exchange system. The deionized solution is then pumped to hold tanks to await charging to the hydrogenation autoclaves.

Hydrogenation

Merck has several autoclaves for use in the sorbitol process. These were designed by Merck for this process; are stainless steel clad, jacketed for water cooling, and equipped with agitators. The vessels are built to take pressures up to 2000 p.s.i.

Adjacent to the autoclaves are catalyst make-up units. The catalyst is prepared just prior to hydrogenation from Raney nickel—an aluminum-nickel alloy (about 50% nickel by weight). It is made active by dissolving the aluminum from the matrix with warm (60° C.) 25% caustic soda. After the aluminum is dissolved from the matrix, the solution is treated with deionized water to remove sodium aluminate which is formed during the caustic soda treatment. The catalyst is then charged to an autoclave as a slurry by nitrogen.

Deionized dextrose solution—about 3000 pounds of dextrose per charge—is then added to the autoclave and agitation started. Hydrogen flow is turned on and the reaction begins. The hydrogenation takes place at 1000 p.s.i. and requires up to 3 hours to complete. During the reaction, the process temperature is controlled below 150° C. About 1800 cubic feet of hydrogen are needed for each 1000 pounds of dextrose charged.

When the reaction is complete, the catalyst is allowed to settle to the bottom of the autoclave. The pressure is reduced by venting the hydrogen back to the gas holder and then, the reduced pressure is used to blow the supernatant sorbitol to a dual filtering system.

Merck Makes Own Hydrogen

Merck makes the hydrogen for the sorbitol process electrolytically at Danville using conventional cells and 28% potassium hydroxide as the electrolyte. But, during peak demands, Merck supplements in hydrogen output with trailer hydrogen.

The Danville plant has two banks of cells and each cell can make 1.3 cubic feet of hydrogen per minute. Hydrogen produced is stored in a gas holder until needed in the process; oxygen made during electrolysis is vented to the atmosphere.

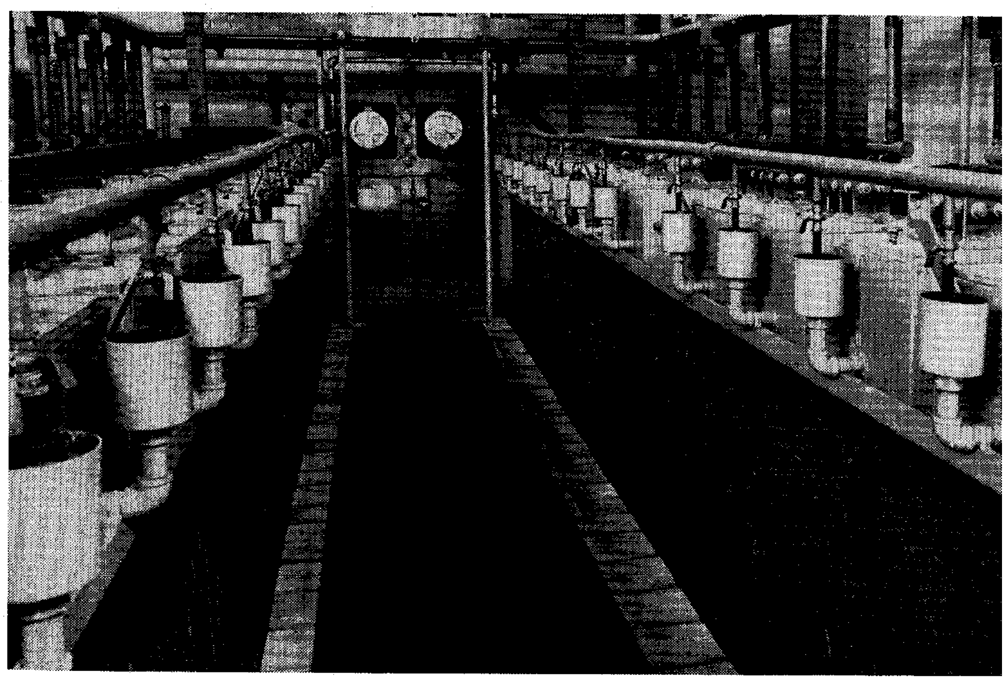
When needed, the hydrogen is freed of all traces of oxygen and passed through a four-stage compressor which builds the pressure up to 3500 p.s.i. This compressed gas then flows to the autoclaves in use.

The first is a Rigimesh—micrometallic filter. The catalyst is pyrophoric so it is separated from the sorbitol solution then washed back to the autoclave without coming in contact with air. The sorbitol solution is passed through a sparkler filter and any catalyst picked up here is inactivated and stored underwater. Meanwhile, the sorbitol solution is pumped to storage tanks to await further processing.

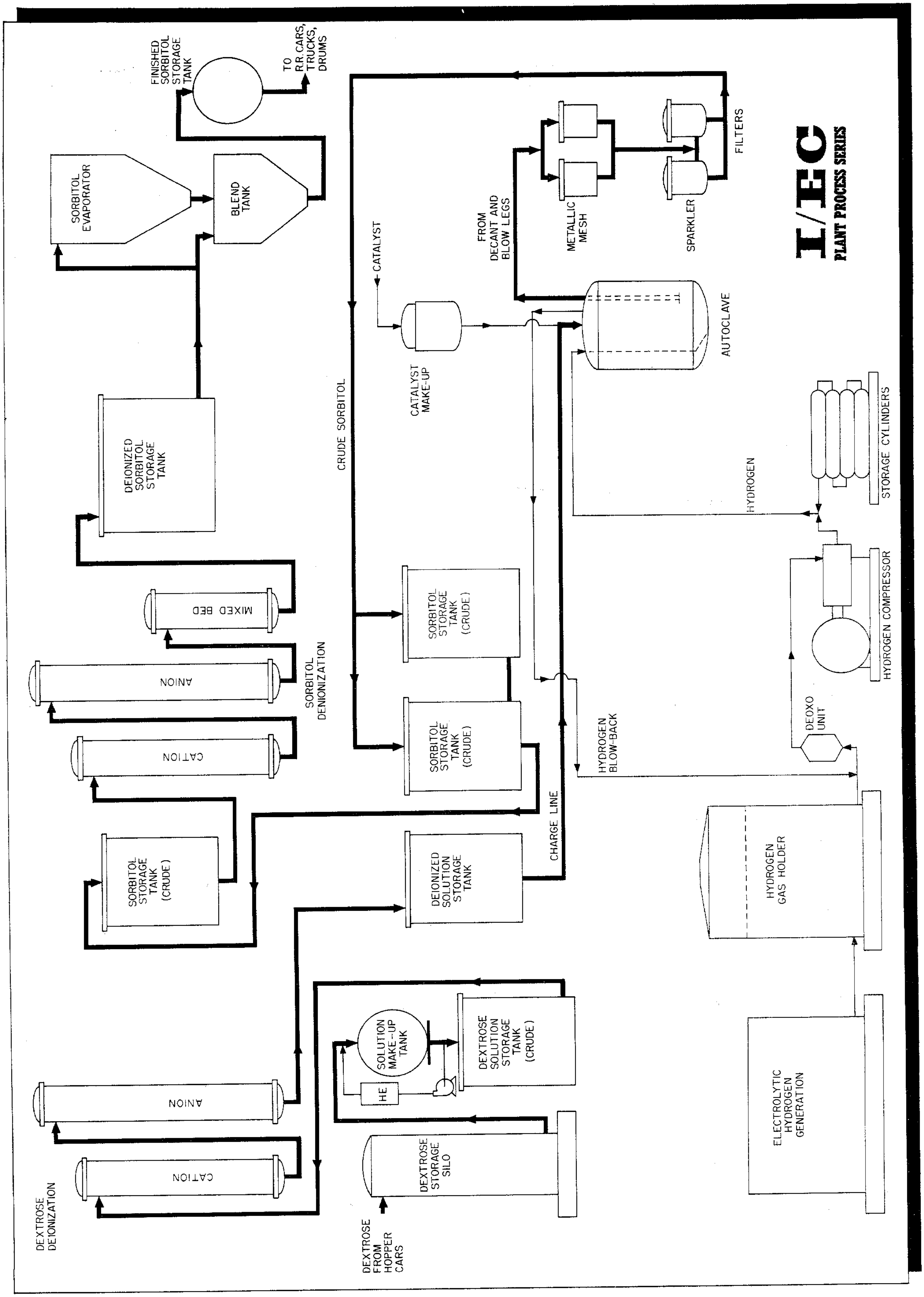
Deionized for Purity

The freshly-made sorbitol solution contains some impurities such as nickel from the hydrogenation. These are removed and the sorbitol purified by passing it through a three-stage deionization system–cationic–anionic-mixed bed.

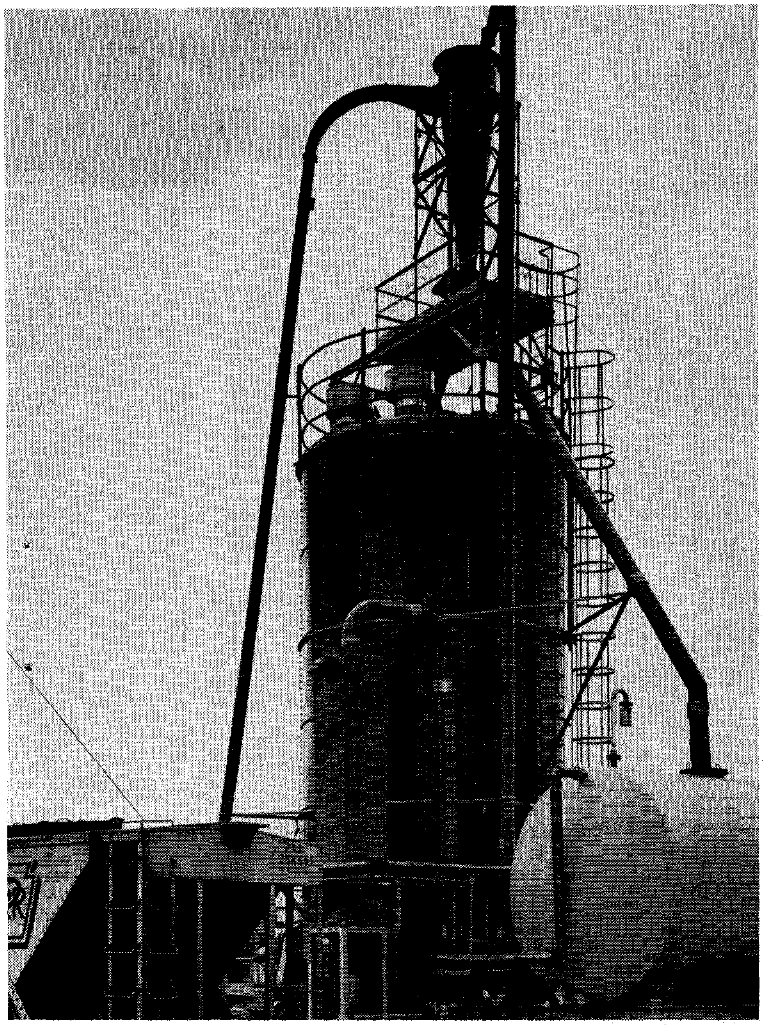
The deionized solution contains 50% sorbitol which is all right for captive use by Merck. But Merck's commercial sorbitol is a 70% solution and this is made by evaporating the deionized sorbitol at 45° to 50° C. under a 50- to 80-mm. vacuum. The 70% solution is then pumped to storage tanks for shipment to customers. It is shipped in tanks cars, tank trucks, or in 55-gallon drums.



Hydrogen for the sorbitol process is made electrolytically at Merck's Danville plant



Flowsheet for the manufacture of sorbitol, Merck and Co., Inc., Danville, Pa.



◀ Storage silo at Danville, Pa., plant of Merck. Dextrose is stored in this glass-lined silo prior to conversion to sorbitol

Running dextrose from make-up tanks through deionization columns. The recorder is checked to show the progress of the operation

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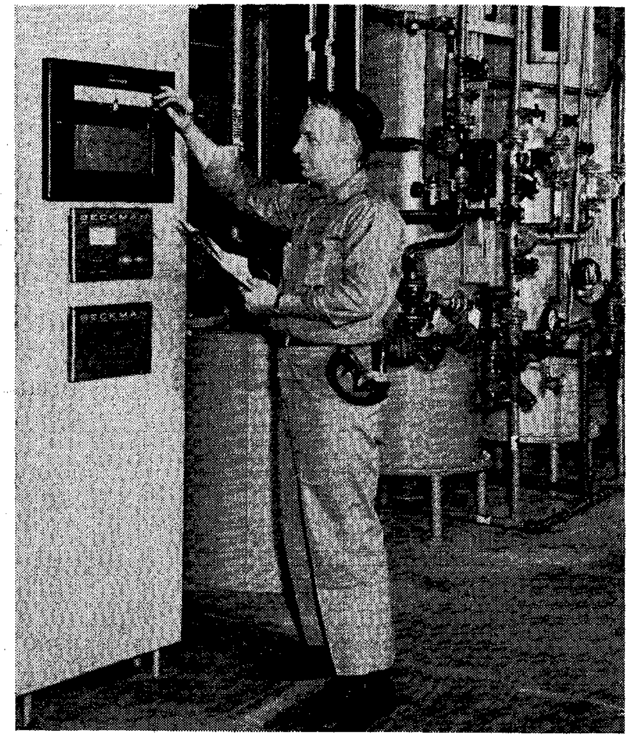

Top view of the autoclave. The flange is being tightened on the sorbitol reactor just before the charging of the first batch

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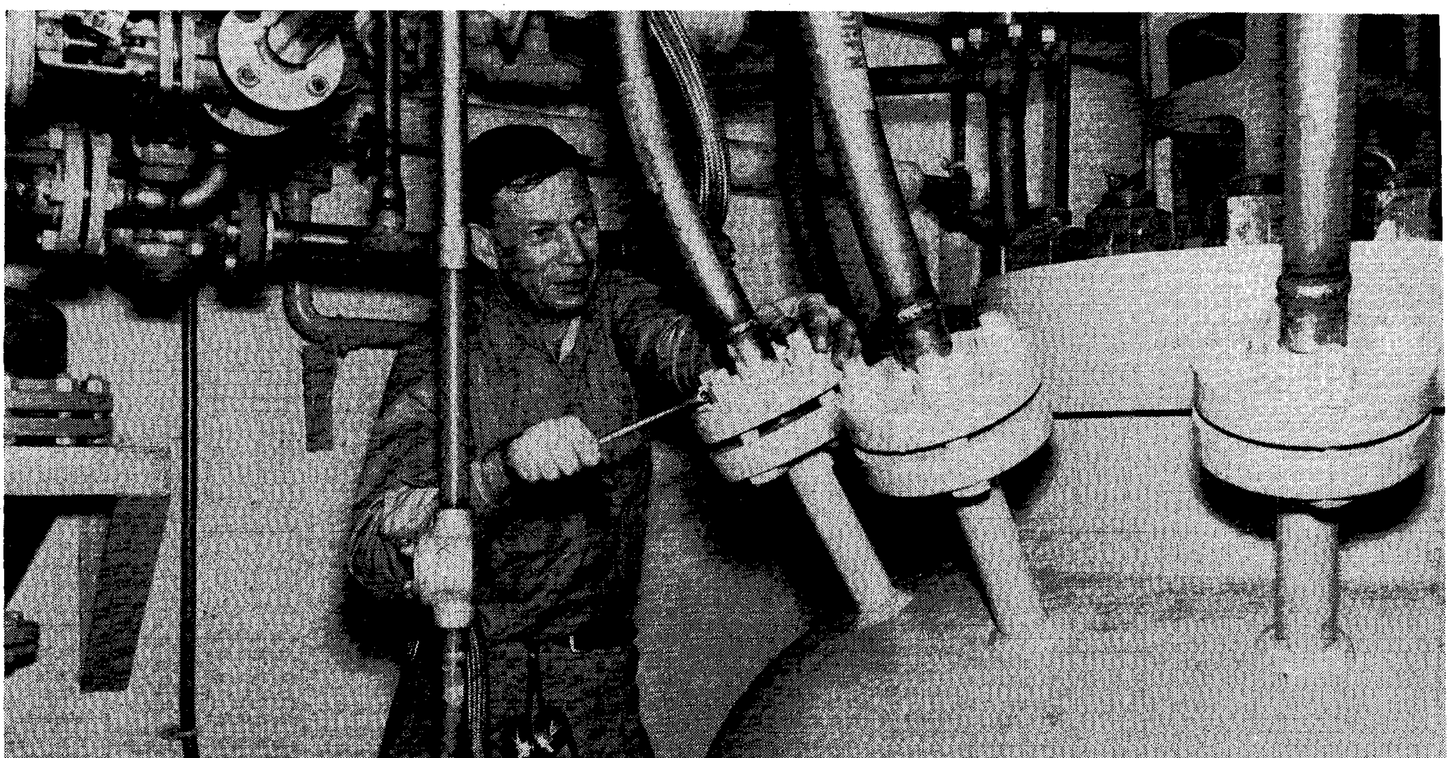
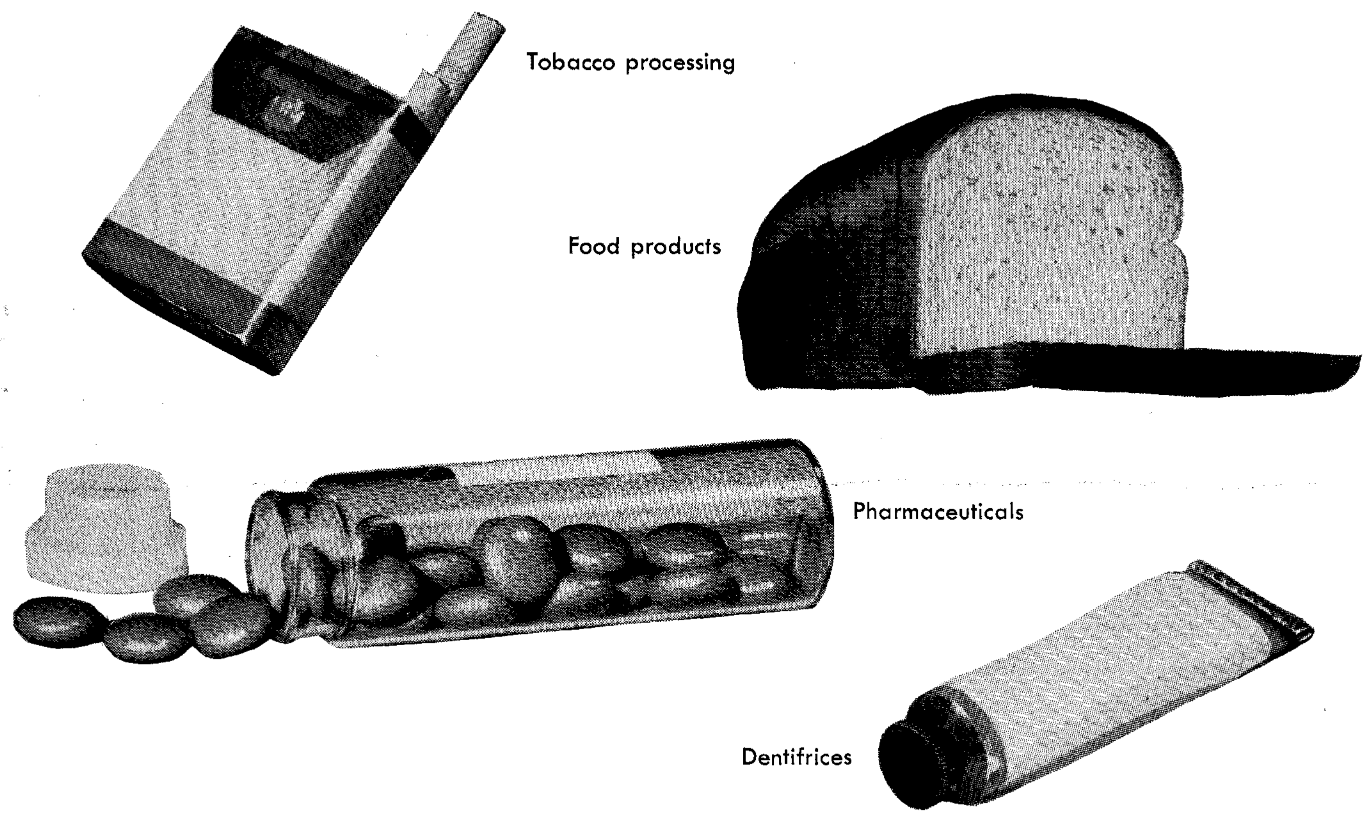


Sorbitol Uses



Sorbitol's uses cross a wide spectrum of pharmaceutical, cosmetic, and industrial applications. Except where used to make vitamin C, sorbitol competes for markets with glycerol as a bodying agent, plasticizer, moisture conditioning agent, and other uses in the food field. Sorbitol competes with pentaerythritol and other polyols in the resin field.

Back in 1925, glycerol represented 97.5% of the polyol market; by 1945 it was down to 40%, and now is about 20%. Glycerol's price ranges from 28 to 30 cents a pound (depends upon grade), while sorbitol (70% solution) runs 18 cents a pound. On a solid basis it is equivalent to 26 cents a pound.

Vitamin C (ascorbic acid), surface active agents, and food additives consume 55% of the sorbitol produced. Most of Pfizer's and Hoffmann-La Roche's sorbitol goes to make vitamin C as do substantial amounts of Merck's output. Typically, sorbitol is converted to ascorbic acid by a fermentation process which converts sorbitol to D-sorbose using an acetic acid bacteria. The sorbose is oxidized to L-xylo-2-keto-gulonic acid. When this intermediate is heated in acid solution, the free 2-keto-gulonic acid group is lactonized to produce ascorbic acid.

Vitamin C production reached 4.5 million pounds in 1959 and output is expected to rise again this year. Further output gains are expected as vitamin C demands grow for therapeutic use and as vitamin C supplementation of fruit juices and other foods continues to increase.

In pharmaceutical applications, sorbitol has a myriad of uses including sugar replacement in preparations, as sorbitol is more stable than sugar in some applications. It is also used to make organic and inorganic derivatives as well as a clarifying agent and embalming fluid.

As sorbitol does not affect buccal membranes, it is used to compound dentifrices and cosmetics.

Another well known use for sorbitol is to make surface active agents called Spans and Tweens. These are fatty acid esters of sorbitans which are made of sorbitol by Atlas.

Sorbitol's End Use Pattern Shapes Up Like This

	%
Pharmaceuticals	10
Ascorbic acid	25
Surface active agents	15
Food field	15
Dentifrices and cosmetics	10
Adhesives	5
Resins	5
Miscellaneous (explosives, textile conditioners, paper finishing agents, etc.)	15

Spans and Tweens get the largest use in the pharmaceutical industry as emulsifying and wetting agents and are also used in various foods.

Food use of sorbitol is in some flux now, due to Food and Drug Administration regulations. At one time the limit was 15% but this has been cut to 7%. This is not significant for many food uses but is important in candies—particularly diatetic candies—and in ice cream. Merck along with others has appealed this ruling.

Wrapping up the many uses for sorbitol are adhesives and resins. The adhesives are primarily plasticizers of softeners. Resins made from sorbitols are alkyd types, but of late this market has declined because of competition from pentaerythritol and glycerol-based materials.

All things considered, the sorbitol market has seen its greatest spurt in Merck's opinion. No new outlets are about to crop up which should hike the market. But there is enough growth remaining to assure a steady 5 to 10% increase in demand—and this is a level satisfactory to Merck.

Acknowledgment

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