

One Hundred Years of Commercial Food Carbohydrates in the United States

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Initiation and development of the industries producing specialty starches, modified food starches, high-fructose sweeteners, and food gums (hydrocolloids) over the past century provided major ingredients for the rapid and extensive growth of the processed food and beverage industries. Introduction of waxy maize starch and high-amylose corn starch occurred in the 1940s and 1950s, respectively. Development and growth of the modified food starch industry to provide ingredients with the functionalities required for the fast-growing processed food industry were rapid during the 1940s and 1950s. The various reagents used today for making cross-linked and stabilized starch products were introduced between 1942 and 1961. The initial report of enzyme-catalyzed isomerization of glucose to fructose was made in 1957. Explosive growth of high-fructose syrup manufacture and use occurred between 1966 and 1984. Maltodextrins were introduced between 1967 and 1973. Production of methylcelluloses and carboxymethylcelluloses began in the 1940s. The carrageenan industry began in the 1930s and grew rapidly in the 1940s and 1950s; the same is true of the development and production of alginate products. The guar gum industry developed in the 1940s and 1950s. The xanthan industry came into being during the 1950s and 1960s. Microcrystalline cellulose was introduced in the 1960s. Therefore, most carbohydrate food ingredients were introduced in about a 25 year period between 1940 and 1965. Exceptions are the introduction of maltodextrins and major developments in the high-fructose syrup industry, which occurred in the 1970s.

KEYWORDS: Alginates; carrageenans; cellulose-based gums; guar gum; high-amylose corn starch; high-fructose syrups; modified food starch; waxy maize starch; xanthan

This paper reviews major developments in food carbohydrate ingredients over the past century from an industrial standpoint. It focuses on the patent literature and on introductions of products and processes, excluding later improvements to the basic products and processes. It also focuses on developments originating in the United States and U.S. patents. As will become evident, most of the significant advances have occurred over the past 70 years, in fact, during a 25 year period (1940–1965). The major developments in the modification of carbohydrates for nonfood applications also occurred during this period, but are not covered in this review. Neither are processes that did not result in commercial products.

Of course, in terms of tonnages, the major refined carbohydrate food ingredients are starch and sucrose. Most of the current starch-producing companies have their roots in companies that were founded before 1908, so their history is not covered here. It can be found in ref 1.

A spontaneous mutant of maize (corn) called waxy maize, a mutant that produces an all-amylopectin starch (2, 3), originated in China and was first reported in 1908. Within a year, it had been brought to the United States, where it was maintained in

agricultural experiment station nurseries as a curiosity (4). However, the early days of World War II (even before the United States entered the war) endangered the supply of tapioca starch from Southeast Asia. The loss of this desirable food ingredient initiated a search for a starch that would give similar clear, nongelling pastes. Waxy maize starch was found to be a suitable replacement for tapioca starch. Hybridization and commercialization quickly followed. Corn breeders at Iowa State University converted waxy maize into a high-yielding hybrid. Commercialization was a joint effort of the American Maize Co. and the National Starch Products Co., which arranged for a waxy maize crop to be grown under contract. Waxy maize starch was first produced commercially in 1942. Pastes of native waxy maize starch have high viscosity and a long texture. They are only slightly cloudy and exhibit a very low tendency to gel, making them more like the pastes made from tapioca and potato starch than those made from normal corn and other normal cereal starches. Waxy maize starch became the base starch of choice for many food applications in the United States. However, pastes of native waxy maize starch are too stringy and cohesive and break down too easily under shear to be acceptable for some, in fact, many, food applications. However, properly modified waxy maize starch produces pastes of good clarity and stability and a relatively high viscosity (see later discussions on cross-linking and stabilization

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of starch). Today, waxy maize starch is the most widely used base starch for making modified food starches in the United States, so the development of waxy maize starch as a commercial product was a major development in the food starch industry.

In the mid-1940s, research was initiated at two locations, the goal of which was to produce the counterpart to waxy maize starch, that is, a starch containing mainly or entirely amylose molecules. One project was that of Roy Whistler and Herb Kramer at Purdue University (5, 6). Other research involved the Northern Regional Research Laboratory, ARS, USDA, and cooperating breeders (7–9). Quickly, it was determined that the high-amylose (ha) gene found by Kramer et al. (5) and the amylose extender (ae) gene characterized by Vineyard and Bear (7) were the same gene (10). Hybridization of corn containing the ae gene followed and resulted in increases in both starch yield and amylose content. In 1958, a consortium of Bear Hybrids, American Maize Products Co., and National Starch and Chemical Co. commercialized the first high-amylose maize hybrid containing 53% apparent amylose content and now known as amylo maize-V (11, 12).

Modified food starches were developed for three reasons: to minimize negative aspects of starch in terms of pasting and paste properties, to enhance the positive attributes of starches in either their native or cooked states, and to provide functionalities that native starches cannot provide. Before the 1930s, little starch was used in foods. (Uses of starch prior to 1928 and prior to 1954 are described in refs 13 and 14.) In foods, starch was used in baking powders, pie fillings, sauces, and puddings (15). In the 1930s, Kraft Foods began extending mayonnaise with a paste containing normal corn starch and arrowroot starch. Later, combinations of normal corn starch and tapioca starch and normal corn starch and locust bean gum were employed (16).

Before the 1940s, there were many attempts to derivatize starch, but almost all reactions were done on nongranular starch (17–19). There are two major kinds of chemical modification—cross-linking and substitutions that result in paste stabilization (20, 21). Oxidation, acid-thinning, and various kinds of pregelatinization are also employed (20, 21).

Starch molecules within granules are cross-linked by reacting them with bifunctional reagents. The purpose of cross-linking is to strengthen granules, largely, but not entirely, to make the starch more tolerant to food-processing conditions (high temperatures, high shear, low pH). As early as 1919, Kerb reported treatment of soluble starch with phosphoryl chloride (POCl_3 , phosphorus oxychloride) (22). Later, others reacted soluble starch with bifunctional reagents. According to Wurzburg (23), however, Bryant, who claimed the manufacture of a corn starch product in which “the viscosity of the starch paste is increased” by treatment of the starch with limited amounts of hypochlorite during manufacture, was probably the first to have practiced cross-linking within granules (24). In the patent issued to Bryant, it is also stated that, as a result of the hypochlorite treatment, the starch was “rendered more thick boiling than ordinary starch”. However, introduction of cross-linked starch products effectively dates to 1943. The story as told to me by Otto Wurzburg is the following. The National Starch Products Co. routinely bleached imports of tapioca starch with hypochlorite. A shipment was received that, after bleaching, produced unique cooked paste characteristics. Someone was perceptive enough to realize that these characteristics were desirable and potentially useful. That realization initiated a study to determine what was different about this lot of tapioca starch, and it was found that it had a higher content of protein than did other lots. That finding led to a patent issued to A. D. Fuller in 1943 (25). The Fuller patent claimed that addition of a protein, especially gelatin, to starch, followed by

treatment with an oxidant such as hypochlorite resulted in a product that had the properties of a lightly cross-linked starch. At about the same time, George Felton and Herman Schopmeyer of American Maize Products Co. claimed reaction of granular starch with phosphoryl chloride and achieved a greater degree of resistance to breakdown during cooking (26), in what is probably the first commercial reaction of granular starch with a derivatizing reagent.

Particularly after the latter revelation, use of a large number of bifunctional reagents was explored. Those reagents that resulted in commercial cross-linked modified food starch processes and products are the following. Moses Konigsberg of the National Starch Products Co. claimed the use of epichlorohydrin in 1950 (27). This reagent was used to make diether cross-linked starch products until it was voluntarily discontinued by the member companies of the Corn Refiners Association to ensure worker and consumer safety. In 1957, Ralph Kerr and Frank Cleveland of the Corn Products Refining Co. described the use of sodium trimetaphosphate (STMP) to make distarch phosphate (28). Carlyle “Corky” Caldwell and Otto Wurzburg, also of the National Starch Products Co., used adipic–acetic mixed anhydride to produce dicarboxylic acid ester cross-links (1953) (29). Cross-linked starch products became widely used in spoonable salad dressings, the commercial baking of pies, canned pie fillings, and canned products such as cream-style corn. Cross-linked waxy maize starch became the starch ingredient of choice for canned soups, sauces, gravies, and many other products.

A second major group of products made by derivatizing hydroxyl groups is that of the products known as stabilized starches or substituted starches. Development of stabilized/substituted starches originally was the result of a need for pie fillings that were more stable to cold temperatures (16). Corky Caldwell of the National Starch Products Co. used acetic anhydride to prepare low-DS granular starch acetates (1949) (30), although nongranular starch acetates had been known for many years before that (17, 18). Jack Tuschoff and Clifford Smith of the A. E. Staley Manufacturing Co. claimed the use of vinyl acetate to effect a transesterification reaction for the same purpose (1960) (31). Use of vinyl acetate for acetylating starch was voluntarily discontinued by the member companies of the Corn Refiners Association because the byproduct of its reaction with starch is acetaldehyde. (Both epichlorohydrin and vinyl acetate are still allowable reagents for making modified food starch in the United States and are used elsewhere in the world.) Preparation of the partial hydroxypropyl ether of starch was first described by Carl Kessler and Erling Hjermstad of Penick & Ford Ltd. (now Penford Products Co.) in 1950 (32), but hydroxypropylated starch products were not commercialized until the 1970s. Preparation of monostarch phosphates via esterifying starch with orthophosphate salts was claimed by Hans Neukom of the International Minerals & Chemical Corp. (1958) (33) and by Ralph Kerr and Frank Cleveland of the Corn Products Co. (1960) (34), who also claimed use of sodium tripolyphosphate (STPP) for the same purpose (1959) (35). Preparation of monostarch phosphates from STPP and distarch phosphates (cross-linked starch) from STMP received a major boost from publication of a thorough analysis of their reactions by Paul Seib and co-workers, beginning with a 1993 paper (36). In general, pastes made from stabilized/substituted starches have a reduced tendency to undergo retrogradation (setback) and to exhibit the negative characteristics associated with retrogradation.

A special kind of substituted starch is its octenylsuccinate ester, first described by Corky Caldwell and Otto Wurzburg of the National Starch Products Co. in 1953 (37). These products, also known as OSA starches because the reagent used to make them is

octenylsuccinic anhydride, have interfacial activity. Some forms of OSA starches have been developed as replacements for gum arabic.

The key to development of these modified starch products was development of practical ways to react starch in aqueous slurries while maintaining granule integrity, thus allowing recovery of the modified starch product by filtration or centrifugation and removal of reaction byproducts by the same filtration or centrifugation technique, followed by washing with water. The nature of the corn wet-milling industry changed dramatically with the development of these processes. From this review, it is obvious that the leaders in the early development of cross-linked and stabilized starches were National Starch Products Co. (later to become National Starch and Chemical Corp.) and Corn Products Co. (later to become the Corn Products Refining Co., then CPC International, Inc.).

Use of acids to hydrolyze starch is a technology that is more than 100 years old, but in 1923, a patent was issued to Bill Newkirk of the Corn Products Refining Co. for the first commercially viable process for producing pure crystalline glucose (dextrose) from starch hydrolysates (38).

Before 1938, corn syrups were produced exclusively by acid-catalyzed hydrolysis of corn starch and, as a result, suffered from off-flavors and color. A revolutionary process for converting starch into corn syrup that used both acids and a fungal enzyme preparation that contained a mixture of a glucoamylase (amyloglucosidase) and an α -amylase was claimed by Julian Dale and David Langlois of the A. E. Staley Mfg. Co. in 1940 (39). Compared to previous products, the 65-DE (65% dextrose equivalence) syrup was sweeter, less bitter, more fluid, and less likely to crystallize. Today, thermostable α -amylases, first developed in the 1970s (40, 41), are used exclusively to saccharify starch. Use of specific enzymes also allowed, for the first time, the production of special syrups such as high-maltose syrups (42, 43). A history of the beginnings of the use of enzymes to effect hydrolysis of starch has been written (44).

The early history of high-fructose corn syrups has also been written (45–49). An enzyme (which was actually a xylose isomerase) that catalyzes the isomerization of glucose to fructose was reported in 1957 by Richard Marshall and Earl Kooi of the Corn Products Refining Co. (50); Marshall then applied for a patent for the enzyme (51). However, production of xylose isomerase was first commercialized in Japan (52). Clinton Processing Co., which was then a division of Standard Brands, Inc., licensed a xylose isomerase from San Matsu, a Japanese sugar company, began selling small amounts of the enzyme in 1967, and developed a practical process for making corn syrup containing both glucose and fructose. The company also produced a 42% fructose syrup (HFCS-42) in 1967. In 1968, the A. E. Staley Mfg. Co., the second company in the isomerization business, obtained a sublicense for the technology, but by 1972 had developed its own technology (49). By 1971, a glucose isomerase was described (53). By 1974, the first generation of immobilized forms of glucose isomerase, the first commercial application for immobilized enzyme technology in any process anywhere in the world, was claimed (47, 48, 54–56). Before the end of the 1970s, large-scale chromatographic separations that allowed concentration of fructose to make syrups with fructose concentrations of greater than the equilibrium concentration of 42% were introduced (57). These chromatographic separations are now continuous processes (57). Large-scale commercial production of high-fructose corn syrup containing 55% fructose (HFCS-55) began in 1978. Within less than a decade, HFCS-55 had replaced sucrose in most soft drinks containing a nutritive sweetener.

Maltodextrins were introduced as food ingredients when Fred Armbruster and co-workers of the Corn Products Refining Co.

developed an acid–enzyme process for making them (58). A major advance in the production of maltodextrins was the all-enzyme process that resulted from the work of Alpha Morehouse and co-workers at Grain Processing Corp. (59).

An important director of research that led to the development of some of the products from corn starch mentioned above was A. Larry Elder of the Corn Products Refining Co. Larry chaired the Agricultural and Food Chemistry Division of the American Chemical Society (ACS) in 1956, received its award for Advancement of Application of Agricultural and Food Chemistry in 1986, and was President of ACS in 1960.

Also during about a 60-year period from about 1935 to about 1995, the processes for wet-milling of corn to produce corn starch and byproducts and various processes for making modified starches were modernized in ways that could be called revolutionary.

Two processes for the preparation of cold-water-swelling, granular, native, and modified starches originated in the early 1980s. One developed by General Foods Corp. used a specially designed atomization nozzle for a spray-dryer (60). The other developed by James Eastman of the A. E. Staley Mfg. Co. involved heating starch slurries in aqueous alcohol (61).

The number of plants producing potato starch in the United States peaked before 1908 (62), the earliest date covered by this review, but one development involving potatoes needs to be mentioned. The origin of the modern process for manufacturing a flake form of instant mashed potatoes dates to a patent issued to two researchers at the Eastern Regional Research Center, USDA (63). A product made by this process was first marketed in 1946.

Cellulose ethers were already being made in Europe when commercialized production of methylcellulose by the Dow Chemical Co. began in 1938 (64).

The first patent for the preparation of carboxymethylcellulose (CMC) was issued in Germany in 1918. Hercules, Inc., began commercial production of CMC in the United States in 1943 (65). Its sales grew rapidly due to applications based on its special properties, although it was originally produced as a replacement for natural gums (65).

Patents related to the preparation of hydroxyalkylcelluloses date to 1950. In 1964, two patents were issued to Gene Klug of the Hercules Powder Co. for the preparation of hydroxypropylcellulose (66, 67). The product was commercialized in 1966.

The first patent on the preparation of microcrystalline cellulose was issued to Orlando A. (“Landy”) Battista and Patricia Smith of American Viscose Corp. in 1961 (68) following its serendipitous discovery. That patent was followed closely by one issued to Battista, a chemist whose quotations are widely known and who holds 58 U.S. patents, in 1962 on “food compositions incorporating cellulose crystallite aggregates” (69).

Sustained commercial production of sodium alginate in the United States began in 1929 by the Kelco Co. (70). A milk-soluble product introduced by the Kelco Co. in 1934 became the most important ice cream stabilizer of the time. A patent for the preparation of propylene glycol alginate, a product that is less responsive to calcium ions, was soluble in acidic solutions, and (as opposed to nonesterified alginates) had emulsion-stabilizing activity, was issued in 1947 to Arnold Steiner (71), who led the development of algin products in the early years of the industry. Later developments in alginate products occurred under the leadership of W. H. (Bill) McNeely.

A red seaweed from which carrageenan is extracted was being used in foods in Ireland hundreds of years ago. Isolation of the polysaccharide was first reported in 1837, and a patent for purification of the extract was issued in 1871 (72, 73). The modern

carrageenan industry began along the northeast coast of the United States. The first carrageenan-producing company was Krim-Ko Corp., followed by Jacques Wolf and Co. and Kraft Foods, all production facilities being built to provide a stabilizer for chocolate milk. The demand for carrageenan products increased rapidly, and the industry grew accordingly. In 1946, Algin Corp. of America began operation of a third plant in Rockland, ME. In 1958, Algin Corp. and Seaplant Corp. merged to form Marine Colloids, Inc., the world's largest producer of carrageenans. Marine Colloids was acquired by FMC Corp. in 1977. The R&D leader in this field was Leonard Stoloff, who chaired the ACS Division of Agricultural and Food Chemistry in 1961 and received its Award for Distinguished Service in 1986. Stoloff was Chief Chemist at Krim-Ko Corp. and then at SeaPlant Corp. and finally directed research at Marine Colloids.

During the 1940s, the Institute of Paper Chemistry set out to find a replacement for locust bean gum, a valuable beater additive in the papermaking process, because World War II effectively cut off its supply (largely from Spain and Italy) (74). In 1945, guar gum was identified as a possible replacement, and investigations to that end began. Purdue University was asked to grow an experimental crop, and General Mills Inc. was enlisted to process the beans. After this work indicated the promise of guar gum (75–78), Stein Hall and Co. and General Mills, Inc., undertook its commercialization. Stein Hall and Co. developed a process that resulted in improved properties and higher viscosities. Commercial amounts of guar gum became available in 1953 (78); food uses of it could then be investigated.

The pectin industry seems to have developed simultaneously in the United States and Europe in the 1920s and 1930s. In the United States, Hercules Inc., using lemon and lime peels as the source of pectin, was the major producer.

In the 1950s, Allene Jeanes and James Sloneker led a project to screen the organisms in the extensive culture collection of the Northern Regional Research Laboratory, ARS, USDA, for producers of water-soluble polysaccharides of potential commercial importance (79). The polysaccharide with the most interesting properties appeared to be that produced by *Xanthomonas campestris* NRRL B-1459. Work on its structure was undertaken in the 1960s, but its structure was not solved until the next decade (80, 81). The Kelco Co. began pilot production of this polysaccharide (xanthan) in 1960; semicommercial production began in 1961 and full commercial production in 1964 (79). Today, xanthan is used extensively as an ingredient in food products, often because of the high degree of pseudoplasticity and the viscosity, suspension, and emulsion stability imparted to aqueous systems into which it is incorporated.

It was during the decade of the 1960s that regulations were first established under the Federal Food, Drug, and Cosmetic Act administered by the U.S. Food and Drug Administration for the kinds and amounts of reagents that may be used to make "food starch-modified" and the kinds of food gums (hydrocolloids) that may be used as food ingredients.

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