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Corn Starch: Present and Potential Uses in Industry

by Dr. Charles R. Russell

Domestic consumption of corn starch products, including unmodified and modified starches, in industrial or nonfood applications, amounts to approximately 3 billion pounds per year. Although this figure is impressive, it is small compared to the large amounts of petroleum and natural gas consumed in the production of synthetic polymers, plastics, rubber, fibers, films, protective coatings, adhesives, industrial alcohols, ethylene glycol, and related large-volume organic chemicals. Rising prices and diminishing supplies of petroleum and natural gas have intensified interest in starch, as well as other renewable raw materials, to satisfy more of the needs of the chemical industry.

Prospects for greatly expanding the use of starch as an industrial raw material are good because it is comparatively inexpensive and can be converted readily into many products by chemical and biochemical means. Such an expansion in the use of corn starch should not put a strain on the supplies of corn needed for feeds and foods for the following reasons: Only 1.6 percent of our 1975 corn crop would be consumed in producing the 3 billion pounds of starch now filling industrial needs, the protein and oil fractions obtained in the production of starch from corn by wet milling are channeled into feed and food outlets, respectively, and furthermore, more corn can be grown if needed. Let us consider current industrial applications of starch and starch products, opportunities for expanding these applications, and certain trends and developments that could lead to large new industrial outlets for corn starch.

About 90 percent of the present industrial usage of starch is accounted for by products employed in making and coating paper and paperboard, as adhesives and as sizes in the manufacture of textiles. Because these applications have been reviewed in detail \(^1\)–\(^3\), only a brief account of them is given here.
Starch in Papermaking

In papermaking, wet-end additives including starch products, other natural polymers or gums, and certain synthetic polymers are introduced into aqueous slurries of papermaking pulp to (1) improve drainage of the wet sheet or mat on the forming wire, (2) improve formation or distribution of fibers in the sheet, (3) enhance dry strength of the paper, (4) facilitate retention of clay and other pigments in filled paper, and (5) impart wet strength to some types of paper.

Before the advent of cationic starches (chemically modified starches), unmodified starch was the principal product introduced at the wet end to increase dry strength of paper. Usually about two to three weight-percent of unmodified starch on a dry pulp basis gives the desired effect. Unmodified starch has been partially replaced by cationic starches because they are retained more completely by the pulp fibers than unmodified starch. Cationic starches are also good retention aids for clay and other pigments required in making filled papers. With cationic starch, a level of addition around 0.5 weight-percent is generally sufficient to give the desired strength increase and to maintain strength when fillers are added.

Substitution of cationic starches for unmodified starch also reduces BOD and suspended solids levels in white water. However, in a move to further reduce pollution of water from papermills, more starch is being applied as a surface size rather than as a wet-end additive.

The end use requirements for paper and paperboard dictate whether or not a surface size is applied. Surface sizing improves: (1) strength properties of the sheet; (2) writing and printing characteristics, particularly ink holdout; and (3) erasability. The principal starch products in surface sizing are enzyme-converted starch, jet-cooked starch, hydroxyethylated starch, oxidized starch, acid-modified starch, or cyanoethylated starch. The amount of size picked up by the paper varies from one to four percent.

Several viscosity grades of starches are needed to meet the range of surface-sizing requirements. The desired viscosity levels are attained either by partially depolymerizing starch through application of high temperature and shear to aqueous pastes (steam-jet cooking) or by treatment with enzyme, acid, or an oxidant. In surface sizing, starch paste at a concentration of two to twelve percent solids, is applied to the sheet at the size press, and excess paste is squeezed out by the size press rolls before the sheet is dried. In tub sizing, a comparatively slow process conducted off the paper machine and usually restricted to the highest quality papers, solids content may run up to 20 percent.

Starch in Adhesives

The largest single outlet for starch-based adhesives involves the application of clay and other pigment coatings to paper. Paper is coated to improve its printability, appearance, and brightness, as well as to increase its opacity. The same reasons for coating paperboard apply except for improvement of opacity which is inadequate in uncoated boards. Representative paper products that are coated are magazine stock, bag paper and paperboard for packaging consumer goods. Starch products and synthetic latices are the major binders or adhesives in pigment coatings. An aqueous dispersion containing the pigment, a dispersing agent and minor amounts of additives are combined with the adhesive to form what is referred to as a coating color.

Solids content of coating colors, including adhesives and pigment, range from about 30 to 70 percent depending on the weight of coating that is to be applied. Starch-based adhesives are usually used at a level corresponding to about 18 weight percent dry starch product on a pigment basis. Enzyme-converted starch, oxidized starch, and dextrins, as well as hydroxyethylated starches and starch acetates, are the principal coating adhesives. Enzyme conversion is done on site, but the other starch modifications are supplied by starch manufacturers and are tailored to meet exacting requirements, particularly rheological behavior of coating colors with different solids content during high-speed coating on various types of coaters. Those most widely used are roll, blade, and air-knife coaters.

In addition to pigment coating, large volumes of starch-based adhesives are also consumed in the production of corrugated boxboard, laminated board, and paper bags. The major component in corrugating adhesives is unmodified starch. Either the carrier- or no carrier-adhesive system is employed. In the carrier system, starch is suspended in an aqueous paste of cooked cereal starch. In the no carrier system, raw starch is swollen enough by pretreatment to keep it suspended in the aqueous phase. Both systems contain sodium hydroxide and borates to facilitate gelatinization of the raw starch granules and to improve tackiness of the adhesive.

The unique property of starch granules to gelatinize and to take up water from the adhesive under the influence of heat is called upon to provide the initial tack needed to keep the assembled board together until it has had time to dry.

Starch-based adhesives are also used in the production of laminated paperboard, paper bags and sacks, spiral wound tubes, and gummed labels and tapes. The principal starch products for making these adhesives are unmodified corn starch, hydroxyethylated starches, dextrins, oxidized starch, waxy maize starch, acid-modified starch, and starch acetates. Other significant applications for starch-based adhesives include their incorporation as binders in gypsum, mineral, and insulating boards, and acoustical tile.

Total starch shipments to the paper industry for basic papermaking, on-machine coating, and converting operations in 1972 was reported to be 2.5 billion pounds. It was estimated that thirty-one percent of this volume, 775 million pounds was for off-machine coating and fabrication of corrugated boxboard, laminated paperboard, paper bags, and similar operations on paper after it was made. A figure of 500 million pounds of starch product was reported for coating adhesives. The most prevalent opinion is that the volume of starch products going into basic papermaking, on-machine coating, and converting consists of, in decreasing order, surface sizing, coating, corrugating plus laminating, and wet-end addition. The paper industry has just about recovered from the drastic production that bottomed out in 1975, therefore, the 1977 figure should not be far off at present.

As to prospects for expanding sales of starch products to paper and board mills beyond that expected through growth of the industry, two opportunities stand out: the
development of starch products to replace latices used in paper and board coatings, and the development of a starch-based product that will impart sufficient rigidity to corrugated boxes to enable them to withstand prolonged exposure to high humidity.

Starch in Textiles

The third largest industrial outlet for starch products is in the textile industry—mainly as a size to strengthen warp yarns and to improve resistance to abrasion during weaving. Starch products are also employed in the finishing of fabrics. Starch products sold to the textile industry include unmodified starch, acid-modified starch, hydroxyethylated starches, unmodified and modified high-amylose starches, starch acetates, oxidized starch, and dextrins. Total sales for textiles in 1972 was approximately 275 million pounds. Since then, there appears to have been little change in either the total sales figure or the distribution of starch products within it.

Unmodified starch is modified at the textile mill to reduce its viscosity. The most common processes for this purpose are: conversion with enzyme, application of high shear to cooked pastes, and steam-jet cooking. Pastes for warp sizing usually contain about 9 percent by weight of starch product and around 0.5 percent softening agent. Yarns spun from staple fibers, such as cotton, when sized with traditional starch products, usually carry from 10 to 15 weight percent starch product on a dry basis. Modified derivitized starches are used to size synthetic fiber cotton blend yarns. After weaving, the cloth, except for certain such grades as denim, must be desized before dyeing, printing, and other operations are carried out. Desizing produces large volumes of wastewater that has a high 5-day BOD. Because of this, some textile mills began several years ago to shift to polyvinyl alcohol (PVA) and carboxymethylcellulose (CMC) for warp sizing. However, mills are faced now with new regulations on organic matter content in wastewater and are having trouble getting rid of PVA and CMC because they biodegrade slowly compared to starch. Since starch is readily digested (converted to carbon dioxide and water) by microorganisms in sewage systems it may regain some of the markets lost to PVA and CMC. Development of starch products that would bond permanently to the fabric and neither interfere with dyeing, printing, and other operations nor detract from the quality of the cloth would be desirable. High-amylose starches, derivatives thereof, and synthetic polymers are used to size glass fibers.

The textile industry also consumes significant amounts of unmodified and modified starches in finishing processes to increase fabric stiffness, to change the hand (feel) of the fabric, and to improve appearance.

Other Applications

In this category are: flocculating agents, anticaking agents, mold-release agents, dusting powders, thickening agents, and raw material for the production of chemicals and explosives.

Potential Markets

New opportunities for the utilization of starch products in many areas appear to be opening up as a consequence of increasing prices and shortages of petroleum and natural gas. For example, the production of industrial-grade ethanol from starch by fermentation may soon be competitive with that made from ethylene. Fermentative production of other large-volume organic chemicals from starch—such as acetone, butanol, and 2,3-butylene glycol (a chemical readily converted to butadiene)—could also come into the picture, if the projected price increases for petroleum are borne out. In addition, a number of advances in applied research on starch have been made during the past several years that appear to have excellent potential for: (1) increasing utilization of starch, (2) conserving petroleum products, (3) saving energy, and (4) providing ecologically oriented materials. These products and processes are: (i) graft polymers of starch, starch-based urethane foams and plastics, starch-derived polyols for use in alkyd resin production, starch xanthide (a substitute for carbon blacks in rubber), a low cost process for making powdered rubber by starch encasement of rubber particles, and starch-extended plastics and films.

Starch graft polymers that are powerful thickening agents for aqueous systems and good flocculating agents for a variety of suspended solids in process waters and wastewaters have been prepared. Also, a graft polymer of starch has been developed that will absorb up to 1,400 times its weight of water, yet not dissolve. This polymer, called Super Slurper, exhibits excellent utility as: (1) an absorbent in soft goods (diapers, bedpads, and the like), (2) a moisture-holding coating for seeds and roots of seedlings to facilitate sprouting of seeds and survival of seedlings, and (3) a moisture-holding and erosion control agent in soil. Super Slurper is now being produced on a limited scale, and steps are being taken to implement large-scale production.

Economical starch-based polyols (glycol glycosides) have been developed that can replace up to 85 percent of petroleum-based polyols in alkyd resins with no loss in quality of the resins. Currently, about 600 million pounds per year of alkyd resins in the United States alone serve as protective coatings (paint) on automobiles, metal and wood furniture, refrigerators, and stoves. The same starch-based polyols employed in making alkyd resins
also serve as excellent replacements for petroleum-derived polyols in the production of rigid urethane foams. Foams designed for insulation of buildings must be flame retardant. A significant advance in flame retardant technology has been achieved by replacing conventional polyols in urethane foams with brominated allyl glucoside derived from glucose. Use of urethane foam is experiencing a remarkable growth rate, particularly in construction, and is projected to reach the billion pound per year level in 1980.

Starch xanthide is a good substitute for low and medium grades of carbon black used to reinforce rubber. Current domestic use of carbon blacks in rubber is more than 3 billion pounds annually. The xanthide can also be made to merely coat the rubber particles to yield powdered rubber. This has good potential for commercialization because powdered rubber requires only about one-half the energy to mix and process as does conventional slab rubber.

Significant advances toward the development of biodegradable films for crop mulching, have been made by incorporating starch into synthetic polymer films. Water soluble starch-polyvinyl alcohol film has already been developed and commercialized which can be made into laundry bags that will dissolve in the wash. The film was designed for hospitals and nursing homes to keep the laundry staff from contacting contaminated bedding and clothes. Up to 40 percent starch has also been incorporated into rigid polyvinyl chloride plastics without reducing tensile strength significantly. All such plastics containing 12 percent or more of starch give indications of at least partial biodegradability when inoculated with soil microorganisms.

A recent advance is the development of crosslinked starch xanthates that are highly effective in removing many heavy metals from wastewaters. In view of the advances in starch technology made during the past few years, it would appear that with imagination and effort, many new starch products can be developed. Also, starch will undoubtedly be in greater and greater demand as a chemical raw material as our irreplaceable supplies of petroleum and natural gas continue to dwindle.

BIBLIOGRAPHY


Department of Agriculture researchers examine a sample of "super slurper," a new form of corn starch which can absorb 1,400 times its weight of liquid. "Super slurper" was recently cited as one of the 100 most significant new products of 1975 by Industrial Research magazine.