Corn and Wheat Starch

Starch, the main constituent of grain flours, is the most important industrial cereal product, and the most plentiful and widely used of the starches is cornstarch. Although most of the products from corn milling go into food and feed, the industry also produces 4.5 billion pounds of starch annually, largely for nonfood purposes. Of this amount, 3.5 billion pounds are used in the paperboard, paper, and related industries, where starch serves both as an adhesive and coating.

Several hundred million additional pounds of cornstarch products are consumed each year by the textile industry, chiefly as a warp sizing to strengthen warp yarns and improve their resistance to abrasion during weaving. Cornstarch and the materials derived from it are used in countless other ways by industry, according to an NRRC starch chemist, "to thicken, stabilize, flocculate, absorb, coat, adhere to, dry, and moisten." He adds that it seems certain that if research continues at current rates, many new and expanded industrial markets for cornstarch will be found in the years just ahead.

Chemical research to find new uses for surplus corn began in 1940 with the opening of the Northern center. An early discovery involved the starch in so-called waxy corn. Most cereal grains are roughly classified as waxy and common, or nonwaxy. The terms do not imply the presence or absence of wax, but rather describe the appearance of the inside of the kernel. Peoria researchers discovered that the starch in waxy corn is composed almost entirely of a constituent called amylopectin. The amylopectin content in nonwaxy varieties is only 73 percent. Waxy cornstarch, unlike nonwaxy, is a competitor with imported tapioca in food and industrial markets, since it produces pastes with similar viscosity and clarity. Peoria researchers developed ways to process the waxy corn and found outlets for the amylopectin starch produced from it. As early as 1942, waxy corn became a profitable commercial crop, grown under contract with an assured market.

A flake of Super Slurper swells into a soft, rubbery chunk that is 99.5 percent water.

Further research disclosed that amylose, the other principal constituent of cornstarch, also has properties of value to industry. A starch composed mostly of amylose, for example, is able to form thin films. A cooperative breeding program soon led to a variety of corn with starch containing more than 70 percent amylose, compared with only 27 percent in common yellow dent corn. Buyers for high-amylose starch were found among manufacturers of glass fibers, paper, products, and specialty films. In a short time, several million pounds of the starch were being produced by the wet-milling industry, and like growers of waxy corn, farmers were producing the high-amylose corn under contract to industry and receiving premium prices.

NRRC researchers in the late 1950's discovered and developed a low-cost process for preparing a new product called dialdehyde starch from ordinary cereal starch. Enthusiasm for dialdehyde starch mounted in the early 1960's, as more and more uses for the product were found by science and industry. It imparted wet strength to paper, including facial tissues; it served as a coating adhesive for other papers; it proved an excellent tanning agent for sole leather. Called by some "a wonder product," dialdehyde starch could also harden gelatin and impart water resistance to glue for making plywood. And it was nontoxic, colorless, and odor free.

What's more, Peoria scientists improved the product in 1974, making it of even greater potential value to the paper industry. What happened? After a brief flurry of interest by U.S. industry, foreign companies began making dialdehyde starch, and today this country must import all it needs. "It was a disappointing outcome for an excellent invention," says a retired Peoria chemist.

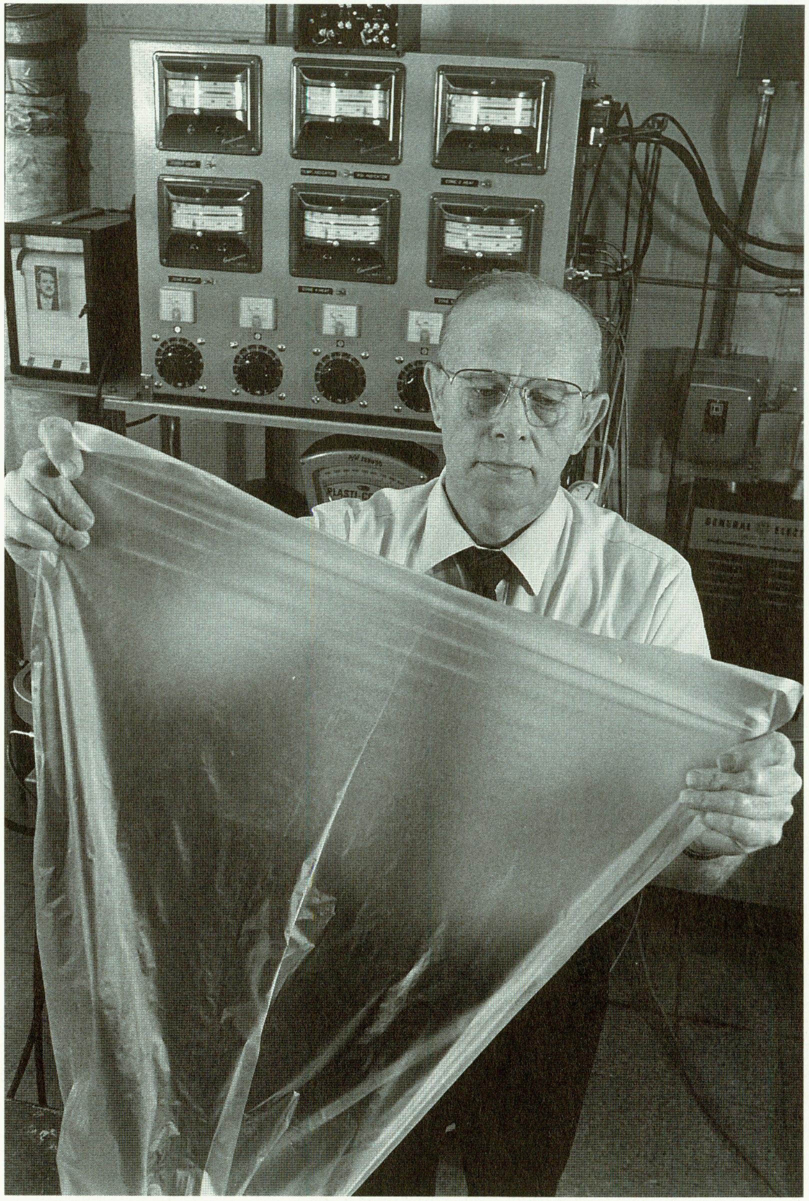
But new uses for starch kept coming in the 1950's and 1960's. Wheat flour was chemically modified to mix readily with water to form a free-flowing paste with less tendency to thicken and gell. The improved properties made it useful as an adhesive and as a coating and sizing for paper and textiles. A versatile product with similar properties was cross-linked dicarboxyl cornstarch, which produces a variety of viscous, pastelike products that also have the desirable property of not gelling

Starch Facts

Starches, like sugars, are carbohydrates, and in many plants, starch is the form in which carbohydrates are stored. Starch is a polymer; that is, a compound in which the molecules are built up by the chemical union of hundreds or even thousands of identical molecules of a simpler substance. In the case of starch, the building block is the simplest of the sugars: d-glucose, or dextrose.

Dextrose is produced by photosynthesis in the green leaves of plants in the presence of sunlight. It combines with itself chemically through a dehydration reaction to make the long-chain starch molecule. Through a simple process called acid hydrolysis, the starch can be broken down again into molecules of dextrose. It can also be digested in the body by enzymes. (See also "Micro-organisms," p. 134.)

Starch occurs as small granules that are easily separated in pure form from the rest of the plant. It was prepared from wheat as early as 184 B.C. In 1840, Orlando Jones, an Englishman, developed wet-milling to recover starch from corn and founded a multimillion-dollar industry. By 1880, his process was used in the United States to produce 200 million pounds of cornstarch a year. Today all cereals can be wet-milled with some variation of the process.



Peoria chemist Felix Otey stretches a sheet of biodegradable plastic film, made from starch and petroleum-based polymers.

A few of the growing number of commercial products containing starch-derived Super Slurper are shown by three of the NRRC chemists who developed it: (left to right) William M. Doane, George F. Fanta, and Edward Bagley. Not pictured is team member M. Ollidene Weaver.

when cooled. And new starch-based polyesters were developed for use in making rigid urethane foams.

One of the most commercially successful cornstarch products to emerge from the Peoria laboratories was developed and improved and improved yet again. Spurred by the oil shortage in the 1970's, scientists were searching for polymers made from farm commodities to replace those derived from petroleum. In one series of experiments, they married starch to a synthetic chemical and created a product able to absorb hundreds of times its own weight in water. The chemical family name was hydrolyzed starch-polyacrylonitrile graft copolymers, but somebody dubbed the absorbent Super Slurper, and the name stuck. After USDA patents were secured in 1976, Super Slurper began to be employed for a variety of practical uses, and the starch-based industry grew rapidly.

One company, which was licensed to use the USDA patents, now markets a product for agricultural uses under the trade name STA-WET. It is used to jacket seeds to accelerate germination and increase yields and to coat the roots of trees before transplanting them. Both techniques hold water where it is needed. Another firm, marketing Super Slurper under the name STA-DRI, uses it to remove water from fuels; still another manufacturer incorporates the product in fuel and oil filters. One company markets baby powders and wound dressings containing the absorbent, and compounds very much like it are being used in disposable diapers and sanitary napkins.

New and original uses are still being found for Super Slurper. An ARS entomologist in Florida recently discovered that the water-hungry product, when added to the soil in citrus groves, keeps dry soil moist so that tiny nematodes can survive during dry spells to kill weevils that chew up citrus tree roots. (The nematodes invade a weevil's gut and release lethal bacteria.) The scientist suggests that commercial companies rear the helpful nematodes and package billions of them alive. Growers could mix them with Super Slurper and apply them to citrus tree roots before planting, he says, providing a grove of trees with built-in weevil control around the roots.

In still other applications, the absorbent compound, which has been improved until it slurps up 2,000 times its weight in water, is being used as an electrical conductor in batteries and in medical and recreational cold packs. The NRRC invention has already led to creation of a $1-billion-a-year industry, and sales could top $3 billion a year before the year 2000.

Another major discovery at the Peoria lab in the 1970's was insoluble starch xanthate (ISX), a starch-sulfur compound used to remove heavy metals from wastewater. Discussed in more detail in the chapter on "Waste Management," p. 28, ISX is now being used to treat processing wastes of the electroplating and circuit printing industries. The compound lowers the heavy metal content of discharge water to allowable levels.

Another NRRC inventor patented several processes in the 1980's for encasing sticky particles of latex in a thin film of starch-based compounds. The result is a lightly powdered latex that is nontacky and free-flowing—both useful qualities in making tires and other molded rubber products. The starch in this application is used in amounts too small to make it a filler, and it has little or no effect on rubber quality. Other NRRC research, however, showed that starch could replace carbon black as a filler in tires and could be used to make rubber in various colors.

The Science of Rheology

Factories that saw boards or punch out sheet metal parts or assemble bicycles all have something in common. The materials they work with don't keep changing their form and density during manufacture. But that isn't true of many other materials, like plastics and bread dough and cheese and confections. During processing, such materials may swell or stiffen or flow or ooze or creep or soften or droop. They present so many special industrial problems that a whole science has developed to study them—a branch of physics called rheology.

The word was coined by a chemist in 1928, and a year later The Society of Rheology held its first meeting. Rheology is defined as "the study of the change in form and the flow of matter, embracing elasticity, viscosity, and plasticity." Rheologists, like scientists in other disciplines, have evolved a vocabulary of their own, including terms like "relaxation rate" and "dilatant," which means expanding in bulk when the shape changes. They often work with viscous materials that are somewhere between the solid and liquid state. In Peoria, rheologists have applied their special expertise to help commercial bakeries bake bread from different wheats; to characterize the properties of starch gels, to manufacture xanthan gum, and to meet similar challenges that involve materials, like rising bread, that change form and shape during processing.

Encapsulating various products in granules of starch is another NRRC-developed process that appears to have an exciting commercial future. The idea was originally developed to allow the slow release of herbicides and other chemical pesticides. There are many benefits to farmers in using such products. Smaller amounts of chemicals are needed to kill weeds and

Twin-Screw Extruders

A tool that has captivated several Peoria researchers during the last 2 years is the twin-screw extruder. Used today in several industries, it consists of two big horizontal screws, which may intermesh or not, rotating in either the same or opposite directions. As the screws rotate, they can mix various high-solids materials and move them along through chemical reactions, eventually extruding them. In the food, feed, plastics, and rubber industries, the extruders have often replaced mixing materials in batches, a step that breaks the continuity of processing. "A twin-screw extruder," explains an NRRC chemist, "represents a low-energy way to process very viscous and hard-to-mix materials in continuous in-line reactions. You can put a complex series of reactions into a closed system."

In the laboratory in Peoria, twin-screw extruders have been used successfully to convert starch to much smaller molecules that act as chemical precursors in making a variety of products, including polyurethane foams. The reverse is also true; extruders have been used to build onto starch molecules, to increase their molecular weight.

Twin-screw extruders can also be used on an industrial level to make starch graft polymers, including Super Slurper. "It used to take an hour or more to make a batch of the product," says the chemist. "With a twin-screw extruder, it can be made in a continuous process in a matter of minutes. In terms of capital cost per pound, it is far cheaper to make Super Slurper with a twin-screw extruder than in batches." Another successful NRRC application is in encapsulating various chemicals, including pesticides, in a starch for slow release. The whole process can be carried out in a single operation with extruders.

"Extruders are wonderful, flexible processing tools," concludes the scientist. "You can change their pitch, alter their speed, run them forwards or backwards, drop in chemicals to react at any point in the process, and add sections to knead the materials." In current NRRC research, they are being used to produce starch-plastic premixes for blown films.

insects, pesticides stay active longer, and they cause less pollution because they are not washed away or leached into the ground as easily as uncapsulated chemicals. The starch jackets also protect the pesticides from decomposition from sunlight and rain.

To encapsulate a herbicide, cornstarch is cooked in a jet of steam to gelatinize the starch; then the chemical is mixed in. After drying, the mixture can be crumbled into free-flowing granules or ground to any size of particle.

Since its initial development, NRRC researchers have come up with many more uses for starch-encapsulation of liquids and solids. Their patented invention employs a low-amylose matrix that, like other cornstarch products, can be used in foods. As a result, says a Peoria chemist, "the number of products that could be profitably encapsulated is limited only by the imagination. You could use slow-release capsules for insect lures, plant growth regulators, fertilizers, medicines, vitamins, and food flavorings and colorings. And all of them using a product made from surplus corn!"

In 1990, two NRRC researchers reported that adding starch and sugar to a spray of *Bacillus thuringiensis* (Bt) helped prevent the bacterium from being washed off plant leaves by rain. Bt is a biocontrol that is effective against several insect pests of crops. Without the sugar-starch mixture, Bt remained on corn leaves for only 4 days before becoming ineffective. With the mixture, it stayed put and kept killing European corn borers for up to 19 days, rain or shine.

Much of the most sophisticated chemical research conducted at the Northern laboratory in the last few years has been directed toward incorporating starch into plastic films derived from petroleum. Many farmers and gardeners today blanket the soil between crop rows with black plastic mulch to warm the soil and retain moisture. Millions of pounds of plastic films are sold each year for this purpose. The trouble is that the plastic doesn't biodegrade in the soil. It has to be removed when no longer needed and burned or buried. A similar problem exists with plastic trash bags buried in landfills. They remain there indefinitely. The inclusion of enough starch in the plastic films, reasoned Peoria chemists, might well make the mulch and trash bags biodegradable.

Research along these lines has so far led to one invention that is clearly a success. Technology developed by NRRC scientists is being used by a company in Indiana to produce starch-based laundry bags that will dissolve in hot water. The products are finding a ready market in hospitals, where the water-soluble bags protect patients and hospital workers from the danger of cross-contamination from soiled linens. Laundry can be placed directly into washing machines in sealed bags, which soon disappear.

A more difficult research task is the development of trash bags that will break down in the soil. Two major chemical approaches have been used to include starch in the formulas, and both produce plastics with satisfactory strength. As early as 1985, studies showed that it is possible to devise starch-plastic formulations that can withstand the strain of extrusion-blowing into plastic film. The films, however, are only partially biodegradable. The higher the proportion of starch in the plastic, the more it will either disintegrate or break down into simpler compounds. That part of the formulation derived from petroleum, however, biodegrades much more slowly. Researchers still hope to crack the puzzle. Or it may be that someday, labeling for plastic bags will disclose the percentage of the product that will biodegrade.

Recent experiments have used wheat starch instead of cornstarch in trials with biodegradable plastic films. One type of wheat starch granule is less than half the size of a granule of cornstarch and, theoretically at least, could be used to make thinner plastic films. “The first need,” explains a Peoria chemist, “is a practical way to sort out the really small granules that would go into such plastics.” Researchers at the Southern center in New Orleans think they may be able to handle the sorting for Peoria with their liquid cyclone, originally used to remove gossypol glands from cottonseed meal.