

Corn Starch



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Each day of the year, in some manner or another, every American's life is touched by one of our most abundant renewable resources, corn starch. From the clothing we wear to the food on our table, corn starch is a component of tens of thousands of manufactured products that define our modern lifestyle.



FOREWORD

The use of starch is chronicled in records of the early Egyptians, who manufactured papyrus using a starch coating. Roman records indicate that those early innovators found uses for starch in foods, medicine, cosmetics and fabrics. It was not until the middle of the nineteenth century, however, that the process for large-scale efficient extraction of starch from corn was developed. The development and continual improvement of this process has enabled the corn refining industry to offer American consumers abundant supplies of starch tailored to meet the most exacting needs of individual customers.

Our twelfth edition of *Corn Starch* reviews the chemistry of the starch granule, describes how corn refiners extract starch from the corn kernel, how it is treated to produce special products and reviews handling and analytical procedures for starches. We hope that you will find this guide useful and will not hesitate to contact the Corn Refiners Association, if we can provide you with further information on starch and its products.

John W. Bode
President & CEO
Corn Refiners Association

Readers are advised that the information and suggestions contained herein are general in nature and that specific technical questions should be referred to the Association or member companies. Questions as to the price and/or availability of the products described should be directed to individual Association members.



INTRODUCTION

The corn plant (*Zea mays*) is a high-capacity, factory for efficiently converting large amounts of radiant energy from the sun into stable chemical energy. This energy is stored as cellulose, oil and starch in the corn plant and in the corn kernel.

The corn plant is also one of nature's greatest multipliers. Approximately four months after planting, a single kernel of corn weighing about one one-hundredth of an ounce will yield 800 kernels weighing eight ounces. In comparison to this 800-fold seed multiplication in corn, wheat will produce a 50-fold yield per seed planted.

By careful genetic control, corn has been developed which can grow in the temperate and semi-tropical areas throughout the world. With annual production of corn topping 10 billion bushels, the United States ranks as the world's largest grower of corn. Since the corn grain averages about 70-72% starch (dry basis) this enormous quantity of corn provides

an almost unlimited raw material supply from which starch may be produced.

In 1844, Colgate & Co. built small corn starch factories at Jersey City, New Jersey, and Columbus, Ohio. In 1848, the much larger Kingsford Cornstarch Plant was built in Oswego, New York. Since that time, starch technology has steadily improved and production has increased many-fold. Today, corn starch dominates the world's industrial and food starch markets.

This booklet presents a brief, simplified description of the manufacture of starch by the corn refining (wet milling) process, a summary of the physicochemical properties of starch that make it of such great value to mankind and general information about how starch is used in food and industrial applications. We hope you find this information useful. If you wish further information on starch, corn or corn refining, please contact the Corn Refiners Association or its member companies.

Starch exists as a major carbohydrate storage product in all plants containing chlorophyll. In the process known as photosynthesis, green plants extract energy from sunlight to form glucose from carbon dioxide and water. Glucose fuels plant growth processes and is the primary building material for plant support structures such as cellulose and hemicellulose. When the plant reaches maturity, the reproduction cycle begins, culminating in pollination and formation of the starch- and oil-rich seed embryo. Starch and oil exist in the corn kernel to supply energy to the germinating seed. Starch is a carbohydrate polymer made by the linking of glucose units end-to-end into very long chains, similar to the stringing together of pearls in the making of a pearl necklace.

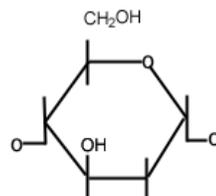
Newly-synthesized starch is layered around a hilum nucleus within the plant cell, in structures called granules (Figure 1). Starch granules vary in size and shape, characteristic of specific plant sources. Figure 2 shows the comparative sizes and shapes of granules from six common starches. Starch molecules are oriented within granules in specific crystalline patterns. This is illustrated in Figure

3, showing the Maltese cross pattern characteristic of these crystal structures, viewed in aqueous suspension under polarized light.

The highly structured nature of the starch granule is demonstrated by its great strength. After all the pulverizing, pumping, centrifugal circulation and physical attrition in the wet phases of the corn wet milling operation, followed by drying, grinding and mechanical or air transportation of the dry starch, practically all of the granules remain intact. Granule integrity also persists in both modified and derivatized starches.

Isolated starch is typically a dry, soft, white powder. It is insoluble in cold water, alcohol, ether and most organic solvents. Starch, if kept dry, is stable in storage for indefinite periods. Though starch granules are physically durable, they can be disrupted quite easily. If granules in water suspension are gradually heated, they begin to absorb water. The granules hydrate, increase in size and finally lose their structural integrity. This results in loss of characteristic birefringence and opacity, an increase in

STARCH AND THE STARCH GRANULE



α -D-glucopyranose unit



Figure 1
Layers of starch formed around the hilum

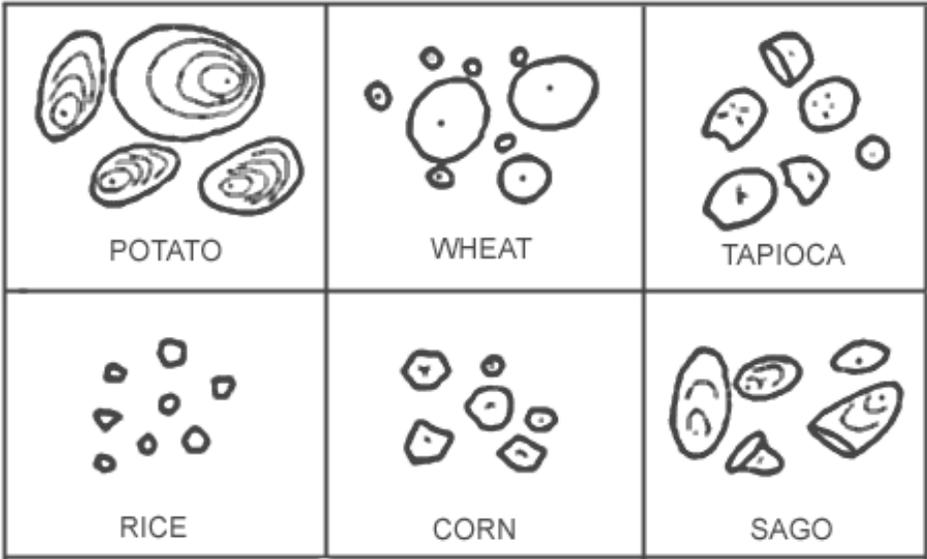


Figure 2
Shape of six common starch granules

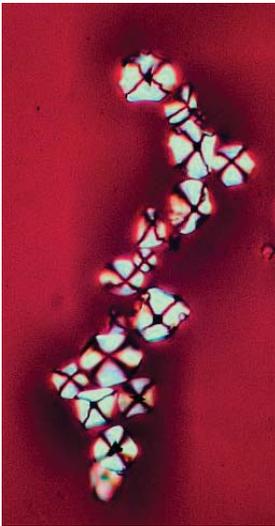


Figure 3
Corn starch photographed under polarized light. Note typical “Maltese cross” pattern

viscosity, and the eventual formation of a paste or gel. This process is referred to as starch *pasting* or *gelatinization*. The temperature at the which gelatinization of a starch occurs — the *gelatinization temperature* — is dependent upon such factors as starch concentration, pH of the suspension, rate of heating, the presence of certain salts, and the specific procedure being followed. Under well-defined conditions, starches can be classified using gelatinization temperature as a means for differentiation.

The properties of the starch granule are dependent upon the arrangement of the bonds which link glucose units to one-another within the starch molecule itself. The starch molecule is a

homopolymer of repeating anhydroglucose units joined by an alpha-glucosidic linkage, the aldehyde group of one unit being chemically bound to a hydroxyl group on the next unit through hemiacetal linkages. In most starches the alpha-1,4-linkage predominates, with only occasional 1,6-linkages. The 1,4-linkages yield straight chain starch molecules called *amylose*, while the 1,6-linkages serve as the branching point in branched-chain starch molecules called *amylopectin* (Figure 6). The proportions of these two types of starch molecules are established genetically and are relatively constant for each species of starch. For example, corn starch contains 27% of the linear amylose polymer, potato starch 20%, and

tapioca starch 17%.

Plant geneticists have learned to manipulate genetic controls in corn and have developed commercial varieties of corn that contain all branched-chain starch amylopectin molecules are called *waxy maize*. At the other extreme, a variety containing as high as 70% straight chain amylose molecules is grown commercially, and is called *high amylose* corn. 82% and higher amylose hybrids have recently been announced. The granules of waxy maize gelatinize much like normal corn starch. High amylose corn, on the other hand, will not gelatinize even in boiling water, but must be pressure cooked or hydrated by treatment with dilute sodium hydroxide. More detailed discussion of the effect of these variations in molecular structure is presented later.

The inherent properties of the starch granule can be altered by mild chemical treatment and/or derivatization. Oxidation with sodium hypochlorite, for example, decreases the gelatinization point in direct proportion to the quantity of chemical used. Similar effects are observed when starch is derivatized with ethylene oxide or other reagents. In

contrast, starch derivatives can be made in which the granule will not gelatinize at all when exposed to the severe conditions of moist heat and pressure.

The granular structure of starch, one of nature's fascinating architectural forms, is a vital element in the flexibility of commercial starches to fill specific product needs.

Corn kernels have three main parts: the seed coat or pericarp, the starchy endosperm, and the embryo, commonly called the germ (Figure 4). The pericarp is the outer skin or hull of the kernel which serves to protect the seed. The endosperm, the main energy reserve, makes up about 80% of the total weight of the kernel. It is about 90% starch and 7% gluten protein, with the remainder consisting of small amounts of oil, minerals and trace constituents. The embryonic germ contains a miniature plant made up of a root-like portion and five or six embryonic leaves. In addition, large quantities of high energy oil are present to feed the tiny plant when it starts to grow, as along with

THE CORN WET MILLING PROCESS

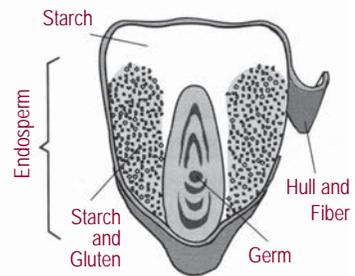


Figure 4
A kernel of corn

many substances required during germination and early development.

The corn wet milling process is illustrated in Figure 5, in which the kernel is separated into its component parts, and those parts are then further subdivided and refined.

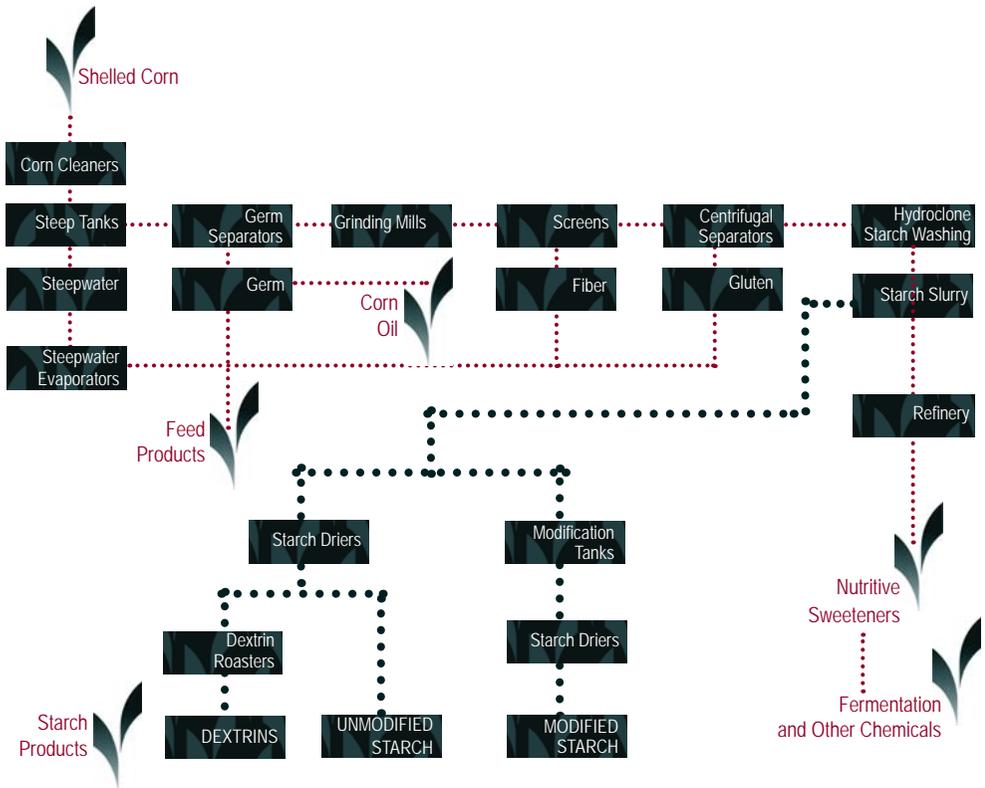
Corn wet millers buy shelled corn that is delivered to the plant by truck, barge or rail car. Normally #2 grade corn is purchased, based on USDA standards. Incoming corn is cleaned to remove

extraneous material such as pieces of cob, foreign seeds, stray metal, and fine grit. It then is conveyed to storage silos, holding up to 350,000 bushels, until ready to go to the refinery.

Cleaned corn is transported to large tanks called *steeps*. Warm water (125°-130°F) containing small quantities of dissolved sulfur dioxide is circulated through the steeps for approximately 24-48 hours to soften the kernel. Sulfur dioxide and water react during steeping

Figure 5

The corn wet milling process



to form sulfuric acid, which controls undesirable fermentation and assists in separation of starch and protein. During steeping, the soluble components are extracted from the intact kernel. At the conclusion of steeping, water is drained from the kernels and concentrated in multiple effect evaporators to yield concentrated *steepwater*.

This protein-rich extract may be used as a nutrient for microorganisms in the production of enzymes, antibiotics and other fermentation products.

Most steepwater, however, is combined with fiber and gluten in the production of animal feed ingredients. Further information on feed products produced by corn wet millers may be found in the booklet *Corn Wet Milled Feed Products*, available on the Corn Refiners Association website, www.corn.org.

Softened corn kernels next pass through mild attrition mills to loosen the hull and free the germ from the starch-rich endosperm. Water is added to the attrition mills and a thick slurry of macerated kernels and whole germ results. Because the germ at this stage contains 40-50% oil, it is lighter than the endosperm and hull. Centrifugal force is used to

isolate the germ.

Clean, separated germ is dried and the crude oil is removed by mechanical presses and/or solvent extraction. The crude oil may be refined to yield a fine quality salad and cooking oil or a raw material for the preparation of corn oil margarines. Extracted germ meal is used in animal feed. Further information on production and use of corn oil may be found in the booklet *Corn Oil*, available on the Corn Refiners Association website, www.corn.org.

The remaining mixture of hull and endosperm then passes through a series of grinding and screening operations. Large hull particles are retained on screens and removed, while finer protein and starch particles pass through. The hull is added to animal feed or washed and milled in the production of refined corn fiber (bran).

The water slurry of starch and gluten protein is next separated by centrifugation. Because starch and gluten differ widely in buoyant density, nearly complete separation is obtained. Typical operations yield a gluten stream containing over 60% protein, while the starch

stream is over 99% starch. The gluten is dried and sold as gluten meal (60% protein).

The white, nearly-pure starch slurry is further washed to remove small quantities of solubles. At this stage the starch slurry may be further processed to make any common (unmodified) corn starch or converted to make sweeteners or fermentation products. Various modified or derivatized starches may be produced by treating the slurry of washed starch with chemicals or enzymes. After treatment, the products are recovered by filtration or centrifugation and the starch is dried.

in water, combining with individual water molecules. As the molecules hydrate, they increase in size, immobilize much of the water present, thicken the aqueous system and form a paste. The first useful physicochemical property, thickening, gives many food products such as puddings, gravies, sauces and pie fillings their desired physical characteristics. This property is also useful in many industrial starch applications.

The second useful physicochemical property is the ability of the starch paste to disperse and suspend other ingredients or particulate matter. In many foods, fats and proteins are suspended and/or emulsified in starch pastes. In coatings for paper and in some adhesives, clay particles are suspended in thick starch pastes.

When starch pastes are allowed to cool, they thicken and can congeal into a semi-solid gel. The third useful physicochemical property, gel formation, provides the body typical of starch-based puddings, salad dressings and some types of adhesives.

The fourth useful physicochemical property of starch paste is its ability to produce strong adhesive



PHYSICOCHEMICAL PROPERTIES OF STARCH

What is starch? Starch is a highly functional carbohydrate in its unmodified state. It is also a highly reactive carbohydrate, which may be modified physically, chemically or enzymatically to meet specific needs.

Starches have four major physicochemical properties that make them useful in food and industrial applications. Both types of starch molecules—amylose and amylopectin (Figure 6)—are polyhydroxy compounds and hydrate when heated

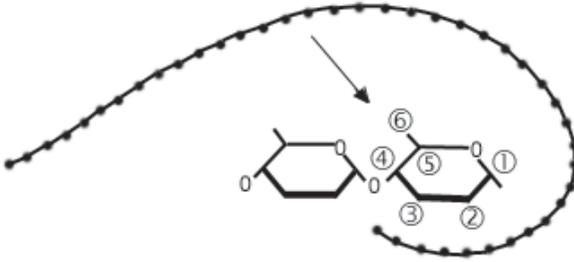
films when spread on smooth surfaces and dried. The major industrial uses of starch, such as paper coating and sizing, textile sizing, corrugated board manufacture and all adhesive applications utilize this property.

These four important properties vary in degree from one starch source to another. When the structures of linear and branched starches were elucidated and methods were

developed for detecting and quantifying the two types of molecules, their functional properties were finally explained.

Straight chain amylose molecules tend to line up parallel to each other in solution. As the solution cools, there is less energy available to keep the molecules apart. The hydroxyl groups on parallel amylose molecules

Amylose



Amylopectin

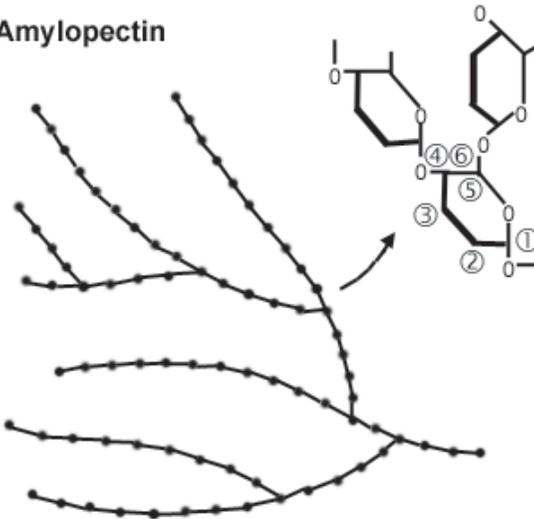


Figure 6

Amylose (top) and Amylopectin (bottom) molecules

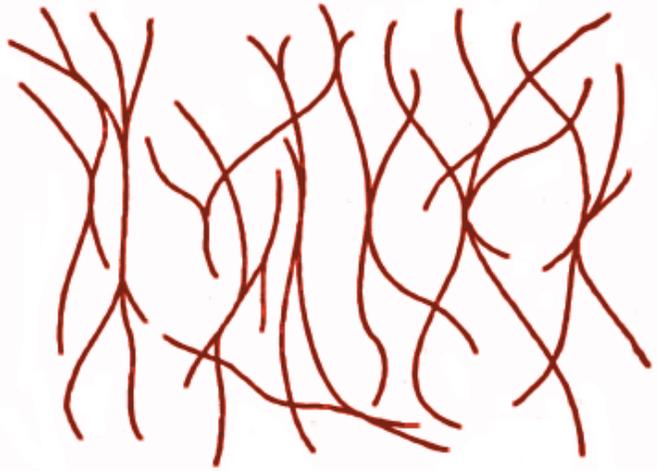


Figure 7
Micelle formation in
amylose molecules

exert attractive forces and the molecules are pulled together. This phenomenon, illustrated in Figure 7, is often referred to as retrogradation. The overall result is a gelled paste. The oriented areas are called micelles. Starches with a high percentage of amylose are difficult to gelatinize because of the extra energy needed to hydrate and disintegrate the firmly-bonded, crystalline aggregates of amylose. After gelatinization such starches form firm gels and when properly prepared, yield strong, tough films.

At the opposite end of the functional spectrum are the

waxy starches, which are nearly 100% amylopectin. They gelatinize easily and yield nearly-transparent, viscous pastes that retrograde slowly to weak gels. Between these extremes is found a wide range of natural starches as well as many starch modifications and derivatives. Based on the behavioral diversities of native starches, the starch chemist, by selection of the proper raw material, followed by application of selected modification or derivatization techniques, can devise products with a broad range of functional characteristics.

UNMODIFIED, REGULAR, NATIVE OR COMMON CORN STARCH

If the starch produced by the corn wet milling process is simply dried, it is called a common, regular or unmodified corn starch. It is available in various physical forms: corn starches may be sold as fine or coarse powders, as flakes, as pearls or be agglomerated to larger particles.

Slight variations can be introduced into unmodified starch by adjusting pH, by mild heat treatment, or by adding small quantities of chemicals or adjuvants before or after drying. Such starches will then perform more effectively in specific applications. For example, common starch intended for enzyme conversion may be adjusted to a specific pH and small amounts of inorganic salts that facilitate enzyme action may be added. Starches for food use are also often pH adjusted.

More unmodified corn starch is sold than any other type. It is used in the manufacture of corrugated board, coated and sized paper, paperboard, adhesives, salad dressings, beer, canned foods, dry food mixes (such as puddings, cakes, baking powder, etc.),

molding starch, laundry starch, etc.

Unmodified corn starch, when cooked, has such great thickening power that pastes containing more than 4-5% solids are too thick to handle. Further, such pastes gel very rapidly when cooled. For many uses higher solids-containing pastes with reduced tendency to thicken or with the ability to form softer gels are required.

The chemical composition of starch — highly oxygenated carbon compounds — make starch an excellent product for use as a chemical feedstock. Many industrial products, which today are derived from petrochemical feedstocks, are increasingly being synthesized from starch or cellulosic feedstocks. Examples of current commercial products of this type include the use of corn starch in the production of biodegradable plastics.

GENETIC VARIATIONS OF CORN STARCH

Many applications require starches in which properties other than viscosity have been modified. For many years, tapioca starch was the choice for puddings, fruit fillings and certain types of hard biscuits. When the



COMMERCIAL CORN STARCHES

supply of tapioca became short during the late 1930's, and later became unavailable, intensive research was begun to develop a genetic variety of corn that contained starch with properties similar to tapioca starch. A type of corn first found in China in 1908 and maintained as a genetic curiosity was called waxy corn because of its waxy appearance. The starch in this corn had properties similar to starch from tapioca.

An active breeding program was begun in 1956-57 to develop a commercial variety of corn that retained the waxy maize characteristics. By 1944, sufficient waxy maize was grown to demonstrate that it could be processed by the wet milling method to yield a starch that was a satisfactory replacement for tapioca.

Waxy maize starch, which is essentially 100% amylopectin, yields pastes that are almost clear when cool, non-congealing, and when dried in thin films, yields a translucent, water-soluble coating. Waxy starches are used for thickening a wide variety of prepared foods. Most commercial waxy starches are modified by crosslinking and/or derivatization to further enhance their

advantageous properties.

The development of waxy maize encouraged geneticists to look for a mutant that might yield a starch with a much higher amylose content than regular corn. Such a starch, it was postulated, should be an excellent film former and might be spinnable into a fiber. Genetic research ultimately resulted in the commercial development of two corn hybrids, one containing about 55%, the other about 70% amylose. Recent research has resulted in developing starches with greater than 80% amylose. The ultimate goal is to have native hybrid corn starch with 100% amylose.

High-amylose granules are smaller than those from regular or waxy maize corn and they often have unusual shapes. Some granules do not gelatinize or lose their birefringence even when boiled for a long time. However, they will gelatinize in dilute alkali or alkaline salts, or when heated in water under pressure at elevated temperatures. The solutions must be kept hot or the amylose quickly gels and retrogrades. High amylose starches are used to produce sizes for textiles and to produce quick-setting

confectionery gums. High amylose starches appear to be resistant to human digestion (hence, “resistant starches”) and may find application in reduced-calorie food products.

Active research programs are now being conducted into new methods to alter the genetic makeup of corn to produce starches which have the characteristics and functionality of the starch derivatives discussed below. Several are now commercially available. The genetically engineered starches allow processors to use fewer chemicals in their production, and to claim “native” labeling in addition to their unique functionality and their contribution to the development of new foods.

MODIFIED STARCH

Native starches have certain inherent features for use in the development of foods, pharmaceuticals and industrial products. Among other advantages, they are readily available, generally low in price, and yield a simple, consumer-friendly label when listed in an ingredient panel.

However, the advent of more sophisticated processing systems made it apparent that the natural properties of

raw starches could not meet the demanding processing requirements of increasingly sophisticated product formulations.

In order to meet such manufacturing requirements, starch chemists developed modified starches. The techniques and chemicals used to manufacture food and industrial modified starches have been thoroughly researched and tested to ensure safety and functionality. Modified food starches are strictly defined and regulated by the United States Food and Drug Administration (FDA) in 21 CFR Chapter 1, paragraph 172.892, and industrial modified starches are covered by 21 CFR Chapter 1, paragraph 178.3520.

Acid-modified corn starch

The first method used commercially to reduce the viscosity of starch pastes was the acid-modification process patented by Duryea in 1899. In this method, a starch-watersuspension is agitated while being subjected to mild treatment with dilute mineral acid at temperatures elevated but below the starch gelatinization temperature, for varying periods of time. When tests show the desired viscosity has been reached, the acid is neutralized with

sodium carbonate and the starch is filtered, washed and dried. In this manner a series of starches yielding pastes of decreasing viscosity are produced.

The primary reaction taking place during acid-modification is hydrolysis of glucosidic bonds in starch molecules. This limited and controlled hydrolysis produces two important consequences. First, since the starch molecule is so large, only a small amount of cleavage is needed to markedly reduce viscosity. Second, disruption of bonds within the granule weakens the granule structure. Like the parent starch, all acid-modified starch pastes have reduced viscosities when warm, yet have a strong tendency to gel when cooled. This suggests that acid-modification reduces chain length but does not substantially change the molecular configuration. When starch fragments reorient, the cooled pastes can and will set to firm gels. These so-called acid-modified or thin boiling starches are used in large quantities in textile warp sizes, especially for cottons and cotton polyester blends. The starch pastes, applied to warp yarns and dried, serve as an adhesive to

bind the fibers in the warp giving increased strength and resistance to abrasion needed in the loom during weaving. The lower viscosity acid-modified starches are also used in calendar and size press applications in the paper industry to enhance printability and abrasion resistance of the paper surface. This ability to form firm gels is utilized by the confectioner in the manufacture of starch-based gum candies.

Oxidized corn starch

A second method for reducing the viscosity and altering the properties of starch is oxidation. Although oxidizing agents such as chlorine, hydrogen peroxide and potassium permanganate can be used, oxidized starches produced by the corn wet milling industry are almost exclusively made using sodium hypochlorite as the oxidizing agent.

As in the case of acid-modification, aqueous starch suspensions under continuous agitation are treated with dilute sodium hypochlorite containing a small excess of caustic soda (NaOH). The reagent solution is added slowly to the starch suspension in a reactor which is maintained at about 120°F.

Cooling water in the reactor jacket or external heat exchangers remove heat generated during the oxidation reaction. When the correct amount of reagent has been added and sufficient time for reaction has elapsed, the viscosity of the starch is determined. When the desired degree of oxidation is reached, the starch slurry is treated with a reducing agent such as sodium bisulfite to remove excess hypochlorite, adjusted to the desired pH, filtered, washed and dried. Products with a wide range of modification can be produced.

Oxidized starch retains its original granule structure and is still insoluble in cold water. It is extremely white due to the bleaching action of the sodium hypochlorite. In addition to having decreased viscosity, oxidized starch pastes are relatively clear and show a reduced tendency to thicken or set back when cooled. When dried, oxidized starch films are clear and tough. Because the highly oxidized starches give relatively clear pastes at high solids, they are sometimes referred to as gums.

Treatment of starch with sodium hypochlorite brings about a random oxidation of a limited number of hydroxyl groups to carboxyl or carbonyl groups, with the resulting

rupture of the adjacent glucosidic bond. Since the oxidation occurs in the presence of excess sodium hydroxide, the carboxyl groups are neutralized, resulting in a sodium salt. Since the sodium salt of the carboxyl group is bulkier than the parent hydroxyl group, it is postulated that the tendency of the amylose molecules to associate and retrograde into gels is reduced. The major uses for oxidized starches are in the paper industry as tub, size press and calendar sizes; in the textile industry as warp sizes and as components in adhesives. They are used in food applications where high solids, low viscosity and a creamy body are desired, such as in bakery fillings. Oxidized starches perform well in batters and breadings due to good adhesion to meat products.

Dextrins

Dextrins are produced from starch by dry heating or roasting unmodified starch with or without an acid or alkaline catalyst. In this process, unmodified starch, dried to about 5-7% moisture, is usually acidified with very small amounts of mineral acid and placed in heated, agitated vessels called

reactors or roasters. The temperature is increased at a controlled rate and then maintained at a maximum temperature for varying lengths of time. The resulting product is cooled, blended and sometimes aged. Another dextrinization method utilizes a fluid bed, in which unmodified starch is placed in a reactor and suspended or “fluidized” in a stream of heated air. The starch is then acidified and, as in the conventional or “roaster” process, heated under controlled conditions of time and temperature until the desired end product is attained. With several degrees of freedom possible in such processes, a range of dextrans with widely varying properties is produced.

During dextrinization, the granule is not destroyed but granule integrity is disrupted. When dextrans are suspended in water and heated, the granules swell and then undergo a “peeling” action, separating into layers that eventually break free and disperse. The extent of occurrence of this behavior varies with the degree of conversion of the dextrin.

Dextrans differ from other modified starches in that, not only are they reduced in viscosity, but they also

have appreciable cold water solubility, reduced tendency to gel and increased reducing power. High solids solutions of some of the more highly converted dextrans produce tacky, quick-setting adhesives used in making all types of paper products (bags, laminates, paper boxes, paper tubes and envelopes).

There are several theories regarding what takes place during the dextrinization process. The process reduces the strength of the chemical bonds, which give the starch granule its integrity and brings about generalized molecular scissions that both reduce molecular size and alter molecular arrangement. In those cases where acids are present, simple hydrolytic cleavage is believed to occur. A combination of hydrolysis, recombination and formation of new glucosidic linkages likely accounts for altered paste viscosities and congealing characteristics.

There are three major types of dextrans: white, yellow and British gums. Depending on the processing conditions involved, there may be many subtypes.

White Dextrans

The first type, white dextrans, have a white color similar to original corn starch, but

have reduced viscosities, and cold water solubilities ranging from 5 to over 90%. White dextrans produce light colored pastes that set to soft but definite gels. The lower solubility products yield pastes similar to the most highly acid-modified thin-boiling starches. The higher solubility white dextrans (40-90%) can be used at much higher concentrations to yield very soft gels.

Yellow Dextrans

Yellow or canary dextrans are the second type. By using less acid, higher temperatures and more time, dextrans with high water solubility and a distinct yellow color can be produced. The yellow dextrans are used to produce high solids pastes (40-60%) that are very tacky and, when applied in thin films, dry rapidly. They make excellent adhesives, especially for paper products.

British Gums

British gums, the third type, are produced by adding little or no acid to very dry starch and then roasting a long time with slowly increasing temperature. They are tan to light brown in color and have a distinct caramelized odor. A range of products results, varying from low to high solubility. The pastes prepared from these dextrans

vary from nearly solid gels through very soft gels to viscous liquids.

Cyclodextrans

Although similar in name to dextrans, cyclodextrans are produced through quite different processes and have different uses. Cyclodextrans are produced through treatment of starch with a glucosyltransferase enzyme. The resulting water-soluble product takes the physical shape of a hollow cone, with an interior cavity of different sizes depending on the production method. A unique property of the interior of the cone is its hydrophobic nature, enabling cyclodextrans to be used to encapsulate a wide variety of compounds.

Uses for cyclodextrans include encapsulation for controlled flavor release, masking odors and tastes, stabilizing emulsions, increasing foaming power, and controlling or masking color. These properties are finding increasing applications in chemical, pharmaceutical and food markets.

Starch derivatives

Since the starch molecule contains many primary and secondary hydroxyl groups, it can be modified by chemical

derivatization.

Unlike the modifications thus far discussed, derivatization may or may not reduce the viscosity of the parent starch. Derivatization is used to impart different properties to the derivative than those of the parent starch. This allows the derivative to meet more effectively the requirements of specific end uses.

Countless starch derivatives have been described in technical literature and in patents, but only a limited number are manufactured and used commercially.

The derivatization of starch differs from most chemical modifications of polymers in that the changes in properties are attained with very slight changes in the molecule itself. In fact, all commercial derivatives are prepared under such mild conditions (usually in aqueous suspensions) that the starch granules retain their integrity. This allows the products to be handled in processing and application in much the same manner as the common starches previously discussed. Starch derivatives are usually prepared by adding the desired reagent to an agitated suspension of corn starch in water. By adjusting the pH of the slurry with an alkali, and sometimes with a catalyst,

the mild reactions proceed on the ungelatinized starch at only slightly elevated temperatures. After sufficient reaction time, the derivatives are recovered by filtration or centrifugation, washed with water, dried and packaged.

Two basic types of derivatives are prepared commercially:

Crosslinked/inhibited

Crosslinked starches, sometimes referred to as inhibited starches, are made to overcome the sensitivity of starch sols to shear and processing conditions. This is accomplished by treating starch in the granule state with trace amounts of bifunctional agents capable of reacting with hydroxyl groups on two different molecules within the granule.

Reagents such as phosphorus oxychloride or sodium trimetaphosphate may be used as crosslinking agents. Very small amounts of these agents can exert a marked effect on the behavior of the cooked starch. The degree of crosslinking controls the rate and extent to which starch swells on cooking. Crosslinking decreases the sensitivity of starch sols to temperature, agitation and acids, improving resistance to loss in viscosity.

Stabilization

Starch is stabilized against gelling by using monofunctional reagents. These reagents react with hydroxyl groups on the starch to introduce substituent groups that interfere with intermolecular association between starch molecules. Certain reagents may also introduce specific functionality into starches, e.g., increasing their water combining capacity or viscosity, or imparting a positive charge to the starch molecule.

Hydroxyethyl starches—To produce hydroxyethyl starch, a starch slurry is adjusted to an alkaline pH and a salt is added to suppress the tendency of the starch to gelatinize. Ethylene oxide in varying quantities is added slowly to the agitated slurry and allowed to react for the proper time. Most hydroxyethyl starches are also acid-modified to reduce their viscosity. The hydroxyethylated starch is recovered by filtration, washed and dried. The introduction of the hydroxyethyl group reduces the gelatinization temperature of the starch and results in clear, stable pastes. Hydroxyethyl starches are widely used in surface sizing and coating paper.

Cationic starches—Reaction of corn starch with tertiary or quaternary amines yields quaternary ammonium or amino alkyl starches. When dispersed, these starches exhibit positively charged particles that are strongly adsorbed by negatively charged cellulose fibers in the manufacture of paper. Less starch is used; but, more importantly, nearly all of the cationic starch in solution is adsorbed by the paper, leaving very little in the effluent going to the waste disposal system. This greatly reduces the biological oxygen demand (BOD) load. In addition, cationic starch promotes the retention of filters and pigments in the sheet while reducing the loss of very fine paper fibers. The additional retained fiber and the ability of the starch to bond the cellulose fibers together give greatly increased internal strength to the sheet. This substantive characteristic of cationic starches makes them useful also as surface sizes and as an adhesive in pigmented coatings. With the growing use of recycled paper stock in the manufacture of paper, more highly treated cationic starches are necessary to give strength and fiber retention properties. Computer printer paper requires higher cation treated starches to yield

properties needed to function properly.

Starch acetates—Corn starch can be acetylated with acetic anhydride or vinyl acetate under carefully controlled conditions of pH, temperature and time. After reaction, the starch is isolated by filtration, washed and dried. Sufficient acetyl groups are introduced to prevent retrogradation of the starch paste. Acetylated starches are used to size textile warps, yielding tough, yet flexible yarns. The reduced tendency to congeal makes starch acetates easy to pump and to apply at the slasher.

Starch acetates are also used as food starches. For example, waxy maize starch can be crosslinked with phosphorus oxychloride and then acetylated with acetic anhydride or vinyl acetate to produce an excellent thickener, texturizer or stabilizer used in preparing a wide variety of products.

Starch succinates—The use of succinic anhydride instead of acetic anhydride yields starch succinates, which are also used as thickening agents for foods. The 1-octenyl succinic ester is also prepared and has affinity for fats and oils superior to that of other derivatives. These starches

act as emulsifiers in such products as salad dressing, flavors and beverages.

Starch phosphates—Starch can be esterified with monosodium orthophosphate or sodium tripolyphosphate to yield starch phosphates which produce gels that are more stable than those produced from the parent starch. The phosphorylated starches are used mainly in preparing food products.

Hydroxypropyl starches—Propylene oxide added to an alkaline starch suspension reacts with the starch to yield hydroxypropyl derivatives. When made in accordance with 21 CFR 172.892, hydroxypropyl starches are used in food products where low temperature or frozen stability is needed. Hydroxyethyl starch can only be used in food packaging and industrial applications.

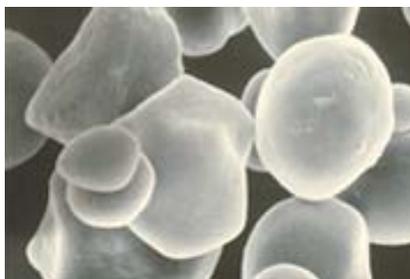
Other starch derivatives—Starch can be etherified by treatment with acrolein. Such ethers may then be esterified with either acetic or succinic anhydride. Starches are also esterified with phosphorus oxychloride and then etherified with propylene oxide.

Pregelatinized starches

Suspensions of most starches and starch derivatives can be gelatinized and dried to yield a broad variety of pregelatinized starches. This is normally done on a single drum dryer with applicator rolls. The starch slurry is heated to gelatinize it, instantaneously dried and ground to desired granulation requirement. These products can be dispersed in cold water with agitation to yield pastes comparable to those obtained by cooking the raw starch. The pregelatinized starches make possible the production of many unique food and industrial products that do not require heat for preparation. “Instant” adhesives and “Instant” starch-based puddings are examples of these types of products. New types of cold-water soluble (CWS) starches are made using aqueous/alcohol reaction, which causes the granule to swell and retain its structure without being ruptured. Such starches yield easier to use, smoother bodied products. Newer mechanical processes being used are spray drying and extrusion. Often these procedures involve the application of several treatments.

Bleached starches

Even though starches are quite white, certain uses require starches that are stark white. Such products are manufactured from starches by treating them with small amounts of such agents as hydrogen peroxide, peracetic acid, ammonium persulfate, potassium permanganate, sodium chlorite or sodium hypochlorite. The conditions of application are designed to whiten without producing any detectable chemical change in the starch. The bleached starch is recovered on continuous filters or centrifuges, washed with copious amounts of water to remove traces of inorganic salts formed from the bleaching agent, dried and packaged. Bleached starches perform functionally in the same manner as the parent starch but are lower in microbiological population due to the bleaching agents used. They are used in the manufacture of pills and body powders.



Corn starch photographed at 3000x.



STATUS OF STARCHES UNDER FEDERAL REGULATIONS

The Food and Drug Administration has proposed to affirm the “generally recognized as safe” (GRAS) status of food grade unmodified or common starches as well as pregelatinized starches. In addition, the same regulations proposed affirming the GRAS status of unmodified starches with differing amylose/ amylopectin contents, such as high amylose and waxy corn starches. These proposals are found in 50 FR 12821-12825. Corn starches have been affirmed as GRAS for use in food contact surfaces in 21 CFR 182.70 and 182.90. Dextrins have also been affirmed as GRAS by the Food and Drug Administration. Regulations covering dextrins may be found in 21 CFR 184.1277.

Two specific regulations promulgated by FDA cover the bleached, the modified and the derivatized starches approved for use in foods and in food packaging. These regulations specify the treatment approved, set limits for either the quantity of modifying agent used in preparing the product and/ or the amount introduced into the starch. They also specify the names to be used for modified starch

in ingredients lists. In the ingredients list on the label of a finished food, the name is, “food starch- modified.” The two regulations are: Food starch-modified — 21 CFR 172.892; and Industrial starch-modified — 21 CFR 178.3520.

For food starch-modified, these regulations cover acid-modified, bleached, oxidized, esterified and etherified starches, and starches treated with various combinations of these treatments.

For industrial starch-modified, the regulations cover starches treated by similar methods, as well as irradiated starches and starches treated with specific surface-active agents. Industrial starch-modified regulations specify the use of these products as a component of articles for food packaging, processing and storage.

In addition to regulatory actions by the Food and Drug Administration, various groups such as the *Food Chemicals Codex*, *U.S. Pharmacopeia* and the *National Formulary* have issued guidelines and specifications for starches, modified starches and dextrins intended for specific uses.

Dry starches are available in multiwall paper bags and in rail car or bulk truck shipments. Other containers such as paper drums, metal and rubber containers of various sizes, and corrugated boxes can be used but require special arrangements between user and supplier. Bulk bags up to 2000 pounds may be useful for industrial users, while smaller bags (25 and 50 lb.) are available for retail customers. Bulk installations vary in size from those with capacity for a few thousand pounds to those with capacity to handle several bulk rail hopper cars of starch at one time.

Because starch is a finely divided organic material, handling conditions that create dust may increase the risk of explosion. Explosion prevention measures include the use of non-sparking metals, explosion proof electrical motors and eliminating sparks, flames and hot surfaces in starch handling areas. Compliance with OSHA, EPA and local safety and health regulations is required.

Starch from a dry bulk handling station can be transported to points of use throughout a plant by properly designed air, vacuum and mechanical systems. Dry starches can also be slurried in water and pumped to the point of use. Because starch settles rapidly from water, continuous agitation or recirculation is necessary to maintain a suspension. Proper design of both dry and wet starch handling systems is necessary. Starch manufacturers will supply engineering assistance in designing such systems.

Starch is very stable and can be stored for long periods if kept dry. Like many other organic materials, however, it will degrade and decompose if allowed to become damp. Because starches are somewhat hygroscopic, they will vary in moisture content depending upon the humidity of the atmosphere in which they have been stored. Storage should avoid areas where aromatic products are stored, as starches can readily pick up flavors.



SHIPPING AND HANDLING DRY STARCHES

COOKING PROCEDURES FOR STARCHES

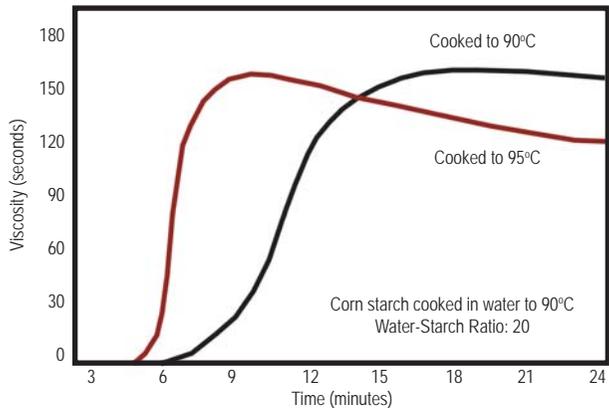
Most applications for starches require that they be suspended in water and then heated above the gelatinization temperature. The viscosity of the resulting paste is dependent on many variables, such as starch type, solids concentration, pH, amount of agitation during cooking, rate of heating, maximum temperature reached, time held at that temperature and the presence of other ingredients in the suspension.

As pointed out earlier, gelatinization temperature will vary with the type of starch selected for use. Further, the observed gelatinization temperature of a specific starch may vary with the physical conditions imposed upon the system. As shown in Figure 8, if starch under certain specific conditions of concentration, pH and agitation is heated

in a water bath maintained at 90°C, the observed gelatinization temperature and the resulting viscosities are not the same as with the bath maintained at 95°C. The 90°C cook reaches its maximum viscosity in about 18 minutes and then remains relatively constant. The 95°C cook, on the other hand, reaches its maximum in just over 9 minutes, but then gradually decreases in viscosity. The granules subjected to the more rapid temperature rise reach their maximum expansion and then begin to rupture with a resulting loss of viscosity. Adverse starch breakdown can be reduced or prevented by using a low level of crosslinking.

The effect of agitation on the gelatinization and breakdown of corn starch is shown in Figure 9. In this experiment a 5% starch suspension at

Figure 8
Effect of temperature on gelatinization



room temperature was placed in a water bath maintained at 90°C and agitated at two different speeds. The solid line shows that the paste agitated at 100 rpm required approximately 18 minutes to reach its maximum viscosity and then remained constant for the last three minutes. In contrast, the suspension agitated at 200 rpm reached a maximum viscosity after 6 minutes, followed by a rapid viscosity decrease and then a continued, but much slower, viscosity decrease. In the 200 rpm cook, improved heat transfer caused the temperature to rise at a faster rate and the granules to gelatinize more rapidly. The mechanical action of the 200 rpm agitator, however, ruptured the swollen granules resulting in a sharp drop in viscosity. Continued agitation brought about only slight viscosity decrease after the granules were mechanically ruptured. Crosslinking

reduces viscosity loss due to shearing of the granule by use of agitators, pumps and homogenizers.

The effect of pH on corn starch gelatinization and breakdown is demonstrated in Figure 10. The reference sample at pH 4.0 yields a typical cooking curve for normal corn starch. Increasing the pH to 7.0 caused more rapid gelatinization, but yielded a comparable viscosity in the cooked paste. Increasing the pH from 4.0 to 7.0 increased the ability of the starch granule to hydrate and gelatinize, but did not provide sufficient alkalinity to produce appreciable viscosity breakdown after gelatinization. However, when the pH was increased to 10.0 with alkali, gelatinization occurred in a much shorter time due to an increased rate of hydration

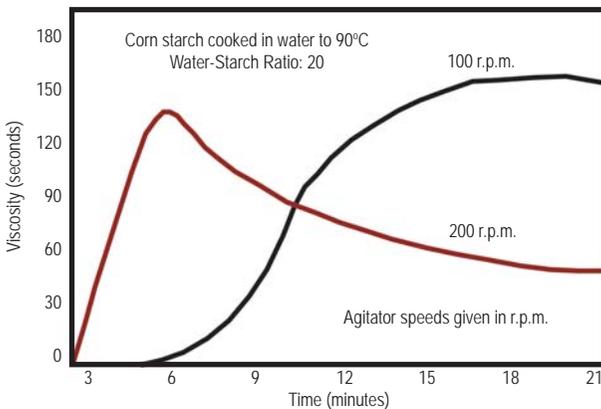


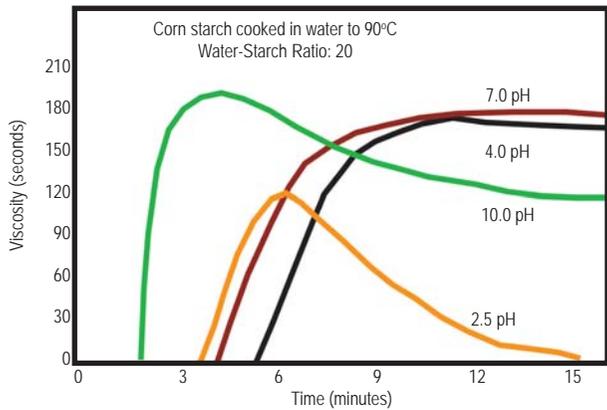
Figure 9
Effect of agitator speed on gelatinization

of the starch molecules. The higher alkalinity also ruptured some of the swollen granules with a resulting loss of viscosity. Although not shown in Figure 10, if the starch had been dispersed in 2% sodium hydroxide solution, it would have gelatinized without any added heat to a relatively stable, but less viscous paste than that produced by heating at pH 10.0.

The final curve on Figure 10 shows the viscosity behavior of a starch suspension adjusted to pH 2.5. Gelatinization began much like the suspension at pH 7.0, but the paste attained a lower maximum viscosity and then underwent a rapid and continuing loss of viscosity. At pH 2.5 and at temperatures approaching 80°C the starch molecules probably undergo glucosidic

cleavage, weakening the entire granular structure, which ultimately disintegrates yielding water-dispersible fragments of lower molecular weight. The effects of other materials in the solution on the rate of gelatinization of starch and the characteristics of the resulting pastes also can be observed. For example, when cooked in 10% sucrose solutions, starches gelatinize less rapidly and form less viscous pastes, since sucrose binds water so that less is available for granule gelatinization. When the diastatic enzyme alpha-amylase is present, marked decreases in viscosity occur. If beta-amylase is present, the viscosity drops and up to 60% of the starch may be converted to maltose. If glucoamylase is present, the starch may be converted to over 95% glucose. Another method for preparing starch

Figure 10
Effect of pH on
gelatinization



pastes involves continuous pressure cooking, often referred to as jet cooking. In this process the starch suspension is mixed with steam and then injected into a pressure vessel, where it is held for a very short period of time at temperatures over 100°C and at pressures higher than atmospheric. The paste is then flashed down to atmospheric pressure, with resultant evaporative cooling and concentration. If desired, some modification of the starch may be obtained by adding small quantities of specific chemicals to the starch slurry before injection into the cooker. This allows the user to alter the properties of the starch paste in a continuous process to meet the requirements of his specific use, but it does mean that the user must assume responsibility for controlling the degree of modification accomplished.

Since starch properties can also be altered by derivatization and modification, almost unlimited variations can be obtained. This versatility has made possible the development of many specialty starch products designed for specific fields of application. It is impossible to discuss the many products

commercially available in this brief discussion. Typical applications for food and industrial starches, and dextrans are included at the end of this booklet. Any reader wishing assistance with these products is encouraged to contact individual member companies of the Corn Refiners Association. They would be pleased to offer assistance in selecting the correct product and in recommending proper methods of application.

Cooked starches may be used hot, at room temperature or chilled. The proper conditions for altering the temperature must be applied to the hot paste if the desired results are to be obtained. Conditions are often designed for a specific application, but some general guidelines follow:

1. Hot starch pastes continue to lose viscosity if maintained near boiling temperatures. They should be cooled to the temperature at which they are to be used immediately after cooking.
2. Starch pastes lose viscosity in direct proportion to the force of agitation. If viscosity is to be maintained, gentle



but thorough agitation should be used after cooking.

3. Starch pastes increase in viscosity as they are cooled. The amount of agitation applied during cooling affects the physical characteristics of the cooled paste. Continuous agitation during cooling yields pastes smoother in texture and with fewer tendencies to gel than those not stirred. Conversely, maximum gelling demands that no agitation be applied during cooling.

4. Undercooked starch pastes yield gels that release water upon standing. Though often referred to as “weeping,” as the more correct term is *syneresis*. Selection of the proper starch product, thorough cooking and proper cooling eliminates syneresis.

5. Dilute starch pastes, particularly those of unmodified and acid-modified starches, may develop a distinct cloudiness. This cloud is the result

of *retrogradation* of the amylose polymer in the starch. Retrogradation is the process of molecular alignment and dehydration that produces large, loosely bound molecular aggregates. Given sufficient time and no agitation, these aggregates may precipitate (settle). Clouding and precipitation can be prevented by keeping starch pastes at a temperature of about 170°F with gentle, continuous agitation. Oxidized, certain derivatized and most dextrinized starches have reduced tendency to retrograde. Waxy starches do not exhibit this retrogradation phenomenon to any marked degree.

6. Due to the ready accessibility of sugars, starch pastes are excellent media for the growth of many airborne microorganisms. If stored at or near room temperature for more than 24 hours, preservatives must be added to prevent fermentation, loss of viscosity and eventual spoilage.

Starch pastes of all types are susceptible to hydrolysis by amylolytic enzymes resulting in shorter polymer chain lengths and sharply reduced viscosities. Enzyme hydrolysis is widely used, particularly in the textile and paper industry and in the preparation of corn syrups and dextrose.

Cotton warp yarns are commonly sized with starches to give them the needed strength for proper weaving. However, the starch must be removed from the woven cloth before it is dyed. A diastatic enzyme (alpha-amylase) that rapidly hydrolyzes starch to short, water soluble fragments is used for this purpose. The enzyme is applied to wet cloth, allowed to stand for the correct period of time to permit the enzyme to act on the starch, and the solubilized hydrolysates are then washed from the cloth with warm water.

Paper manufacturers use large quantities of starch that is enzyme converted in the paper mill. The enzyme conversion process allows the papermaker to replace the modified or derivatized starches with unmodified starch for some applications. It also allows the papermaker to custom convert starch

to the viscosity required for specific applications. In a typical paper or textile mill, bulk starch is automatically scaled into converting equipment, where it is slurried in water at the correct concentration (35-40% starch suspensions for high solids conversions). The starch slurry is adjusted to the desired pH, alpha-amylase is added and a programmed heat cycle is set in operation. In a typical conversion cycle, steam is applied to a closed, jacketed, agitated vessel heating the starch suspension to 80°C in 15 minutes. This swells the starch and initiates rapid enzyme conversion. The conversion is held at 80°C for 45 minutes and then heated to about 105°C in 15 minutes. The elevated temperature is maintained for 30 minutes to inactivate the enzyme and thoroughly disperse the starch.

At the conclusion of the 105°C holding period, the starch is cooled to the temperature at which it is to be used by one of several means. If it is intended for use as a tub size or for application at the size press on a paper machine, it will quite likely be cooled by dilution with cold water. Pigments or other chemical aids may be added



ENZYME CONVERSION OF STARCH

simultaneously with the dilution water.

If the conversion is intended for use in preparation of a pigmented coating for paper, it is cooled by adding it to a “clay slip” which is a high solids mixture of clay or other pigments with dispersing agents, dyes and other chemical aids. Since paper coating is accomplished at very high speeds, the rheological properties of the starch-clay-chemical mix (coating color) must be carefully controlled.

Primary control of the final viscosity of enzyme-converted starch is achieved by varying the quantity of enzyme utilized, but variation of the physical conditions imposed upon the system also affects the characteristics of the converted starch. Batch systems are often employed, but continuous systems are also in use commercially.

Generally, starches used for enzyme conversion are unmodified and are specially

prepared for this use. They are usually pH adjusted and buffered; small quantities of various adjuvants are incorporated in the slurry before drying and special drying techniques may be used.

The major use for enzyme-converted starch occurs right in the wet milling plant, where each year billions of pounds of starch are converted to nutritive carbohydrate sweeteners. These processes utilize alpha-amylase, beta-amylase, glucoamylase, debranching enzymes and isomerases. They are discussed in a booklet entitled *Nutritive Sweeteners from Corn*, available on the Corn Refiners Association website, www.corn.org.

Enzyme treatment today is frequently used to prepare starch for subsequent derivatization and processing steps, which result in the creation of products with unique physical and functional properties.

The chemical literature contains descriptions of countless methods for determining the chemical and physical properties of starch.

The Corn Refiners Association, through its Technical Affairs Committee, has spent many years developing and standardizing analytical procedures for starch and starch derived products which are practical and effective. The committee actively continues its work on standardization of analytical procedures today.

As a result of this extensive work, the Corn Refiners Association publishes these analytical procedures and

makes them available to the public. These methods are published in *Analytical Methods of the Member Companies*, available from the Association's website, www.corn.org.

By cooperation with the Association of Official Analytical Chemists many of these methods are available through that organization's reference publications as well.

The Corn Refiners Association has published many analytical procedures applicable to unmodified and modified starches and dextrans, sweeteners and corn byproducts.



ANALYTICAL EXAMINATION OF STARCH

CORN REFINING INDUSTRY PRODUCT USE

| | Unmodified starch | Modified starch | Dextrins | | Unmodified starch | Modified starch | Dextrins |
|------------------------------|-------------------|-----------------|----------|-----------------------------|-------------------|-----------------|----------|
| ALCOHOLIC BEVERAGES, BREWING | | | | Vinegar | ✗ | | |
| Beer, liquor | | ✗ | | Worcestershire sauce | | ✗ | |
| BEVERAGES, NON-ALCOHOLIC | | | | CONFECTIONERY & GUM | | | |
| Carbonated | | ✗ | | Chewing gum | ✗ | ✗ | ✗ |
| Protein drinks | | | ✗ | Chocolates | ✗ | | |
| Fruit drinks & juices | | ✗ | ✗ | Confectionery | ✗ | ✗ | ✗ |
| Powdered mixes | ✗ | ✗ | ✗ | Licorice | ✗ | ✗ | ✗ |
| BAKING, SNACK FOODS | | | | Marshmallows | ✗ | ✗ | ✗ |
| Baking powder | ✗ | ✗ | | Nougats | ✗ | ✗ | ✗ |
| Bars, energy & snack | | ✗ | | FATS AND OILS | | | |
| Biscuits | ✗ | ✗ | ✗ | Margarine | ✗ | ✗ | ✗ |
| Breads & rolls | ✗ | ✗ | ✗ | Pan coatings | ✗ | | |
| Cakes | ✗ | ✗ | ✗ | FORMULATED DAIRY PRODUCTS | | | |
| Cookies | ✗ | ✗ | ✗ | Cheese spreads & foods | ✗ | ✗ | ✗ |
| Crackers | ✗ | ✗ | ✗ | Coffee whitener | ✗ | ✗ | ✗ |
| Doughnuts | ✗ | ✗ | ✗ | Condensed milk | | | ✗ |
| Extracts and flavors | | ✗ | ✗ | Frozen cream | ✗ | ✗ | ✗ |
| Food coloring | | | ✗ | Yogurt | | ✗ | |
| Frosting, icing, glazes | ✗ | ✗ | ✗ | ICE CREAM & FROZEN DESSERTS | | | |
| Pies | ✗ | ✗ | ✗ | Frozen puddings/custards | ✗ | ✗ | ✗ |
| Potato chips | | ✗ | ✗ | Ice cream or milk | ✗ | ✗ | ✗ |
| Powdered sugar | ✗ | ✗ | | Powdered mixes | ✗ | ✗ | ✗ |
| Pretzels | ✗ | ✗ | ✗ | Sherberts, water ices | ✗ | ✗ | ✗ |
| Spices | | | ✗ | JAMS, JELLIES, PRESERVES | | | |
| Yeast | ✗ | | | Fruit butters | ✗ | ✗ | ✗ |
| CANNED FRUITS & VEGETABLES | | | | Jams | | ✗ | ✗ |
| Fruits & berries | ✗ | ✗ | | Jellies | | ✗ | ✗ |
| Fruit fillings | ✗ | ✗ | | Marmalade | | ✗ | ✗ |
| Soups | ✗ | ✗ | ✗ | Preserves | | | ✗ |
| Tomato sauces | ✗ | ✗ | ✗ | MEAT PRODUCTS | | | |
| Vegetables | ✗ | ✗ | | Bologna | ✗ | ✗ | ✗ |
| CEREALS | | | | Breakfast meats | | ✗ | |
| Cereals | ✗ | ✗ | ✗ | Chicken products | | ✗ | |
| Cereal bars | ✗ | ✗ | ✗ | Dried meats | | ✗ | |
| CONDIMENTS | | | | Fish, seafood | ✗ | ✗ | |
| Catsup | ✗ | ✗ | | Hotdogs | | ✗ | |
| Gravies | ✗ | ✗ | ✗ | Mincemeat | ✗ | ✗ | ✗ |
| Mayonnaise | ✗ | ✗ | | Sausages | ✗ | ✗ | |
| Mustard | ✗ | ✗ | | Surimi | ✗ | ✗ | |
| Oriental sauces | ✗ | ✗ | ✗ | MIXES, PREPARED | | | |
| Pickles, pickle products | | ✗ | | Cake mixes | ✗ | ✗ | ✗ |
| Relishes | | | | Cookie, brownie mixes | ✗ | ✗ | ✗ |
| Salad dressings | ✗ | ✗ | ✗ | Dessert mixes | ✗ | ✗ | ✗ |
| Sauce mixes | ✗ | ✗ | ✗ | Dried foods | ✗ | ✗ | ✗ |

CORN REFINING INDUSTRY PRODUCT USE

| | Unmodified starch | Modified starch | Dextrins | | Unmodified starch | Modified starch | Dextrins |
|------------------------------|-------------------|-----------------|----------|-------------------------------|-------------------|-----------------|----------|
| Eggs, frozen or dried | ✗ | ✗ | ✗ | Coatings (food & drug) | ✗ | ✗ | ✗ |
| Frosting, icing mixes | ✗ | ✗ | ✗ | Cough drops | ✗ | ✗ | ✗ |
| Gelatin mixes | | ✗ | ✗ | Drugs | ✗ | ✗ | ✗ |
| Gravy mixes | ✗ | ✗ | ✗ | Medicinal syrups | ✗ | ✗ | ✗ |
| Instant breakfast foods | ✗ | ✗ | ✗ | Pharmaceuticals | ✗ | ✗ | |
| Instant tea | | ✗ | ✗ | TOBACCO | | | |
| Pancake, waffle mixes | ✗ | ✗ | ✗ | Tobacco | | ✗ | ✗ |
| Quickbread mixes | ✗ | ✗ | ✗ | ANIMAL FEED | | | |
| Seasoning mixes | ✗ | ✗ | ✗ | Cat | ✗ | ✗ | ✗ |
| Soups, dried | ✗ | ✗ | ✗ | Cattle | ✗ | ✗ | |
| SYRUPS & SWEETENERS | | | | Dog | ✗ | ✗ | ✗ |
| Chocolate, cocoa | ✗ | ✗ | ✗ | Fish | ✗ | ✗ | ✗ |
| Dessert toppings | ✗ | ✗ | ✗ | Swine | ✗ | | |
| Fruit and table | ✗ | ✗ | ✗ | CHEMICALS | | | |
| Low calorie sweeteners | | ✗ | ✗ | Acetic Acid | ✗ | | |
| Soda fountain | ✗ | ✗ | ✗ | Agrochemicals | ✗ | ✗ | |
| MISC. FOODS | | | | Dispersing agents | ✗ | ✗ | |
| Baby Food | ✗ | ✗ | ✗ | Enzymes | ✗ | ✗ | |
| Desserts (puddings/custards) | ✗ | ✗ | ✗ | Fermentation processes | ✗ | ✗ | ✗ |
| Dietetic preparations | ✗ | ✗ | ✗ | Food acids | ✗ | ✗ | |
| Invalid feedings | ✗ | ✗ | ✗ | Industrial alcohol | ✗ | ✗ | |
| Peanut butter | | | ✗ | Insecticides | ✗ | ✗ | |
| Precooked frozen meats | ✗ | ✗ | | Organic solvents | ✗ | ✗ | ✗ |
| Rice & coffee polish | ✗ | | ✗ | Pharmaceuticals | ✗ | ✗ | |
| HOUSEHOLD NEEDS | | | | PAPER, PAPER RELATED PRODUCTS | | | |
| Air freshener | | ✗ | | Abrasive paper & cloth | ✗ | ✗ | ✗ |
| Batteries | | ✗ | | Bookbinding | ✗ | ✗ | ✗ |
| Briquettes | ✗ | ✗ | ✗ | Envelopes | ✗ | ✗ | ✗ |
| Cleaners | | ✗ | | Glassine | ✗ | ✗ | ✗ |
| Crayons & chalk | | ✗ | ✗ | Labels | ✗ | ✗ | ✗ |
| Diapers | ✗ | ✗ | | Paper | ✗ | ✗ | ✗ |
| Laundry care | | ✗ | | Parchment | ✗ | ✗ | ✗ |
| Matches | | ✗ | ✗ | Printing inks | ✗ | ✗ | ✗ |
| Metal cleaner | ✗ | | | Straws | ✗ | ✗ | ✗ |
| Trash bags | ✗ | ✗ | | Wallpaper | ✗ | ✗ | ✗ |
| Twine, cord, string | ✗ | ✗ | | PASTE ADHESIVES | | | |
| PERSONAL CARE | | | | Adhesives | ✗ | ✗ | ✗ |
| Cosmetics | ✗ | ✗ | ✗ | Binders, binding agents | ✗ | ✗ | ✗ |
| Deodrant | | ✗ | | Glues | ✗ | ✗ | ✗ |
| Hair styling products | | ✗ | | Gums | ✗ | ✗ | ✗ |
| Surgical dressings | ✗ | ✗ | | Mucilages | ✗ | ✗ | ✗ |
| PHARMACEUTICALS | | | | Pastes | ✗ | ✗ | ✗ |
| Antibiotics | ✗ | | ✗ | TEXTILE | | | |
| Asprin | ✗ | ✗ | | Cord polishing | ✗ | ✗ | |

CORN REFINING INDUSTRY PRODUCT USE

| | Unmodified starch | Modified starch | Dextrins | | Unmodified starch | Modified starch | Dextrins |
|---------------------------|-------------------|-----------------|----------|-----------------------------|-------------------|-----------------|----------|
| TEXTILES cont. | | | | MINING/METALLURGY | | | |
| Dyes & dyeing | ✗ | ✗ | ✗ | Electroplating | | ✗ | |
| Oilcloth | ✗ | ✗ | | Galvanizing | | ✗ | |
| Printing | ✗ | ✗ | ✗ | Metal plating | | ✗ | |
| Sizing materials | ✗ | ✗ | ✗ | Ore refining, separation | ✗ | ✗ | ✗ |
| Textile | ✗ | ✗ | | MISC. INDUSTRIAL | | | |
| Windowshades, shade cloth | ✗ | ✗ | ✗ | Boiler compounds | | ✗ | |
| BUILDING MATERIALS | | | | Explosives | ✗ | ✗ | ✗ |
| Cardboard | ✗ | ✗ | | Filters | ✗ | ✗ | |
| Ceramics | ✗ | ✗ | ✗ | Fireworks | ✗ | ✗ | ✗ |
| Coatings (wood, metal) | ✗ | ✗ | | Leather tanning | | ✗ | |
| Cork products | ✗ | ✗ | | Lubricating agents | | ✗ | |
| Fiberglass | ✗ | ✗ | | Oil-well drilling | ✗ | ✗ | |
| Fiberboard, plywood | ✗ | ✗ | ✗ | Plastics, incl. degradable | ✗ | ✗ | |
| Glass or rock wool | ✗ | ✗ | | Protective colloids | | ✗ | ✗ |
| Laminated | ✗ | ✗ | ✗ | Refractories | | ✗ | |
| Linoleum | ✗ | ✗ | | Rubber (cold process) | ✗ | | |
| Paints and varnishes | ✗ | ✗ | | Shoes | | ✗ | |
| Tile, ceiling | ✗ | ✗ | ✗ | Tires (rubber) | ✗ | | |
| Wall treatment compound | | ✗ | | Water recovery (industrial) | | ✗ | |
| Wallboard | ✗ | ✗ | ✗ | | | | |



GLOSSARY

To aid in the understanding of industry-specific information in this booklet, technical terms are explained in the text at the points where they are first used. For reader convenience, definitions of some of the more difficult terms and of terms having special meanings in the corn refining industry are listed here.

Amylose – A starch molecule made up of glucose units chemically arranged in long straight chains.

Amylopectin – A starch molecule made up of glucose units chemically arranged into branched chains.

Anhydroglucose units – The basic $C_6H_{10}O_5$ unit that occurs repeatedly in all starch molecules.

Aqueous – Containing water.

BOD – Biological oxygen demand, the measure of the amount of oxygen in a body of water used over a period of time through bacteria and plankton activity to stabilize decomposable organic waste.

Brabender – Amylo-viscograph unit used to measure viscosity.

Carbohydrate – A chemical compound composed of carbon, hydrogen and oxygen (starch, sugar and cellulose are three of the most common examples).

Congeval – To change from a liquid to a semi- solid, non-fluid mass.

Convert – To change to a lower molecular weight form, as by dextrinization, hydrolysis, etc.

Corn – The seed from commercially grown maize (*Zea mays*) used primarily for animal feed and corn-derived food and industrial products; not sweet corn.

Derivative – A product obtained by reacting starch with a chemical compound, resulting in unique physical and functional properties.

Enzyme – Any of a class of protein molecules that catalyze specific biochemical transformations, as in the conversion of starch to glucose.

Fluidity – Reciprocal of viscosity.

Fractions – The two types of molecules found in starches--- linear and branched; amylose and amylopectin.

Gel – A firm, semi-rigid, cooled starch paste resembling a jelly; to form a gel.

Gelatinize – To cook starch in aqueous suspension to the point at which swelling of the granules take place, forming a viscous sol.

Genetics – A branch of biology dealing with hereditary variations in plants and animals. As an applied science, it is used to improve corn by breeding desired characteristics into new varieties.

Glucosidic cleavage – The hydrolysis of a glucose polymer whereby water is the agent, which, under acid or enzyme catalysis, acts to split apart the glucosidic bond holding adjacent glucose units together and regenerates an hydroxyl group on each glucose component.

Granule – The small, grain-like storage particle produced in plants, consisting of starch molecules arranged in characteristic patterns.

High amylose starch – A starch containing over 50% amylose (usually 55-70%).

Hydrate – A molecular-water association.

Hydrolysis – Process of splitting a molecule into smaller parts by chemical reaction with water.

Hydroxyl (OH) group – A chemical radical consisting of one oxygen and one hydrogen atom.

Hygroscopic – Readily absorbing and retaining moisture.

Kernel – A whole grain or seed of a cereal, especially corn.

Linkage – The specific bonding arrangement by which molecules are joined to form larger molecules.

Micelles – The tight bundles into which linear starch molecules and the linear segments of the branched molecules are drawn together.

Molecule – A unit of matter; the smallest portion of a compound that retains chemical identity with the substance in mass.

Mutant – An offspring different from its parent in some well-marked characteristic.

Oxidation – The act of oxidizing which is brought about by increasing the number of positive charges on an atom or the loss of negative charges.

pH – A measure of the acidity or alkalinity of a solution, pH 7 being neutral, lower values acid and higher values being alkaline.

Polymer – A very large, complex molecule formed by chemically joining a large number of identical smaller units (or monomers) in a repeating pattern.

Retrogradation – Dehydration and reversion of cooked starch from a paste to a condition of insolubility.

Slurry – Suspension of starch in water, with or without other components of corn.

Stable – Term indicates that the starch paste does not change appreciably in viscosity, clarity or texture with age.

Starch paste – The thick, viscous, smooth suspension formed by cooking starch in a water suspension to a point above its gelatinization temperature.

Steepwater – Water containing dissolved protein, minerals and other substances in which corn has been soaked or “steeped” during the initial stages of the corn refining process.

Suspension – A heterogeneous mixture of an insoluble granular or powdered material with a fluid.

Synthesize – To build up a compound by the union of simpler compounds or of its elements.

Viscosity – Term used to indicate the resistance of liquids to flow; often used to describe the thickness of a starch paste.

Waxy maize – A variety of corn, the starch content of which consists solely of branched molecules.

Wet milling – A process for separating corn into its component parts using a water-sulfur dioxide system.



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