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Industrial Starch Chemistry

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1 Introduction

Starch is a polymeric carbohydrate composed of anhydroglucose units and is extracted in granular form from the organs of certain plants. The word ´starch´ may be derived from the Anglo-Saxon ´stearc´ and has the meaning of strength or stiffness. Starch granules are deposited in the seeds, tubers, roots and stem piths of plants, as a reserve food supply during periods of dormancy, germination and growth. The microscope reveals that starch is composed of tiny, white granules, ranging from about 1 to 100 microns (= micrometer) in diameter. Size and shape of the granules are peculiar to each variety of starch.
Figure1 shows schematically the appearance of various starches. After cellulose, starch is the next most abundant compound synthesized by plant cells. It is a ´renewable´ substance; a new supply of starch is grown annually.

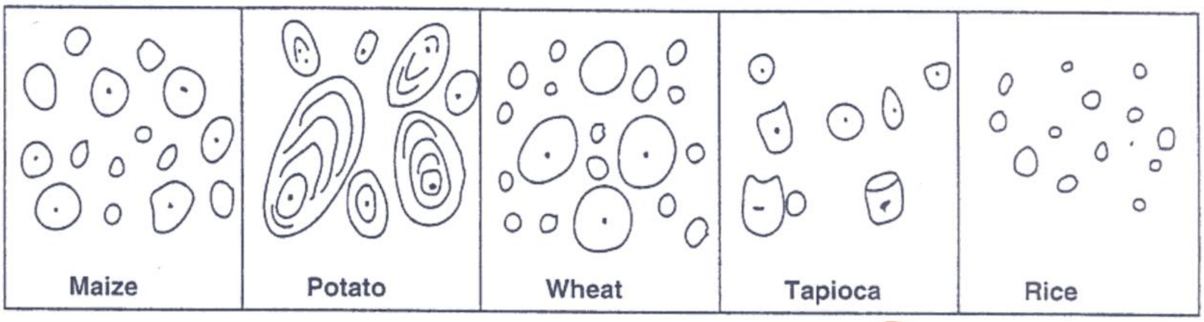

Figure 1 – Microscopic appearance of various starches

The commercial sources of starch are the seeds of cereal grains (maize, wheat, sorghum and rice), tubers (potato), roots (tapioca, sweet potato and arrowroot) and the pith of the sago palm. Each starch is described according to its plant source as maize starch, potato starch, tapioca starch, wheat starch, etc. The properties of the starch vary with the plant source from which it is derived. The starch industry uses a combination of grinding and wet purification techniques to manufacture starch with a purity of about 98-99.5 %. In the manufacturing process, starch is separated from the other constituents of the milled raw material such as fibres, proteins, sugars and salts.

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Starch can be considered to be a condensation polymer of glucose. The glucose units in the starch polymer are present as anhydroglucose units (AGU). If starch is treated with acids or certain enzymes, it is broken down into its constituent glucose molecules. Similarly, glucose is generated when starch is used as a food by animal and man.

Starch is not a uniform material. Most starches contain two types of glucose polymers: (1) a linear chain molecule termed amylose and (2) a branched polymer of glucose termed amylopectin. These two fractions occur in differing amounts in starches from various botanical sources. Amylose comprises 15-30 % of the common starches.

Starch granules are insoluble in water below 50 °C. When a suspension of starch in water is heated beyond a critical temperature, the granules absorb water and swell to many times their original size. The critical temperature, at which this occurs, is known as the pasting or gelatinization temperature (about 55 to 80 °C; depending on the type of starch). When heating is continued, the swollen starch granules begin to desintegrate into swollen starch aggregates. The viscous mass, resulting from the swelling and the colloidal dispersion of starch in an aqueous medium, is termed starch paste.The process, involving the transformation of a starch into a starch paste, is termed gelatinization. True solubilization of all the starch molecules occurs when the paste is cooked at temperatures of 100-160 °C. When cooked starch pastes are allowed to stand, the phenomenon known as retrogradation (synonym: setback) can take place and this is manifested in the formation of a gel or precipitate.

Native starch can be modified by physical, chemical and/or enzyme treatment to alter its properties or to impart new ones.

The ability of starch products to produce a viscous paste when heated in water is its most important practical property. The hydrocolloidal poperties of starch make it suitable for a great variety of applications. Starch and its derivatives are widely used in the manufacture of foods, paper, textiles, adhesives, pharmaceuticals and building materials

2 Sources of starches

2.1. Biosynthesis of starch

Green leaves of plants contain chlorophyll, which is able to absorb light quanta and utilize the energy to catalyze the formation of glucose and oxygen from carbon dioxide and water. This process is known as photosynthesis and may be written as follows (simplified):

$$6\,H_2O \quad + 6\,C0_2 \xrightarrow{\text{light/chlorophyll}} C6H_{12}0_6 + 6\,0_2$$

water + carbon dioxyde glucose + oxygen

Starch is formed in the leaves of plants by condensation polymerization of glucose with the aid of starch synthesizing enzymes. This process may be written as follows (simplified):

$$n\,C_6H_{12}0_6 \xrightarrow{\text{enzymes}} (C_6H_{10}O_5)n \quad + \; n\,H_2O$$

glucose starch + water

During active photosynthesis (during the day) the starch is accumulated in the leaves in the form of tiny granules of about 1 micron in diameter (leaf or transistory starch). During the night, this leaf starch is partly broken down by enzymes and transported in the form of sugars (mainly sucrose) to other parts of the plant. Some of these sugars are reconverted in to starch in the seeds, tubers and roots of various plants (storage starch). It is from these sources that the commercial starch is obtained.

Starch molecules are synthesized in plants from sugars. The true mechanism for the biosynthesis of amylose and amylopectin is not entirely clear. The enzymes phosphorylase (P-enzyme), starch synthetase and a branching enzyme (Q-enzyme) are, or may be, involved in starch biosynthesis.
Nowadays most starch scientists believe that starch synthetase is the true chain-lengthening enzyme in normal starch biosynthesis. The branching enzyme is responsible for the synthesis of the branching points in the amylopectin molecules. How amylose escapes from branching in the obvious presence of branching enzyme is still a question.

Development of starch granules commences with the accumulation of poorly organized material of unknown chemical composition. At a certain moment there is the deposition of a minute amount of insoluble polysaccharide, which acts as a nucleus for further starch deposition. This nucleus is the botanical center (hilum) of the granule, around which the granule is grown. Initial growth gives nearly spherical granules. As the granules are enlarged they often become elongated or flattened. The starch molecular chains grow in an orientation perpendicular to the growing surface of the starch granule. As the dissolved glucose units are linked to the growing starch polymer they simultaneously solidify. During the growing of the starch granule there is an increase in the proportion of amylose and an increase in molecular size of both amylose and amylopectin

2.2. Occurrence and manufacture of starches

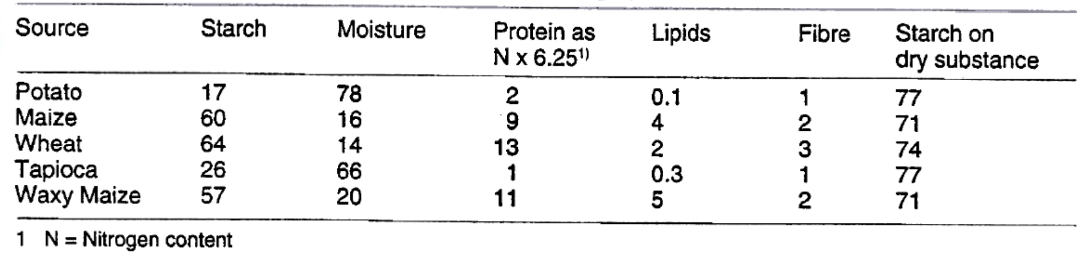
Starch occurs in practically every type of tissue of green plants: leaves, roots, tubers, seeds and fruits. Storage of starch takes place in the underground organs of various plants, for example potato, sweet potato, tapioca, arrowroot and canna. The trunk of the sago palm becomes filled with a starch bearing pith during its growth. The seeds of many plants contain starch as a reserve nutrient, for example grasses, rice, wheat, maize, sorghum, barley and oat. Starch constitutes the major portion of the carbohydrates of legume seeds (peas, beans, lentils). Starch occurs also as a component of many fruits, for example unripe apples, bananas and green tomatoes.

Certain mutants of maize, rice and sorghum are cultivated for their special starch characteristics. The waxy cereals (waxy maize, waxy sorghum, waxy rice) contain starch with no amylose fraction (100 % amylopectin). Plant breeders have developed varieties of maize with 50-80% amylose in the starch granules (amylomaize).

Despite the great variety and wide distribution of starch in nature, the number of major sources for industrial production of starch is comparatively small. The major sources of commercial starch are: maize, potato, tapioca and wheat. Smaller quantities of starch are also produced from waxy maize, sorghum, waxy sorghum, rice, sago, arrowroot, sweet potato and mung beans.

The composition of the raw materials varies according to such factors as age, soil, variety and climate. A typical analysis of the various raw materials is shown in Table 1.

Table 1 - Composition of raw materials (in % by weight)



Source	Starch	Moisture	Protein as N x 6.25[1]	Lipids	Fibre	Starch on dry substance
Potato	17	78	2	0.1	1	77
Maize	60	16	9	4	2	71
Wheat	64	14	13	2	3	74
Tapioca	26	66	1	0.3	1	77
Waxy Maize	57	20	11	5	2	71

1 N = Nitrogen content

The roots and tubers differ from the cereals in that they have considerable higher moisture content, but lower lipid content. The starch content, calculated on a dry basis, is for all raw materials about 70-80 %.

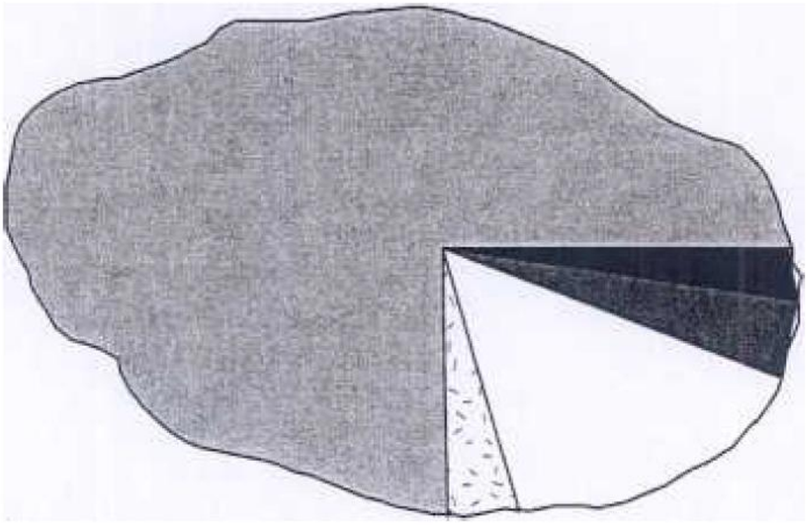
In addition to the components mentioned in Table 1, the raw materials contain other compounds such as sugars, salts, acids and pentosans. Figure 2 shows the composition of potatoes (next page).

The potato starch manufacturing process is simple (see Fig. 3). The potatoes are washed and ground by a rasping machine. The rasped potato is then passed through rotating sieves. The fibres are retained and are discharged as potato pulp (potato fibres). The remaining starch slurry contains soluble compounds (sugars, proteins, acids, salts) and fine fibres. These are separated by further treatment through continuous centrifugal separators or hydrocyclones and fine sieves. The purified starch slurry is used for the production of potato starch derivatives or is dewatered and dried. The manufacture of the root starches (tapioca, sweet potato, arrowroot) is similar to the manufacture of potato starch

2.3. Varieties of starch

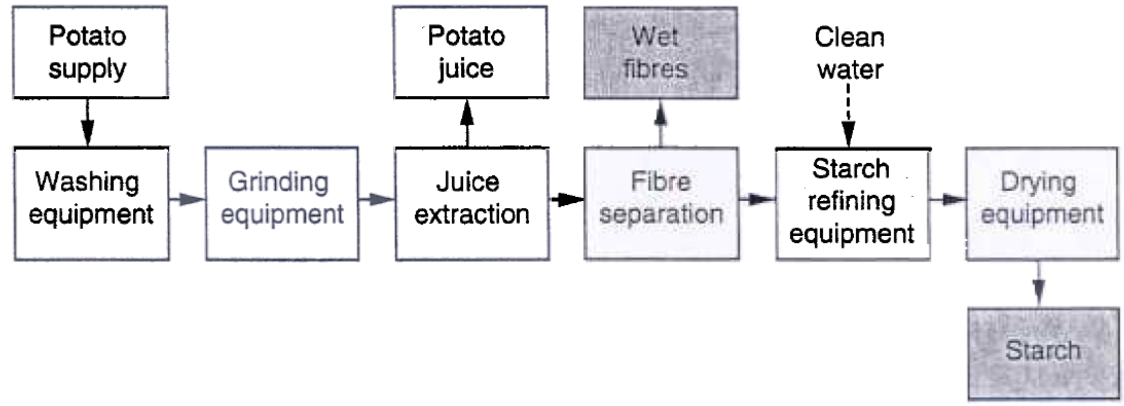
Irrespective of the source, all starches occur in nature as minute granules, each having its inherent characteristics, size and shape. The source of a starch can be identified from its microscopic appearance (see Figure 1). Table 2 shows the size and shape of starches from
different origin.

Figure 2 – Composition of the potato (in percent by weight)



▒	water	78 %	
■	protein	1 %	(dissolved in potato juice)
▩	amino acids + amides + sugars + organic acids + salts	3 %	(dissolved in potato juice)
□	starch	17 %	(solid component)
▭	fibres	1 %	(solid component)

Figure 3 – Potato starch manufacturing process



The commercial starches can be divided into three groups. The first group comprises the tuber (potato), root (tapioca, arrowroot, sweet potato) and pith (sago) starches. The second group comprises the common cereal starches (maize, wheat, sorghum, rice). These two groups are distinctly different from each other with respect to chemical composition and physical properties. The third group comprises the waxy starches (waxy maize, waxy sorghum, waxy rice). These starches are obtained from cereals, but the physical properties of the waxy starches are similar to those of tapioca starch

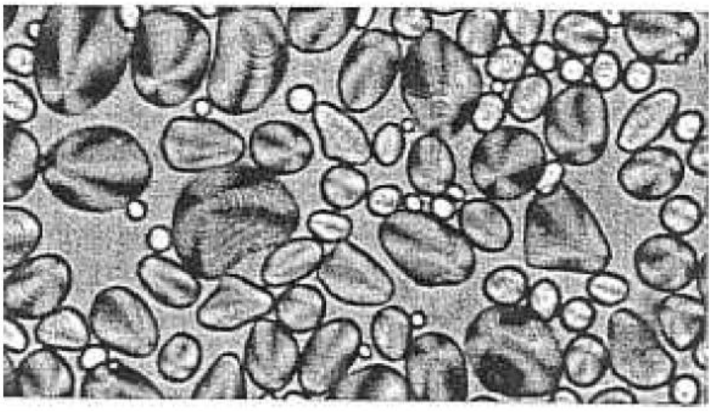
2.3.1 Potato starch

Potato starch granules are oval in shape, with pronounced oystershell-like striations around an eccentrically placed hilum (see Figure 4).

Table 2 – Starch granule properties

Starch	Type	Size; diameter; range (micron)	Size; diameter; number average (micron)	Size; diameter; weight average (micron)	Shape
Potato	tuber	5-100	28	40	oval, spherical
Maize	cereal	2-30	10	15	round, polygonal
Wheat	cereal	1-45	8	25	round, lenticular
Tapioca	root	4-35	15	25	oval, truncated
Waxy Maize	cereal	3-26	10	15	round, polygonal

Figure 4 – Potato starch (under polarized light)



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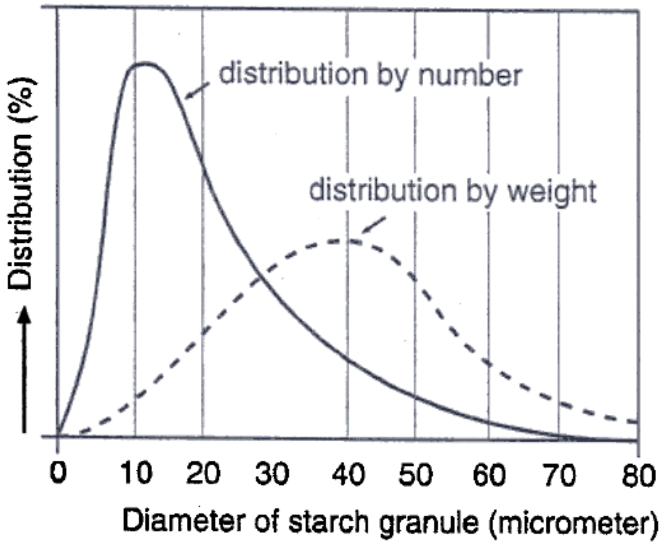
Potato starch has the largest granules of any commercial starch. Figure 5 gives the particle size distribution (by number and by weight) of potato starch (schematic). Special strains of potato have been developed, which give a high starch yield. About 3% of the world crop of potatoes is used for the production of potato starch. The world production of potato starch is approximately 2 million tons, of which 500.000 tons are produced in the Netherlands. Potato starch products are a.o. used in the manufacture of food and feed products, paper, textiles, for the production of adhesives and as special additives in drilling muds

Figure 5 – Size distribution of potato starch granules



2.3.2 Maize starch

(Synonyms: corn starch; regular corn starch; in the USA and some other countries the term corn starch is commonly used.

Maize starch granules are medium-sized and round or polygonal in shape. One gram of Maize starch contains about 1,000,000,000 granules. One starch granule contains about 10,000,000,000,000 starch molecules. The specific area of maize starch is about 300 m2/kg.
Only about 6 % of the annual world maize crop is used for the manufacture of starch. The world production of maize starch is about 16 million tons, of which about 8 million tons are produced in the United States. Maize starch accounts for over 75 % of the total world production of starch. About 70 % of the produced maize starch is converted into glucose syrup, glucose-fructose syrup and dextrose. Large quantities of maize starch are also used in the production of corrugated board and paper.

2.3.3 Wheat starch

Wheat starch consists of two types of granules: the smaller spherical granules (1-10 micron) and the larger lenticular granules (20-45 micron). The large starch granules in wheat flour average about 10 % of the total granule number while accounting for about 90 % of the starch granule weight. Wheat starch is produced in many countries as a by-product in the manufacture of wheat gluten. Only 0.4 % of the world crop of wheat is processed to starch and gluten. The world production of wheat starch is about 2 million tons. Wheat starch is used in the baking industry, in the production of adhesives and for conversion into starch sugars.

2.3.4 Tapioca starch

(Synonyms: cassava starch; manioc starch)
Tapioca starch granules are round or truncated at one end to form kettle drum shapes. Tapioca starch is manufactured from the root of a tropical plant called cassava, tapioca or manioc. The world production of tapioca starch is about 2 million tons. It is produced in Thailand, Vietnam, Brazil, the Philippines, Nigeria, Malaysia and Angola. Tapioca starch is a typical root starch and is used in the production of food products and adhesives

2.3.5 Waxy maize starch

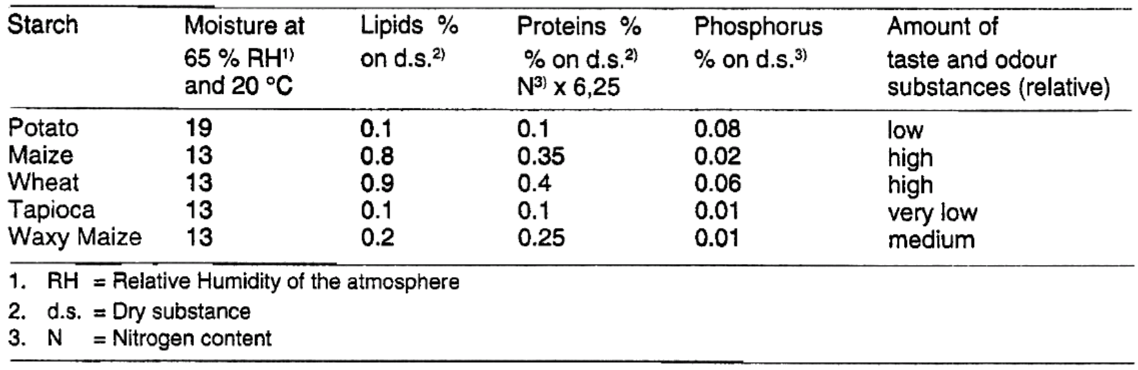
(Synonyms: waxy corn starch; amioca)
Maize starch and waxy maize starch are identical under the microscope. Waxy maize starch is produced from waxy maize, a special botanical type of maize.To prevent cross-pollution with regular maize, waxy maize must be grown in relatively isolated fields.
Starch from waxy maize consists solely of amylopectin. It is produced mainly in the United States. The rheological properties of waxy maize starch resemble most closely those of tapioca starch. Waxy maize starch products are used in the manufacture of adhesives and as thickeners in various food products.

3 Composition and properties of starches

3.1. Chemical composition of starch granules

Starch granules contain usually 10-20 % moisture and small amounts of proteins, lipids and traces of inorganic materials. Table 3 gives the average chemical composition of various commercial starches.

Table 3 – Average chemical composition of starch granules



Starch	Moisture at 65 % RH[1] and 20 °C	Lipids % on d.s.[2]	Proteins % % on d.s.[2] N[3] x 6,25	Phosphorus % on d.s.[3]	Amount of taste and odour substances (relative)
Potato	19	0.1	0.1	0.08	low
Maize	13	0.8	0.35	0.02	high
Wheat	13	0.9	0.4	0.06	high
Tapioca	13	0.1	0.1	0.01	very low
Waxy Maize	13	0.2	0.25	0.01	medium

1. RH = Relative Humidity of the atmosphere
2. d.s. = Dry substance
3. N = Nitrogen content

3.1.1 Moisture

The moisture content of starch products depends on the relative humidity (RH) of the atmosphere in which they have been stored. If this humidity decreases, the starches will give up moisture; if the RH increases, they will absorb moisture. The equilibrium moisture content of starch is also dependent on the type of starch product. Under normal atmospheric conditions, most commercial native starches contain 10 to 20 % moisture. The equilibrium moisture content of all starches is low at a low relative humidity of the atmosphere. At a RH of zero, the moisture content of the starches nears to zero. At a RH of 20 %, the moisture content of all starches is about 5-6 %.

3.1.2 Lipids (fatty substances)

The tuber (potato) and root (tapioca) starches contain only a very small percentage of lipids (about 0.1 %), compared with the common cereal starches (maize, wheat, rice, sorghum), which contain 0.8 - 1.0 % lipids. The fatty substances in the cereal starches are predominantly free fatty acids (in maize and waxy maize starch) or phospholipids (in wheat starch). The free fatty acids consist mainly of palmitic, linoleic and oleic acid.
The presence of lipids in the common cereal starches has a profound effect on the physical properties of these starches. The lipids exist as an amylose-lipid inclusion complex in the granules. The linear fraction of the starch molecules (amylose) forms helical clathrates with polar fatty substances, such as the higher fatty acids. The amylose-lipid complexes are insoluble, but dissociate when heated in water above a given temperature. The dissociation temperature is indicative of the strength of bonding and depends on the type of complexing agent. The amylose-lipid complexes tend to repress the swelling and solubilization of the cereal starch granules. Elevated temperatures (above 125 °C) are required to disrupt the organized native amylose-lipid structure in the cereal starch granules and to solubilize the amylose fraction. The presence of fatty substances can create problems in the use of maize and wheat starch products, because of the tendency to become rancid on storage.

3.1.3 Proteins

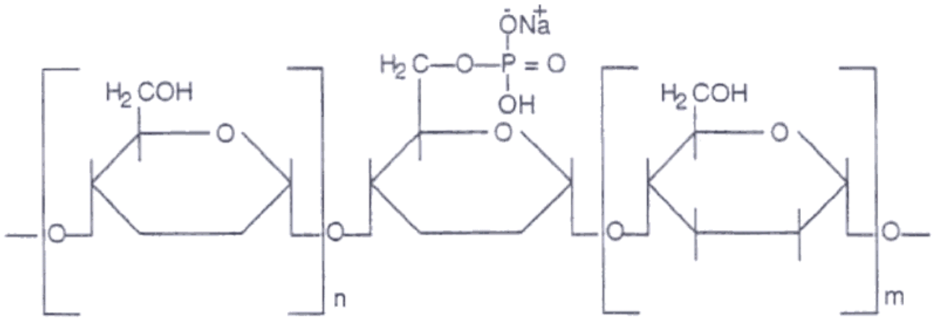
The amount of proteins as shown in Table 3 (calculated as N x 6.25) includes real proteins, but also peptides, amides, amino acids, nucleic acids and enzymes which may be present in the starch granules.The tuber (potato) and root (tapioca) starches contain only a small amount of proteins (about 0.1 %), compared with the cereal starches (maize, wheat, waxy maize), which contain 0.2 - 0.4 % proteins. Because of the residual protein, the cereal starches may have a mealy flavour and odour and also a tendency to foam. The small granules of wheat starch contain much more protein (1.6 %) than the large granules (0.1 %).

3.1.4 Phosphorus

The phosphorus in the cereal starches is mainly present as phospholipids. The root starches (tapioca) contain a very low amount of phosphorus compounds. Potato starch is the only commercial starch, which contains an appreciable amount of chemically bound phosphate ester groups. The ester phosphate groups are bound to the C-6 position of glucose-units of the amylopectin molecules in potato starch (see Figure 6).

The amount of phosphate groups in potato starch ranges from1 phosphate group per 200 to 400 glucose units. This corresponds with a degree of substitution (DS) of about 0 .003 to 0.005. The phosphate substituent confers the properties of a polyelectrolyt on potato starch amylopectin when dispersed into aqueous solutions. The mutual repulsion of the charged groups forces the molecule to expand. The phosphate groups can be considered as ion exchanging groups.

Figure 6 – Ester phosphate groups in potato starch and monostarch phosphate



3.1.5 Flavour and odour substances

The pregelatinized common cereal starches (maize, wheat) have a relatively raw cereal flavour. These starches impart cereal-type flavours to the foods in which they are incorporated. Potato and tapioca starches contain only a low amount of flavour substances and this may be due to their low lipid and protein content.

3.2. Amylose and amylopectin

Starch is a carbohydrate composed of carbon, hydrogen and oxygen atoms in the ratio 6:10: 5, $(C_6H_{10}O_5)_n$. Starch can be considered to be a condensation polymer of glucose, consisting of anhydroglucose units. The glucose units are linked to one another through the C-1 oxygen, known as glucoside bond. The glucoside linkage is stable under alkaline conditions and hydrolysable under acid conditions. The glucose unit at the end of the polymeric chain has a latent aldehyde group and is known as the reducing end group. Most starches are a mixture of amylose and amylopectin, each having a wide range of molecular sizes. Starches of different origin have different amylose to amylopectin ratios, as Table 4 shows. Table 4 shows also the average degree of polymerization (DP) of both fractions in various starches

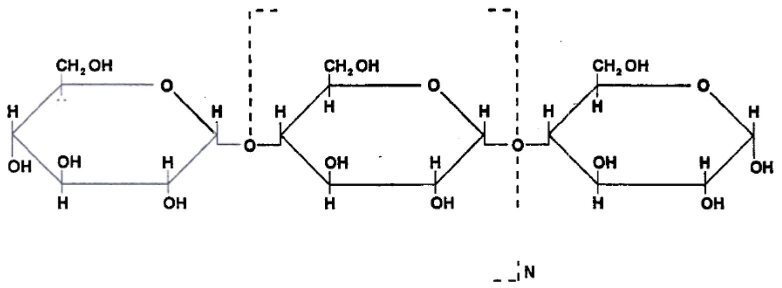
Table 4 – Amylose and amylopectin contents and degree of polymerization of various starches

Starch	Amy-lose	Amylo-pectin	Average DP amylose	Average DP amylopectin
Potato	21	79	4000	2,000,000
Maize	28	72	1000	2,000,000
Wheat	26	74	1000	2,000,000
Tapioca	17	83	4000	2,000,000
Waxy Maize	0	100		2,000,000

3.2.1 Amylose

Amylose is a linear polymer containing up to 6000 glucose units, connected by 1,4 linkages
(see Figure 7).

Figure 7 – Linear chain structure of amylose molecules



Enzyme studies indicate perhaps a trace amount of branching in the amylose molecules or in a portion thereof. The ratio amylose: amylopectin is fairly constant for a given species of starch. Maize and sorghum starch have a much higher amylose content (about 28 %), compared with the tuber and root starches (potato, tapioca, arrowroot), which contain only about 20 % amylose. The waxy starches contain no amylose fraction. Amylomaize starch may contain up to 80 % amylose.

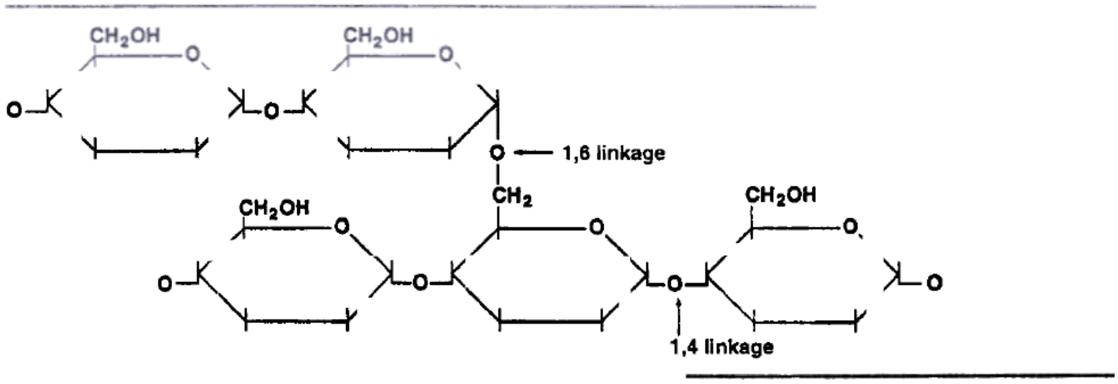
Amylose covers a range of degrees of polymerization, depending upon the source of the starch. The amylose molecules of potato and tapioca starch have a substantially higher molecular weight than maize and wheat starch amylose. The amylose fraction of potato starch has a degree of polymerization (DP) ranging from 840 to 22,000 glucose units. The amylose fraction of maize starch has a DP-range of about 400 to 15,000 glucose units.

Amylose forms inclusion complexes with iodine and various organic compounds such as butanol, fatty acids, various surfactants, phenols and hydrocarbons. These complexes are essentially insoluble in water. It is believed that amylose complexes by forming a helix coil around the complexing agent. The complex of amylose with iodine gives a characteristic blue colour, which is used to establish the presence of amylose-containing starch

3.2.2 Amylopectin

Amylopectin has a highly branched structure, consisting of short linear chains with a DP ranging from 10 to 60 glucose units. The average DP of these chains is about 22. They are connected to each other by alpha-1,6-linkages (see Figure 8).

Figure 8 – Structure of amylopectin branching points



The glucose units with an alpha-1,6-linkage are the branching points of the amylopectin molecule and make up about 5 % of the total glucose units in amylopectin. The average length of the outer chains of amylopectin before reaching a branch point is about 14 glucose units. The average chain length of the inner branches is about 8 glucose units. A portion of the branches are separated by only one glucose unit. This suggests the presence of regions of dense branching. Probably amylopectin has a cluster-type structure. The branch points are arranged in tiers of some kind (see Figure 9).

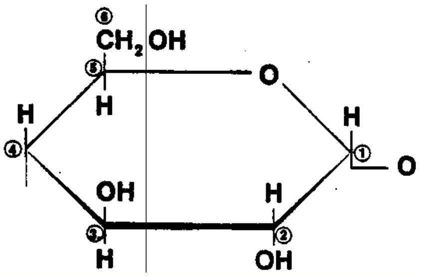
Figure 9 – Model of amylopectin molecule, R = reducing end-group

Amylopectin is one of the largest molecules in nature with an average degree of polymerization of about 2 million (corresponding with an average molecular weight of about 400 million). Apparently, there are no substantial differences between the average molecular weight of the amylopectin molecules of various kinds of starch (see Table 4). The molecular weight of amylopectin is about 1000 times as high as the molecular weight of amylose

3.2.3 Glucose unit

The glucose units of the starch molecules contain a primary hydroxyl group on carbon-6 and a secondary hydroxyl group on carbon-3 and carbon-3 (see Figure 10).

Figure 10 – Glucose unit



Starch molecules have a multitude of hydroxyl groups, which impart hydrophilic properties to the starch and lead to the dispersibility of starch on heating with water. However, these hydroxyl groups also tend to attract each other, forming hydrogen bonds between adjacent starch molecules and thus preventing the dissolution of starch granules in cold water

3.3. Structure and organization of starch granules

Viewed under polarized light, the starch granules usually show a strong interference cross (malteser cross), centered through the "hilum. This suggests a radial organization of some sort.
The Characteristic X-ray diffraction patterns of the starch granules prove that there are areas of crystallinity in the starch granules. The starch molecules are arranged in the granules in a radial fashion toward the hilum (see Figure 11).

Figure 11 – Micellar organization within starch granules

Whenever linear segments of the starch molecules parallel one another, hydrogen bonding forces pull the chains together into associated crystalline bundles or micelles (see Figure 12). It appears that crystallinity and structural integrity of the starch granule are essentially due to the amylopectin component. The large amylopectin molecule participates in both the crystalline micelles and the less organized regions.

Figure 12 – Micelle within the starch granule

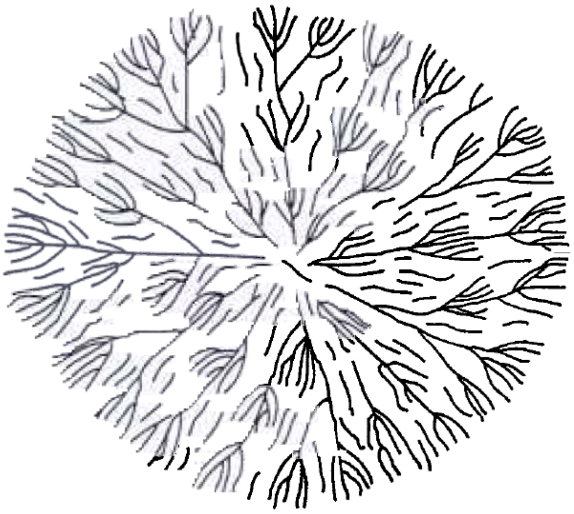
The starch granules are organized into more or less crystalline regions and amorphous regions, the transition between these regions is a gradual one.
The regionis of micellar crystallinity hold the granules together. Because of their radial orientation, they are responsible for both the optical polarization and the X-ray spectrum.The orientation of the crystalline micelles perpendicular to the granule

surface implies that the molecular axes of the starch molecules are also arranged in this fashion. Figure 13 shows a schematic model of the organization of a starch granule.

The amorphous regions are those where chain folding or multiple branching occur, preventing the formation of ordered polymer structures.

The areas of crystallinity in the various native starches comprise about 25-50 % of the total volume of the starch granules. In the tuber and root starches, solely the amylopectin molecules constitute the crystalline structure. The amylose in these starches is present in the amorphous state and can be readily leached out preferentially from the granule. In the cereal starches, the amylopectin fraction is the most important element of the crystalline structure.
A portion of the amylose molecules in the common cereal starches is present as a complex with lipid molecules. This complex forms a weak crystalline structure and could be involved in the structural network of the granules. The amylose-lipid complex provides some reinforcement of the cereal starch granules that could retard granule swelling.

Figure 13 – Schematic model of the structure of a starch granule



3.4. Swelling and gelatinization

3.4.1 General observations

Native starches are insoluble in water below their gelatinization temperature. This is a very important property, which enables an easy extraction of the starch granules from their plant source in aqueous systems. In addition, the native starches can be chemically modified in suspension in water and recovered in purified form by filtration, washing with water and drying.

Starch granules are insoluble in cold water due to the hydrogen bonds, formed either directly via neighbouring alcoholic OH-groups of the individual starch molecules or indirectly via water bridges. The hydrogen bonding forces are weak, but there are so many hydrogen bonds in a starch granule that it does not dissolve in cold water.

When starch granules are heated in water to progressively higher temperatures, a point is reached where the polarization-cross starts to fade at the hilum, and this phenomenon rapidly extends to the periphery of the granule. Simultaneously, the granule starts to swell irreversibly. The term "gelatinization" is applied to this loss of polarization and concurrent initiation of swelling. The initial swelling takes place in the amorphous regions of the granule, disrupting the weak bonding between the starch molecules and hydrating them. The tangential swelling disrupts the orderly radial organization of the micelles and the granule loses its polarization. As the temperature of the aqueous starch mixture rises, more hydration occurs in the amorphous regions and the hydrogen bonds in the crystalline regions begin to be disrupted. The granules continue to expand to a greatly swollen reticulated network, still held together by persistant micelles which have not been disrupted (see Figure 14).

A portion of the amylose molecules leach out into the aqueous substrate. The viscosity increases to a maximum that corresponds to the largest hydrated swollen volume of the granules.

Extensive swelling is associated with disruption of the crystalline areas. In the first stages of gelatinization the shorter micelles dissociate, while the longer micelles will persist to higher temperatures. As the heating and agitation of the mixture continues, the swollen starch granules begin to rupture and collapse, yielding a viscous colloidal dispersion of swollen granule fragments, hydrated starch aggregates and dissolved molecules. Figure 15 gives an impression of the swelling, disruption and colloidal dispersion of a starch granule during gelatinization.

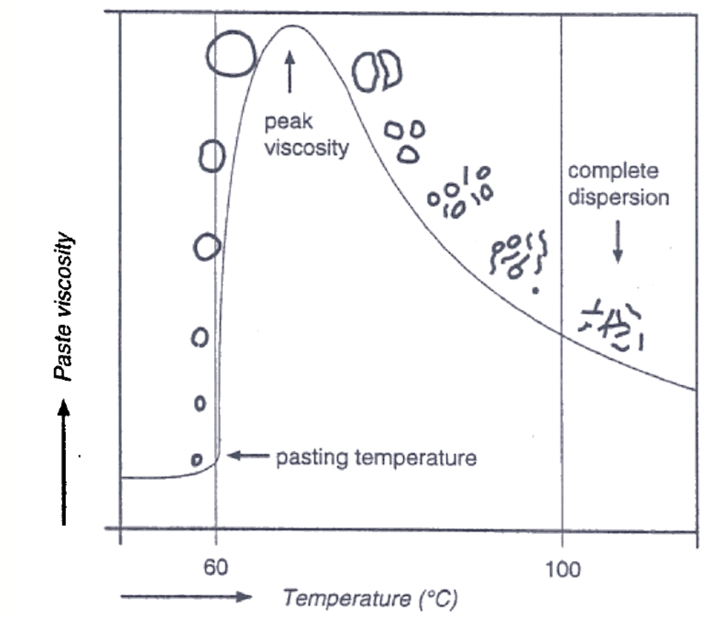
Figure 14 – Micellar oranization within swollen starch granules

Upon raising the temperature of a starch suspension, the first granules will start to gelatinize at a certain temperature. Other granules in the same suspension, usually smaller in size than the first ones, start to gelatinize at higher temperatures. This implies that the gelatinization process of a starch suspension cannot be defined as to take place at a certain temperature, but rather during a certain temperature range.

3.4.2 Brabender visco-amylograph

The ability of the starch granules to swell and subsequently disrupt is of great technological importance. According to a well-known method the viscosity changes during cooking of a starch paste can be followed with the help of a Brabender visco-amylograph.

Figure 15 - Swelling, disrupfion and dispersion of a starch granule during gelafinizafion

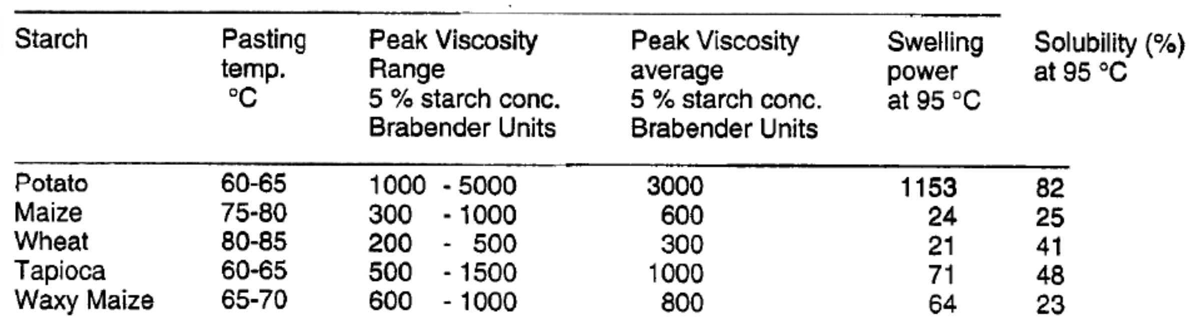


This apparatus measures the viscosity of starch-water dispersions that are stirred and heated at a uniform rate, held at any desired temperature for a specific time and then cooled at uniform rate. A suspension of starch in water is transferred to the sample cup of the Brabender visco-amylograph. The instrument is started and the temperature of the sampie is increased at a rate of 1.5 °C per minute. Heating is continued until the sampie reaches a temperature of 90 °C or 95 °C and the sampie is maintained at this temperature for 20, 30 or 60 minutes, while stirring and recording the viscosity continuously. The paste is then cooled to 50 °C or 25 °C at a rate of 1.5 °C per minute and held for e.g. 1 h. at this temperature while stirring. Brabender viscosity curves are characteristic and different for each type of starch as shown in Fig 16.

Initially, no viscosity effect is noted as the suspension of starch is heated until the pasting temperature is reached. The temperature at which the viscosity begins to rise is termed pasting temperature. Appreciable granule swelling must occur before the viscosity is sufficiently high to be recorded by the Brabender instrument.

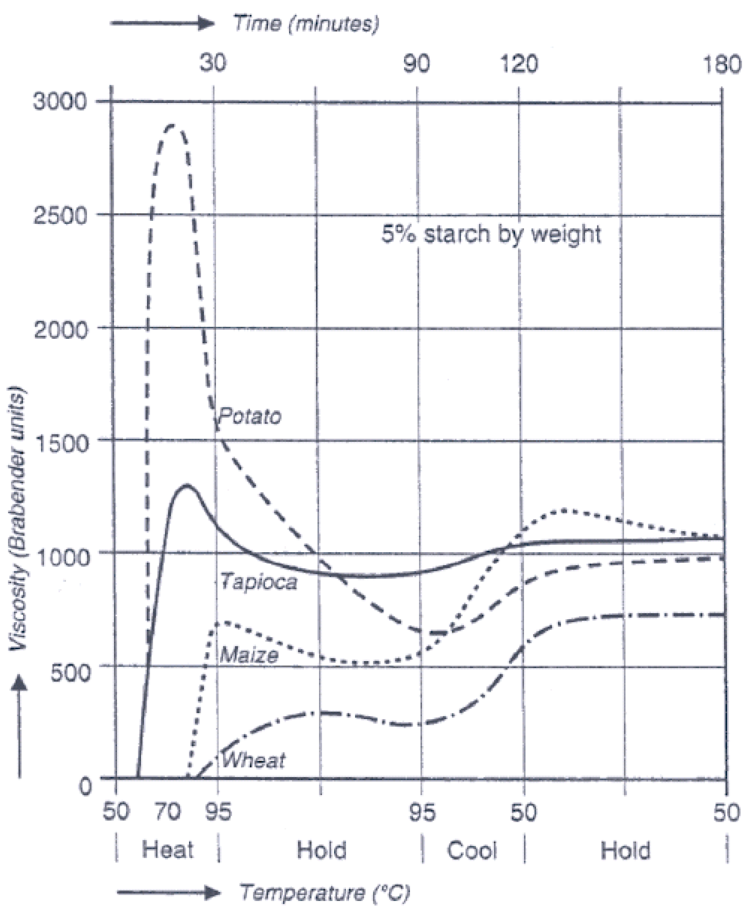
As shown in Table 5 and Figure 16, potato and tapioca starch have a lower pasting temperature than maize and wheat starch.

Table 5 – Gelatinization characteristics of native starches



Starch	Pasting temp. °C	Peak Viscosity Range 5 % starch conc. Brabender Units	Peak Viscosity average 5 % starch conc. Brabender Units	Swelling power at 95 °C	Solubility (%) at 95 °C
Potato	60-65	1000 - 5000	3000	1153	82
Maize	75-80	300 - 1000	600	24	25
Wheat	80-85	200 - 500	300	21	41
Tapioca	60-65	500 - 1500	1000	71	48
Waxy Maize	65-70	600 - 1000	800	64	23

Figure 16 - Brabender viscosity curves of native starches

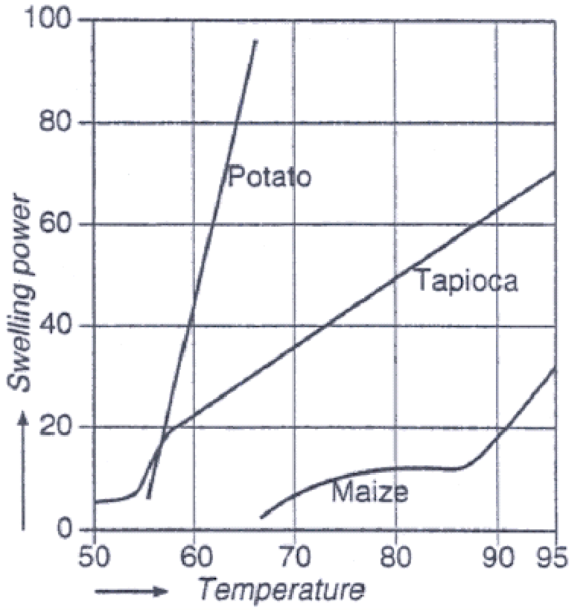


As the temperature of the starch sample is increased, the granules swell to impinge on each other and increase the viscosity of the starch paste. This process continues until the "peak viscosity" is reached. The peak viscosity is the highest viscosity that the user may encounter during preparation of a starch paste. Tuber and root starches show a sharper rise in viscosity during cooking and a higher peak viscosity than the common cereal starches do. Typical values for the peak viscosity (in Brabender Units = BU) are shown in Table 5 (starch concentration 5 %). Potato starch shows the highest peak viscosity. Maize starch gives a relatively low peak viscosity because the granules are only moderately swollen. Tapioca starch and the waxy starches swell to a greater extent than maize starch. Wheat starch shows a very low peak viscosity. The peak viscosity is a measure of the thickening power of a starch. On further cooking and stirring at elevated temperatures, the cohesive forces in the swollen granules become excessively weakened and the structure of the paste collapses. The fragile swollen granules break down and thin out as a result of granule fragmentation under shear. The tuber and waxy starches break down in viscosity more rapidly and drastically than the common cereal starches do. The next part of the Brabender curve shows the behaviour of starch pastes upon cooling from 95 °C to 50 °C. The increase in viscosity during cooling is a measure of retrogradation (set-back) due to association of amylose molecules.

3.4.3 Swelling power and solubility

If an aqueous suspension of starch is heated above the gelatinization temperature, the granules undergo a progressive swelling. The granules swell in a pattern peculiar to the particular starch. The extent of swelling can be determined by suspending a weighed starch sample in water, heating for 30 minutes in a thermostated bath, then centrifuging, decanting the aqueous supernatant solution and weighing the precipitate of swollen granules. Swelling power, at the pasting temperature used, is calculated as the weight of sedimented swollen granules per gram of dry starch. The swelling power can be determined over the entire pasting temperature range (about 50 - 95 °C) at intervals of 5 °C. The swelling power is then plotted against the temperature of pasting, to give characteristic curves as shown in Figure 17.

Figure 17 – Swelling patterns of native starches



The swelling power at 95 °C of various native starches is shown in Table 5. The solubility can be determined by evaporation to dryness of the supernatant solution above mentioned.
The solubility is expressed as the percentage (by weight) of the starch sample that is dissolved molecularly after heating in water at 95 °C during 30 min. Potato and tapioca starch show the highest solubilization. The lipids in the cereal starches reduce the solubilization.

On heating in water, the granules of potato, tapioca and waxy maize starch desintegrate more rapidly than the granules of maize and wheat starch and consequently they more quickly reach the homogeneous condition necessary for many uses.

Maize starch shows a relatively slow, restricted two-stage swelling property. This suggests two unequal sets of bonding forces within the granule, the weaker relaxing below 75 °C, the stronger above 85 °C. The amylose-lipid complexes in maize starch inhibit granule swelling.
Defatted maize starch swells more freely and uniformly.

Potato starch undergoes a very rapid and exceptionally high swelling at relatively low temperatures, indicating weak internal bonding. This is partly due to the presence of ionizable esterified phosphate groups, which assist swelling by reason of mutual electrical repulsion. The rapid single-stage swelling at relatively low temperature is typical starch polyelectrolyte behaviour. It is conceivable that hydrogen bonding in potato starch granules partly occurs through hydrate water bridges instead of by strong direct association of starch molecules. Although the bonding forces in the potato starch are weak, they are comparatively extensive, immobilizing the starch substance within the granule even at high levels of swelling. Potato starch granules swell several hundredfold before extensive solubilization of starch molecules into the aqueous phase occurs.

Root starches swell at lower temperatures and to a greater extent than the common cereal starches. This shows that the degree of association in root starches is less than in the common cereal starches. Waxy maize starch swells much more freely than regular maize starch, since waxy maize starch contains no amylose-lipid fraction to reinforce the molecular network within the granule.

3.4.4 Molecular solubilization of starch

The organized micelies of the starch granules are quite persistent, and starches cooked at about 95 °C for one hour may still contain highly swollen, hydrated starch aggregates. True solubilization of all the starch substance does not occur normally unless the paste is cooked at temperatures of 100 - 160° C (dependent upon the type of starch). Tuber, root and waxy starches can be cooked to a completely dissolved state at about 100 °C; maize starch requires about 125 °C and amylomaize starch about 150 °C. By super-temperature heating (100-160 °C), as in an autoclave or in a commercial steam-jet cooker, the micelles dissociate to give a low-viscosity starch solution.

3.4.5 Jet-cooking of starches

Cooking starch slurries (suspensions) by the batch method was commonly used until about 1950 (see Figure 18). At that time continuous cooking systems were introduced. Jet-cookers utilize direct steam injection (see Figure 19).

Jet-cooking is a continuous method of pasting starch in which steam under pressure mixes completely with starch slurry, rapidly heats it and cooks it within a few seconds. The cooked starch paste is then delivered directly to the point of use (see Figure 20).

Jet-cookers are used in the starch industry and in various starch-consuming industries (paper, food and adhesives industry). By cooking starch slurries at high temperatures (100 - 175 °C) and pressures in jet-cookers, the starch granules are fragmented and dispersed more extensively than by cooking at conventional temperatures in batch cookers(below 100 °C). The first types of jet-cookers were described in 1937-1938. Only after 1950 jet-cookers were used on an industrial scale. Various forms of apparatus may be used. In special jet-cooker systems starch is simultaneously cooked and oxidized, or cooked and enzyme-modified

Figure 18 – Batch system for the preparation of cooked starch

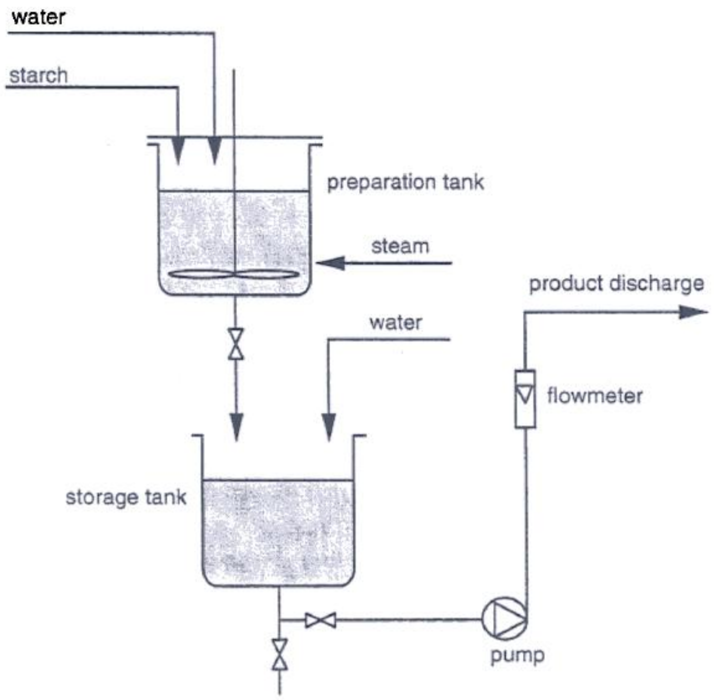
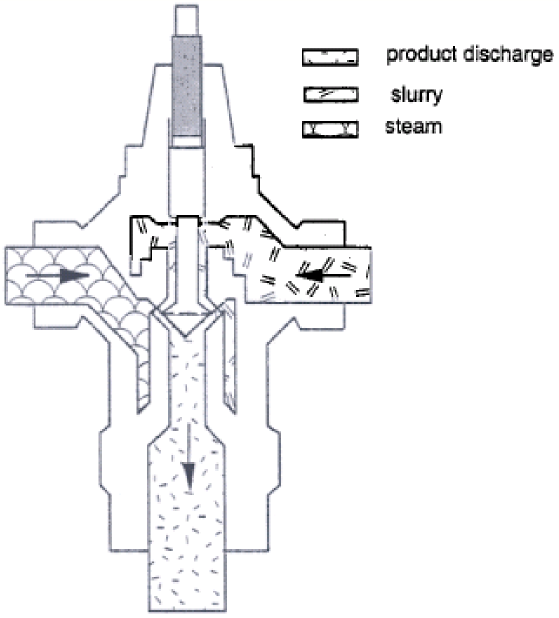


Figure 19 – Schematic drawing of a jet cooker

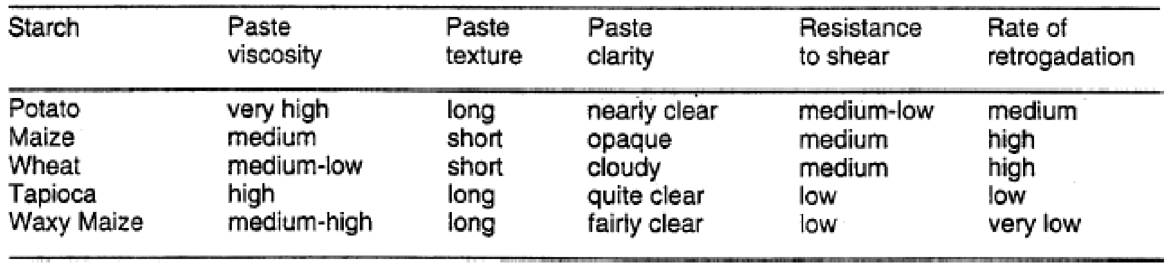


3.5. Starch pastes

The properties of a starch paste are determined by the variety of starch, the type of modification, the cooking procedure and the presence of other materials. Careful attention must be given to controlling the conditions of cooking in order to obtain the desired properties consistently. The factors involved are cooking equipment, starch concentration, temperature, time, intensity of agitation and pH.

Starch pastes may contain unswollen granules, partly swollen granules, swollen granules, fragments of swollen granules, swollen starch aggregates, dissolved starch molecules and retrogradated starch precipitates. Some properties of starch pastes, which are obvious important for the user are: the viscosity, the texture, the paste transparency and the resistance to shear. The paste properties of starches from different botanical sources differ from each other, as in shown in Table 6.

Table 6 – Properties of pastes of native starches



Starch	Paste viscosity	Paste texture	Paste clarity	Resistance to shear	Rate of retrogadation
Potato	very high	long	nearly clear	medium-low	medium
Maize	medium	short	opaque	medium	high
Wheat	medium-low	short	cloudy	medium	high
Tapioca	high	long	quite clear	low	low
Waxy Maize	medium-high	long	fairly clear	low	very low

3.5.1 Paste viscosity

The viscosity of a starch paste reflects the work required to displace swollen starch particles past one another. The viscosity is determined by the type of starch, the cooking procedure and the starch concentration. The highest viscosity of a starch paste is shown by the peak viscosity of the Brabender curve (see Figure 16 and Table 5). Generally, potato starch shows a higher paste viscosity than the other starches (compared at the same conditions). This may be explained by the influence of the phosphate groups in potato starch. A higher phosphate content in potato starch results in a higher viscosity. The root and waxy starches have a higher paste viscosity than the common cereal starches (as is shown in Table 6). In order to obtain a starch paste with a given viscosity, a lower amount of potato starch is needed than with tapioca starch, maize starch or wheat starch

3.5.2 Texture of starch pastes

Generally, maize starch pastes consist of granules that are not very swollen, in contrast to the potato starch pastes in which the granules are fully stretched and swollen. The swollen granules of potato starch are weakly bonded internally and shear will cause the paste to elongate to ´strings´, snapping back when released. The texture of potato starch pastes can be described as cohesive, visco-elastic, long bodied, stringy, fluid and rubbery. The texture of pastes of the root and waxy starches is similar to that of potato starch, but generally less cohesive and less visco-elastic. The texture of pastes of the common cereal starches can be described as non-cohesive, short, soft, heavy bodied or salve-like (see Table 6).

3.5.3 Clarity of starch pastes

On thermal gelatinization, the initial opacity of an aqueous suspension of starch decreases and the paste becomes progressively more transparent. The clarity of the final paste is dependent upon the type of starch (see Table 6). Pastes of tuber -, root - and waxy starches are much clearer than those of the ordinary cereal starches; potato starch undoubtedly gives the clearest paste.

In general, paste clarity is directly related to the state of dispersion and the retrogradation tendency of the starch. The pastes of the common cereal starches (maize, wheat, sorghum, rice) are described as opaque, cloudy, dull or flat. The pastes of the tuber (potato), root (tapioca, arrowroot, sweet potato) and waxy starches are described as translucent, clear or transparent.

3.5.4 Resistance of starch pastes to shear

The viscosity of a starch paste may be reduced by mechanical shear (agitation, mixing. stirring), which tears apart the swollen granules. Root, tuber and waxy starches cook readily to give greatly swollen, fragile granules, which easily break down and thin out during stirring. The common cereal starches cook more slowly, swell to a lesser degree, and show a moderate resistance against viscosity breakdown by agitation (see Table 6). The resistance under shear can be tested by stirring starch pastes for e.g. 20 minutes and then determining the viscosity.
After stirring, tapioca and waxy maize starch show the lowest viscosity, potato starch is intermediate and maize starch shows the highest remaining viscosity. The introduction of a very few chemical cross-linkages within the granule tightens up the molecular network, restricts granule swelling and hence stabilizes the viscosity of starch pastes against breakdown by agitation

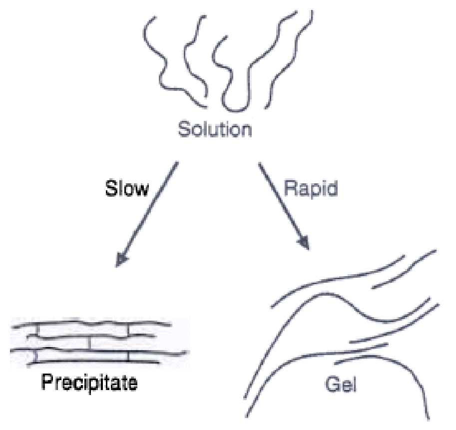
3.6. Retrogradation

If a dilute starch solution stands for prolonged time, it gradually becomes cloudy and eventually deposits an insoluble white precipitate. If more concentrated starch dispersion is allowed to cool, it rapidly sets to an elastic gel. These are both processes of retrogradation, whereby the starch substance goes from a dissolved and dissociated state to an associated condition. In starch granules, mainly the amylopectin molecules constitute the crystalline micelles. In contrast, retrogradated, crystalline starch material is composed mainly of amylose molecules. The mechanisms of retrogradation are schematically shown in Figure 21.

Retrogradation of starch pastes or starch solutions may have the following effects:

- Increase in viscosity;
- Development of opacity and turbidity;
- Formation of insoluble "skins" on hot pastes;
- Precipitation of insoluble starch particles;
- Formation of gels;
- Syneresis of water from the paste (weeping).

Figure 21 – Mechanism of starch retrogradation (amylose)



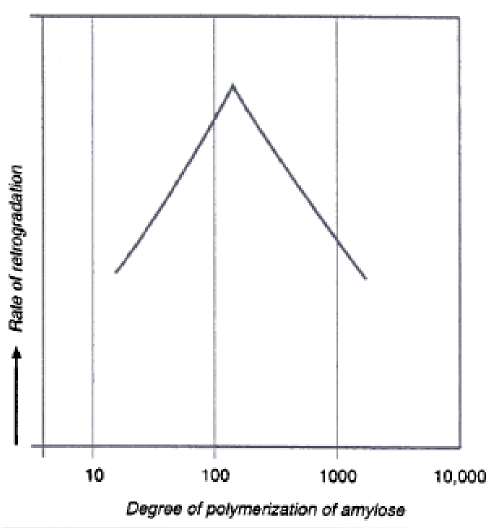
Retrogradation is a complex process and depends on many factors such as type of starch, starch concentration, cooking procedure, temperature, storing time, pH, cooling procedure and the presence of other compounds. Retrogradation of starch dispersions is generally favoured by low temperatures and by high starch concentrations. The retrogradation rate is fastest at pH 5-7, decreasing at higher and lower pH. Retrogradation does not occur at pH above 10 and is slow below pH 2. Retrogradation is retarded by the salts of monovalent anions and cations and by urea.

3.6.1 The role of the amylose fraction

Amylose is considered primarily responsible for retrogradation processes, and this is the most significant property of this fraction. Dissolved amylose molecules can orient themselves in a parallel alignment, so that a large number of hydroxyl groups along one chain are in close proximity to those on adjacent chains. When this occurs, the hydroxyl groups form associations through interchain hydrogen bonds, and the amylose chains are bound together to form aggregates that are insoluble in water. In dilute solutions, the aggregated chains of amylose precipitate. In more concentrated dispersions, the aggregated amylose entraps the aqueous fluid in a network of partially associated starch molecules, forming a gel. In both instances X–ray diffraction patterns show that a crystalline organization is formed. A temperature of 100 - 160 °C may be required to redissolve retrograded amylose particles in water.

There is a relationship between the chain length of the amylose molecules and the ease and kind of retrogradation. Amylose exhibits a maximum rate of retrogradation (minimum in solubility) at a degree of polymerization (DP) of about 100-200 glucose units (see Figure22).

Figure 22 – Rate of retrogradation of amylose (schematic)



The rate of retrogradation decreases with longer and shorter amylose molecules. Long amylose molecules do not readily move into tight association with other chains and have difficulty in lining up with their neighbours over long intervals. Amylose molecules smaller than the optimum length do not associate as completely and are too short to give a gel.

3.6.2 The role of amylopectin

Amylopectin is much less prone to retrogradation than amylose. The association of dissolved amylopectin molecules is strongly inhibited by their highly branched structure. Therefore, amylopectin tends to be soluble, forming solutions that do not gel under normal conditions. Under extreme conditions of high starch concentrations or freezing temperatures, the branched fraction may undergo retrogradation effects. These effects are attributed to the association of the outer chains of the amylopectin molecules. These associated branches may contain about 20-30 glucose units. For example, the staling of bread has been traced to associative bonding between the outer branches of the amylopectin fraction. In pastes or solutions of the common starches (containing amylose and amylopectin) the presence of the branched amylopectin fraction has a moderating influence on the retrogradation of the linear amylose fractions, slowing down its precipitation and diminishing its gel tendencies.

3.6.3 The role of lipid substances

The 'normal' retrogradation occurs generally on cooling and storage of starch pastes at temperatures of 70 °C and below. There is, however, another form of retrogradation, which occurs during storage of maize starch solutions at relatively high temperatures (75-95 °C) and takes the form of a precipitate of regularly sized particles. High temperature retrogradation is observed when maize starch is gelatinized at temperatures of 120-160 °C with a jetcooker and the resultant paste is stored at 75-95 °C. The precipitated particles are formed from inclusion complexes of maize starch amylose with free fatty acids which occur naturally in maize starch. Precipitation, caused by high temperature retrogradation, did not occur when de-fatted maize starch, waxy maize starch or potato starch were gelatinized above 120 °C and stored at 70-95 °C. The complex of amylose with the higher fatty acids is not formed above 95 °C, which would indicate that dissociation of such a complex takes place above 95 °C.

3.6.4 Retrogradation of various native starches

The rate of retrogradation of different native starches is shown in Table 6. A measure of the retrogradation is the increase in viscosity, after cooling starch pastes from 95 °C to 50 °C, as shown in the Brabender curves (see Figure 16). The common cereal starches (maize, wheat, sorghum, rice) retrograde more quickly than the tuber (potato) and root (tapioca, arrowroot, sweet potato) starches. The waxy starches show the lowest rate of retrogradation.

Maize starch pastes and maize solutions retrograde relatively fast. The high amylose content (28 %), the relatively small molecular size of the maize amylose molecules (DP between 400 and 15.000), and the high lipid content (0.8 %) are important factors which promote retrogradation. A substantial portion of the starch molecules in maize starch pastes is usually present as an associated amylose-lipid complex with reduced hydration capacity. This relatively inert portion does not contribute to the binding force or thickening power of the maize starch paste. The other common cereal starches (wheat, sorghum, rice) show similar retrogradation effects as maize starch.

Potato starch dispersions show only a moderate tendency towards retrogradation. This is attributed to the low amylose content (21 %), the great length of the potato amylose molecules (DP between 840 and 22.000) and the low lipid content (0.1 %). The root starches have a low (tapioca) to moderate (sweet potato, arrowroot) tendency towards retrogradation.
The most practicable method for preventing retrogradation effects is to derivatize the starch molecules with a small amount of ether or ester groups. The introduction of only two or three of such groups per 100 glucose units (degree of substitution 0.02-0.03) prevents side-by-side alignment of linear chains.

3.7. Starch films

In foods, starch products are generally used in the form of a paste, usually for thickening purposes. Most of the industrial, non-food uses of starch products involve cooking of starch in water and application of the resulting paste to a solid surface, followed by drying of the film or coating. The function of the starch may be as an adhesive (to cause two surfaces to stick together), or the cooked starch paste may be used to give a smooth film or coating over paper sheets or textile fabrics. The starch film must have certain specific properties to qualify it for the intended use. These properties include plasticity, internal strength, solubility in water, response to humidity, film transparency and gloss.

Films of potato and tapioca starch products have a greater flexibility, a higher tensile strength, a higher elongation before rupture and a higher toughness than films of maize and wheat starch products.

For a number of applications it is necessary that the applied starch film dissolves fast and at low temperatures in water. This is the case when remoistenable starch films of gummed papers are wetted with water and when sized textile yarns are desized. Starch films obtained from different types of starch vary both in solubility and rate of retrogradation. Films of starch products obtained from potato, tapioca or waxy starches redisperse in water more readily and more completely than films of starch products obtained from the common cereal starches (maize, wheat, sorghum, rice). The low solubility of films from the common cereal starches is attributed primarily to the influence of the amylose fraction, in combination with a high content of lipids. The small amylose molecules of the cereal starches will retrogradate during drying of the film, not only becoming insoluble itself, but likewise entangling the amylopectin molecules in an insoluble network. The root, tuber and waxy starches are much less prone to retrogradation and, therefore, the films of these starches dissolve readily in water.

Starch products are used as remoistening adhesives on gummed papers, like envelope flaps, gummed labels, postage stamps and gummed tape. The starch film should retain its water solubility for considerable periods of time. Starch films obtained from maize starch show an excessive loss of adhesive properties on ageing. This appears to be due to retrogradation of starch molecules, which slowly develops in the film, thereby lowering its solubility and hence its adhesiveness. Tuber, root and waxy starch products give starch films which retain their adhesiveness for long periods of time.

Films of starch products made from potato, tapioca or waxy starches have greater clarity and higher gloss than films of starch products made from maize or wheat starch products. During drying and ageing, films of maize starch and wheat starch undergo retrogradation, whereby the amylose molecules associate into insoluble micelies which impart both opacity and fragility to the film.

4 Starch modifications

General aspects - why modified starches?

Very often native starch is not the best product in a particular application or process. Modifications of native starches are carried out to provide starch products with the properties needed for specific uses. Modification of native starch properties is an important factor in the continued and increased use of starch products to provide thickening, binding, gelling, adhesive and/or film-forming functionality. The various ways of modification of native starch are designed to change one or more of the following properties:

- Pasting temperature;
- Solids-viscosity relationships;
- Gelatinization and cooking characteristics;
- Resistance of starch pastes to breakdown in;
- Viscosity by acids, heat and/or mechanical shear;
- Retrogradation tendencies;
- Ionic character;
- Hydrophilic character.

Methods of modification

The modification of native starch may involve a change in physical form, a controlled degradation and/or the introduction of chemical groups. Table 7 gives the various methods of starch modification

Table 7 – Modification of starch

No	Type of modification	Main objectives	Treatment
1	Pregelatinized starch	Cold water dispersibility	Drum-drying; Extrusion
2	Low-viscosity starches	Lower viscosity	a, b, c or d
	a. Dextrins	Lower viscosity Range of viscosity stability	Dry heat treatment with acid
	b. Acid-modified starch	Lower viscosity High gel tendency	Acid hydrolysis (suspension)
	c. Oxidized starch	Lower viscosity Improved viscosity stability	Oxidation (in suspension or paste)
	d. Enzymatically modified starch	Lower viscosity	Alpha-amylase (paste)
3	Crosslinked starch	Modification of cooking characteristics	Crosslinking in suspension
4	Stabilized starch	Improved viscosity stability	Esterification Etherification
5	Combinations of modifications 1, 2, 3 and/or 4	Combinations of objectives 1, 2, 3 and/or 4	Combinatons of treatments 1, 2, 3 and/or 4
6	Starch sugars	Sweet saccharides	Acid and/or enzymes

Reaction techniques for chemical starch modification

The industrial reaction techniques tor the chemical modification of starch can be divided into three groups:

- Reactions in aqueous gelatinized starch pastes;
- Reactions with dry or semi-dry starch granules:
- Reactions in suspensions of ungelatinized starch granules in water.

Properties of native starches retained in modified starches
By chemical and/or physical modification, the properties of the native starches are altered.
The relative differences between the native starches (mentioned in the chapters 'Sources of
Starches', page 6 and 'Composition and properties of starches', page 10) are however more or less retained in the corresponding modified starches. The distinctive composition and properties of the various native starches are clearly present in the modified starches produced from these native starches (chemical composition, pasting temperature, paste viscosity, paste clarity, retrogradation tendencies, starch film properties, solubility, adhesivenes and application ability).

4.1. Pregelatinized starches

Pregelatinized (precooked) starches are used when a starch product that is swellable (soluble; dispersible) in cold liquids without cooking is required. Pregelatinized starches are manufactured by the starch producer by means of drum-drying (starch suspensions or starch pastes) or extrusion (semi-dry starch). Pregelatinized starches are mostly produced on steam heated roller drums of the single or double type. Extrusion is used to a lesser degree.
In fact, in the manufacture of pregelatinized starches the starch is precooked for the user.
Precooked starches have practical importance for users who do not have the facilities for cooking starch. Typical applications of pregelatinized starches are convenience foods (instant puddings), wet-end additives in paper making, wallpaper adhesives and drilling muds.

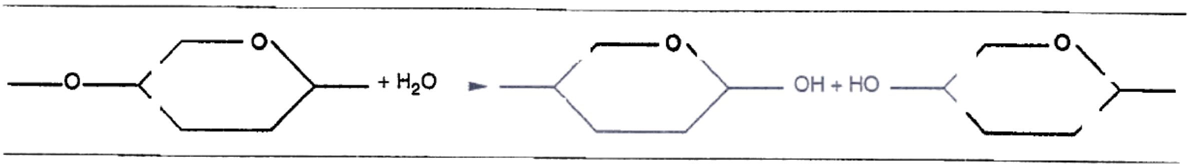
Pregelatinized starches can be made from any native or modified starch. Except for their cold water solubilty, slightly lower viscosity and lower tendency to gel, the properties of the pregetatinized starches are similar to those of the parent starch.
The common cereal starches (maize, sorghum, wheat) contain unsaturated lipids. In the intact granule, these lipids are protected from oxidation. In the pregelatinized cereal starches, lipids may develop rancid flavours on storage (due to oxidation)

4.2. Low-viscosity starches

Low-viscosity starches are produced by controlled degradation of native starches. Low viscosity starches can be gelatinized (cooked) in water at higher concentrations (10-65 % by weight) than native starches (maximum about 10 % by weight).
Low-viscosity starches are needed in applications where a high-solids starch paste with a pumpable and workable viscosity is required. The high viscosity of a cooked dispersion of a native starch requires a large amount of water (low starch concentration) to provide a workable viscosity for pumping, mixing and applying the paste to a substrate (e.g. paper, textiles). This low-solids starch paste would require large quantities of energy and a longer drying time to obtain a dried product.

Low-viscosity starches are obtained when the starch is subjected to a treatment which results in rupture of some of the glucosidic bonds in the starch molecules. As a consequence, the viscosity of the starch product will decrease. The hydrolysis of a glucosidic bond is shown in Figure 23.

Figure 23 – Hydrolysis of a glucosidic bond of a starch molecule



The commercial conversion processes for the production of low-viscosity starches are carried out by acids and heat (dextrins), acids (acid-modified starches), oxidizing agents (oxidized starches) or alpha-amylase (enzymatically modified starches). The comparative viscosity ranges of the native and low-viscosity starches, in terms of parts of water per part of dry starch to give roughly the same hot viscosity, are shown in Table 8.

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Table 8 – Viscosity ranges of native and low-viscosity starches (expressed as parts of water per part
of dry starch to give about the same hot viscosity after cooking)

Starch product	Viscosity range
Potato starch	23-24
Waxy maize starch	21-23
Tapioca starch	19-21
Maize starch	14-16
Wheat starch	12-14
Oxidized starches	3-12
Acid-modified starches	2-11
Enzymatically modified starches	2-11
British gums	1-11
White dextrins	1-5
Yellow dextrins	1-2

4.2.1 Dextrins

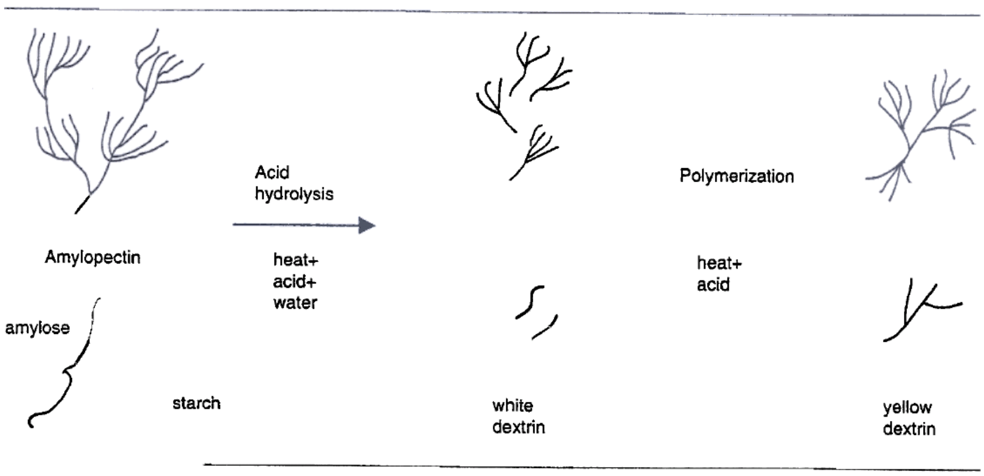
(= roasted starch = pyrodextrins)
It was a purely accidental discovery that was to play the biggest role in the development of dextrin. In September 1821 a fire broke out in a textile mill near Dublin in Ireland. Potato starch was stored in an adjacent building, which was partially destroyed by the fire. The brown-coloured powder which was left after the fire was found to be soluble in water and to give a sticky solution. It was then discovered that the same result could be obtained by heating starch in an iron pan. If this story is true, and it seems proper authenticated, it is slightly ironic that the roasted starch became known as British gum. Later (in 1833), the roasting of starch in the presence of sulphuric acid was further Investigated by Biot and Persoz, who examined the products obtained and gave the name "dextrin" to the gummy material they separated because of the direction of its optical rotation.

Dextrinization is the roasting of dry starch, mostly in the presence of small quantities of acid.
Native starch (10-20 % moisture) is mixed with the required quantity of acid (usually hydrochloric acid). The next step is a drying process to reduce the moisture content of the starch down to about 5-12% (white dextrins) or below 5% (yellow dextrins). The subsequent dextrinization process is carried out in rotating roasting kilns or in fluidized bed systems. When the reaction is complete the dextrin is dropped into a vessel and cooled. Finally the product is remoistened (untill about 10% moisture), sieved and bagged.

During dextrinization the starch molecules are first randomly hydrolyzed to short fragments, the so-calied "white dextrin" stage (see Figure 24). Thereafter the fragments recombine giving a bush-like structure (yellow dextrins).

Dextrins can be made from all the commercial native starches; however, the ease of conversion and the quality of the dextrins vary with the type of native starch. The manufacture of a high-quality dextrin requires a high-quality base starch with a low level of proteins, lipids and other impurities. Potato starch and tapioca starch convert easily to yield dextrins that give dispersions of excellent clarity, stability and adhesiveness. Dispersions of maize dextrins do not show the clarity of potato and tapioca dextrins and tend to thicken rapidly on storage.

Figure 24 – Mechanism of dextrinization



The yellow dextrins are the most highly de-polymerized low-viscosity starches. Their degree of polymerization (DP) is approximately in the range of 20 to 50. Because of their low DP it is possible to make fairly free flowing solutions or pastes, which contain up to 65 % solids.

4.2.2 Acid-modified starches

(= acid-converted starch = thin-boiling starch = acid-fluidity starch)
C.J.Lintner (Germany) was the first (in 1886) who described the suspension treatment of starch with acids. He treated a starch suspension with a 7.5 per cent aqueous solution of hydrochloric acid for 7 days at room temperature. Then the starch was washed free of acid with water and dried. The material has referred to ever since as Lintner's starch. It is used as substrate in enzyme assays and as indicator for iodometric titrations.

The suspension process is widely used in the starch industry. Starch is suspended in a dilute acid solution (such as hydrochloric or sulphuric acid) and maintained at a temperature varying from room temperature to just below the pasting temperature. The suspension is stirred until the potential viscosity of the suspended starch is reduced to the desired level. The suspension is then neutralized (e.g. with alkali or sodium carbonate), washed and dried.

Properties
The acid-modified starch (suspension process) differs from its parent native starch in the following respects:

- Lower hot-paste viscosity (lower average molecular weight);
- The acid degradation involves mainly a scission of the starch molecules to lower-molecular weight fragments. There is an increase of the number of linear molecules, which are smaller than the amylose molecules of the native starch. The result is an increased tendency of the gelatinized starch solution to increase in viscosity and form a gel upon cooling and standing;
- Less granule swelling during gelatinization in hot water.

4.2.3 Oxidized starch

(= chlorinated starch = oxystarch = thin-boiling starch)
Starch can be oxidized by a number of oxidizing agents (oxidants) such as sodium hypochlorite (NaOCl), calcium hypochlorite, ammonium persulfate, potassium persulfate, hydrogen peroxide, peracetic acid, potassium permanganate, sodium chlorite, perborates and chlorine (in water: hypochlorous acid). The oxidation reaction may be carried out in an aqueous starch suspension or in a gelatinized starch paste.

Depending on the type of oxidant and the conditions of the reaction, carboxyl (COOH) and carbonyl (C=O) groups are introduced, while at the same time depolymerization occurs.
Oxidation is the only treatment in which one modification reagent causes two important chemical modifications (depolymerization + introduction of carboxyl groups). Although the oxidation affects both amylose and amylopectin molecules, the carboxyl and carbonyl groups formed on the amylose chains have the main influence on the reduced tendency to retrogradation and gelling of these products in solution.

Bleaching may be considered as a very light oxidation. The products indicated as oxidized starches contain more than 0.1 % added carboxyl groups, while bleached starches contain 0.1 % added carboxyl groups or less.
The degree of substitution (DS) of commercial oxidized starches is in the range of 0.01 to 0.04 for carboxyl groups (1 to 4 carboxyl groups per 100 glucose units) and 0.005 to 0.01 for carbonyl groups (0.5 to 1 carbonyl group per 100 AGU).

The commercial production of oxidized starches by the starch industry (suspension-reaction) involves treating an aqueous starch suspension with a sodiumhypochlorite solution.
Essentially sodium hypochlorite (NaOCl) is made by diffusing chlorine into a cool solution of sodium hydroxide. The reaction proceeds as follows:

$$2\ NaOH + Cl_2 \ \rightarrow \ NaOCl + NaCl + H_2O$$

The reaction of sodium hypochlorite with starch may take place according to the following equation:

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$\text{St-CH}_2\text{OH} + \text{NaOCl} \rightarrow \text{St-COOH} + \text{NaCl}$

Starch + Sodium hypochlorite -> Oxidized starch + Salt

Oxidized starches are sometimes called chlorinated starches because of the reagent used, although no chlorine is introduced into the starch.

Since about 1870 Elliot & Crabtree Ltd. of Manchester were using hypochlorite solutions in order to bleach imported sago starch, which was used in the Lancashire textile industry for sizing purposes. Since about 1930 the industrial production of oxidized starches has increased rapidly.
Today, hypochlorite oxidized starch is probably the most important starch derivative (starch sugars not included). The production of oxidized starches in the starch plant involves treating an aqueous starch suspension (35-45 % solids) with sodium hypochlorite solution (containing 5 to 10 % available chlorine) at pH 8 to 10 and 15 to 38 °C. When the required level of oxidation (degradation) is reached, the reaction mixture is neutralized to pH 5-6.5 to remove impurities, solubilized starch and by-products of the reaction. The reaction product is washed on continuous vacuum filters or in hydrocyclones. Finally the product is recovered by filtration and dried.
Oxidative conversion by users of starch (especially in the paper industry) can be realized by adding an oxidant to starch slurry and then cooking the starch in continuous systems. The starch is gelatinized and simultaneously oxidized. Hydrogen peroxide and potassium or ammonium persulfates are the preferred oxidants in the continuous thermochemical conversion processes.
Thermochemical conversion of starch involves continuously forming of cooked oxidized starch solutions by subjecting a starch suspension to temperatures of 100-175° C in the presence of an oxidizing reagent for a short period of time (0-2 minutes). Jet-cookers or other apparatus for the continuous cooking of starch under pressure may be used (see Figure 33 on page 45).

Properties of oxidized starches (suspension-reaction)
Oxidized starches differ from their parent native starches in the following respects:

- Lower hot-paste-viscosity (lower average molecular weight);
- Lower rate of retrogradation of cooked pastes (because of carboxyl groups introduced in the amylose molecules);
- Lower pasting temperature, faster rate of gelatinization, lower peak viscosity;
- Higher clarity of pastes, solutions and films;
- Lower tensile strength of dried films;
- Whiter granules; improved flavour; lowered bacterial count;
- Anionic character (carboxyl groups).

4.2.4 Properties of bleached starches (suspension reaction)

Bleached starches differ from their parent native starches in the following respects:

- Bleached starches are whiter because of the bleaching treatment (removal of most proteinaceous impurities) ;
- Improved flavour and odour;
- Bleached starches may have a very low bacterial count;

4.2.5 Enzymatically modified starch

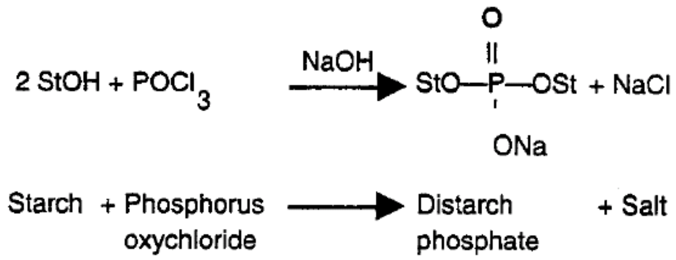
In the continuous enzyme conversion process starch slurry containing a heat-stable alpha amylase is gelatinized instantaneously by direct steam injection (jet-cooker) and discharged continuously to a holding column where the enzyme thinning reaction takes place. Then the thinned paste is pumped from the column and the enzyme is deactivated by heating (in a jetcooker) to an elevated temperature. The resulting paste can directly be pumped to the point of use.

4.3. Crosslinked starches

(= crossbonded starches = inhibited starches)
One of the most important types of starch modification is that resulting from the action of bi- or polyfunctional reagents capable of reacting with more than one hydroxyl group, thus forming crosslinks or bridges from one starch molecule to another. Treatment of ungelatinized starch granules with crosslinking reagents has had particularly valuable use. What appears to take place is a crosslinking of starch molecules in the starch granule, with a resulting tanning or toughening of the granule. At increasing degrees of crosslinking the ungelatinized starch granules become more and more resistant to gelatinization. In most cases a relatively low degree of crosslinking of about one crosslink per 100 to 2000 anhydroglucose units is used. With an average degree of crosslinking corresponding to about one on every 20 glucose units, starches are obtained which show extremely limited ability to swell on cooking.

4.3.1 Distarch phosphate

In the method of Felton and Schopmeyer (from 1940), 0.15 to 0.25 % phosphorus oxychloride (based on starch) is added slowly to a slurry of about 40 % starch in water at a pH of 10 and a temperature of about 25 °C. Upon completion of the reaction, the pH is adjusted to neutral and the granular starch product is filtered, washed and dried. The reaction takes place according to the equation

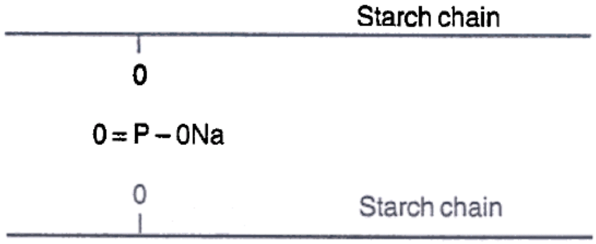


$$2\ StOH + POCl_3 \xrightarrow{NaOH} StO-\overset{\overset{O}{\|}}{\underset{ONa}{P}}-OSt + NaCl$$

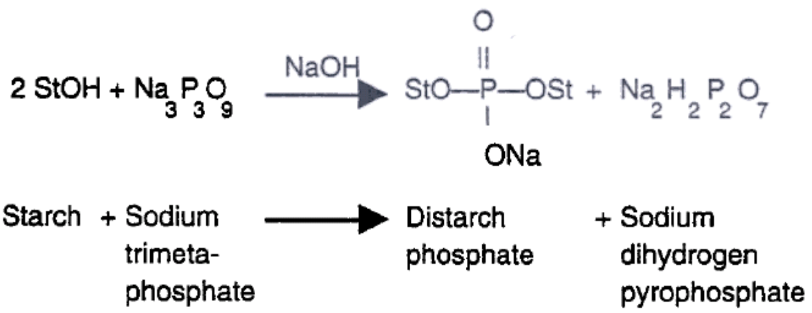
$$\text{Starch} + \text{Phosphorus oxychloride} \longrightarrow \text{Distarch phosphate} + \text{Salt}$$

The structure of distarch phosphate is given in Figure 25, demonstrating the crosslinking of two starch chains by means of a phosphate bridge.

Figure 25 – Structure of disctarch phosphate



Kerr and Cleveland described in 1954 the crosslinking of ungelatinized starch in an aqueous alkaline suspension with sodium trimetaphosphate. Esterification with trimetaphosphate salts requires more rigorous conditions than does esterification with phosphorusoxychloride. Thus a distarch phosphate may be prepared by heating starch slurry (adjusted to a pH of 10 to 11), containing 2 % sodium trimetaphosphate (based on the weight of the starch) to 50 °C for 1 hr. The pH is adjusted to neutral and the granular distarch phosphate is filtered, washed and dried. The reaction takes place according to equation:

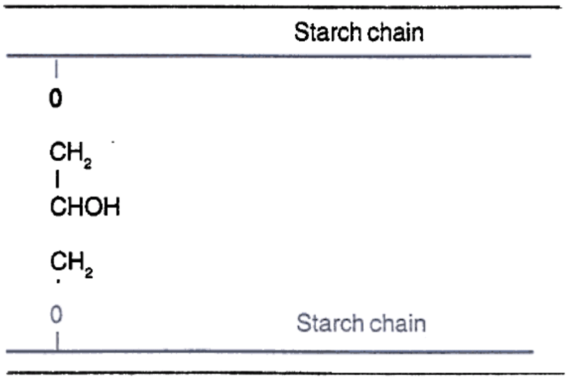


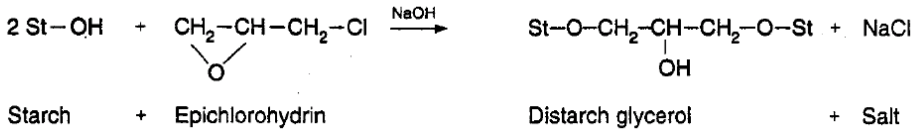
4.3.2 Epichlorohydrin-treated starch

(= distarch glycerol)

M. Konigsberg discovered in 1945 that epichlorohydrin could react with ungelatinized starch granules in aqueous systems to give crossbonding to the molecules. The obtained modified starch has properties similar to those obtained with phosphorus oxychloride. The reaction with epichlorohydrin takes place according to equation below. The structure of distarch glycerol is given in Figure 26, demonstrating the crosslinking of two starch chains by means of a glycerol bridge.

Figure 26 – Structure of distarch glycerol





4.3.3 Other crosslinking reagents

Adipic acid anhydride was found to give crossbonded starch derivatives with properties analogue to those described for phosphorus oxychloride and epichlorohydrin treated starches.

The action of borax in starch pastes (increased viscosity and stability) is probably also a case of weak crosslinks. Borax is the most important single substance to modify pastes of starch products. The unknown man who first discovered the effect of borax on starch adhesives has made the most outstanding contribution in this field.

4.3.4 Properties of crosslinked starches

Crosslinked starch differs from its parent native starch in the following respects:

- The starch granules have an increased resistance to swelling and gelatinization;
- A higher viscosity of the cooked paste is attained;
- Increased resistance of starch paste viscosities to the thinning effect of prolonged agitation, heat or low pH;
- Reduction of the cohesive, rubbery, elastic characteristic of starch pastes from starches such as potato, tapioca and waxy maize to give smooth, salvelike, creamy pastes.

4.4. Stabilized starches

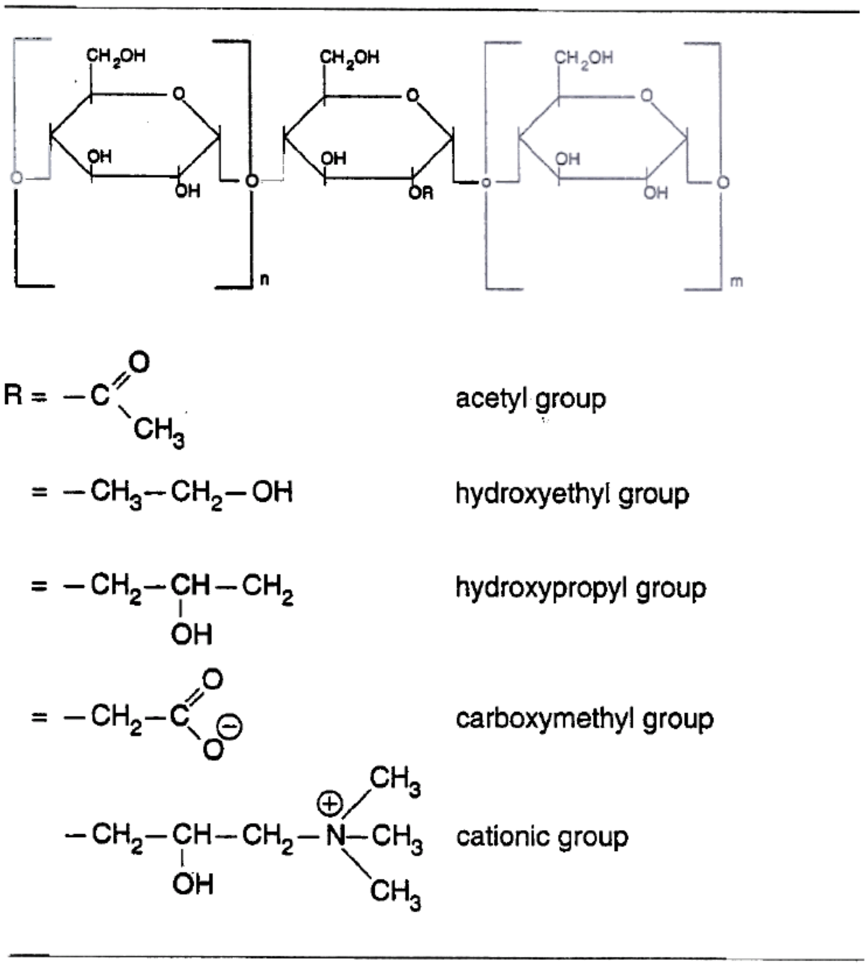
(Starch esters; Starch ethers)

General aspects

Stabilized starches are usually made by reacting starch with etherifying or esterifying reagents in the presence of an alkaline catalyst. The number of introduced substituents is indicated as degree of substitution (DS). The DS is defined as the average number of substituents per anhydroglucose unit (moles substituent per mole of AGU). Thus, a starch derivative with a DS of 0.05 contains 5 substituents per 100 anhydroglucose units (average value). Generally, the commercial starch esters and starch ethers have a DS below 0.2 (lower than 20 substituents per 100 AGU).

The substituent groups of a partially substituted starch derivative are distributed among the three hydroxylg roups (C-2, C-3 and C-6) of the anhydroglucose units of the starch molecule (see Figure 10 and Figure 30). The distribution is determined by the relative reactivity of the hydroxyl groups and the nature of the substitution reaction. The substituents in the commercial starch acetates, hydroxyalkyl starches, carboxymethyl starches and cationic starches are predominantly attached to the C-2 of the anhydroglucose units. The remaining substituents are located mainly at the C-6 position with only negligible substitution at C-3.
Figure 27 gives the structure of these stabilized starches with a low DS. In contrast, cyanoethyl starch and monostarch phosphate are substituted predominantly on the C-6 position.

Figure 27 – Structure of stabilized starches with low DS



The reaction of starch with monofunctional esterifying or etherifying reagents is a method of introducing side-chains, in other words: adding irregularities to the starch chains (see Figure 28). Irregularities on the starch chains (and in particular on the linear amylose molecules) inhibit the formation of ordered structures in the starch paste, so retrogradation is retarded (increased viscosity stability). Therefore starch ethers and starch esters are often designated as stabilized starches. Retrogradation decreases when more substituent is introduced in the starch chains. The object of crosslinking starch is mainly the crosslinking of amylopectin molecules in order to reduce the rate of swelling of the starch granules. In contrast, the object of monofunctional esterification or etherification of starch is mainly the introduction of side chains in the linear amylase molecules to reduce the rate of retrogradation of starch solutions.

Non-ionic, anionic and cationic side-chains can be introduced. Although a large number of starch esters and starch ethers have been prepared, only a few are produced on a commercial scale. This section will only deal with those of most commercial interest.

4.4.1 Starch esters

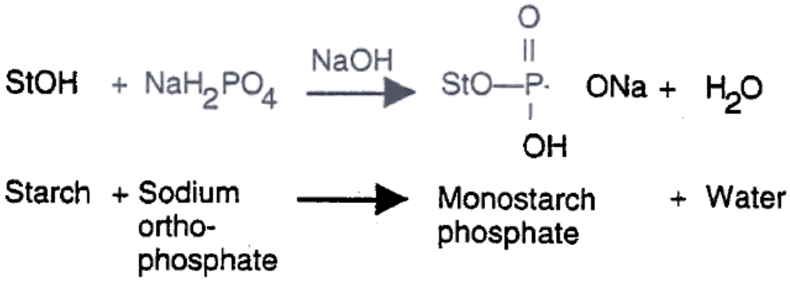
Monostarch phosphate

In monostarch phosphate only one of the three acidic functions of phosphoric acid is esterified with a starch hydroxyl group (predominantly the C-6 hydroxyl groups; see Figure 6). The monoesters have been referred to as starch phosphate monoesters, or simply as starch phosphate, but are more properly described as starch dihydrogen (or disodium etc.) phosphate.

Monostarch phosphates are prepared by semidry reactions of starch with phosphoric acid or water-soluble salts of ortho-, pyro- and tripolyphosphoric acid. This techniquew as first used in 1943 by Jülicher and Appelt. They heated a semidry mixture of starch, urea (e.g. 12% on starch) and phosphoric acid (e.g. 5% on starch) during 2-3 hours at 140 °C.

The reaction of starch with phosphating reagents appears to proceed faster and easier in the presence of urea. Therefore, the reaction may be carried out at lower temperatures and/or during a shorter time and/or with a lower amount of phosphating reagents. The monostarch phosphates obtained (with urea) have a lighter colour and contain less free phosphates as impurity.

In the Neukom-process the starch is impregnated with the phosphate salt solution by suspending in the solution and then filtering; by spraying the solution on the dry starch; or by mixing the solution with the wet filter cake. The pH values of the phosphate solutions vary from pH 5 to 8.5 depending upon the particular phosphate used. The phosphate impregnated starch is dried (to 8-15 % moisture) and then heated (roasted) at temperatures of 120-175° C for 1-15 hours. The reaction takes place according to the equation:



$$\mathrm{StOH} + \mathrm{NaH_2PO_4} \xrightarrow{\mathrm{NaOH}} \mathrm{StO{-}}\underset{\mathrm{OH}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}ONa} + \mathrm{H_2O}$$

The phosphation reaction generally runs to a DS of 0.02 to 0.15. The resulting products contain between 1 and 5 % phosphorus. The industrial production of monostarch phosphates may be carried out in the same kind of apparatus as is used in the production or dextrins, for example in rotating kilns or fluid-bed systems.

Properties of monostarch phosphates

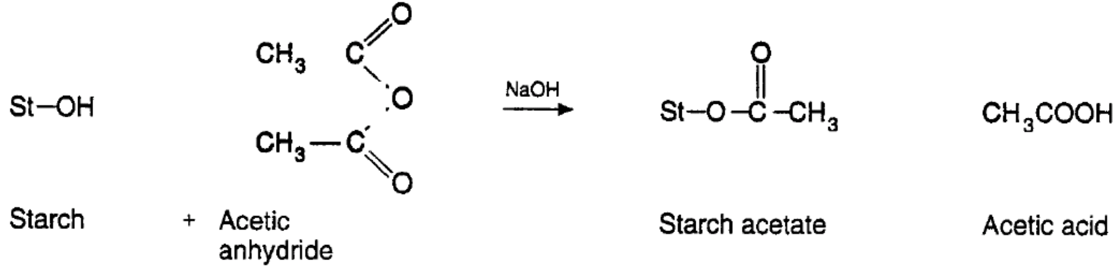
Monostarch phosphate differs from its parent native starch in the following respects:

- The monostarch phosphates tend to become cold-water-dispersible at DS greater than about 0.07. Products with a DS of 0.01-0.07 have a lowered pasting temperature.
- Undepolymerized, purified monostarch phosphates form dispersions with a higher viscosity than that of the native parent starch (because of the ionic nature of the phosphate group). For example, a 1.8 % paste of monostarch phosphate has about the same hot viscosity (as measured by the standard Scott test) as a 4.3 % paste of the parent starch. When during the phosphation reaction some hydrolysis of the starch occurs (acid conditions) the resulting monostarch phosphates (dextrin-phosphates) will have a lower viscosity as compared with the parent starch.
- Monostarch phosphates are anionic polyelectrolytes. The viscosity of solutions of these starches is reduced in the presence of salts.
- Monostarch phosphates may be precipitated from solutions by treatment with soluble salts of aluminium etc.

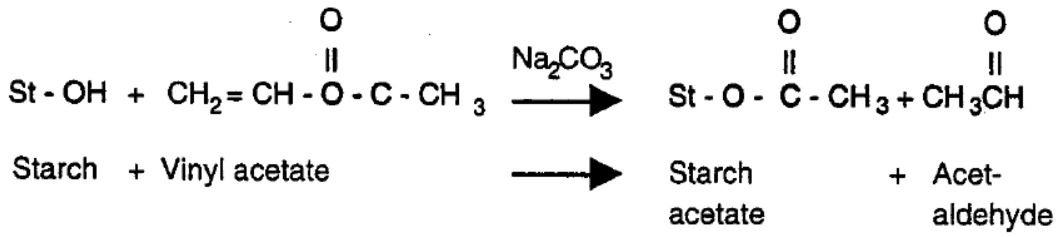
- When gelatinized by cooking in water, the monostarch phosphate forms a viscous, clear, non-gelling paste which has long, cohesive flow characteristics.

Starch acetate
(= acetylated starch)
Encouraged by the easy reaction of phosphorus oxychloride on granule starch in aqueous suspensions (discovered in 1940), it was only natural to look at other water reactive reagents. Acetic anhydride was one of the first reagents to be tried. It reacts with starch according to the equation below.

In 1945 Caldwell described the preparation of starch acetates in granular form by reaction of starch in aqueous suspension with acetic anhydride under alkaline conditions. Successful acetylation depends upon maintenance of conditions that favour acetylation over acetic anhydride hydrolysis without appreciable hydrolysis of starch acetate. The reaction is carried out at a pH controlled at 7.5 to 9.0 at room temperature with slow addition of acetic anhydride. Reaction efficiency is about 75 %. The products are recovered by neutralization to pH 5 with dilute acids, filtration, washing and drying. Ungelatinized starch acetates containing up to 5 % acetyl groups (DS about 0.2) can be obtained. Beyond this level the granules begin to swell and filtration becomes difficult.



Another reagent, patented by Smith and Tuschhoff in 1957, is vinyl acetate. It reacts with
starch according to equation:



$$St-OH + CH_2=CH-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Na_2CO_3} St-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3\overset{O}{\overset{\|}{C}}H$$

Starch acetates are manufactured by treatment of aqueous starch suspensions with vinyl acetate. The reaction is run at about 35-40 °C and pH 9-10 during about 60 minutes. Sodium carbonate is used as catalyst and buffer. Reaction efficiency is about 70 %. The products are recovered by neutralization, filtration, washing and drying. The reaction appears to be a transesterification with acetaldehyde as a by-product.

Properties of granular starch acetates
Starch acetate differs from its parent native starch in the following respects:

- Lower rate of retrogradation of cooked pastes. At relatively low DS the parallel orientation of amylose molecules and of the outer branches of amylopectin is hindered;

- The pasting temperature is progressively lowered as the DS is increased;
- Pastes are clearer and have a longer, more cohesive texture;
- Films (formed by drying thin layers of colloidal solutions) have greater clarity, higher gloss, more flexibility, larger elongation before rupture, less cracking tendency and easier solubility.

Other starch esters

Granular starch succinates may be obtained by treating ungelatinized starch granules in an aqueous alkaline suspension with succinic anhydride. Octenylsuccinate half-esters of starch are made by treatment of aqueous starch suspensions with octenyl succinic anhydride. The introduction of hydrophobic groups at low DS-levels (0.01-0.1) imparts some hydrophobic properties to the starch without destroying the water-dispersibility. The hydrophobic –hydrophilic balance imparts useful emulsifying and emulsion stabilization properties.

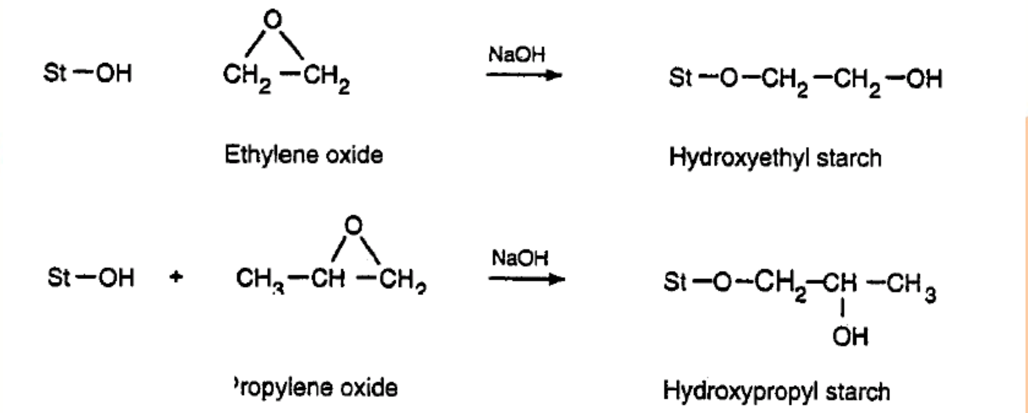
If an intimate blend of urea and a starch containing 5-10% moisture is heated at 90-120 °C, a low DS nitrogen-containing starch derivative is produced. The product is assumed to be a starch carbamate (St-O-CO-NH_2). The reaction is promoted by the addition of potassium acetate.

4.4.2 Starch ethers

Various reaction techniques are used in the production of starch ethers. In general, etherifying agents are relatively slower to react with ungelatinized starch granules as compared to esterifying agents. The high efficiency of the alkaline suspension reaction is caused by the concentration of alkali on the starch granules (adsorption).

Hydroxyalkyl ethers

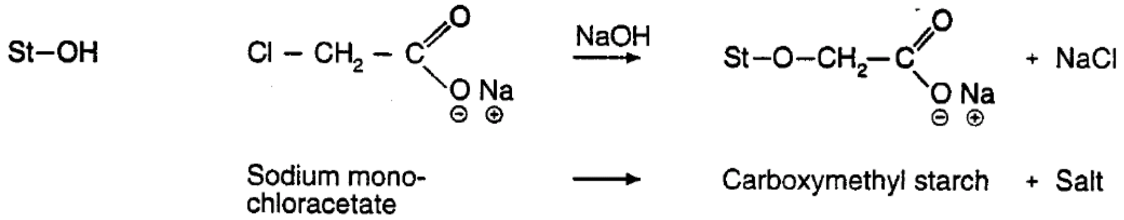
Since about 1945 considerable attention has been given to the preparation of purified granular starch ethers with low DS. Low-DS (0.03-0.10) granular hydroxyalkyl starch ethers are prepared by treating aqueous starch suspensions (about 40 % d.s.) with alkylene oxides (ethylene oxide, propylene oxide) in the presence of alkalies (sodium hydroxide, calcium hydroxide) at temperatures up to 50 °C. The reactions take place according to equations:



A reaction temperature of 25 °C requires a reaction time of about 24 hr., but this time can be shortened by the use of higher temperatures. Sodium sulfate or sodium chloride is required in high concentrations to prevent swelling of the starch so that the granular starch remains filterable. The hydroxyalkyl starches are recovered by filtering, washing and drying. The surprising efficiency of the reaction is caused by the adsorption of the alkaline catalyst on the starch granules. This specifically promotes starch etherification rather than formation of ethylene glycol. The basic process is described by Kesler and Hjermstad in 1946.

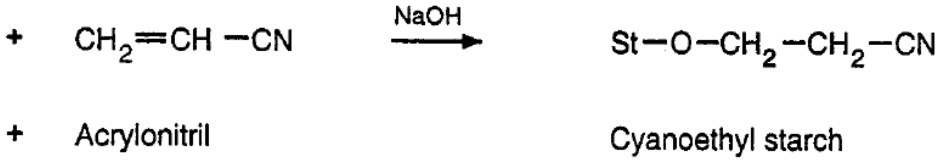
Carboxymethyl starch

Highly water-soluble carboxymethyl starch ether (usually obtained as the sodium salt) is manufactured by the reaction of starch with monochloroacetic acid or sodium monochloroacetate in the presence of sodium hydroxide. The reaction takes place according to the equation



Cyanoethyl starch

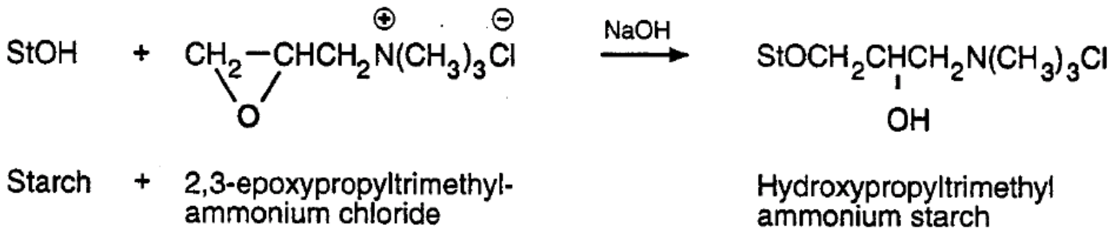
The reaction of starch with acrylonitril in an aqueous alkaline suspension was patented by T.E. Sample in 1955. The obtained low-DS cyanoethyl starch is isolated by filtration, washing with water and drying (DS of e.g. 0.05). The reaction takes place according to the equation:



Cationic starch ethers

The early synthesis of cationic polysaccharides was directed almost entirely to the preparation of amino-cellulosederivatives. It was not until about 1950 that serious efforts were made to synthesize cationic starch derivatives for industrial use. Diethylaminoethyl chloride was found to react readily with granule starch with alkaline catalysts under such conditions that no gelatinization of the starch takes place.

Quaternary ammonium alkyl ethers of starch are made by reacting starch under alkaline conditions with 2,3-epoxypropmethylammonium chloride(a) or chloropropyltrimethylammonium chloride (b). Reagent (b) is converted into reactant (a) (epoxy group) under alkaline reaction conditions. The reaction takes place according to equation:



The cationic ether derivatives are usually made by treating the starch in an aqueous alkaline suspension with the reagent at temperatures of 20-50 °C for 8 to 16 hr. Then the pH of the
Reaction mixture is adjusted to about 3 to 7 with dilute acid and the product is recovered by filtration, washing and drying. The cationic starches can be made by semi-dry reactions as well in mixers or extruders. The reaction can also run on gelatinized starch (batch or continuous).

Properties of starch ethers in general (nonionic, anionic, cationic)
Starch ethers differ from their parent native starch in the following respects:

- Reduced retrogradation of cooked pastes. Not all substituents are equally effective in decreasing retrogradation phenomena. A long side-chain is more effective than a short one. A side-chain with anionic end-group is more effective than a nonionic side-chain of about the same length;
- The gelatinization temperature is lowered. Cold-water-swelling of hydroxyethyl starch granules begins at a DS of about 0.3. Granules of quaternary ammonium alkyl ethers swell in cold water at a DS of about 0.07;
- Pastes have a longer, more cohesive texture;
- Improved properties of dried starch films (increased solubility, clearer films, more flexible films, higher gloss, more continuous films).

Specific properties of carboxymethyl starch
- The carboxymethyl anionic substituents convert the starch to a polyelectrolyte which shows increased solubility and viscosity in the absence of electrolytes (salts, acids).
- Carboxymethyl starch can be insolubilized by reaction with polyvalent ions (such as aluminium, ferric and cupric ions) leading to precipitation or gelling of dispersions or insolubilization of films.

Specific property of cationic starch ethers
As cationic macromolecules cationic starches are attracted to and retained by oppositely charged particles or surfaces (anionic materials) such as cellulose fibres and glass.

Specific property of nonionic starch ethers
The starch acetates and the hydroxyethyl, hydroxypropyl and cyanoethyl ethers of starch are nonionic and their dispersions (pastes, solutions) are therefore not subject to the solubility and viscosity effects which dissolved electrolytes and water hardness have on polyelectrolyte polymers.

4.5. Combination of treatments

Often one type of starch modification is not sufficient to obtain the desired properties for a certain application. By combining two (= dual treatment) or more treatments the desired properties may be obtained. Usual modification combinations are:

a. Crosslinking + stabilization
b. Stabilization+ controlledd egradation
c. Esterification+ etherificationo r etherification+ etherification (all monofunctional)
d. Crosslinking + pregelatinization

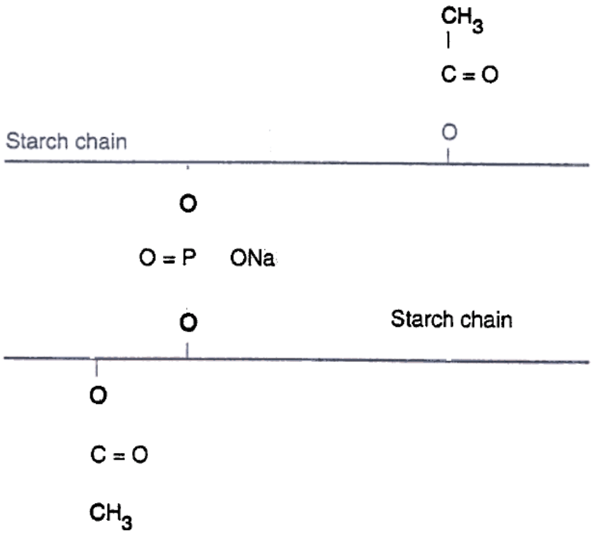
a. Crosslinking + stabilization

A crosslinked granular starch with repressed or "inhibited" swelling properties may be used as base material for monofunctional esterification or etherification (stabilization). Crosslinking + monofunctional esterification may also be carried out simultaneously in an aqueous alkaline suspension. The dual-treated starches give slow retrogradating pastes (because of the ester and ether groups) with increased viscosity (because of the crosslinking). The structure of an acetylated distarch phosphate is given in Figure 29.

b. Stabilization + controlled degradation

In order to obtain lower-viscosity starch esters or ethers the native starch may be oxidized or acid-modified prior to esterification or etherification. It is also possible to depolymerise starch esters or ethers by acid-modification, dextrinization or enzyme modification to obtain products with the desired viscosity. Starch pastes of these dual-treated derivatives have a lower viscosity and a lower tendency to retrogradation as compared with the native parent starches.

Figure 29 – Structure of acetylated distarch phosphate



c. Combination of esterification + etherification or etherification + etherification (all monofunctional)

Mixed cationic-anionic starch derivatives (amphoteric starches) containing both anionic (carboxymethyl; carboxyl; phosphate) and cationic (tertiary amino alkyl; quaternary ammonium) groups may be prepared. These products may have a predetermined isoelectric point and protein-like properties. Starch derivatives carrying both hydrophilic and hydrophobic substituents are used as foaming agents in aqueous systems.

d. Crosslinking + pregelatinization

Crosslinked starches and crosslinked stabilized starches may be pregelatinized by drumdrying. These pregelatinized starches are used in convenience foods, in various adhesives and as textile printing thickeners

4.6. Starch sugars

When starch undergoes complete acid and/or enzyme hydrolysis it splits quantitatively to glucose. Glucose syrups are concentrated aqueous solutions of a hydrolysate in which the conversion has not proceeded to completion. The reaction can be checked and stopped at various intermediate stages. Consequently, glucose syrups contain glucose, maltose and a mixture of higher sugars.

Glucose and dextrose are synonymous in the chemical sense. However, industrially it is usual to employ the name dextrose to describe the pure crystalline product. The name glucose syrup is employed to describe the products of incomplete hydrolysis.

The method for expressing the relative composition of glucose syrups is based on the determination of the dextrosee quivalent (DE). The DE is defined as total reducing sugars expressed as dextrose and calculated as a percentage of the total dry substance. The DE value is inversely related to the degree of polymerization (DP). Starch has a DE of virtually zero, whereas the DE of dextrose is defined as 100. An indication of the DP of a starch hydrolysate is obtained by using the formula: DE x DP = 120.

The starch sugars (starch hydrolysates) may be classified as follows:

Glucose syrups, which may be classified as follows:

- Low-DE glucose syrup: DE 25-37;
- Intermediate glucose syrup: DE 37-57;
- High-DE glucose syrup: DE 58 and higher;
- Maltose syrup: maltose content at least 40% (on d.s.);
- Dried glucose syrups (DE 20 or more);
- Total sugar (= solid glucose = chip sugar = masse);
- Isoglucose (= glucose-fructose syrup);
- Dextrose (anhydrous or monohydrate);

In the production of starch hydrolysates the following catalysts may be used:

- Acids (hydrochloric acid, sulphuric acid, oxalic acid)
- Alpha-amylase (from malt, bacteria or fungi)
- Beta-amylase (from malt or bacteria)
- Glucoamylase (= glucosidase = amylogrucosidase = gamma-amylase; from fungi)
- Isomerase (= glucose isomerizing enzyme; from bacteria)
- Debranching enzyme (= pullulanase = isoamylase = amylo-1,6-glucosidase; from bacteria)

The present glucose industry had its beginning from the work of Kirchhoff in 1811. Gottlieb Sigismund Constantin Kirchhoff was a German chemist working in a Russian laboratory. He discovered that starch could be converted by heating with dilute acids into sweet sugars. This discovery was accidently, since his object had been to prepare a substitute for gum arabic. The three types of product obtained by Kirchhoff by heating potato starch with dilute sulphuric acid (syrup, solidified hydrolysate and dextrose separated from the syrup) are still commercial products in the form of glucose syrup, total sugar and crystalline dextrose. His results were immediately duplicated by many chemists and in less than a year following the announcement of his discovery, the commercial manufacture of starch sugars had been established in Germany. Kirchhoff was also among the first (in 1815) to report the conversion of starch to maltose syrup by the action of cereal malt amylase on a paste of potato starch. Since 1811, at least 50 % of the world production of native starch has been converted into starch sugars (glucose syrup, dextrose, isoglucose).

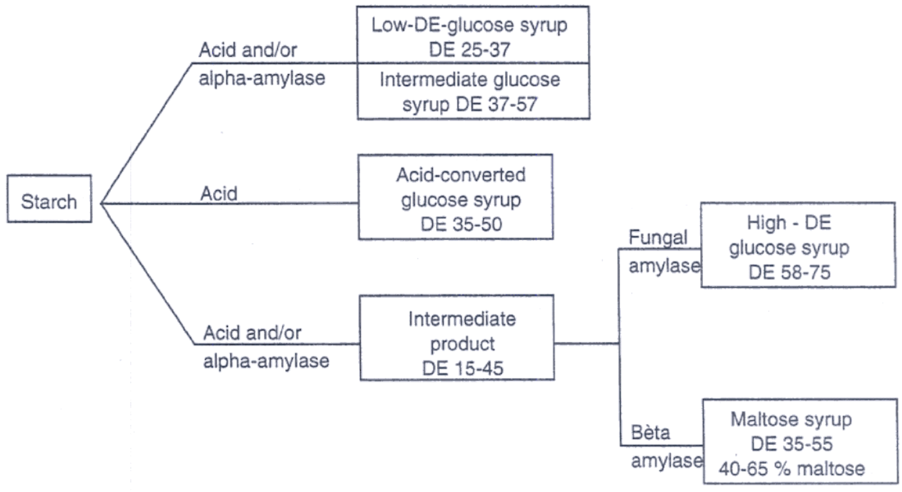
4.6.1 Glucose syrup

Acid hydrolysis of starch is an 'at random' action and the resulting syrup is only a function of the degree of conversion. Enzyme hydrolysis of starch is a patterned action and the composition of the resulting syrup is a function both of the degree of hydrolysis and the kind of enzyme used. The 4 customary amylases (alpha-amylase, beta-amylase, glucoamylase, isoamylase) show distinctly different patterns of hydrolysis. One or more of these enzymes may be used in conjunction with acid in the hydrolysis of starch to produce syrups of very specific composition and having definite physical and chemical characteristics. Georg Wulkan was the first (1932) to describe the production of acid-enzyme converted glucose syrups. Other types of acid enzyme converted glucose syrups are the high-DE glucose syrups, and the low-DE glucose syrups.

4.6.2 Maltose syrup

The use of malt (or malt extract) in the preparation of maltose syrups was the first application of enzymes in the starch industry. Maltose and dextrins appear as the main products of hydrolysis. Malt contains alpha-amylase and beta-amylase. It has been used in breweries for hundreds of years. A generalized pathway tor the production of glucose syrups, dextrose and isoglucose is shown in tigure 30 and 31.

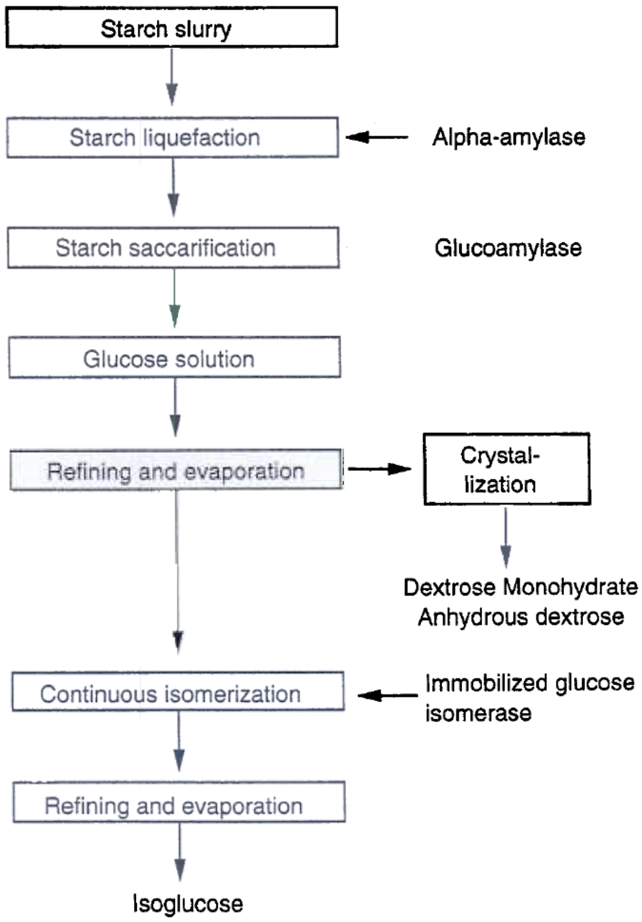
Figure 30 – Production of glucose syrups



4.6.3 Starch liquefaction

Before starch can be effectively converted by glucoamylase, it must first be gelatinized and thinned. Liquefaction is the term used to describe the dispersion of starch molecules in aqueous solution, followed by partial hydrolysis. This process is accomplished by heating the starch in a water slurry above the gelatinization temperature and partially hydrolysing (to DE 5-20) the solubilized starch with either acid or alpha-amylase. The object of this treatment is to reduce the starch to a manageable, essentially completely soluble and non-retrogradable form.

Figure 31 – Production of dextrose and isoglucose



4.6.4 Dextrose

W.B. Newkirk introduced the concept of conducting the crystallization of dextrose monohydrate at a controlled rate in the presence of substantial amounts of seed crystals. The operation was most economically carried out by leaving in the crystallizer 25 to 30 % of a finished batch to act as a seed for the syrup of a succeeding batch. Good agitation is needed. The crystals were suitable for separation from the mother liquor by centrifugation and washing. The first commercial production of crystalline dextrose monohydrate began in 1921. Newkirk also invented a method for the manufacture of crystalline dextrose anhydrous.

4.6.5 Isoglucose

In 1956, Marshall described a process for converting dextrose to fructose using xylose isomerase isolated from Pseudonomas hydrophilia. This process appeared to US-technologists more like a scientific curiosity than a commercially promising process. The real transfer of emphasis from the scientific level to the industrial technological level occurred in

1965 when Takasaki and Tanabe (Japan) published the details of their proposed commercial process in which isomerase-containing cells of Streptomyces albus were reused in a sequence of batch reactors or used continuously in columns. Developed originally by

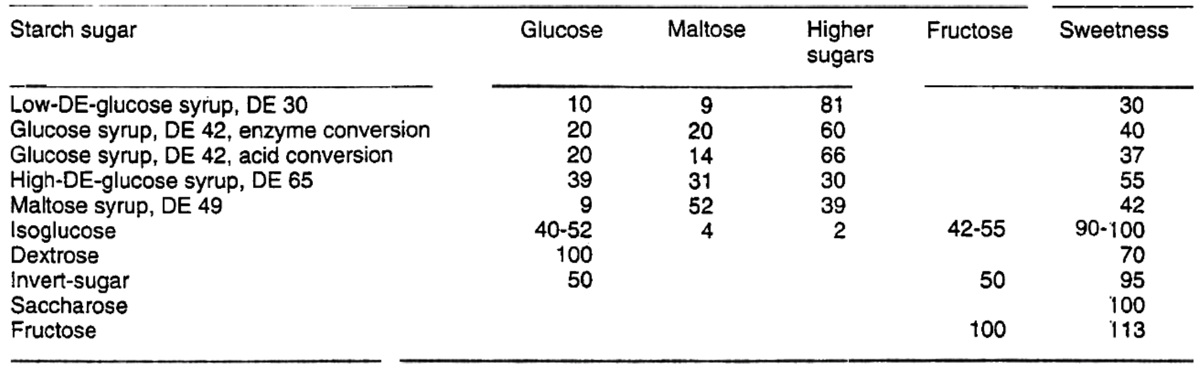
Japanese biochemists, the isomerization process has been improved and commercialized in the USA by the Clinton Corn Processing Company. They were in commercial production of syrup of 15 % fructose content in 1967 and 42 % fructose content syrup in 1968. At first the process was batch operated, but in 1972 it was converted into a system using an immobilized isomerase in a continuous process. Commercialization occurred about 10 years after discovery of the enzyme used.

Isoglucose is essential a 50-50 liquid mixture of glucose and fructose and is similar in composition and sweetness to liquid invert sugar. Its acceptance in the sweetener market and its economic impact on the starch industry has been sensational.

4.6.6 Composition and sweetness of starch sugars

Table 9 summarizes the composition (% by weight on dry substance) and relative sweetness of various starch sugars. The sweetness of a 10 % (by weight) aqueous solution of a starch sugar is compared with the sweetness of a 10 % aqueous solution of saccharose (saccharose sweetness is 100).

Table 9 – Composition and sweetness of starch sugars



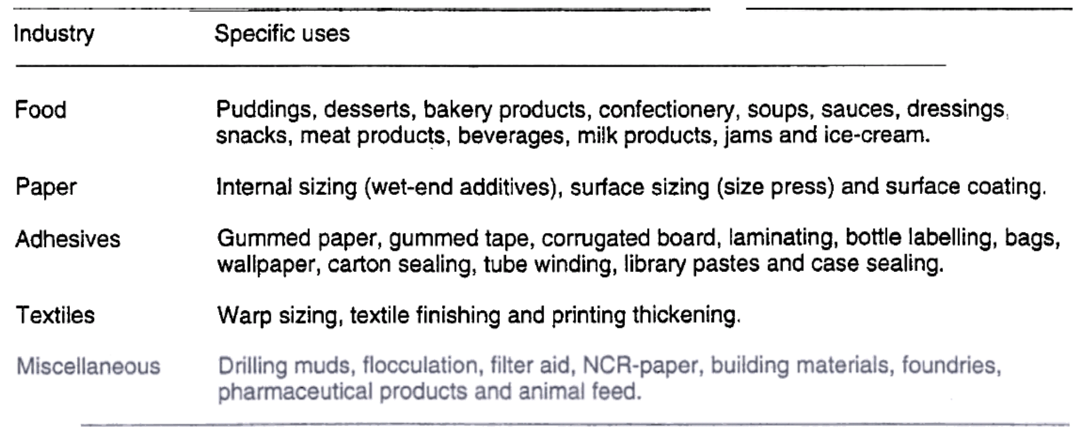
Starch sugar	Glucose	Maltose	Higher sugars	Fructose	Sweetness
Low-DE-glucose syrup, DE 30	10	9	81		30
Glucose syrup, DE 42, enzyme conversion	20	20	60		40
Glucose syrup, DE 42, acid conversion	20	14	66		37
High-DE-glucose syrup, DE 65	39	31	30		55
Maltose syrup, DE 49	9	52	39		42
Isoglucose	40-52	4	2	42-55	90-100
Dextrose	100				70
Invert-sugar	50			50	95
Saccharose					100
Fructose				100	113

5 Applications of starches

5.1. General aspects

To obtain starch products meeting the specific requirements for a particular application modification of the inherent properties of native starches is often required. By choosing the type of starch (potato, maize, tapioca, wheat, waxy maize) and the type of modification (controlled degradation, crosslinking, stabilization and/or pregelatinization) a suitable starch product can usually be developed. Important performance factors are gelatinization characteristics, thickening power, gelation, viscosity stability, binding and adhesive characteristics, emulsion stabilization properties and film-forming abilities.

Table 10 – Main areas of application for starch products



Industry	Specific uses
Food	Puddings, desserts, bakery products, confectionery, soups, sauces, dressings, snacks, meat products, beverages, milk products, jams and ice-cream.
Paper	Internal sizing (wet-end additives), surface sizing (size press) and surface coating.
Adhesives	Gummed paper, gummed tape, corrugated board, laminating, bottle labelling, bags, wallpaper, carton sealing, tube winding, library pastes and case sealing.
Textiles	Warp sizing, textile finishing and printing thickening.
Miscellaneous	Drilling muds, flocculation, filter aid, NCR-paper, building materials, foundries, pharmaceutical products and animal feed.

There are considerable differences between the chemical composition and the physical properties of starch products (native and modified) of different biological origin (potato, maize, tapioca, wheat, waxy maize). Consumption patterns for different kinds of starch vary widely from industry to industry and from country to country. Economic considerations as well as functional properties dictate which starch will be used. Table 10 shows the main areas of application for starch products

5.2. Governmental regulations

The use of modified starches and other starch derivatives in foods and as a component of articles intended for use in manufacturing, packing, processing, preparing, treating, packaging, transporting or holding food is restricted by legislation. The governments have issued regulations specifying the reagents, the amount of these reagents and the amounts of residual reagents and residual by-products that are cleared in treating starch to make modified starches suitable of direct addition to foods and/or suitable of coming in contact with food. There are also regulations relating to the migration limits of starch products (including residual reagents and residual by-products) as components in articles, packaging materials and adhesives that can come in contact with food. Examples of residual by-products in chemically modified starches are chlorohydrins (resulting from the use of reagents such as ethylene oxide, propylene oxide, epichlorohydrin and/or cationic reagents) and acetaldehyde (resulting from the use of vinyl acetate as reagent). The quality and purity of chemically modified starches and other starch products must meet performance standards and comply with manufacturing practices specified in national and international regulations. Each country has its own regulations and these vary considerably. The full regulations should be consulted before using starch derivatives.

5.3. Foods

The use of starch products as a food ingredient is usually not based on their nutritional value, but on their functional value. Food starches impart to the food system certain desirable properties such as texture or ´mouthfeel´ thickening, geling, binding and stability. The selection of the starch or modified starch for a particular food system will be determined by the processing requirements and the characteristics required in the finished food product.

Potato and tapioca starch products yield starch pastes with a good clarity and a bland flavour, which make them useful in many food applications. They contain only small amounts of proteins and lipids. In contrast, maize and wheat starch products contain substantial amounts of residual proteins and lipids which may impart undesirable off-flavours to the food products.

5.3.1 Puddings, desserts and custards

Home-made cooked puddings require a starch that has (after cooking by the consumer) a smooth short texture, such as maize starch. The cooked pudding mixture is poured into cups or dishes and allowed to cool and gel.

Pregelatinized crosslinked starches are used in many kInds at dry blends, mixed by the consumer with water or milk. Instant pudding is an important outlet tor these materials. Pregelatinized crosslinked potato and tapioca starch are generally employed as basic materials for instant puddings and instant desserts. To obtain the desired structure of the pudding, the native starch must be crosslinked to avoid complete granule disruption on the drum-dryer, which would result in a cohesive, slimy texture of the pudding or custard.
Pregelatinized potato and tapioca starch products are essentially the blandest starches and do not have off-tastes associated with the pregelatinized cereal starches.

The Dutch dairy factories sell custard, or so called ´vla´, in bottles or paper packages. The custard is produced in continuous cooking systems in which the cooking time is very short, so that a high temperature (above 100 °C) is necessary. Crosslinked granular starches are used as thickeners. Native starches cannot be used, since the granules would be disrupted, which would result in an unattractive structure of the custard.

5.3.2 Bakery products

Crosslinked starches (potato, tapioca, waxy maize) and crosslinked stabilized starches (including the pregelatinized versions) are used as thickeners in bakery custard, pie fillings, fruit fillings, cream toppings and bakery creams.

Wheat starch is employed in the baking industry to reduce the wheat flour content and hence the protein content of pastry, biscuits and certain cakes (wheat starch as diluent for wheat gluten). Pregelatinized starches are employed in dry cake mixes to be mixed by the consumer with water or milk.
Powdered native starches are used as dusting powder in the bakery industry. To maintain the efficiency of prepared baking powder du ring storage, the acid and the bicarbonate must be kept dry and kept as far apart as possible, even though they are mixed. The preferred method is to use a redried native starch as a diluent (at 15 to 40 % of total baking powder).

5.3.3 Confectionery

Low-viscous potato, tapioca and waxy maize starches are suitable as binders in gum-type confections (liquorice gums, fruitgums and winegums). The candy industry also uses a large amount of acid-modified starch in gelied confectionery such as jelly beans, jelly candies and orange slices. The starch is cooked with the sugar and syrup to a fluid sol, which is cast in starch moulds where setting and drying occur. The essential contribution of the starch is to form a rigid gel on cooling. Acid-modified starch is commonly used because of its tendency to retrogradate and gel, and because it can be cooked at high solids to give a workable viscosity.

Powdered native starches are employed in moulding beds in the manufacture of gum candies and other cast confectionery. The starch is usually redried to about 5-10 % moisture to absorb some moisture from the cast pie.

5.3.4 Soups (dry soup powders; canned soups)

Native potato starch or crosslinked potato starch are preferred as thickeners in dry soup powders, capable of reconstituting to a cream-like soup in hot water. Potato starch has a low pasting temperature and gives the desired cream-like character to the soup, while not imparting any undesirable taste to the reconstituted product. Preferably, a redried potato starch with a moisture content of 6-12 % is used. It acts not only as a thickener, but also protects the other ingredients of the dry soup powder, because it attracts water vapour more readily. Redried oxidized potato starch is used in dry soup powders, for the preparation of thin clear soups (consommé types of soup). Pregelatinized starches are employed as thickeners in vending soups.

Potato, tapioca or waxy maize starches are preferred as base starches to make a retort starch for the production of canned soups and other canned products. In thick soups a crosslinked stabilized starch is preferred. Crosslinking is necessary to retain a high viscosity during sterilization; stabilizing maintains the rheological properties of the soup on storage. Thick-thin retort starches give a high viscosity in the initial stages of soup manufacture, but lose their viscosity in the sterilization phase and give a thin clear soup.

5.3.5 Sauces and dressings

Potato starch and crosslinked potato starch are used as thickening agents in dry sauce bases, capable of reconstituting to a sauce in hot water.

Starch pastes serve as stabilizers for oil emulsions in salad dressings. Since these are generally of low pH, the starch must resist the viscosity breakdown by acid cooking (vinegar) and also high shear forces which occur in homogenizing the formulation. Wheat starch and crosslinked starches are employed here.

Pregelatinized starch products are used in dry gravy and sauce bases, mixed with hot water by the consumer.

5.3.6 Snacks

The manufacture of expanded, extruded potato snacks involves the basic steps of forming a dough of suitable composition, extruding the dough and cutting the extruded dough into piecelets (pellets) to form a so-called" half-product". This half-product can be cooked (fried) to effect expansion of the product, resulting in a crispy, expanded snack product. The dough is generally formed by admixing with water a dry mix of a dehydrated potato product (flakes; granules), ungelatinized starch (preferably potato starch), pregelatinized starch (preferably pregelatinized potato starch) and salt.

In the manufacture of puffed snacks (not potato-based) the dough binder is preferably derived from potato, tapioca or waxy maize starch.

5.3.7 Meat products

Starches are used as binders in emulsion meats such as bologna and sausage to keep meat, fat and juices together. One of the best binders for bologna and frankfurters is potato starch. It has a low gelatinization temperature, which permits it to absorb water in the early stages of cooking and smoking operations in the meat processing.

Certain types of canned processed meat contain added starches and spices. These types of product require to be retorted in the can for sterilization. The purpose of the starch is to give bulk and prevent shrinkage of the can contents during the heat treatment. Unmodified potato starch is often preferred for this purpose.

5.3.8 Starch sugars

Glucose syrup, dextrose and/or isoglucose are utilized in the production of various foodstuffs such as confectionery, bakery products, beverages, milk products, canned products, jams, beer and ice-cream. The most significant properties of the starch sugars in these applications are: bodying, browning reaction, hygroscopicity, prevention of sugar crystallizations, sweetness and viscosity.

5.4. Paper

The paper industry is the largest industrial non-food consumer of starches. Starch is used in three applications:

- As an additive to the pulp before the paper sheet is formed (internal sizing; wet-end addition; beater sizing);
- In surface sizing of paper;
- In surface coating of paper.

5.4.1 Internal sizing

(wet-end addition)

The principle of making paper is simple. A very dilute suspension of cellulose pulp in water is filtered on a fine wire screen to drain most of the water, leaving a wet fibrous mat which is pressed to remove more water and then dried. Starches are added to the pulp primarily to increase the dry strength of the paper. They may also be used to increase the retention of fillers and pigments. The starch forms a bond between the individual pulp fibres.
The starch is usually added as dispersion produced by cooking the starch directly before use or using a pregelatinized starch. The starch can be cooked at the site of application in continuous steam-injection cookers (jet-cookers).
Pregelatinized (drum-dried) starches are used in mills where starch cooking facilities are not available. Borax and other additives are added to the starch before drum-drying. Monostarch phosphates are effectively retained in the wet sheet in the presence of alum. They are useful in acid paper-making systems.

Since 1960 there is an increasing use of cationic starches for internal sizing. Cationic starches are retained for virtually 100 % on the pulp, because of their attraction to the anionic cellulose fibres. The advantages of cationic starches are a greater contribution to the strength of the paper, higher starch retention and a higher retention of anionic fillers. Potato starch contains naturally occurring phosphate groups which permit it to show improved properties when utilized as a paper additive for internal sizing. Cationic potato starches are so much more effective than cationic maize starches, that they are produced in the United States on a large scale.

5.4.2 Surface sizing

In the paper industry, most starch is used for surface sizing. Application of non-pigmented starch pastes to the nearly dry sheet is referred to as surface sizing. A continuous film of gelatinized starch is deposited on the sheet and the sheet is then dried. The size is employed to anchor the surface fibres and particles, so that dusting and linting will not occur. A surface sizing treatment of paper improves the strength and surface properties for printing and writing. The surface properties desired are improved appearance, surface strength, scuff resistance, printability, erasability and resistance to the penetration of fluids and inks into the sheet.

Starch is the most used surface sizing agent. The starches employed in the sizing operation are low-viscosity types, since the native starches are too high in viscosity to provide enough solids in the sizing solution. The conversion (controlled degradation) can be carried out by the starch producer or in the paper mill at the site of application.

The following starch products may be used in surface sizing:

- Oxidized starches;
- Oxidized starch esters or ethers;
- Enzyme-converted (batch or continuous process) native starches, starch esters or starch ethers (conversion in the paper mill);
- Thermochemical-converted (continuous pasting and oxidation) native starches (conversion in the paper mill).

5.4.3 Surface coating

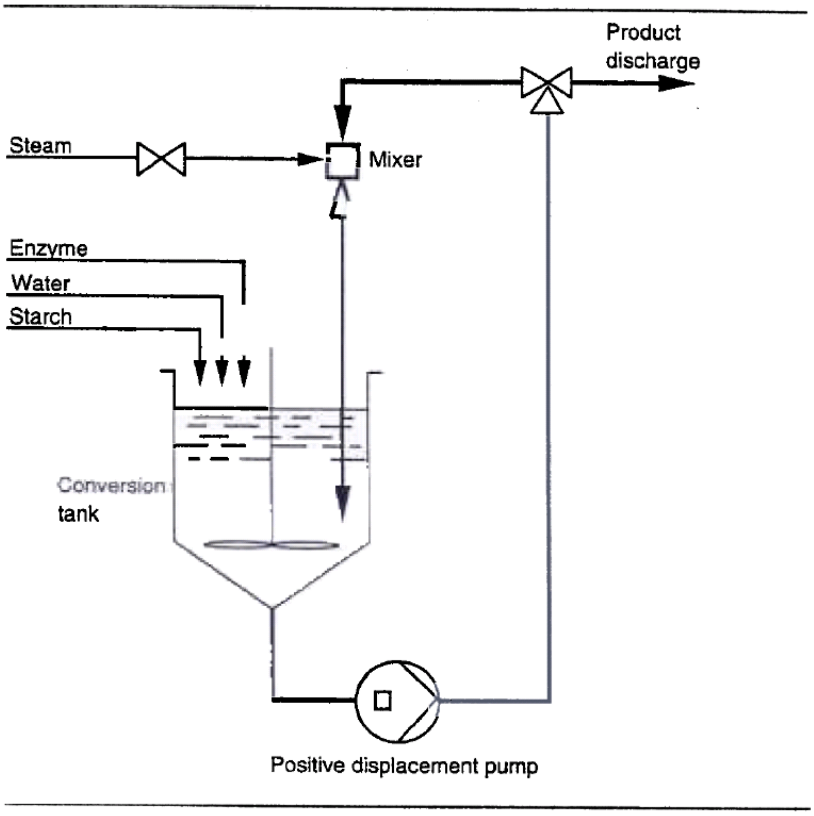
In surface coating a layer of white pigment particles (clay, satin white, calcium carbonate or titanium dioxide) is applied to the surface of paper and paperboard to obtain a white smooth surface. Starch products are used as a binder to bind the pigment particles to each other and to the base paper. In this application the following low-viscosity starch products may be used:

- Oxidized starches;
- Oxidized starch esters or ethers;
- Monostarch phosphates;
- Enzyme-converted starches (conversion in the paper mill);
- Thermochemically converted starches (conversion in the paper mill).

Enzyme conversion and thermochemical conversion of starches in the paper mill

During the past several years, improvements in starch conversion techniques enabled many paper mills to convert granular native or modified starches by enzyme conversion or thermochemical conversion.

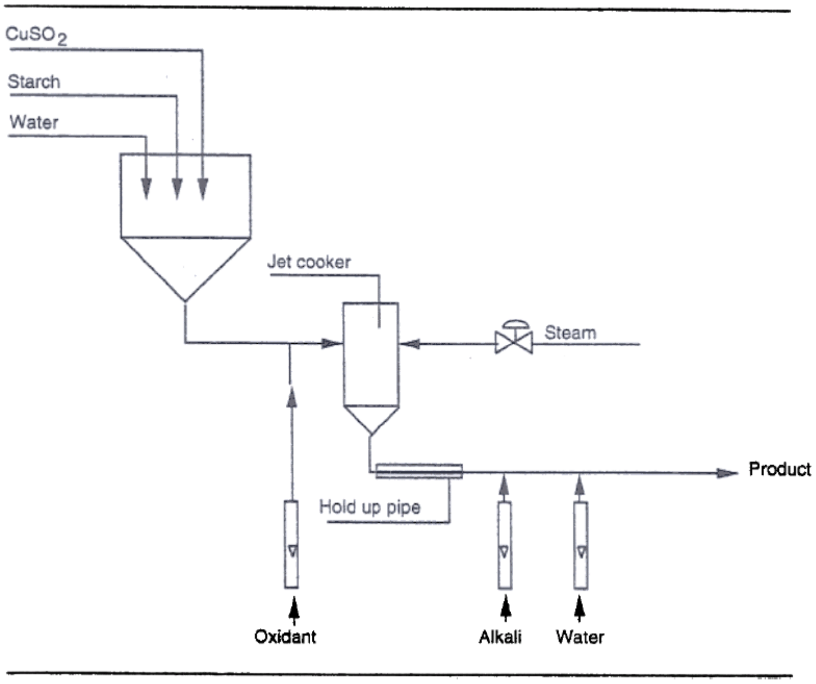
Figure 32 – Enzymatic circulation converter



Enzymatic conversion can be practized either batchwise or continuous. Figure 32 represents an enzymatic circulation converter. The starch and water are metered into the conversion tank and turned into slurry with the aid of a high-speed agitator. When the slurry has obtained its pre-set temperature and pH, the enzyme (alpha-amylase) is metered in. The slurry is pumped to the mixer where it is blended with steam and then recirculated back to the conversion tank. The temperature during the enzyme conversion may be about 70 °C (for potato starch) to about 78 °C (for maize starch). A major advantage of this system is that any viscosity peaks are smothered prematurely. When conversion has been completed and the enzyme activity stopped, the starch solution is pumped to a storage tank by the circulation pump.

Figure 33 represents a system for thermochemical conversion of starch. In the application of continuous thermochemical conversion, slurry of starch is prepared with a small amount of copper sulphate which is used as a catalyst. The slurry is drawn into the narrow slit of a special steam injection valve where the slurry is heated with excess steam. Just ahead of the ´jet-valve´ an oxidizing substance (such as hydrogen-peroxide or ammonium persulphate) is metered in. The thermochemical conversion temperature may be about 120-140 °C (for potato starch) to about 150-160 °C (for maize and wheat starch). After the jet there is a holding tube for a hold-up time of about 0.5 minute, at the end of which neutralizing alkali and cooking water are added to maintain pH, concentration and temperature at their desired levels.

Figure 33 – Thermochemical conversion of starch



Various types of starches may be used in enzyme conversion and thermochemical conversions such as potato starch, maize starch and wheat starch. These starches differ in their response to the conversion processes. Potato starch undergoes conversion more readily (at lower temperatures and/or with lower amounts of enzyme or oxidizing agents) than maize starch which is easier to convert than wheat starch. The converted potato starch solutions are water white and are substantially free from foam, off-flavours and sludge forming tendencies. The high content of lipids (0.8 %) and proteins (0.3-0.5 %) in maize and wheat starch may result in the formation of foam, off-flavours and sludge in the converted starch solutions.

5.5. Adhesives

Starch-based adhesives are excellent to fix porous hydrophylic materials together, such as paper and paperboard They can be used in all applications where both surfaces are paper or paperboard, or one is paper and the other metal or glass. Maize, potato, tapioca, wheat and waxy maize starches are used as basic raw materials in the manufacture of adhesives. Each of them imparts its own characteristics to the final adhesive. Borax is used to modify some types of starch-based adhesives to increase viscosity, stability and cohesive nature of the starch paste.

5.5.1 Gummed paper

Dextrin adhesives are used in the gummed paper industry to bring a thin layer of remoistening gum on paper used for the manufacture of postage stamps, gumming stamps, labels and envelopes. Potato and tapioca dextrins give films of good solubility (remoisten ability), neutral flavour, light colour and excellent adhesive properties.

5.5.2 Gummed tape

Potato, tapioca and waxy maize thin-boiling starches are used as water-remoistenable adhesives on gummed tapes. The native starches are modified to give low viscosity (by controlled degradation) and viscosity-stability (by esterification or etherification) at about 50 % solids. These starch products have replaced animal glue in many areas of gummed tape manufacture.

5.5.3 Corrugated paperboard

An enormous quantity of maize starch is used in the manufacture of corrugated board. A mixture of native starch, borax, sodium hydroxide and water is suspended in a paste of cooked starch (carrier). After the adhesive is applied to the flute tips and subsequently heated, the native starch gelatinizes in place (in situ). The gelatinized starch fixes together a corrugated strip of paper and a smooth surfaced liner. This process was developed in 1935 by Jordon Bauer of the Stein-Hall Company. Maize starch is the predominant starch in this process, but other starches (potato, tapioca, wheat) could also be u-sed, as dictated by economics and local availability.

5.5.4 Vegetable glue

(Pflanzenleim, plantenlijm, alkali converted adhesives)

Alkaline gelatinization of potato and tapioca starch yields stringy, rubbery, viscous dispersions. These dispersions may be neutralized and drum-dried. The obtained vegetable glues are used in:

- Laminating paper to board;
- Bottle labelling;
- Aluminium foil-to-paper laminations;
- The manufacture of paper bags.

5.5.5 Bag adhesives

One of the largest consumers of starch adhesives is the paper bag industry. Most of the starch is used in the manufacture of grocery and multi-wall paper bags. Numerous starch adhesives are employed such as pregelatinized starches, vegetable glues, dextrins, acid-modified starches, cooked native starches, borated dextrins, starch ethers and oxidized starches.

5.5.6 Wall covering adhesives

Packaged adhesives are used by contractors and by home-owners to apply their own wallpaper. The "do-it-yourself" wallpaper adhesive must have excellent viscosity stability, good slip for easy application and good tack. Pregelatinized potato starch ethers are used for this application.

5.5.7 Other adhesive applications

Borated dextrins give high tack with good ageing characteristics and good adhesion and machining properties. They are used in case sealing, carton sealing, tube winding and laminating applications. Non-borated dextrins and vegetable glues are used in bottle labelling. Potato white dextrin is preferred in library pastes.

5.6. Textiles

The principle uses of starch products in the textile industry are:

- Sizing of warp yarns (warp sizing);
- Finishing of textile fabrics;
- Carrying dye and chemicals in printing pastes.

5.6.1 Warp sizing

After the various fibres have been converted into a continuous length of yarn, the warp yarn undergoes a sizing operation to provide a protective coating which increases the tensile strength and improves abrasion resistance during weaving. The warp sizing operation involves passing the strands of yarn into a hot size solution, then through squeeze rolls to remove the excess size and finally over steam-heated rolls to dry the sized yarn. The size binds the loose fibres tightly to the surface of the thread and thereby strengthens the warp to resist abrasion during weaving. After the fabric is woven, the size is removed.
The warp sizing process requires a polymer that is easy to disperse ih water, giving noncongealing, non-foaming size solutions which deposit non-tacky, flexible and tough films on the yarn. Starch products are widely used for sizing natural fibres (e.g. cotton) and the blends of synthetic with natural fibres. Since the viscosity of the native starch is generally too high, it must be converted to the required viscosity. Acid-modified starches, oxidized starches, oxidized starch esters and ethers (acetates, hydroxyethyl, hydroxypropyl, cyanoethyl, carboxymethyl ethers) and pregelatinized starch ethers are used in warp sizing. The stabilized starches (esters and ethers) are generally easier to disperse, have lower pasting temperatures, give stable viscosities and tend to give better film properties. They are also more readily removed in the desizing operation. Potato starch products produce films that are tougher and more flexible than the films of the corresponding cereal starch products and are preferred in sizing fine-count yarns.

5.6.2 Finishing textile fabrics

Starch products are traditionally used as finishing agents for completed textile fabrics to add weight, smooth, stiffness and strength to the cloth. The starch product fills in the interstices of the weave, thereby improving the "hand", body and general appearance of the cloth. The finishing operation involves passing the fabric through a dilute starch solution, squeezing and then drying.The starch finish is non-durable since it does not resist washing. Starch finishing is used for inexpensive fabrics, work clothing, white goods, book cloth, window shades and interlinings. Native starches, white dextrins, oxidized starches and acid-modified starches are used in textile finishing.

5.6.3 Printing

The function of starch products in textile printing is to thicken the solution of the dye and to act as a carrier for the colour. The thickener is used to provide good dispersion of the expensive dyestuff and helps to give a sharp transfer of the dye pattern to the cloth. Modified starches, such as dextrins and drum-dried crosslinked starch ethers, are used for this purpose (alone or in combinationw ith other thickeners).

5.7. Miscellaneous applications

5.7.1 Drilling muds

When bores are being drilled for the establishment of oil wells, a composite drilling mud is pumped down through the hollow drill and passes across the face of the drilling bit and then upwards into the bore. The purpose of the mud is to lubricate and cool the bit, to convey the drillings away upwards and to form an impervious wall around the bore hole. The mud is recirculated after the drillings have been removed. The muds consist of clay with additives to give necessary colloidal properties. Modified starches are used in the mud to give the correct viscosity and water-holding capacity. Since it is not convenient to have starch cooking equipment on an oil-drilling site, the usual product is a cold-water-swellable starch (drum-dried or extruded).

Preferably, pregelatinized potato starches (native or etherified) are used as fluid loss reducers and viscosifiers for drilling muds. They are superior to corresponding maize or wheat starch products. The choice is a balance of starch cost and water-holding capacity.

5.7.2 Flocculation applications

Flocculation agents are used in sewage treatment, water purification and as a sludge conditioner. Pregelatinized starches are employed as secondary flocculants in the purification of water for human consumption and for industrial waste water treatment. In most instances, potato based flocculation agents provide superior results as compared to corresponding products based on other starches. The flocculation efficiency of potato starch products has been related to their content of negatively charged phosphate ester groups. Although the ionic charge is not high, in aqueous solutions the repulsion of these charges very likely helps to untangle the individual starch molecules and to extend their sphere of influence. This extension or uncoiling of the branches of the anionic potato starch molecules would aid the flocculation of suspended particles by a bridging mechanism.

5.7.3 Various applications

Alimentary liquids (beer, cider, brewery yeasts and fermented liquids) are filtered with the use of potato starch and/or tapioca starch as a filter aid. Potato starch is preferred because of its large granule size.

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The large granule portion (15-40 micrometer) of wheat starch is useful as protective material for pressure sensitive microencapsulated coatings (NCR-carbonless copy paper).

Native starches are used as binders in ceiling tiles, fibreboard, insulating board and wall panels. They are incorporatedin the forming of the tile from slurry of wood fibre or mineral wool (silicate fibres). When the wet, formed tile is dried by heating, the starch gelatinizes and binds the tile together. Potato starch and tapioca starch are very effective as binders, thanks to their low pasting temperature and rapid increase in viscosity when the pasting temperature is reached.

Pregelatinized wheat starch products are used as binders in sand moulds for foundries.

Starch products are employed as binders, fillers and desintegrants in pharmaceutical tablets. Carboxymethyl potato starch ethers are very useful as desintegrants.

6 References

1. Industrial Starch Chemistry – Ir. J.J.M. Swinckels