Technical Bulletin

Borates in starch and dextrin adhesives

1. Introduction

The use of starch as an adhesive is not new. Literature reports that among many other uses the Egyptians used a starch adhesive as a bonding agent in the making of papyrus. Even today, we still prepare our own adhesive for use around the home. For example, the hanging of wallpaper can be done with an adhesive paste (starch) made by cooking some flour and water to the right consistency. Currently, starch- or dextrin-based adhesives are a most significant segment of the adhesive industry.

2. Sources

Starch is a natural polymeric product and is found in practically all plants. It serves as one of the essential foods for both animals and humans. Potatoes, wheat, and other grains were initially used as available sources of starch for domestic and industrial uses. Today, the principal sources of most commercial starches are corn, potato, tapioca, and wheat.

3. Chemistry of starches

This chemistry of starch based adhesives has become quite complex and many technological advances have been and are being made.

A major breakthrough in starch chemistry was made in the late 1930s when the Stein Hall* process was developed, replacing sodium silicate with a starch-based adhesive in the production of corrugated paper and paperboard. This process was covered by three basic U.S. patents: 2,051,025; 2,102,937; and 2,212,557.

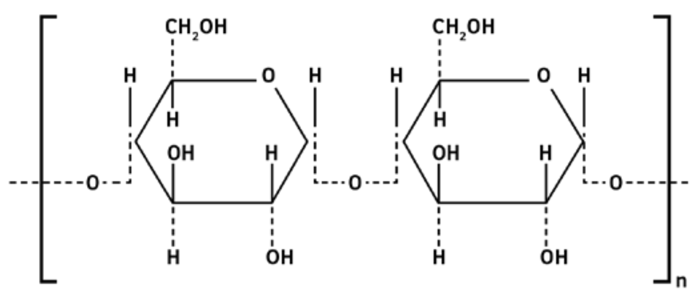
4. Chemistry of starch and starch-based adhesives

The specific effect of borax decahydrate, sodium metaborate or *Optibor*® boric acid in the preparation of adhesives from commercial starches is based upon the following chemical changes.

*The Stein Hall Process is so well known in the industry that a detailed discussion is not presented here. Should there arise specific questions in this area, substantial data is available on request. The process is still used today, but many improvements have been made to meet the ever increasing demands of the paper industry.

The chemical makeup of the starch polymer is shown in Figure 1.

Figure 1. Molecular structure of the starch polymer



In addition to the linear structure shown, the amylopectin portion of starch contains branched chains formed from the same recurring unit of Figure 1. In areas where several chains lie parallel, hydrogen bonding is extensive and crystalline regions are formed. This is shown in Figure 2.

Borates in starch and dextrin adhesives

When starch is heated with an aqueous solution of soda ash or caustic soda, swelling occurs as water penetrates the granule producing a complex system of starch nets filled with water molecules. The alkali hastens this process by breaking hydrogen bonding between starch chains and also through the formation of hydroxyl (alcohol) groups (Figure 3). The crystalline regions are dissipated in this process and a starch paste is formed.

When starch is treated with borax decahydrate, *Neobor*® borax pentahydrate, *Optibor* boric acid or sodium metaborate, more extensive chemical changes are brought about. Interchain linkages are probably formed through the borate anion structure as shown in Figure 4, resulting in desirable modifications of the physical properties of the system.

Figure 2. Arrangements of crystalline regions (heavy lines) and the primary valence chains uniting these in a single layer of a starch grain.

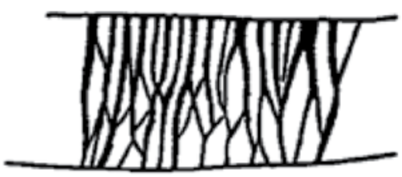
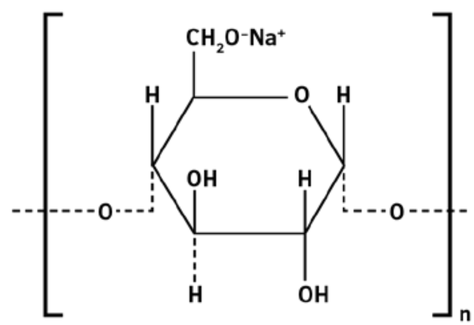
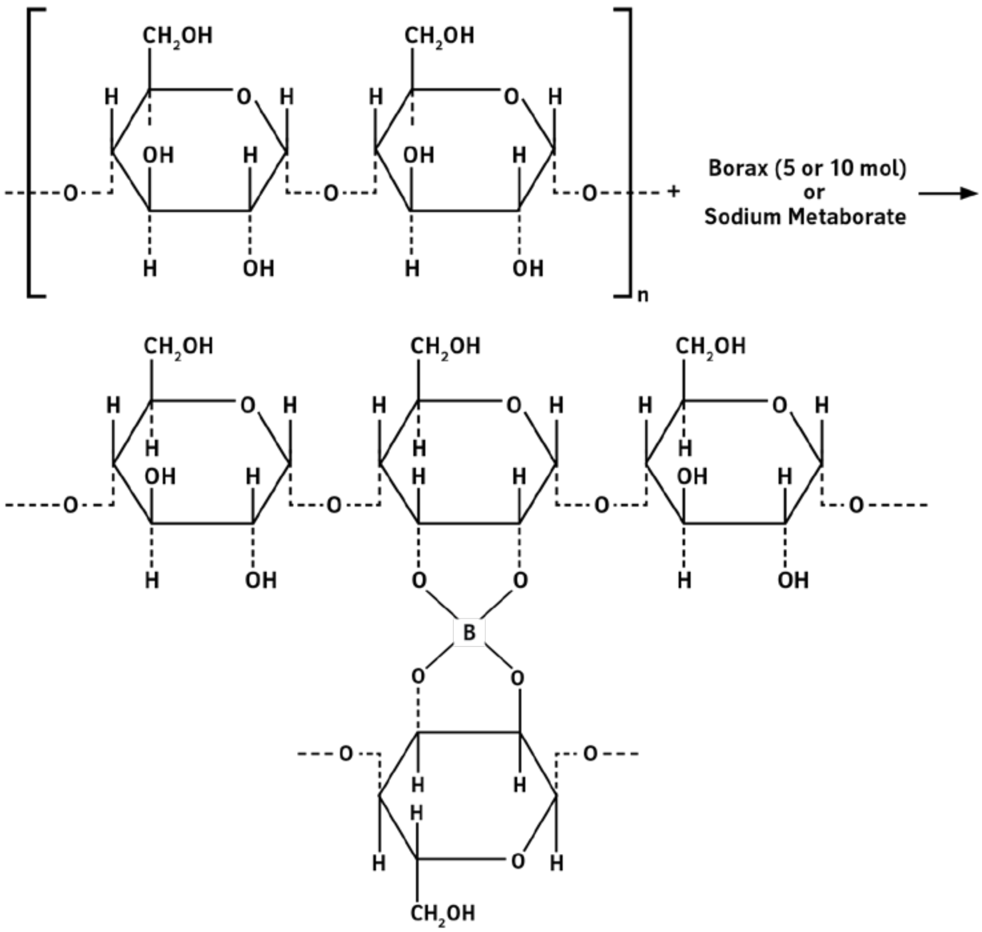


Figure 3. Reaction product of starch polymer and caustic soda.



Borates in starch and dextrin adhesives

Figure 4. The resultant complex molecule shown in Figure 4 is much larger than the graphical representation, extending its various branches in all directions. The structural formula is given to exhibit the linking mechanism only.



It is this change in the polymeric structure of the starch molecule, to a more highly branched chain polymer of higher molecular weigh. This in turn produces an adhesive with increased viscosity, quicker tack and better fluid properties. These qualities are essential for use in corrugated paperboard machines and other forming operations, where quick tack is vital at a reasonably low temperature to maintain the high operating speeds of such manufacturing procedures.

Starches can be broken down readily and inexpensively into a variety of degradation products using enzymes, acids, oxidizing agents and heat. These degradation products are hydrophilic and adhesive and can further be made into a wide range of adhesives of different viscosity and concentration adaptable to machines over a wide range of industrial applications.

Borates in starch and dextrin adhesives

Skeist (Reference) classified these degradation products as follows:
• Boiling starches
• Oxidized starches
• Dextrin

Dextrins may be further broken down to:
• White dextrin
• Canary
• Yellow dextrin
• British gums

5. Industrial applications

The starch and starch adhesive industry depends on unique characteristics imparted by the addition of borates in adhesives. A brief description of some important end uses demonstrating the multiplicity of the demanding performance characteristics of adhesives has been summarized from work reported by Irving Skeist in his “Handbook of Adhesives” published in 1964.

5.1 Corrugated boxboard

Skeist (l) makes the following comments and gives a typical starch formula:

“Originality of technical thinking was strongly demonstrated in the conception and development of a practical and efficient process for bonding corrugated board with a starch adhesive. This, the Stein-Hall Process has become the largest outlet for starch in the last quarter century.”

“The process makes starches competitive with sodium silicates. It takes advantage of the natural property of starch to gelatinize rapidly and with maximum viscosity within a limited temperature range. A concentrated suspension of starch granules — a fluid milk — is applied to the flutes of the corrugated board. They are swollen and burst there by the heat of the machine, in situ, in contact with the paper liner. A difficult initial problem was the development of a practical carrier to keep the starch granules in suspension. The answer was found in gelatinizing a fraction of the total starch by caustic soda. Other improvements included lowering the gelatinization temperature of the slurry with caustic; increasing the rate of gelatinization with borax; maintaining optimum viscosity of the ‘milk’ and its stability in the paste pans. Adequate heating was found to be essential since the use of starch required more heat than for silicate. The design and construction of special mixing equipment also evolved for the production of starch-based adhesives.”

“The following is a typical formula and directions for preparing a non-weatherproof paste:”

Two-Tank System - Henry Pratt Mixers - 333 gallons (1,260 L). Starch: corn

Upper Mixer (No.1)
(1) Add 400 lb (182 kg) of water which will bring the level to about 25 inches (63.5 cm) from top.
(2) Add 80 lb (36.3 kg) of starch and mix for 3 minutes.
(3) Dissolve 17 lb (7.7 kg) of caustic soda in 3 gallon (11.4 L) water in suitable containers; stop agitator and add this solution; start agitator and mix thoroughly.
(4) Heat with live steam to 160°F (or 71°C) and agitate for 15 minutes.
(5) Add 500 lb (227 kg) of cold water and agitate which should bring the level to about 6 inches (15.2 cm) from top.
(6) This diluted mixture is the completed carrier and is ready for use in the lower mixing tank (No. 2). Lower Mixer (No. 2):
(7) Fill with 1,520 lb (690 kg) of water, ie, about 18 inches (45.7 cm) from top.
(8) Add 10 lb (4.5 kg) of bentonite and mix thoroughly.
(9) Add 17 lb (7.7 kg) of Borax and mix until dissolved (2 to 3 minutes).
(10) Add 505 lb (229 kg) of starch and mix well until thoroughly dispersed.

(11) Drop contents of upper tank (No. 1) slowly into lower tank (No. 2) and agitate until viscosity reaches about 35 seconds. This is on the standard Stein-Hall viscosity tube.
(12) Add 1 one quarter (0.95 L) of formaldehyde or 1 lb (0.45 kg) of "Dowicide."
(13) Pump to storage tank.

Note: If heavier paste is desired, increase the quantity of starch in step 2 (5 lb or 2.25 kg should be ample). If thinner paste is desired, decrease quantity of starch in step 2 (5 lb or 2.25 kg should be sufficient).

"Frequently the entire mixing is done in tank No. 2."

"The vast corrugated board industry uses unmodified starch. The corn starch producers supplying this industry have been active in meeting its needs for ever increasing rates of production and a demand for weatherproof board."

"In other paper gluing fields, adhesive requirements are met principally by modified starches, ie, thin boiling, oxidized, and dextrin, in addition to borax."

5.2 Paper bags (grocery and multi-wall)

One of the large consumers of starch based adhesives is the paper bag industry. Of the many types of bags, grocery and multi wall consume the most adhesive.

Adhesives for grocery bags may be divided into two types: seam and bottom.

A seam adhesive must be fluid, tacky, non foaming and fairly stable in viscosity. It may be derived from a thin boiling starch, an oxidized starch, or from a dextrin. In addition to borax, sodium metaborate, soda ash, and metasilicate, are blended in by the manufacturer. The bag maker may add other chemicals such as caustic soda, clay, or preservative to help achieve the maximum efficiency for the particular type of machine applying the adhesive. A formula working well on one machine will fail on another. Here, as in all other fields of gluing, there is no substitute for practical experience. Fortunately, much information is available from the leading producers and distributors of starch-based adhesives.

Bottom pastes for grocery and sack bags have a number of requirements:

- They should be sufficiently thixotropic to keep the paste roll covered without breaking down appreciably under the roll action
- They should adhere sufficiently and release well from the stencil applying the paste
- They should have enough wet tack to hold the bottoms closed until the bags are bundled, wrapped or weighted
- They must form a good dry bond

The adhesive can be derived from starch and dextrin, or from thin boiling or oxidized starch. Depending on conditions, bottom pastes containing 15-25% solids may be prepared using caustic soda, clay, soap, tallow, and sulfonated oils.

Multi wall bag adhesives are used in the fabrication of large kraft bags having from two to six walls. They may have a variety of configurations: sewn tops and bottoms, sewn bottoms and open mouths, pasted tops and bottoms, or pasted bottoms and open mouths. Three types of adhesives are required: Seam, cross or ply pasting, and bottoming. For seam and bottom operations, the adhesives are further divided into non water resistant and water resistant types.

5.3 Paper boxes

Large amounts of dextrin—mostly borated—are used in making paper boxes. The operations are classified as ending, stripping, tight wrap, and loose wrap.

Ending: This operation involves the formation of the box body. The adhesive must be thin bodied at high solids without being gummy or stringy. Furthermore, it must wet the board without soaking it under pressure. Ending demands very close tolerances in an adhesive.

Stripping: In this operation, the sides and covers of the boxes are wrapped with paper. It is a slow operation involving much skilled handwork. An appreciable time lapse exists between the gumming of the wrap and its application to the box where it is rubbed smooth and the edges turned in by hand. Cold water-soluble adhesives composed of 85-90% dextrin and 10-15% borax are used to a considerable extent, adding 3-4 parts of water per part solids, to the desired viscosity.

In some instances where high quality wrap papers are used, gums from highly soluble thin dextrins are employed at only 2 parts of water. Automatic stripping at higher speeds takes less than 2 parts.

Tight wrap: Die cut papers (wrap) of the exact size and shape for the boxes to be covered are automatically fed one at a time over a glue roll applying the proper amount of adhesive. The wraps then pass along a suction belt which prevent the papers from curling until they reach the operator. This operator controls the number of wraps on the belt so that they will have the correct tack and temper when he puts the boxes or covers on them. At this point they must stick to the boxes or covers. A plunger then presses the boxes through rollers and brushes, completing the operation.

Starch based adhesives used in this process are usually high solubility/low viscosity types blended with borax (10 - 15%) and high in solids (40 - 55%). They must have adequate tack, low foaming, and impart minimum wrapping (dimensional changes). Running temperatures may be as high as 120°F (50°C) thus permitting higher solids and less wrapping.

Loose wrap: This operation is similar to tight wrap except that the adhesive is applied only to the border of the wrap.

5.4 Carton sealing

In this operation the adhesives must seal the top and bottom flaps of small knockdown paper boxes. A variety of adhesives is used. In bottom gluing adhesive is applied by roller to the two long flaps, and the small flaps are turned in. One long gummed flap is turned in and glued to the small flaps, then the other long flap is folded in and glued to the first one. Lastly, the carton is placed on a conveyor and sent to the filling station where the weight of the filling helps to seal the bottom. Although top sealing is more complicated, the principle is similar. The only pressure applied comes from the conveyor belts with none coming from the inside. In this application, adhesive should be free flowing, stable in viscosity and give good closure.

5.5 Case sealing

Case sealing consists of the gluing of both top and bottom flaps of corrugated or solid fiber cases by hand or machine. In machine sealing the adhesive is applied to top and bottom flaps simultaneously in 2 to 5 inches from rolls set horizontally or vertically. The chief factor in the selection of the proper case sealing adhesive is compression time. In one type of case, designed for easy opening, adhesive is applied only to the corners of the flap by cam operation of the gum rolls.

Frequently a case sealing adhesive based on starch modifications will run high in caustic soda content and can be used wherever staining is of little consequence. Liquid starch based adhesives are favored in this trade for both carton and case sealing.

Borates in starch and dextrin adhesives

5.6 Tube winding

This field is a large consumer of liquid starch-based adhesives ie, thin-boiling starches, dextrins, borax, and caustic. There are two main classifications of tubes: Convolute and spiral. A convolute tube is made by winding on a mandrel (similar to the rolling up of a window shade) with the adhesive applied to one or both sides of the paper or board. In automatic winding applications the sheet or board is fed from continuous rolls with one end edge sanded or feathered. Then adhesive is applied to both sides. It is turned on a mandrel, layer by layer typically for three to six wraps. The last wrap has the feathered edge and forms a tube with no sharp break. After the tubes are pushed off the mandrel, they are stacked to dry.

A different type of convolute tube is used for product containers where adhesive is applied to one side only, while a mandrel grips the board and spins the desired number of wraps. The inner surface, in contact with the mandrel, is ungummed. After winding, the tube is given a revolving press operation, at which point it may be labeled by bringing it in contact with the gummed outer surface.

Spiral tubes are wound spiral fashion on a mandrel with an almost unlimited number of plies and may vary from a soda straw to a huge tube for holding concrete. Generally, the innermost ply has no adhesive. Successive plies may have one or both sides gummed while the outermost layer is left without external adhesive to prevent it from adhering to the conveyor belting.

In tube winding, critical adhesives specifications include free flow and the correct tack for the speed of running and length of cutoff.

5.7 Laminated paper board

Once a large consumer of thin-boiling starch and borax adhesive, the laminating of paper has been seriously invaded by synthetic adhesives and clay extender owing to the unusually favorable spreads obtained.

5.8 Gummed tape (water re-moistening)

These adhesives are of a specially modified dextrin type and well plasticized. Critical specifications for tape requires quick and strong initial tack and high permanent strength of bond, together with high gloss and flexibility of film. Tape adhesives based on potato starch, similar to products from waxy maize and tapioca are commonly used.

Vegetable-type tape adhesives are applied hot at high solids (about 50%) to the kraft paper forming the tape rolls.

5.9 Gummed paper (water re-moistening)

Starch based highly soluble adhesives such as dextrins control viscosity by means of enzymes and find considerable use in gumming paper for labels and postage stamps. Film color, shine, and re-moistening properties play important industrial roles, along with viscosity and viscous stability. A workable viscosity at extremely high solids is necessary to provide sufficient weight of dry gum film per ream without excessive wetting and dimensional changes in the paper base. Probably the most familiar and certainly an extensive use of gummed paper made with dextrins is in the manufacture of envelopes.

5.10 Textiles

Second to the paper industry in the consumption of starch is the textile industry. Considered strictly as an adhesive the role of starch and starch based products is here akin to that in paper making where fibers are bound together or coated and surface films are promoted.

Cotton wrap sizing is still a very large field for heavy boiling and thin boiling starch. The sizing of wrap fibers improves weaving efficiency by formation of a tough and readily removable film on the wrap. The low cost of starch has more than counterbalanced its natural deficiencies as a film former in comparison to many of the synthetics.

Borates in starch and dextrin adhesives

However, starch is under increasingly severe competition, and research on starch in wrap sizing has been relatively unproductive. This is true to an even greater degree in other fields in textiles such as finishing. In textiles, the use of starch in large tonnage has narrowed to the sizing of cotton wraps. For the most part, synthetic fiber wraps are incompatible with starch.

In recent years homogenization of heavy boiling corn starch solutions by mechanical means through conversion of high pressure energy to kinetic energy has been successfully applied in many textile mills.

The following are typical wrap size formulations used in southern mills:

Denims

- 80 lb (36.3 kg) of pearl starch to 106 gallons (401 liters) of finished size
- 15 lb (6.8 kg) of softener—tallow, sulfonated oil, calcium chloride
- 2 pints (0.94 liter) of kerosene cooked to 190°F (or 88°C) and homogenized at 2000 psi (136 atmospheres)

Sateen

- 160 lb (72.6 kg) of starch to 225 gallons (852 L) of finished size
- 5 lb (2.3 kg) of a special softener
- 1 pint (0.47 liter) of kerosene
- Cooked to 200°F (or 93°C) and homogenized at 4000 psi (272 atmospheres)

The laundry industry is another substantial consumer of starch (specifically heavy boiling starch). Its adhesive properties combined with stiffening and soil protection can be achieved effectively, attractively, and inexpensively. Wheat starch has been pre-eminent in the laundering of men's shirts. Numerous special laundry starches are produced for this purpose) used both in liquid state and in cold water dispersible form.

Reference

Handbook of Adhesives, Irving Skeist 3rd printing, Rheinhold Publishing Corporation, February 1964.

Borates in starch and dextrin adhesives

About U.S. Borax

U.S. Borax, part of Rio Tinto, is a global leader in the supply and science of borates—naturally-occurring minerals containing boron and other elements. We are 1,000 people serving 500 customers with more than 1,700 delivery locations globally. We supply 30% of the world's need for refined borates from our world-class mine in Boron, California, about 100 miles northeast of Los Angeles. We pioneer the elements of modern living, including:

- Minerals that make a difference: Consistent product quality secured by ISO 9001:2015 registration of its integrated quality management systems
- People who make a difference: Experts in borate chemistry, technical support, and customer service
- Solutions that make a difference: Strategic inventory placement and long-term contracts with shippers to ensure supply reliability

About *20 Mule Team*® products

20 Mule Team borates are produced from naturally occurring minerals and have an excellent reputation for safety when used as directed. Borates are essential nutrients for plants and key ingredients in fiberglass, glass, ceramics, detergents, fertilizers, wood preservatives, flame retardants, and personal care products.

Borax Decahydrate

Optibor®

Neobor®

Sodium Metaborate