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A Comparison

of

the Methods Used to Produce

WATER-RESISTANT STARCH COATINGS

by

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for

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Western Michigan College of Education

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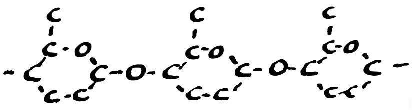
PART I

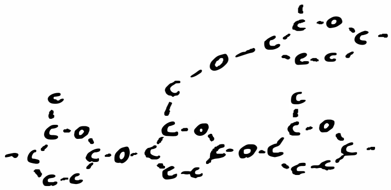
Literature Survey

The use of starch in the coating of paper has been very extensive. The reason being that starch and its conversion products have most of the desirable charactistics of a coating adhesive and are relatively inexpensive. Only one main charactistic is missing in coatings made with starch and that is the lack of water resistance. For many years the paper industry, the adhesive industry, and the textile industry have searched for a method of modifying starch so as to increase its water resistance. A great many processes have developed from these studies. These processes consist of blocking the hydroxyl group of the starch by the use of cross linkage or by the use of a protective water resistant substance either over or mixed through the starch. This is achieved by the use of antimony salts(8, 12, 13), urea formaldehyde resins (6, 7, 9, 14, 15, 21, 22, 29, 33), formaldehyde(23, 24, 2, 27), melamine formaldehyde resins (10, 28, 34), phenol formaldehyde resins (25), chromic salts (4, 5, 16, 17, 18), silicates (1), ester gum emulsion (11), polyvinyl alcohols (30, 31), nitro cellulose (3), latices (32), and various synthetic resins(26). These methods vary in ease of application and results accomplished. There are many other methods of water proofing starch but most of them are not applicable to starch coatings.

To understand the theory of various methods a little knowledge of the structure and nature of starch is valuable. Starch consists of two types of molecules, amylose which is a straight chain molecule and amylopectine which is a branched chain molecule (20).



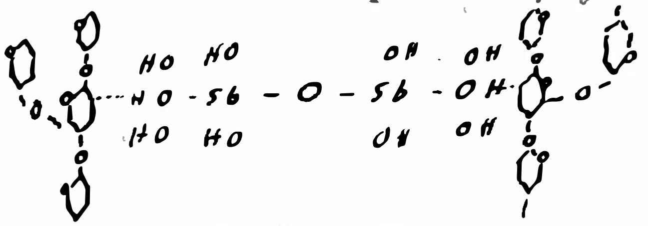
amylose



amylopectin

These molecules are present in different proportions in various starches. In unmodified corn starch the ratio is 25% amylose to 75% amylopectin while waxy maize starch is mostly amylopectin. The amylopectin is the least water soluble and has more of a tendency to form cross linkages. The tendency of starch to disperse in water is due to its hydroxyl groups, therefor the blocking of these groups gives the starch water resistant properties. This is what happens in the first process considered.

The use of antimony salts is discribed by N. M. Frisch and his colleagues in their article(8) and by numerous patents(12, 13). The most useful of the antimony salts is potassium pyroantimonate ($K_2H_2Sb_2O_7$). It can be used on starches modified by wet acid conversion, dextrinization, oxidation, and enzyme conversion but the more degraded the starch the less water resistance to be found in the finished product. The reaction of the salt with starch is through the hydrogen bond, with the elimination of potassium hydroxide.



Judging from this the ratio by weight of starch to salt should be 1.5 to 1, but it has been found by Frisch and his colleagues that 10% of the salt gives good results in the laboratory and in the mill. The amount of water resistance increases with the amount of potassium pyroantimonate used. If the salt is present during the conversion cook, the water resistance will increase but there is a tendency for the mixture to gel. This may be offset by the use of a plasticizer such as urea or dicyandiamide or a thinning agent such as antimony trifloride, ammonium oxalate, or acetic acid.

In the preparation of the coating color the clay is slipped as routine, the starch is converted, and the two are blended. At this point the salt is added. Then the color, defoamer, and plasticizer are mixed into the coating. It is necessary to adjust the pH to the 7.0-7.7 range. The most difficult part of the method is the drying requirements. For good curing the applied coating should be dried for 30-120 seconds at 200-220°F. Any increase in time or temperature will increase the water resistance. Stearate soaps need to be avoided but preservatives, flamproofing agents, and latices are compatible. During the normal storage time, 4-5 hours at 170-180°F., no problems occur.

One of the oldest and best known method of increasing the water resistance of starch is by the use of urea formaldehyde resins. The water soluble or water dispersible type of resin is used, obtainable commercially as a dry powder or as a high concentration solution. The resin combines with the hydroxyl groups of the starch eliminating water and creating cross linkages(7, 19). Thus the more highly converted the starch used, the greater number hydroxyl groups present, and the more resin required to achieve adequate water resistance. The amount of resin needed is low when only starch and resin ✓ are involved but when clay is added the amount of resin increases, due to the dilution effect, to 15-30% of the starch. The clay slip and converted starch are prepared as usual and blended. The resin is added with good agitation at 120°F. or lower and the acid, 10-50% of resin, is mixed in with the resulting pH adjusted to 5-7.

The colloidial change in the starch brought about by the resin also improves many other charactistics such as decreased shrinkage, higher gloss, and increased cohesiveness(22). ✓

This method had a great many problems at first, most of which have been overcome. Some of the remaining problems that should be solved are adhesive strength of starch resin binders, binder systems that would be suitable for higher pH, and a more rapid cure.

There are a few processes whereby formaldehyde is the reaction agent. The aldehyde enters the starch granule to form a complex with the hydroxyl groups. As the starch molecule swells water molecules enter the network and further expand the molecule when heated. As the network expands aldehydes combine with the hydroxyl groups until the chains are loaded with aldehydes. The association is weak and easily reversible but as the reaction proceeds the bond becomes more stable(19).

One of these methods is the treatment of dehydrated starch (275°F. for 20 hours) with commercial formaldehyde, formalin, in equal weights(23). To this mixture is added andacid,such as HCl, to a pH of 2 or lower. If the starch is dried under vacumn of 29-30 inches at 140°C. for 24 hours and then treated as above, a nearly colorless, water resistant adhesive is formed.

Another method involving the use of formaldehyde is by the use of an alkali starch. This starch is prepared by placing 1000 parts of starch in a dextrin cooker and injecting 3.5 parts of ammonia over the space of 1 hour. Heat is gradually raised to 300°F. in 8 hours and maintained for 15 hours with an excess of ammonia and steam being added. For coating, 5-10 parts of the modified starch are mixed with 100 parts water at 70°C. and applied to sheet. Formalin and HCl are then applied separately or together with the amount of formalin equaling the amount of starch and the acid being in the proportion of 2-12 parts by weight of 8.8% HCl to 100 parts of starch.

Melamine formaldehyde resins are in little use. There use is covered by three main patents, Widmer(34), Glarum(10), and Rohm and Haas(28). The starch is reacted with a melamine formaldehyde condensation product and an ammonium salt(34).

A water soluble resin of the phenol formaldehyde group may be used to insolubilize starch. The starch is added to water, 150 grams to 2 liters, and is made basic with 200 cc. of 5% NaOH.

More water, 2 liters, and more NaOH is added. Then 650cc. of phenol and 650 cc. of formaldehyde are mixed in and heated to 200°F for about 45 minutes. By trial and error the reaction is stopped just before a sample of the mixture is insoluble in water. The adhesive is then used in coating and the heat of drying insolubilizes the starch.

There are methods of making starch coating water resistant by the use of chromic salts of complex chromic componds. One of these methods is the process of blocking the hydroxyl groups by the use of chromic salts of organic acids or chromic halides(4). The theory being that the cations of the ionized chromic salts polymerize to form aggrigates of large size upon drying. These combine with and block the hydroxyl groups. The starch is heated with 5-.0% chromic acetate and the solution is applied to coating surface. It is partially dried and passed through alkaline solution after which it is thoroughly dried. The coating after drying should be alkaline.

Another process involves the treating of coated starch with a vapor of 2% by volume of chromyl or stannic chlorides for 1 second to 2 minutes and drying at 35 to 200°C. depending on the time exposed to the heat or treating with a solution of chromyl or stannic chlorides in CCl_4, ethylene dichloride, or n-heptane for one second with subsequent drying at 110°C. for two minutes.(17)

Starch is also rendered water resistant by treatment with a water soluble complex chromium compound of the Werner type. The starch is treated with 5-20% of stearto chromic chloride or abietato chromic chloride at a pH of 4.5-6.0 and then clay is added.(16)

If starch is treated with a soluble sodium silicate, water resistance is increased(1). 100 parts of starch is mixed with 4 parts of a weak organic acid that has in it 0.4 parts of a strong mineral acid. The acids are sprayed into the mixing chamber. The mixture is stored at 30°C. for 36 hours and is neutralized by ammonia spray. 10 parts of meta disilicate, $Na_2Si_2O_5$, is blended into the mixture. 24 parts of this is mixed with 75 parts of water and boiled then blended with clay slip of 100 parts clay in 60 parts of water.

A method of coating was developed by W. L. Graig(11) by which in one tank are mixed 60# of water, 10# 26°Be. ammonia, and 20# dry weight of converted starch, in another tank are mixed 100# of ester gum, 50# of a mineral oil, and 10# of oleic acid. These two are blended and the emulsion diluted with 160# of water . This is incorporated in a mixture of 310# dry weight of converted starch in 1200# coating clay. Upon application this produces a wettable water resistant surface.

Polyvinyl alcohol may be used to protect the starch as in the production of adhesives. Finely divided unswollen starch is suspended in a aquous solution of polyvinyl alcohol, .8-10%. The relation of starch to alcohol being 10:90 to 40:60. They are mixed at 30°C. and are cured at 90-130°C (31).

Polyvinyl alcohol may also be used in a process whereby the paper is treated with a starch solution containing water soluble methylol-melamine, 1-25 parts per 100 parts of starch; a polyvinyl alcohol, 1-25 parts per 75 parts of starch; and an ammonium salt of a mineral acid, and dried(30).

Latices are becoming useful in coatin adhesives and some of these can be incorporated with small amounts of starch(26,32) Appreciable amounts of starch however in a latex or synthetic resin causes the water resistance to lower or become nonexistant.

The starch coating may even be protected by a coating of nitro-cellulose(3).

In conclusion the processes involving the use of antimony salts, urea formaldehyde, and the chromic salts appear to be the best developed methods for increasing the water resistance of starch coatings.

EXPERIMENTAL SECTION.

Introduction. After the various methods of increasing the water-resistance of starch coatings were studied, the author attempted to duplicate the results in the laboratory and therefore obtain a comparison between these methods. It was decided that two experiments should be considered at a time so that some comparison would always be available. The first set was to be the use of urea-formaldehyde resins(7) and antimony salts(8). The other methods were split also but due to the limitation of time and the necessity of setting up standard laboratory procedure by experimentation, only the first set of experiments were studied.

Standard Procedures.

Clay Slurry. The clay slurry was made up in a Day Blender with H T clay and distilled water in a proportion to give a very high consistancy. After considerable agitation, the slurry was diluted to about 70% clay and 0.5% of sodium hexa meta phosphate was added as a dispersing agent. This slurry was used throughout the study with drill press agitation and dilution to make up for evaporation carried out each time there was experimentation. Undissolved particles were removed with a sixty mesh screen.

Starch Conversion. In order to prepare a 20% starch solution, 100 grams of bone dry (111 grams of 11% moisture) corn starch was thoroughly mixed with 400 grams of distilled water and 0.5% of a commercial alpha enzyme (Amyliq Concentrate, Wallerstein Co., New York) was added. This mixture was agitated with a small laboratory mixer equipped with a glass stirrer and was contained in a stainless steel beaker to eliminate any contamination. The temperature was raised by means of a water bath to 76 degrees Centigrade in 30 minutes. This conversion temperature was held for 15 minutes and then the enzyme was killed by boiling the mixture for 10 minutes. Large particles were removed by a sixty mesh screen. Until the starch was used it was kept in solution by agitation.

Preparation of Coating Colors. In order to determine the solid content of the clay and starch mixtures, 10 ml. of each was placed in evaporating dishes and dried. After weighing, the solids per millileter was calculated. From this data the coating colors were prepared. These were made up to a 50% solids content. The starch was calculated as 18% of the clay. The amount of material used for increasing the water resistance was based on a percentage of the starch. The order of addition was clay, starch, dilution water, waterproofing agent, and catalyst if needed.

Coating Procedure. Upon the application of a coating color to a standard sheet by the use of various laboratory methods, and subsequent examination by the use of a black light, it was found that a wire wound doctor blade used in conjunction with a vacuum plate sheet holder was the best method as to even application and reproducable results. The coating was applied to a 8 by 11 inch sheet of 50 lb. (25x36-500) coating raw stock having a size of 20-40 seconds ink penetration.

Curing of Samples. After coating, the samples were dried in a oven at 100 degrees Centigrade for two to five minutes. The oven door was kept open to permit circulation. Samples were tested and then allowed to condition in a room at $\overset{23}{70}$ degrees Fahrenheit and 50% Relative Humidity for a time necessary to bring about full curing.

Wet Rub Test. Various tests were attempted to determine the wet rub resistance of the coatings. Because of the necessity of a swift, easy to perform test, it was decided to use the following; the sample tested was submerged in distilled water at room temperature and rubbed with the finger until coating was removed from the surface. The time from submerging the sample until coating failed was taken in seconds and recorded. This test was not exact and was not reproducable by another operator but for the purpose of comparisons the test was found to be quite sufficient.

Variables. It was decided to vary the material used, per cent of material, curing time, and in some cases the type and per cent of catalyst. All other factors were held constant as far as possible by the use of the standard procedures given above.

Methods Used.

Antimony Salt. The preparation of coatings using potassium pyro antimonate was according to the method outlined in the literature survey (8) and according to the standard procedures set up. The amount of the salt used was based on a percentage of the starch, from 0-20% in increments of five. All the coated sheets were dried for two minutes at 100 degrees Centigrade.

Urea Formaldehyde Resin. The use of a urea formaldehyde resin (7) in increasing the water resistance of starch coatings was done according to the procedures set up. The resin was a 65% solids aquas solution of P-631 Plyamine Resin BU-759, manufactured by Reichold Chemical Company. This resin was added to the coating color in increments of 5% in the range of 0-30% based on the starch. Two catalysts were used, ammonium chloride and diammonium phosphate. Upon the addition of 25% of the ammonium chloride the viscosity of the coating color increased greatly. The use of diammonium phosphate in the range of 25%, caused no change in the physical characteristics of the mixtures. The clay and starch were blended and the resin was added. After agitation the latent acid catalyst was mixed in and samples were coated. The samples were cured in a oven at 100 degrees Centigrade for 2, 3, 4, or5 minutes, tested and stored in a constant temperature-humidity room.

Results.

No results were obtained in the use of the potassium pyro antimonate because of the insolubility of the salt available. It was found that a hydrate of the salt ($K_2H_2Sb_2O_7 \cdot XH_2O$) should be used in these experiments so that enough could be dissolved to bring about a reaction.

The urea formaldehyde resin gave wet rub resistance at certain percentages and after a curing time. It was found that curing in the oven had little effect while curing in a constant temperature-humidity room over a long length of time brought about a reaction.

The effect of curing time on the wet rub resistance of various percentages of urea formaldehyde resin coatings:

%Resin	2 Minutes (oven)	one week	two weeks	three weeks
10%	0 sec.	0 sec.	0 sec.	0 sec.
15%	0 sec.	0 sec.	0 sec.	0 sec.
20%	0 sec.	0 sec.	8 sec.	100 sec.
25%	0 sec.	0 sec.	-	over 300
30%	0 sec.	4 sec.	over 300	25 sec.

The decline of wet rub resistance was due to an excess of catalyst. The results obtained with the use of ammonium chloride showed the same trend but were discarded because of the high viscosity of the coating color.

Conclusions.

It was found that water resistance could be obtained by the use of a water soluble urea formaldehyde resin under certain conditions but that a great many factors were involved. No comparison of methods could be made from the data obtained. Possible the most important aspect of this work was the setting up of standard laboratory procedures that may be useful to others working in this field.

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June 1, 1951

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