

SELECTION OF CONTROLLED RELEASE COATINGS

-STARCHES-

by Harlan S. Hall

In this paper, I would like to discuss the selection of coating materials for controlled release applications. Often, one will have an active material, which has certain desirable properties as a pesticide, and one or more undesirable properties. It is possible, or even likely, that coating (encapsulating) the active with a properly selected film can negate the undesirable properties. The question then is, "How does one select the proper film from the literally thousands available?"

In the brief time allotted, I cannot deal with this question in a comprehensive manner, but I would like to mention some of the classes of materials available and discuss one class in greater detail.

First, let me mention the various types of natural polymers and their derivatives. Starch, or more properly starches, constitutes a large group of natural polymers. This group will be discussed later. Cellulose and its derivatives also constitute a very large group. Cellulose derivatives cover a tremendous range of properties including water soluble, (hydroxypropyl cellulose, methylcellulose, and salts of carboxymethylcellulose) water resistant and durable (ethyl-cellulose, cellulose acetate, and cellulose acetate butyrate), pH sensitive (cellulose acetate phthalate) and even thermoplastic (hydroxypropyl cellulose). Cellulose nitrates and xanthates can be regenerated to yield pure cellulose films (cellophane).

Vegetable gums, exclusive of starches and cellulose, still make up a very large group. Industrial Gums by Whistler divides these gums in subgroups including seaweed extracts (algin, carrageenan), plant exudates (gum Arabic, gum karaya), seed gums (guar, locust bean), and plant extracts (pectin).

Both plants and animals yield proteins including soy protein, zein (corn protein), and collagen and gelatin. I also include amino acid derivatives in this group, such as polyglutamic acid. Casein, milk protein, is an excellent film former and is used in paints and glues. Other animal derived materials include chitosan, derived from chitin, the shell material of crustaceans, and shellac, which is the protective substance secreted by the lac insect of Asia.

Yet another category of materials is waxes. In Industrial Waxes- Vol. I, Bennett lists thirteen commercially important vegetable waxes (candelilla, carnauba), five animal waxes (beeswax, spermaceti), and six specific mineral waxes (montan, ozocerite) as well as a huge variety of paraffin and microcrystalline waxes. Synthetic waxes fill the entire last half of the book.

One last category of natural minerals, which can be used as coating is clays. The variety of clays is almost mind boggling, including kaolinites, montmorillonites, illites, attapulgites, and bentonites.

After all this, we have yet to consider plastics. As everyone here knows, the range of properties available in synthetic polymers is almost without limit. Suffice it to say that it is beyond the scope of this paper to even list them here. For those who wish to pursue this area, the Guide to Plastics published by Modern Plastics lists 35 categories of plastics, and the 1974 edition of Trade Designations of Plastics by the Department of Defense lists over 7,000 entries.

For today, I would like to dwell on one of these categories, starches and their derivatives. If one considers starch as grocery store variety cornstarch, one is overlooking a wide variety of materials, which may be the answer to your problem. Since starches are usable as foods, it is probably natural that a great deal of the available information has been generated by the food industry. Other major resources for information and data on starch derivatives are the paper and adhesive industries.

Before we get into the properties of starches and starch derivatives and the films cast by them let me list the more common sources of starches.

maize	waxy maize
tapioca	potato
milo	arrow root
wheat	rice

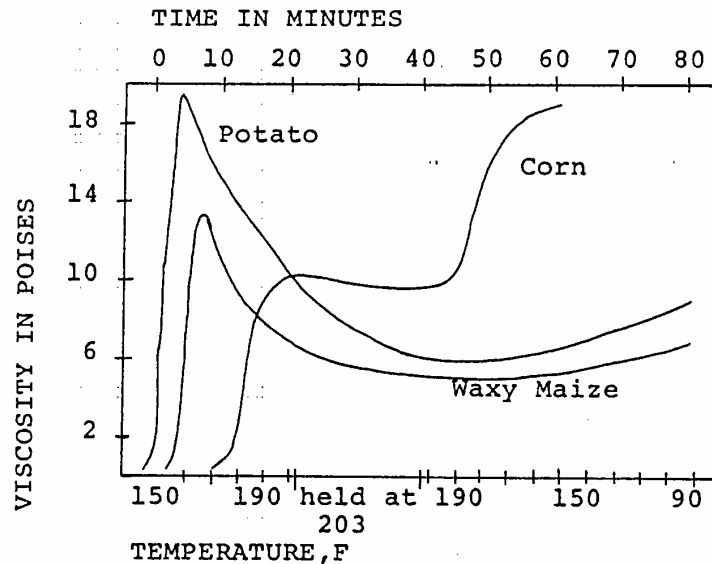
Starches derived from the various sources are not all the same. Starch grains from each source are distinctive enough to be physically separated under a microscope and each has its own characteristics when pasted and cast as a film. Starches vary in grain size, grain shape, gelatinization temperature, proportion of amylose to amylopectin, and film forming properties. The rheological properties of the pasted starches from different sources also varies greatly. Table 1 lists the percent amylose and gelatinization temperature for several unmodified starches. (1)

Table 1: Characteristics of Starch Granules

<u>Starch</u>	<u>Amylose (%)</u>	<u>Gelatinization Temperature (F)</u>
Corn	28	176 degrees
Waxy Corn	0-6	165 degrees
Potato	23	147 degrees
Tapioca	18	145 degrees
Sago	27	165 degrees
Wheat	25	170 degrees
Rice	17	178 degrees

Figure 1 is a graph of viscosity versus temperature for three starches taken through a heating and cooling cycle. When a starch and water slurry is heated, no change in viscosity occurs until the starch granules begin to imbibe water and swell. The temperature at which this begins to occur is the gelatinization temperature. As the cooking cycle progresses, the gelatinization is completed which is shown as a viscosity peak. Further heating results in viscosity drop. When the temperature begins to drop, starches increase in viscosity and many will gel. The ability of starches to gel is a function of the amylose content.

Figure 1:



As Table 1 indicates, starches vary considerably in amylose content. The other major component of starch is amylopectin. Amylose is a linear polymer of glucose and linear chains are capable of molecular association. This association must be overcome to cause starches to gelatinize. This energy input is the cooking or pasting process. When the aqueous paste is allowed to cool, the amylose chains will reassociate, forming a gel. Amylose is capable of forming tough flexible films.

Amylopectin is a highly branched polymer of glucose and its branched structure prevents the formation of hydrogen bonds between polymer chains and is the reason amylopectin does not gel. Because amylopectin cannot form associated networks and gel, it is highly soluble in cold water and does not have the film forming properties of amylose. Pastes of amylopectin are normally much more clear than those of amylose.

Table 2 demonstrates the effect of varying amylose content on the films. Wolff, et al. (3) prepared films varying in amylose content from 95% to 6% and did a series of tests on those films. As the data indicates, the tensile strength, elongation, and folding endurance are proportional to the amylose content.

Table 2: Films From Amylose/Amylopectin

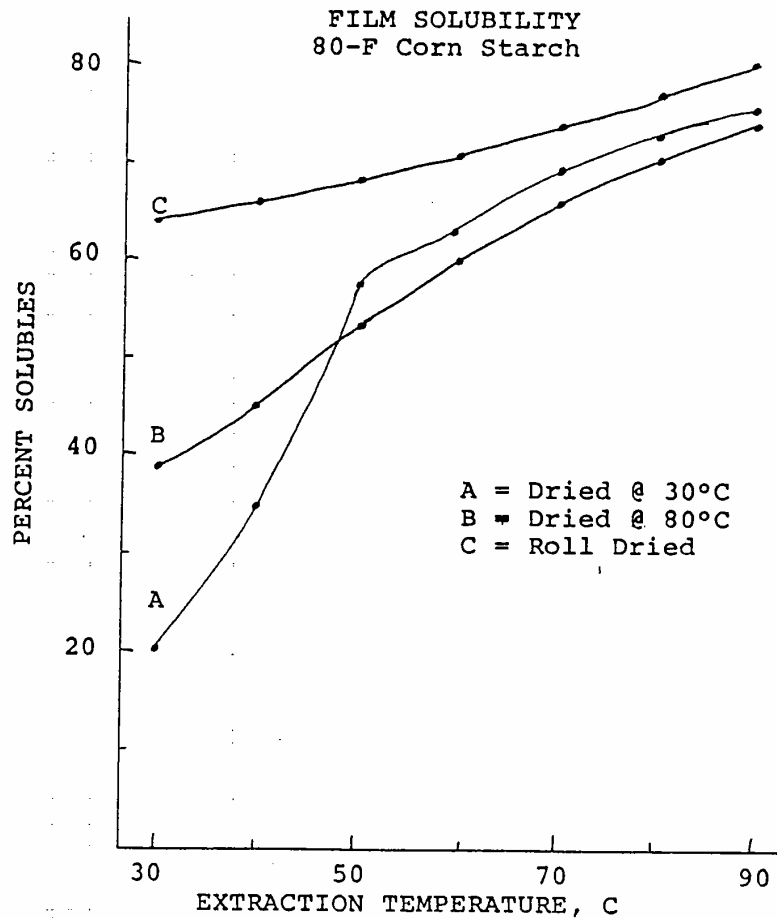
<u>Amylose Content</u>	<u>(Kg/sq. mm) Tensile Str.</u>	<u>Ultimate Elongation</u>	<u>Schopper Folds</u>
95%	7.1	23%	960
77%	6.0	11%	450
50%	6.0	6%	100
24%	5.3	5%	19
6%	5.0	5%	14

Most starches sold are modified in some manner to enhance or introduce particular properties. One of the most obvious modifications is the fractionation of starch into amylose and amylopectin. The problem with this is that one must disrupt the starch grain, cook the starch, to separate the fractions. Many of the other widely used modifications can be performed on the intact starch granule. Other methods used to vary the properties of starches include the formation of ethers, esters, and graft copolymers, acid modification, dextrinizing, oxidizing, and crosslinking. One should note that

starches may be crosslinked in the granular form which will alter the cooking properties, or in the final film which will change the properties of the film.

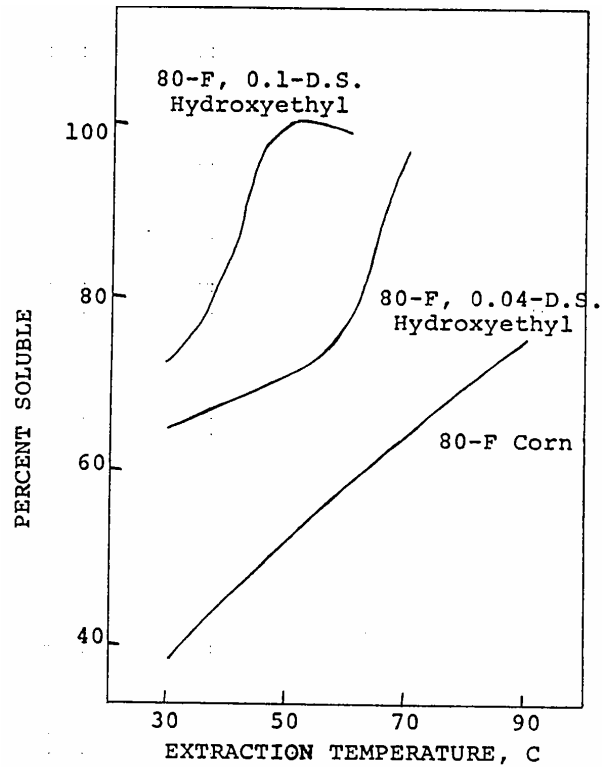
After the starch is pasted, there are still opportunities to alter the film properties. Films of 80-F corn starch (acid modified) were cast by Hull and Schoch. (2) The conditions were standardized except for the drying conditions, which were intentionally varied. Low temperature drying takes longer, allowing the amylose to form a gel network in the drying process. Because of the gel network, films dried at lower temperatures are more difficult to redissolve. This is reflected in Figure 2 showing the solubility of films cast under differing conditions. When the test is performed with water at 30 degrees C, the film dried at 30 degrees C is much less soluble than the film dried at 80 degrees C. As the temperature of the water is increased, the curves converge; indicating that the molecular association of the film dried at a lower temperature is being disrupted.

Figure 2:



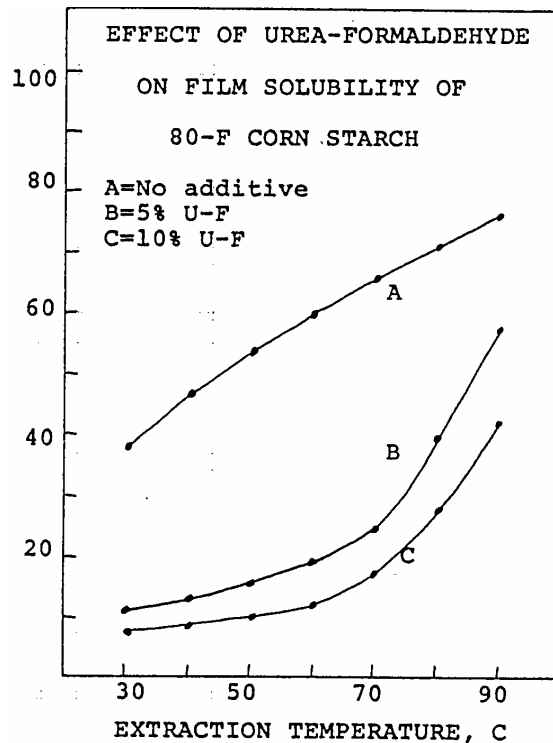
One of the more commonly used modifications of starches is the hydroxyethylation. Hydroxyethyl starch is more water-soluble and forms films of greater clarity than does unmodified starch. Even low levels of substitution have a pronounced effect on the properties of starch, as evidenced by Figure 3 showing the solubility of films prepared from 80-F corn starch, 80-F 0.04 D.S. Hydroxyethyl starch, and 80-F 0.10 D.S. Hydroxyethyl starch. The effectiveness of the Hydroxyethyl substitution in preventing the amylose from forming the gel structure is reflected in the increased cold water solubility of the Hydroxyethyl starch films. (4)

Figure 3:



Crosslinking of starches, as mentioned before, can be done to the starch granules or to the cast film. For this discussion, we will not consider crosslinked granules, which generally do not gelatinize to form workable pastes. Crosslinking agents added to starch films can greatly improve the physical properties of those films. Figure 4 shows increased resistance to water as urea-formaldehyde is added to starch solutions just before the films are cast.

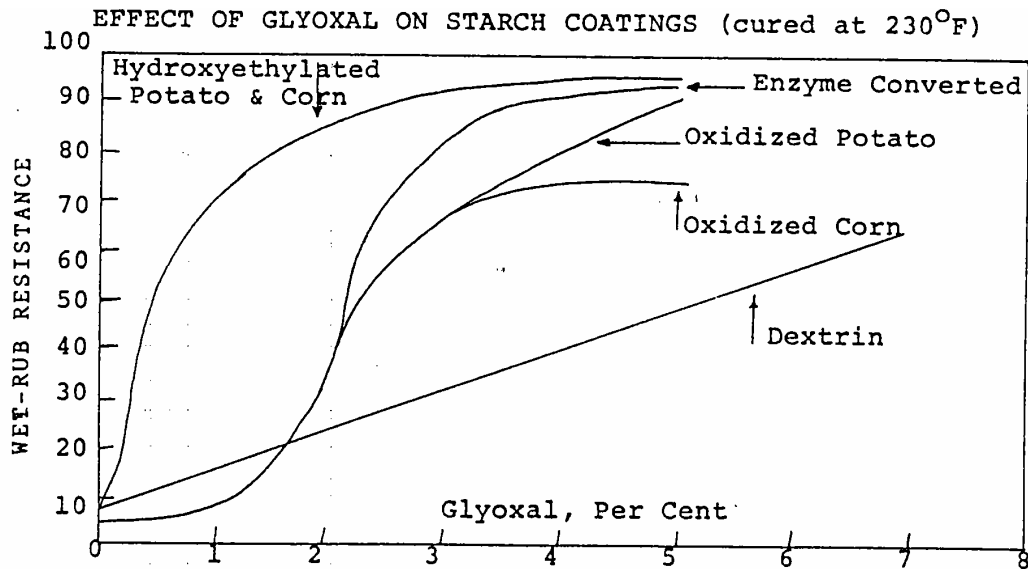
Figure 4:



Glyoxal is used to crosslink starch based paperboard coatings to improve the water resistance, called wet rub. Figure 5 shows the effect of adding glyoxal to five different modified starches. Notice that

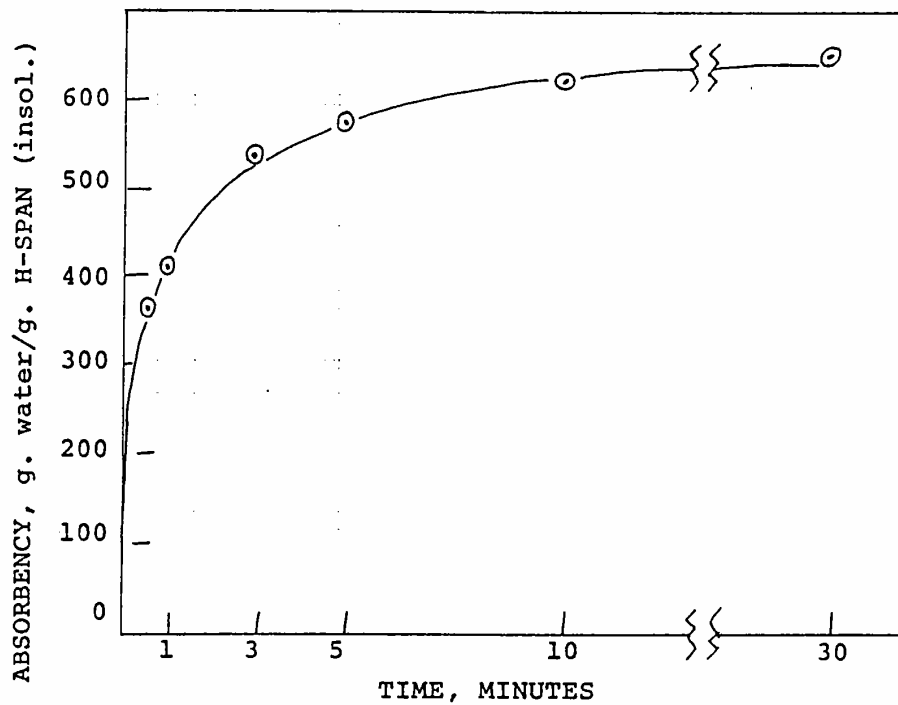
hydroxy ethylated starches are more readily insolubilized than other modified starches. This can be attributed to the fact that hydroxy ethylated starches are more reactive since the substitution prevents molecular association and so reduces steric hindrance.

Figure 5:



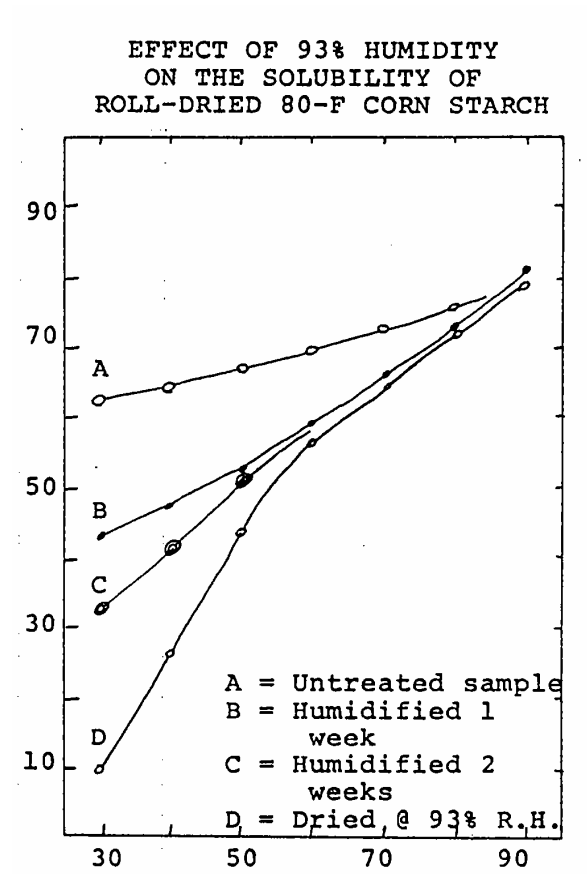
In closing, I would like to present two interesting examples. In 1973, Weaver, et al. of the USDA Peoria, Illinois, and lab presented data on the absorbency of a starch-polyacrylonitrile copolymer. (8) As Figure 6 shows, these polymers are capable of retaining huge quantities of water. They have found application in absorbent diapers and hospital pads.

Figure 6:



The second concerns the aging of starch films under high humidity. As mentioned earlier, films dried slowly at low temperatures will be more water resistant due to the association of amylose molecules. The following graph (Figure 7) is evidence that this association can occur in films when held at high humidity.

Figure 7:



While there is a great deal I have not said concerning starches and starch derivatives, I hope that I have convinced you to consider this underused and relatively inexpensive material.

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