Dextrinization of POTATO STARCH with Gaseous Hydrogen Chloride

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Air-dry starch (about 12% moisture) readily absorbs hydrogen chloride gas but does not permit penetration of the gas through the mass of starch. Both the absorptive capacity and the resistance to penetration of hydrogen chloride gas decreases with the decrease of moisture in the starch. Starch of 3 to 4% moisture content permits absorption and penetration of sufficient hydrogen chloride gas for dextrinization. Satisfactory dextrins can be prepared from partly dried starch and hydrogen chloride gas under proper conditions of temperature, concentration of catalyst, duration of dextrinization.

COMPARATIVELY few studies of the dextrinization of starch have been reported in the scientific literature. Most of the papers are general discussions of the dextrin industry and reviews of methods of manufacture (*4, 5, 8, 11, 12*). Bauer (*1*) in four experiments investigated the effect of acidity and time on the roasting of dextrins. Detailed information on dextrinization is confined chiefly to the patent literature. Numerous patents related to the dextrinization of starch have been granted, most of which claim improvements in dextrinization procedure. The first patent on dextrin in this country was granted to Bloede in 1867 (*2*).

The method used today for dextrinization of starch is substantially the same as that employed for the last forty years or more. It consists in heating or roasting powdered or granular starch which has been treated with a catalyst, usually an aqueous mineral acid. Early in the industry, starch was heated in shallow trays placed in tiers in large ovens. The modern dextrinizer is a cylinder, placed either horizontally or vertically, in which the starch can be agitated or thoroughly mixed during the heating process. Fans are provided for drawing off the excess water vapor and other gases liberated during the roasting of the starch.

The following references are given, not because they are important to the development of the dextrin industry but because the catalyst applied to the starch was in a gaseous or vapor state, as in the method used here. Fielding (*6*) dextrinized starch in a revolving cylinder mounted on trunnions, one of which was hollow. A mixture of atomized acid and steam was conducted through the trunnion to the starch while the cylinder was rotated. Thompson and Morrice (*9*) modified starch by heating it with sulfur dioxide under pressure. Thompson and Berge (*10*) used the combination of sulfur dioxide and steam under pressure to dextrinize starch. Browning and Barlow (*3*) acidified starch for dextrinization by conducting the vapors from boiling concentrated hydrochloric acid into the starch as it was mixed in a rotary converter. Frary and Dennis (*7*) prepared dextrins experimentally by treating 20-gram samples of starch (12.7% moisture) with dry hydrogen chloride. The starch was then heated in stoppered glass tubes.

One of the difficulties in dextrinizing starch is to distribute the small amount of catalyst evenly throughout the comparatively large mass. For example, in some dextrinizations only 1 to 2 pounds of hydrochloric acid are used per ton of starch. The usual method is to spray an aqueous solution of hydrochloric acid into the starch as it is being stirred (*5*). Obviously, regardless of the efficiency of the atomizer or stirring arrangement, this method of distribution cannot give every starch granule an equal portion of acid.

It was thought that the distribution of the catalyst might be improved if it were applied in a gaseous state. We have observed that starch dried to constant weight at about 100° C. would not absorb the minimum amount of hydrogen chloride required for dextrinization even when a large excess of hydrogen chloride was used; on the other hand, air-dried starch (12% moisture) absorbed dry hydrogen chloride readily. This fact suggested that an intermediate moisture content of starch would permit sufficient absorption of hydrogen chloride gas and at the same time allow the gas to penetrate the mass of starch.

EFFECT OF MOISTURE CONTENT ON ABSORPTION

Experiments were designed to determine how the absorption of hydrogen chloride varied with the moisture content of the starch. Starch samples of known moisture content were made by thoroughly mixing air-dried starch (14% moisture) with starch that had been dried overnight at about 100° C. Thirty grams of starch were placed in an open glass tube, 102 cm. long with an inside diameter of 2.7 cm. The tube was held in a horizontal position. The starch was evenly distributed in one end of the tube for a distance of 40 cm., and this end was closed with a one-hole rubber stopper. A known quantity of hydrogen chloride mixed with air was then conducted into the tube at the stoppered end.

Hydrogen chloride was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid at approximately 1 ml. per minute. At the same time a current of air, 700 ml. per minute as measured by a flowmeter, was passed through the sulfuric acid of the generator to carry the hydrogen chloride along and to dilute it with air in the ratio of about 3 volumes of air to 1 of hydrogen chloride. After the required volume of hydrogen chloride had been generated, the air was allowed to flow for another minute and a half. The generator was then disconnected from the tube, and the starch was thoroughly mixed. To determine the quantity of hydrogen chloride absorbed, a 4-gram sample of the starch in water suspension was titrated with 0.1*N* sodium hydroxide solution (phenolphthalein indicator).

Figure 1 shows the variation in the absorption of hydrogen chloride with the moisture content of the starch. Curves A and B, which represent the absorption when 0.36 and 1.46 grams of

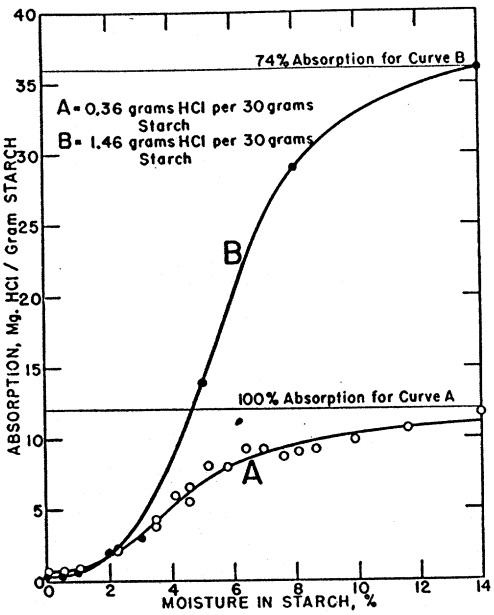

Figure 1. Variation of Hydrogen Chloride Adsorption with the Moisture Content of Potato Starch

hydrogen chloride, respectively, were passed over the starch, show that a comparatively small amount of hydrogen chloride was absorbed by starch with a low moisture content. At 3 to 4% moisture, however, it readily absorbed more than the amount of hydrogen chloride needed for dextrinization. Moreover, up to 4% moisture the amount absorbed from 1.46 grams of hydrogen chloride was not much greater than that absorbed when one fourth as much (0.36 gram) was used. The leveling-off of the curves is partly due to the limited amount of hydrogen chlori present. For example, the highest point on curve *A* represent about 90% of the hydrogen chloride applied, a high figure considering that the starch was not stirred during passage of the hydrogen chloride and that the gas was in contact with the starch for only a short time as it passed through the tube.

TABLE I. PENETRATION OF HYDROGEN CHLORIDE GAS INTO STARCH OF DIFFERENT MOISTURE CONTENTS

Section No.	% HCl Absorbed by Starch with Moisture Content of: 12%	3%	2%	1%	0%[a]
1	1.5	0.94	0.57	0.43	0.25
2	0	0.66	0.50	0.30	0.22
3	0	0.16	0.35	0.24	0.22
4	0	0	0.23	0.14	0.22
5	0	0	0	0.10	0.20

[a] Dried to constant weight at 100° C.

EFFECT OF MOISTURE ON PENETRATION OF GAS

The results of the experiments described above suggested that hydrogen chloride would penetrate much more readily into a mass of starch of low moisture content. The following experiments were made to test this assumption.

A glass tube 102 cm. long with an inside diameter of 2.7 cm. was stoppered at the lower end and mounted in a vertical position (Figure 2). One hundred grams of starch of known moisture content were placed in the tube and made a column approximately 22.5 cm. high. Hydrogen chloride gas was generated in a flask by adding 1 ml. of concentrated hydrochloric acid drop by drop over a 5-minute period to 10 ml. of concentrated sulfuric acid. The hydrogen chloride gas was conducted to the starch by a glass tube which extended to within 15 cm. of the top surface of the starch. To permit displacement of the air during the generation of hydrogen chloride, the tube containing the starch was loosely stoppered at the upper end. After 30 minutes an additional milliliter of concentrated hydrochloric acid was added to the sulfuric acid. Then the tube containing the starch and hydrogen chloride was tightly stoppered. After 24 hours the starch was removed from the tube in such a way that the column could be separated into five sections. The top section was 2.5 cm. long; each of the other four was approximatel 5 cm. Starting at the top, the sections were numbered consecutively from 1 to 5. The quantity of hydrogen chloride in each section was determined. This experiment was carried

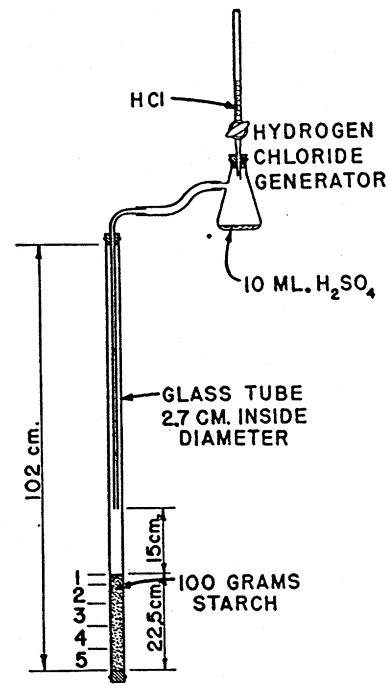

Figure 2. Apparatus for Determining Penetration of Hydrogen Chloride Gas into a Mass of Powdered Potato Starch

TABLE II. PROPERTIES OF POTATO STARCH DEXTRINS PRODUCED UNDER VARIOUS CONDITIONS

Sample No.	Starch, Grams	% Moisture in Starch	HCl Addition: Temp. of starch, ° C.	HCl Addition: Gram/g. of starch	Conversion: Temp., ° C.	Conversion: Min. to attain temp.	Conversion: Time at temp. Hr.	Conversion: Time at temp. Min.	Viscosity, Centistokes[a]	Sugar[b], as % Dextrose
1	349	2	Room	0.0037	95–100	11	1	24	62.4	..
2	500	4	Room	0.0035	95–100	16	1	33	31.4	10.7
3	500	4	Room	0.0035	110–113	9	0	53	29.8	11.7
4	170	4	Room	0.0042	85– 88	10	2	27	38.7	9.1
5	170	4	Room	0.0042	140–142	24	2	6	21.6	11.5
6	157	4	Room	0.0042	140–142	25	0	4	..	10.7
7	170	3	Room	0.0020	135–138	21	0	27	29.6	10.0
8	173	3	Room	0.0015	135–138	21	1	12	40.9	7.9
9	170	3	Room	0.0026	75	..	17	23	..	8.3
10	170	4	95	0.0030	95	..	2	19	34.0	10.2
11	170	4	130	0.0024	130–132	12	1	10	48.5	7.8
12	170	4	Room	0.0025	110–111	8	2	57	..	8.8
13	2600	4	Room	0.0008	179–180	39	2	..	73.0	3.2
14	4100	4	Room	0.0008	180–181	39	2	50	67.2	3.3
15	200	2	Room	0.0008	190	22	0	33	43.5	4.4
16	5000	4	Room	0.0010	190–193	35	1	42	44.9	4.9
17	200	4	180	0.0012	180–182	23	0	42	69.4	4.9
18	200	3	180	0.0013	180	17	1	8	77.9	1.7
19	4875	3	180	0.0009	180–185	31	1	32	48.2	2.7
20	4000	3	180	0.0010	180–185	34	1	36	76.5	3.7
21	200	3	Room	0.0012	180–184	23	0	59	93.0	4.6
22	200	3	Room	..	180	22	1[c]	..	56.8	4.0

[a] Viscosities of 50 per cent water solutions of the dextrins (density approximately 1.22) were determined with a modified Ostwald viscosimeter tube No. 300.
[b] Munson and Walker method (*8A*).
[c] Four minutes before removal from the converter the pH was changed from 2.73 to 4.50 with ammonia gas.

:t with five starch samples of different moisture contents (Table I).

The results show that hydrogen chloride, even in concentrations several times that required for dextrinization, does not penetrate deeply or diffuse into a mass of starch containing 12% moisture; sections 2, 3, 4, and 5 contained no hydrogen chloride. The affinity between this starch and the hydrogen chloride was so great that the surface layer of the starch (2.5 cm.) absorbed all the hydrogen chloride and thus prevented it from penetrating into the mass. In contrast, the hydrogen chloride penetrated the entire length of the dry starch column (22.5 cm.). In the starches with 3, 2, and 1% moisture, respectively, the distribution was intermediate between the two extremes.

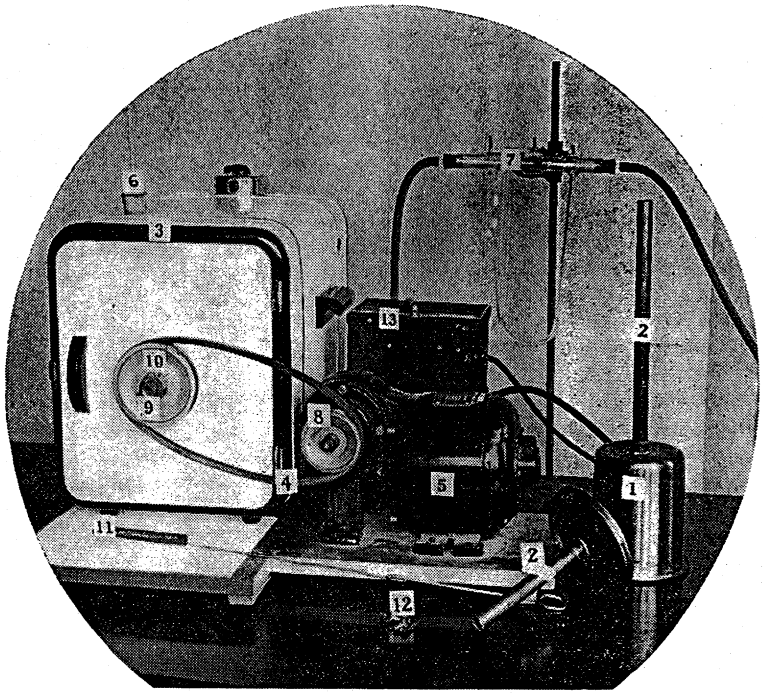

Figure 3. Apparatus for Dextrinizing Starch

1. Stainless steel cylinder
2. Hollow shafts
3. Oven (domestic type)
4. V-belt
5. Gear-head motor
6. Thermometer admitted to interior of oven
7. Flowmeter
8, 10. Pulleys
9. End of hollow shaft
11. Sampler
12. Wing nuts
13. Variable transformer

HYDROGEN CHLORIDE IN STARCH DEXTRINIZATION

The three main factors which influence the dextrinization of starch are: quantity of catalyst present, duration of heating period, and temperature of heating. A change in one factor requires a compensating change in at least one of the others to attain the same degree of dextrinization.

Potato starch was acidified and dextrinized in the apparatus shown in Figure 3. This consisted essentially of a 2-quart, stainless steel, revolving cylinder, 1, supported on hollow shafts and mounted horizontally in an electrically heated oven, the temperature of which was controlled by a variable transformer, 13. This cylinder had an operating capacity of about 200 grams and was rotated at a rate of 35 r.p.m. For larger-scale operations an oven was assembled to accommodate cylinders made from 5- and 8-gallon milk cans, which had operating capacities of 10 and 15 pounds (4.5 and 7 kg.), respectively.

Hydrogen chloride gas was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid at a rate of 3 to 4 ml. per minute. A current of air was bubbled through the sulfuric acid to dilute the hydrogen chloride in the ratio of about 3 parts of air to 1 of hydrogen chloride. The air and hydrogen chloride gas were conducted through flowmeter 7 and the hollow shaft of the cylinder to the starch as it was being mixed in the dextrinizer. The acidity of the starch was determined by titrating 5–10 gram samples as described previously. In most cases the hydrogen chloride was added before heating; in a few cases it was added after the dextrinization temperature had been reached.

The starch was dextrinized by heating until a sample of the dextrin dissolved almost entirely in cold water. The cylinder was then removed from the oven, and the dextrin was emptied into open trays to hasten cooling.

Table II gives the results of dextrinization of potato starch under varying conditions of temperature, duration of heating, and concentration of catalyst. The dextrins were typical of several hundred prepared. The data show that starch dextrinized at low-temperatures (75–142° C.) produced dextrins of low viscosity and high sugar content. On the other hand, the viscosity was higher and the sugar content lower for dextrins prepared at higher temperatures (180–193° C.) and with lower concentrations of hydrochloric acid.

In evaluating these results, it must be remembered that there are no rigid standards for dextrins. Each large consumer has specifications for the particular dextrin used. It has been generally accepted, however, that high viscosity and low sugar content, together with satisfactory solubility in cold water, are the desirable properties of dextrins, particularly for gums that are to be remoistened.

The results obtained when the catalyst was added at room temperature did not differ significantly from those obtained when the catalyst was added at the dextrinization temperature. To some of the samples ammonia gas was added at the end of roasting to prevent overdextrinization of starch and to increase the pH of dextrin; this increase is desirable because it improves taste and odor. It was found, however, that complete neutralization darkened the resulting product. The pH should not be increased above 5.

Some of the best samples prepared in the course of this investigation fully satisfied the specification of U. S. Bureau of Engraving and Printing for dextrins used as adhesive for postage stamps.

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