HETEROGENEOUS REACTION OF GRANULAR STARCH WITH HYDROGEN CHLORIDE

II. Quantitative Studies[1]

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ABSTRACT

Quantitative studies were made on the reaction of dry, granular starch with anhydrous hydrogen chloride gas. The weight, chemical analysis, and cold-water solubility of the products were determined as a function of time of reaction; the water extracts were examined on the same basis. The reaction is easily followed by pressure measurements in a simple Warburg-type apparatus which clearly indicates both the rate and the induction period, as there is a sudden change in rate at the end of the latter. Different starches, such as rice, corn, wheat, and potato had different rates and induction periods, indicating that granule size and structure play a major role in the kinetics. It appears possible to characterize starches, to a certain extent, with this reaction. The reaction appears to be one of diffusion into and disorganization of the granule by the HCl during the induction period, followed by a dehydration reaction; the result is a black, inert, water-insoluble, granular product that appears to be cross-linked.

Qualitative studies of the reaction of granular starch with anhydrous hydrogen chloride gas (1), as well as its reaction with liquid chlorine (2), indicated that heterogeneous reactions with different starches showed marked differences that might well serve to characterize starches. Microscopic studies on the products of the HCl reaction also indicated that the kinetics of the reaction reflected the granular structure of the starch. It seemed propitious, therefore, to investigate the reaction in as quantitative a manner as possible. This second article presents the results and interpretations of this work.

Materials and Methods

The starches used were described in the preceding article of this series (1). All starches were stored at room temperature in closed containers. None of the starches was extracted or treated in any other way than by drying at 110°C. under vacuum before use.

Preparation of Products for Study. The reaction was conducted as previously described (1). Upon completion of the specified reaction time, the product was maintained under vacuum for 1 hr. while in the original flask at 70°C. After its weight was determined, the product was removed from the flask, mixed lightly, and transferred to a tared test tube; it was then further degassed under vacuum in an Abderhalden drying apparatus at 110°C. (boiling toluene) for 23 hr. From the percent loss of weight under this last treatment, the original product weight was corrected to what it would have been

had the transfer been quantitative, for purposes of material balance.

Analyses of Products. Samples, prepared as described above, were analyzed by combustion methods for carbon, hydrogen, and chlorine, by Midwest Microlab, Inc., Indianapolis, Indiana. Oxygen was assumed by difference. It was found that corresponding analyses for chlorine could be obtained by treating the products with water and titrating either the chloride ion or the hydronium ion formed to yield results that agree with those for total chlorine. With products of limited solubility, it was necessary to heat the samples near boiling to liberate this chlorine. Titrations were done with a pH meter to facilitate detection of the end point where dark-colored solutions were obtained.

Extraction of Products with Water. A weighed amount of product (0.2–0.3 g.) was added to a tared, sintered-glass crucible. The crucible was half-filled with cold water and allowed to drain by gravity into a beaker, and was refilled as needed. After about 30 ml. of water had been used, the crucible and contents were placed on a filter flask and washed with 10 ml. more of cold water to complete the extraction. The filtrate was made up to volume for subsequent analysis. The residue was dried at 110°C. and weighed to determine the amount extracted.

Optical Rotation Measurements. Rotations were read with sodium light on a Rudolph Model 80 polarimeter of 0.001° precision. Readings were converted to specific rotations by using the weight of material in solution, such as in the above extractions.

X-Ray Diffraction Studies. Diffraction pictures of the products were compared with starch samples in capillary tubes, on a Norelco X-ray unit. Comparable exposures were used, to detect loss or gain of structure.

Infrared Absorption Spectra. Spectra were determined on a Perkin-Elmer 137 instrument. Both Nujol smears and KBr pellets were tried. Results were best with a 1 to 3% mixture of the product in a KBr pellet.

Pressure Readings. The absorption of HCl was followed by means of readings, to the nearest mm., on a mercury manometer. The stopcock between the manometer and the system was kept closed between readings to minimize reactions throughout between the mercury and HCl, and the connection to the manometer was made of capillary tubing so that there would be less diffusion of HCl into the air in the manometer. Reaction of HCl with mercury is not serious if moisture is kept out of that part of the system.

Results and Discussion

Weight Changes during Reaction. There is an expected gain in weight of the starch during the reaction as the granule absorbs HCl. There is also a later loss of weight beginning at about the end of the induction period, owing mostly to the formation of water from a dehydration reaction.

In this particular sequence a slightly different procedure was employed from that used later. The potato starch was allowed to react with HCl for a given length of time, the gases were pumped off for 7 min. to remove excess HCl and the product was removed and weighed in the reaction flask. The apparatus

was recharged with HCl and allowed to react for another specified time, and the process was repeated.

The weight curve for a typical run at 70°C. is shown in Fig. 1. The product is almost black at the peak of the curve, and moisture begins to appear soon thereafter.
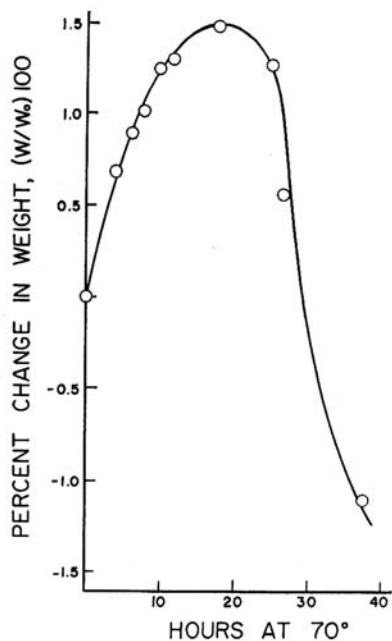

Fig. 1. Change in weight of product during reaction. Peak of curve corresponds closely to end of induction period.
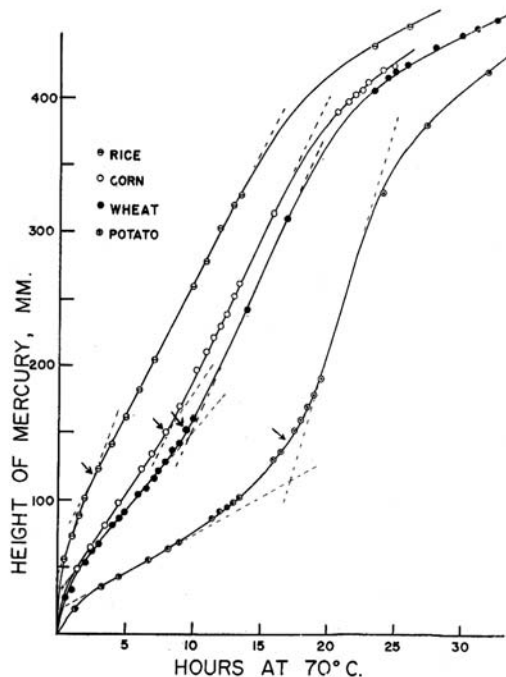
Fig. 2. Pressure curves showing absorption of HCl during reaction for various starches. Intersection of extrapolated straight lines represents end of the induction period. Arrows indicate the appearance of water.

While it is not likely that all the excess HCl was pumped off, the results are sufficient to establish that there is, first, an absorption of HCl, followed by loss of water to give the observed curve. Calculations indicate that mere diffusion of HCl into the starch is not enough to account for the gain in weight; that is, there is definitely some adsorption involved.

Analyses and material balances on products of prolonged runs indicate that only water is eliminated, with the exception of a very small amount of dark-colored, volatile matter that was not identified. The amount of water increases with time up to about 2½ molecules per glucose unit.

Absorption of Hydrogen Chloride. Figure 2 shows curves for the absorption of HCl plotted against time of reaction for four different starches. The curve for potato starch best shows the features characteristic of all the curves.

There is, first, almost instantaneous adsorption of HCl onto the surface of the granule with what appears to be typical Freundlich or Langmuir adsorption. This is completed in a few minutes and followed by relatively straight-line absorption for some 12 hr., rounding off to another, steeper straight-line absorption that eventually curves off.

Similarly shaped curves are obtained for wheat, corn, and rice. It will be noted that the *slope* of the first straight-line portion, comprising most of the induction period, increases in the order: potato, wheat, corn, and rice. At the same time, the *length* of the induction period increases in the opposite order. As pointed out in the preceding paper of this series (1), microscopic observations show that this induction period represents a period of penetration or diffusion of HCl into the granule; hence, granule size should be involved. The average granule diameter increases in the order: rice, corn, wheat, and potato.[4]

The slopes of the second straight-line portion do not seem to be related to granule size, and, in fact, become more nearly equal when corrected for the actual amount of starch used in each case. The determination of the induction period was taken to be the intersection of the projection of the two straight-line portions. For rice starch, the initial slope is greater than the second slope, whereas for the others the opposite is true. Moreover, its induction period is so short and the two slopes so close that the induction period is difficult to determine by this method. It was therefore taken, in this case, to correspond to the appearance of water (2.75 hr.). In most cases, the appearance of water agreed with the induction period as determined by the intersection method within 1 hr., the moisture generally appearing earlier (see arrows on Fig. 2). This is undoubtedly due to the spread of granule sizes in the sample, the smaller granules reaching the end of their induction period earlier than the larger, hence forming water earlier.

This same spread of sizes affects the shape of the curve at the end of the induction period. For potato starch, which not only has the largest granules but also the largest spread of sizes, rounding of the curve is particularly pronounced. In contrast, the granule size for corn starch is much more consistent and its curve shows a much more abrupt transition at the end of the induction period. When potato starch was fractionated into small and large granules, the pressure curves obtained on the separate fractions were much less rounded and more abrupt, like those of corn starch.

It is obvious that some uncertainty exists in the exact determination of induction period and rates by these pressure curves, but they do have more than a qualitative value. The shape of these curves also indicates a certain amount of resolution of consecutive reactions that either occur at rates sufficiently different, or must "wait" for completion of prior steps. The following explanation is offered to explain the observed curves.

After the first rapid adsorption of HCl into the granule surface, a process of diffusion into the granules occurs. Since this is relatively slow compared to the rate at which HCl can adsorb onto the surface, the *bulk* rate of diffu-

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[4] Root mean cube average diameters (100–200 granules) were as follows: potato 32.9, wheat 14.7, corn 12.0, rice 6.8 μ.

sion into the granule will be proportional to this constant amount of HCl on its surface. This, in turn, will be proportional to the surface-to-volume ratio of the particular starch, which therefore varies with the reciprocal of the average diameter. (By "average diameter" is meant root mean cube diameter, to put it on a weight basis.)

The *length* of the induction period, on the other hand, depends upon how far the HCl has to penetrate before it reaches the center of the granule, some sort of relaxation occurring at this point to account for the delay in the formation of water. This assumes that an individual HCl molecule travels into the granule at the same rate, regardless of size or condition of the granule. (Other factors such as degree of organization, aging, etc., will not be considered for the moment.) The length of the induction period, then, will vary *directly* with the diameter.

If the foregoing is assumed to be correct, it should follow that the product of the induction period multiplied by the rate of the reaction during the induction period should thus be constant, the former being directly proportional to diameter and the latter inversely, other factors being the same.

While this is undoubtedly an oversimplification, Fig. 3 shows that some sort of hyperbolic function exists between the rate during the induction period and the length of the induction period, the one decreasing as the other increases, and vice-versa. In actuality, both relationships, rate and length of induction period, vary with granule diameter in the direction postulated, but more in accordance with the square root rather than the first power of the diameters.

As a further check on the effect of granule size, a quantity of potato starch was fractionated into large and small granules: it was stirred in water, the larger granules were allowed to settle, and the smaller ones were poured off into another container. When the process was repeated several times, two fairly homogeneous fractions with average (root mean cube) diameters of 17.2 and 59.3 μ (compared to 38.4 for the original starch) were obtained.

These two fractions were treated with HCl under identical conditions and their pressure curves compared with those of a similar sample of original starch. Because the amounts were necessarily small, a different apparatus was employed and therefore the data cannot be compared with those of Fig. 2; however, they served for comparison with each other.

As expected, the small-sized granules showed the fastest rate and the shortest induction period, whereas the large-sized granules had the slowest rate and the longest induction period. The unfractionated starch was in between. Unfortunately, the unfractionated starch was not treated with water, and showed itself to be more like the large granules, indicating perhaps that the process of fractionation had somewhat activated the starch, partially disorganizing it in the process.

Repeat runs made with many starches indicated that, barring treatments that might age or disorganize the starch, the results were reproducible. It thus seems possible that starches could be characterized by the shapes of their pressure curves. The induction period and rate could be predicted from granule size, and, under controlled conditions, disorganization and other struc-
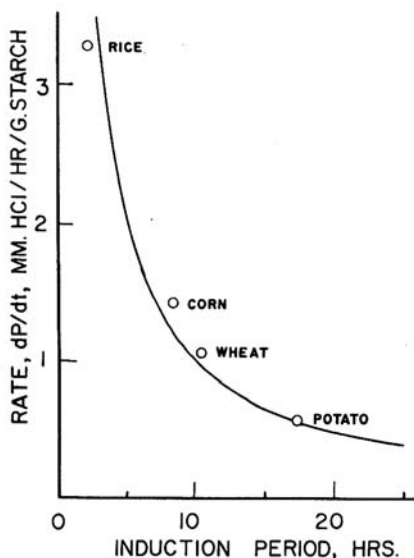
Fig. 3.   Relation between rate of absorption of HCl and length of induction period for various starches. Rates have been corrected for samples of different sizes. Curve is for rate × I.P. = 10.2.

tural changes should be detectable by the changes in the pressure curves.

The increase (except for rice) of slope that generally characterizes the second or dehydration stage of the reaction is possibly due to several things. The primary cause is the sudden formation of water which has resulted from the relaxation of the granule at the end of the induction period, somehow allowing water to be formed, whereas it was not possible until this point. Apparently, a critical number of hydrogen bonds must be severed before the starch molecules acquire enough mobility to approach one another to eliminate water. This water dissolves HCl rapidly in quantities up to saturation, thus increasing the rate of rise of mercury in the manometer. Since this dehydration represents a chemical reaction of the *disorganized* starch, which has suddenly become more readily available for reaction, granule size does not play much part in this new rate. The chemical nature of this latter reaction will be discussed after more evidence has been introduced.

Analysis of the Products. In this particular series the starch was allowed to react at 70°C. and the products were analyzed for carbon, hydrogen, and chlorine after removal of HCl under vacuum at 70°C. for 5.5 hr. In no case was there any increase in carbon content before the end of the induction period, indicating no dehydration reaction. Soon after, however, there was a steady increase in percent carbon and a decrease in percent hydrogen. A material balance on the weight and composition of product and reactant indicated that the loss in weight could be accounted for solely by the elimination of water. Adsorbed HCl was taken into account in these calculations.
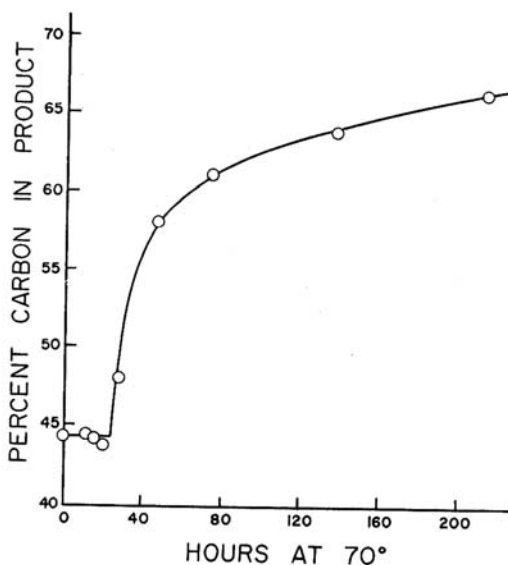
Fig. 4. Change in carbon content during reaction. Values were corrected for chlorine content.

Figure 4 is a plot of percent carbon in the product against time of reaction. The curve confirms that the dehydration reaction begins at the end of the induction period. It also indicates that elimination of water is limited to $2\frac{1}{2}$ or at the most 3 water molecules per glucose unit, rather than the 5 suggested by the molecular formula for starch $C_6H_{10}O_5$. Since one oxygen is involved in the pyranose ring and another in the 1,4-linkage, this is more or less expected, and indicates that the three free hydroxyl groups are involved. The highest percent carbon to date is 64.45% from a sample that was made by reaction of potato starch at 70°C. for 214 hr. The hydrogen in this sample was 4.14%. This corresponds to an average formula of $C_6H_5O_{2.5}$. There was an additional 3.3% Cl, presumably in the form of HCl. This figure corresponds to about 1 HCl unit for 6.5 glucose units.

The chlorine in the product was completely removable with water in the form of hydrochloric acid, either formed by the hydration of adsorbed hydrogen chloride or by the hydrolysis of labile carbon-bound chlorine. It is probable that the majority is due to the former, but the small but perceptible amount of degradation observed would require a corresponding amount of reaction of HCl with the 1,4- or 1,6-linkages that are degraded. This would result, normally, in restoration of the hydroxyl group on carbon 4 or 6, as the case might be, and a chlorine on carbon 1. The latter would be labile enough to hydrolyze readily in water to form hydrochloric acid.

A series of samples taken during the induction period indicated that the amount of chlorine in the product that was not removable at 70°C. increased linearly with time to a maximum value of about 3.4% at about 100 hr. and did not increase further. Some of this chlorine appeared to be removable under

vacuum at 110°C., but only slowly. For example, a product near the end of the induction period, containing only about 1% Cl, was reduced to about 0.5% after 24 hr. under vacuum at 110°C. The residual chlorine might well be carbon-bound, as suggested above in connection with degradation. The chlorine that can eventually be removed at 110°C., but not at 70°C., suggests a strongly adsorbed form of HCl, perhaps similar to the iodine-amylose complex. The stoichiometry for this amount of HCl is within possibility. While HCl is not normally capable of linear polymerization, it is not impossible that a chain
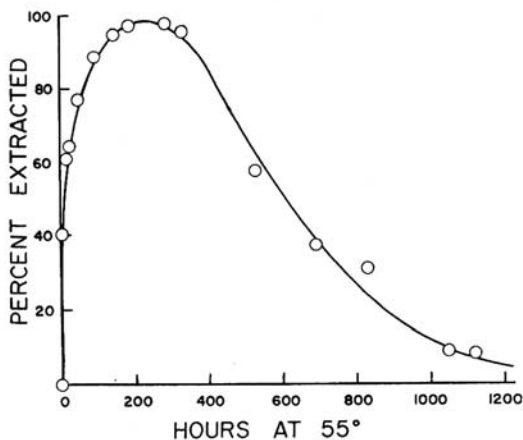

Fig. 5. Change in extractability in cold water during reaction (55° products).

of hydrogen chloride molecules held together by hydrogen bonding in a manner such as H-Cl:H-Cl:H-Cl, etc., might be stabilized by its location within a starch helix. Some of the black might well be due to such a complex, as a noticeable lightening of the products is observed as they lose HCl. The permanent black of the dehydrated starch products beyond the induction period, however, is unaffected by vacuum and might be related to the presence of free radicals (see footnote 5).

Effect of Water on Products. Mention has already been made (1) of the microscopic behavior of granules when treated with water. It was apparent that considerable solubilization of the starch was effected by the reaction, not entirely attributable to disorganization and more likely involving some degradation of the starch into dextrins or sugars.

A quantitative estimate of this solubilization was made by measuring the extent to which the starch became soluble, as described under "Methods." The result on a 55°C. run with potato starch is shown in Fig. 5.

The extraction curve clearly shows maximum solubility near the end of the induction period, followed by a decrease to near insolubility. The products near the peak of the curve were black, as well as all thereafter. Optical rotations on the extracts were unfortunately of uncertain significance, owing partly to some hydrolysis on standing under acid conditions and partly to

lack of sufficiently large readings for good accuracy because of the small solubility of some of the products. No regular trends in the rotations were obtained, and specific rotations ranged from 54° to 176°, indicating the presence of glucose and maltose along with higher sugars. Later work on fresh extractions tested with thin-layer chromatography on cellulose plates indicated that where special precautions were taken to remove adsorbed HCl, no low-molecular-weight sugars were obtained; only dextrins appeared to be present in limited amounts. Products that were not degassed thoroughly to remove HCl changed markedly on standing, indicating that some of the adsorbed HCl was apparently able to move about within the granule.

The decrease in extractability coincides with the evolution of water at the end of the induction period. Whatever the nature of this reaction, it results in polymerization or cross-linking of the starch through water elimination. This could be through hydroxyl-hydroxyl reaction resulting in ether linkages, except that more water is lost than can be accounted for by this alone. Moreover, it is doubtful that such ether bonds would be stable to attack by HCl.

More likely a reaction is involved between a hydroxyl group and a carbon-bound hydrogen, giving rise to carbon-to-carbon bonding[5] in an interglucose reaction. An intraglucose reaction resulting in double bond formation and possible condensation is less likely, since no evidence for unsaturation was found. However, the polymeric nature of the product and the possibility of resonance structures could obscure unsaturation.

The products retain their granular structure throughout the reaction and eventually become insoluble even in hot water. There is also a corresponding increase in hardness, giving the granules a gritty texture unlike that of starch.

X-Ray Diffraction Studies. There is a gradual loss of X-ray diffraction pattern during the induction period from the normal pattern for starch, until by the end of the period no lines can be seen and the product can be considered amorphous. No new lines appear and no regular crystallinity develops during the subsequent polymerization reaction, as no further pattern can be detected.

Infrared Absorption Spectra of Products. There is only a slight change in spectra from starch during the induction period, consisting only in a noticeable decrease of a peak at 6.1 μ and the appearance of new peaks at 5.8 and 6.3 μ. After the induction period there is a relatively large change in the 8- to 16-μ region that characterizes the pyranose ring, with a general undefined absorption in this area obscuring the peaks. The 3- to 5-μ region likewise shows a wide general absorption that obscures any structure. Figure 6 shows a comparison of the spectrum of potato starch with that of a 214-hr., 70°C. product made from it.

It is believed that these general absorptions over these wide regions indicate

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[5] Because of the polymeric nature of starch, it is conceivable that water might occasionally be eliminated where the distances are not quite appropriate for the formation of a carbon-to-carbon bond. In such case a stable free radical might be formed. Preliminary measurements on the electron spin resonance spectra of some postinduction-period products give values of 10^{16} spins/g., corresponding to about one spin/100,000 glucose units. This will be further investigated, but it is cited as further evidence for the possible structure suggested.
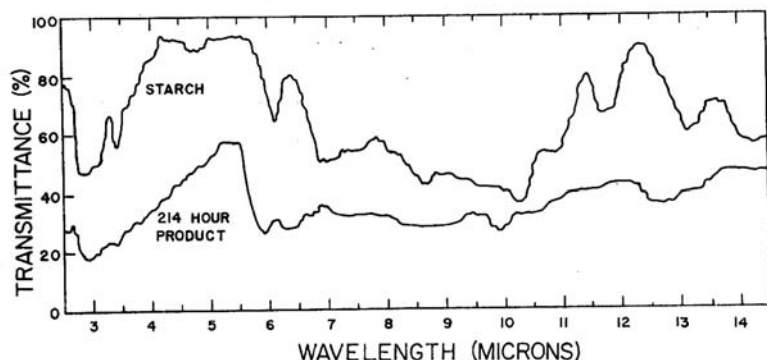
Fig. 6. Comparison of infrared absorption of starch and a 214-hr., 70°C. product. Curve for latter has been shifted down 40% for clarity.

polymerization.   No evidence was found for C-Cl bonding, and structural assignment of the peaks mentioned is as yet uncertain.

Conclusions

The behavior of granular starch in this heterogeneous reaction would seem to best support the trichite structure suggested by A. Meyer (3), in which the starch chains are assumed to be radially arranged, with the increasing area of the cone-shaped sectors of the granule filled with branched chains. The chains are generally believed to be in a helical configuration, in an extended form so that more than one helix can intertwine to form a strand or cable. Because of the great length of the starch molecule and its occasional branching, the many molecules in the granule would thus become interlocked through this splicing process to form the intact structure of the granule.

This radial-helical structure probably persists from the molecule to the granule through successive stages as observed with the electron microscope. It is presumed that hydrogen chloride diffuses radially into the granule, both through these various helical structures and between them, breaking hydrogen bonds as it penetrates. Undoubtedly, similar processes are involved in any heterogeneous reaction of granular starch, and similar kinetics with induction periods should be encountered. It seems likely that studies of such heterogeneous reactions might shed some light on the structure of the starch molecule and its granule.

The quantitative studies reported here support those conclusions based on microscopic examination in an earlier report (1). Particularly, maxima were found in the weight of the product and its extractability in cold water that corresponded with the maximum disorganization noted under the microscope. The evolution of water was also found to correspond roughly to this stage of the reaction. Analyses of the products indicated that an increase in carbon content begins at the end of the induction period.

Finally, mention should perhaps be made of the large number of potential uses that these cross-linked products appear to have. They have the charac-

teristics of a black, spherical, water-insoluble, solvent-insoluble, carbonaceous, porous particle whose size can be varied by starting with starches having granules of various sizes. With their large surface area such particles could well serve as carriers for insecticides or nutrients, or catalysts, or could be used as adsorbants or filter media. They might find use in reprography, particularly since they are somewhat heat-sensitive and show some electrostatic properties, thus possibly substituting for carbon black or blending with it to modify its properties. On treatment with water they yield small amounts of HCl. Products of polymerization, varying in degree, could possibly serve as soil conditioners. The density of these products as compared with that of peat would give them the additional advantage of not floating away with water. The black color could serve to increase the radiation absorption of soils to raise temperatures or to melt snow or ice. It could serve as a good black pigment for inks, paints, or plastics. An inexpensive and potentially useful material has been produced from an abundant natural material—starch.

Acknowledgment

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