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PROCESS OF PRODUCING WATER-REPEL-  
LENT POLYSACCHARIDES AND PRODUCT

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This invention relates to water-repellent polysaccharides and to processes and products for producing them. More particularly, the invention is directed to water-insoluble polysaccharides having hydrophobic surfaces, and to products and processes for imparting hydrophobic character to hydrophilic, water-insoluble polysaccharides comprising exposing them to contact with a chloride of the group consisting of stannic and chromyl chlorides and heating the polysaccharides after such contact.

Increasing the water resistance of polysaccharides has been the object of much investigation and research effort. Such materials, particularly in the form of cellulose or cellulosic derivatives, have greater usefulness for many purposes if they have at least some ability to withstand physical deterioration by water. For instance, unsized paper is a matted web or sheet of cellulose fibers which takes up water very readily and thereupon loses most of its mechanical strength. For most uses of paper this affinity for water is undesirable. It has been avoided by coating, sizing or impregnating the paper. Similarly, other such cellulosic materials as cotton, wood, wood pulp, regenerated cellulose sheet, rayon, jute and hemp have been made water resistant by coating, sizing or impregnating them.

These coating, sizing or impregnating treatments have heretofore consisted of applying to a cellulosic material a hydrophobic substance in such a manner that it is deposited in, on, or around the cellulose in substantial amounts. Enough of the hydrophobic substance must be used to prevent or retard contact between the cellulose and water, the amount used in a particular instance being dependent upon the nature of the coating or size and its manner of application. The application may be a surface coating as when regenerated cellulose sheet is waterproofed by coating its surface with a continuous layer of lacquer, the layer being sufficiently thick to prevent contact between the cellulose and water thereafter applied to the surface of the sheet. The application may be a body size, as when paper is made water-repellent by precipitating a rosin-alum size onto the fibers in the beater before they are webbed so that the size is distributed relatively uniformly through the body of the paper and contact of the fibers with water is thereafter prevented. The application may be a surface size, as when a wax emulsion is worked into the surface of the paper on calender rolls. The application may be a complete impregnation, as when paper is

passed through melted paraffin so that the fibers as well as the interstices between the fibers are completely filled. Whatever the method of application, a substantial amount of a water repellent composition has been required to give cellulosic materials any considerable degree of resistance to water.

Because of the large amounts of coating, sizing and impregnating compositions which it has heretofore been necessary to use in order to improve the water resistance of cellulosic materials, such treatments are usually accompanied by changes in the other physical properties of such materials. The weight of paper is increased, the paper is made brittle or at least less pliable, its color may be changed, or it may be made somewhat translucent, and various other like changes may occur. Similarly, cotton fabrics may acquire a harsh feel. These and various other changes may result from the waterproofing treatment. Sometimes the changes are desirable; sometimes they are objectionable. Since the waterproofing and water repelling agents heretofore used with cellulosic materials have relied for their efficacy upon their own water repellence, it is apparent that objectionable characteristics imparted by them to the treated material cannot easily be overcome.

Now we have found that cellulose and other water-insoluble polysaccharides may be made water repellent by exposing them to contact with a chloride of the group consisting of stannic and chromyl chlorides, and after such contact heating the polysaccharides.

The hydrophobic character imparted to water-insoluble polysaccharides by a process of our invention is similar to the water repellency heretofore obtained by a surface or body size. The surface of the material is made unwettable or difficultly wettable by water. A loose-woven cellulosic fabric such as cotton cloth when treated according to our novel processes is not made entirely impervious to water since water under pressure will pass through the interstices. The individual fibers of the cotton, however, are not wetted, so that when water is poured upon the surface of such cloth it will drain off in preference to passing through the cloth. Closely matted cellulosic materials such as paper, while not made impervious to water by the treatment, are nevertheless rendered so resistant to water that their strength is not decreased by water as it would be if the material were not treated. The term "hydrophobic" as used in describing our invention may therefore be defined broadly as

the property of being able to resist wetting, as contrasted with "hydrophilic" which means the property of being easily wetted by water. Further definition of these terms will appear hereinafter.

The imparting of hydrophobic properties to water-insoluble polysaccharides is accomplished according to a process of our invention by the use of substantially smaller amounts of sizing materials than has heretofore been required with the usual surface or body sizes. For instance, a pure cellulosic uncalendered paper is made water-repellent by treating it with chromyl chloride and heating it to 150° F., the amount of chromyl chloride present in the treated paper being about three-tenths per cent. By this treatment a water repellency is imparted to the paper equivalent to that obtained by incorporating two per cent of a wax emulsion as a calender size into the untreated paper.

From the remarkable reduction in the amount of sizing material required to give water repellency to cellulosic materials by a process of our invention, it appears likely that the products of reaction between the sizing agents and the water-insoluble polysaccharides form an oriented layer of molecules upon the surface of the substance being treated, possibly at the hydroxyl groups, and that this oriented layer is water repellent. The idea that there must be at least some sort of chemical combination between the treated material and the chloride used is further suggested by the fact that chromyl chloride alone reacts violently with water, whereas when used as a treating agent according to a process of our invention the resulting product is water-repellent. It will be understood that while these theories of orientation and combination may be useful in understanding the nature of our invention, other factors than orientation and combination may also contribute to the ultimate results obtained.

When an insoluble polysaccharide is made water-repellent by treatment with a chloride according to a process of our invention, the other physical properties of the material remain substantially unchanged. This is in sharp contrast to the effect of the sizes, coatings and impregnants heretofore available. The explanation may reside in the fact that smaller amounts of the chloride are used, or that the manner of combination of our sizing agents with the material treated is different. Whatever may be the explanation, a decided advantage is obtained in instances where it is desired to impart hydrophobic properties to a material without altering its other characteristics.

The manner of making materials hydrophobic by the processes of our invention and the character of the water repellent materials produced may be better understood by reference to the following illustrative examples. Example 1 shows the use of chromyl chloride for making paper water-repellent.

#### Example 1

A piece of newsprint paper was dried for five minutes at 100° C. It was then exposed to dry air containing two per cent by volume of chromyl chloride vapor for a period of five seconds at about 25° C. The paper was then heated for two minutes in air at 120° C. The treated paper was not wet when dipped in water. Since the paper was not wet, it retained its original opacity so that the print could not show through even after the paper had been immersed for several days. The

strength of the treated paper was not substantially decreased by immersion in water, so that a folded piece of the treated newsprint was easily unfolded and read after several days' soaking. In contrast with these properties untreated newsprint immediately became wetted upon immersion, lost its original opacity, and became a mass of pulp after soaking only two days.

Another form of insoluble polysaccharide which may be made water repellent by our novel processes is regenerated cellulose film. The treatment of this material is described in Example 2.

#### Example 2

A piece of regenerated cellulose sheet was dried for two minutes at 100° C. It was then exposed for one second to dry air containing two per cent by volume of chromyl chloride. The sheet was then heated to 120° C. for one minute.

The treated sheet did not absorb moisture as rapidly as the untreated material, and its surface was markedly water-repellent as illustrated by the fact that drops of water applied to its surface did not spread.

Cotton is another material consisting essentially of insoluble polysaccharides which may be made water repellent by the treatment with a chloride according to a process of our invention as shown in Example 3.

#### Example 3

Cotton cheesecloth was dried for five minutes at 105° C. It was then exposed to dry air containing two per cent by volume of chromyl chloride vapor for five seconds at 25° C. The cloth was then heated to 110° C. for two minutes.

The treated cheesecloth was sufficiently water-repellent to support water to a depth of one-quarter inch on the fabric, while the untreated material was immediately wetted and would support no water. The treated cloth retained its water repellency even after laundering with soap solution and dry cleaning with carbon tetrachloride.

The foregoing examples show the use of chromyl chloride as a sizing agent. Stannic chloride is another chloride which we have found to impart water repellency to insoluble polysaccharides when applied by a process of our invention. Such an application is shown in Example 4.

#### Example 4

A piece of pure unsized cellulose paper was dried at 100° C. for two minutes. It was then exposed to dry air saturated with stannic chloride vapor at 25° C. for five seconds. The treated paper was heated to 120° C. for two minutes.

The treated paper had the characteristics of a sized paper. It did not absorb water as readily as untreated paper and could readily be written upon with pen and ink. By contrast, the untreated paper behaved toward water and ink in the manner of blotting paper.

Stannic and chromyl chlorides may be used to impart water repellency to insoluble polysaccharides according to a method of our invention in solution in an inert solvent rather than by the vapor phase treatments of Examples 1 through 5. The use of such a solvent method is shown in Example 5.

#### Example 5

A piece of pure dry unsized cellulosic paper was dipped in a carbon tetrachloride solution containing one-tenth per cent of chromyl chlo-

ride by weight for one second. The carbon tetrachloride was allowed to evaporate and the treated paper was heated to 110° C. for two minutes.

The treated paper was remarkably water-repellent as compared with a sample of the same original paper stock which had been treated only by immersing in carbon tetrachloride containing no chromyl chloride, drying and heating.

While in the above examples we have shown the application of our novel processes for imparting water repellence to certain specified materials, it will be understood that the processes are broadly applicable to water-insoluble polysaccharides in various forms. Wood, rayon, jute and hemp are examples of other cellulosic materials which may be so treated. Starch and similarly constituted substances which, if they disperse in water at all, form only colloidal dispersions, also may be made water-repellent by this treatment. The art is familiar with various other water-insoluble polysaccharides and to the treatment of these materials also the processes of our invention may advantageously be applied.

Since chromyl and stannic chlorides react with water, the materials which are to be made water-repellent by a process of our invention should be substantially dry before they are treated. The conditions required for drying will of course vary with the material. The art is already familiar with the conditions under which such drying can be effected.

When chromyl and stannic chlorides are applied to insoluble polysaccharides as vapors, the time employed for the treatment and the concentration of the vapor may be considerably varied. Usually the time required will vary inversely with the concentration, higher concentrations requiring shorter treating times. Similarly, when the chloride is applied from solution in an inert solvent, the treating time required is greater at lower concentrations of the chloride in the solvent. Usually contact of the polysaccharide with the chloride for a few seconds is sufficient.

When the treatment is applied from a solution in an inert solvent, the solvent should be one which is relatively resistant to reaction with the chloride used. In Example 5 we have shown the use of carbon tetrachloride. Among other inert solvents which we may use are ethylene dichloride, diethyl ether and n-heptane.

While in the foregoing examples the use of chromyl chloride and stannic chloride is shown separately, we may also use these chlorides together as mixtures, and such mixtures may be applied as either vapors or solutions.

The heat-treatment to which the chloride-treated material is submitted according to a process of our invention may be considerably varied. We have found that in general the time of exposure desirable for the heat treatment varies inversely with the temperature. Thus, in a short time high temperatures accomplish results which lower temperatures require longer exposure to produce.

This time-temperature relationship applies over a considerable range of temperatures. An appreciable water repellency in paper may be developed, for instance, by treating the paper with chromyl chloride vapor and storing the treated paper for a period of a few days at temperatures as low as about 38° C. We have found that by raising the temperature this period of storage is remarkably shortened. Thus, we will ordinarily prefer to use for the heat treatment tempera-

tures of about 50° C. or higher for periods of a few seconds to a few minutes.

It will be understood that the temperature used should not be so high as to cause deterioration of the material being treated. We have found that in most instances satisfactory results are obtained at temperatures not exceeding about 200° C.

The hydrophobic products obtained by the processes of our invention contain the metal ion of the chloride in some form of combination. Whether this is a loose chemical combination, an adsorption, or merely a physical coating, the fact remains that the metallic ion is fixed in the treated material. This is emphasized by the fact that it cannot be washed out by laundering or extraction with carbon tetrachloride. The amount of metal ion present may be considerably varied, depending upon the character of the material treated and the degree of water repellency desired. We have found that a chromium ion retention of from about five-hundredths to twenty-five hundredths per cent based on the weight of the treated material gives satisfactory water repellence while with tin tetrachloride the tin ion retention should be preferably from about one-tenth to one per cent. It will be understood that when reference is made to ions, these ions may be present in combined form, as in the form of chlorides or complex compounds.

The water repellency developed by the presence of a given amount of chromium or tin ion in a polysaccharide is related to the time and temperature of a heating and aging after-treatment as already shown above. This relationship may be expressed mathematically as follows:

$$t = \frac{A}{C} \cdot 2.7183^{\frac{B}{T}}$$

where A and B are constants,  $t$  is the time of the heat treatment, C is weight per cent of chromium ion in the paper, and T is the temperature in degrees absolute used in the heat treatment. From this expression it will be seen that, temperature being constant, increasing the concentration of chromium ion in the treated paper decreases the time required for the heat treatment.

The values of the constants A and B in the above expression are to some extent dependent upon the particular material being treated. For most materials A will have a value in the range from about  $10^{-10}$  to  $10^{-12}$  and B will have a value of from 8000 to 9000, such values being constant for a particular material. For an unsized paper made with about one-third soda pulp and two-thirds sulfite pulp, for instance, we have found the values of A and B, respectively, to be  $10^{-11}$  and 8500. It will be evident that the above expression shows the minimum time of heat treatment desirable, and that somewhat longer times often may be employed advantageously.

While we have described our novel processes and products with reference to particular applications and compositions, it will be understood that without departing from the scope of our invention one skilled in the art may employ numerous processes for imparting water-repellency to water-insoluble polysaccharides using a chloride of the group consisting of stannic and chromyl chlorides.

We claim:

1. A water-insoluble polysaccharide having a hydrophobic surface characterized by the presence thereupon of an orientated layer of thermal

interaction products of the polysaccharide and chromyl chloride.

2. Paper having a hydrophobic surface characterized by the presence thereupon of an orientated layer of thermal interaction products of the paper and chromyl chloride.

3. In a process for imparting hydrophobic character to hydrophilic, water-insoluble polysaccharides, the steps comprising exposing a water-insoluble substantially dry polysaccharide to contact with chromyl chloride in a treating zone, then removing the polysaccharide from the treating zone and thereafter heating the polysaccharide whereby a water-repellent orientated layer of interaction products of the polysaccharide and the chloride is produced on the surface of the polysaccharide.

4. In a process for imparting hydrophobic character to paper, the steps comprising exposing the paper in a substantially dry condition to contact with chromyl chloride in a treating zone, then removing the paper from the treating zone and thereafter heating the paper, whereby a water-repellent orientated layer of interaction product of the paper and the chromyl chloride is produced on the surface of the paper.

5. In a process for imparting hydrophobic character to hydrophilic, water-insoluble polysaccharides, the steps comprising exposing a water-insoluble substantially dry polysaccharide to contact with chromyl chloride in a treating zone, then removing the polysaccharide from the treating zone and thereafter heating the polysaccharide, the time and temperature of heating being related by the expression  $t = A/C \cdot 2.7183^{B/T}$ , where  $t$  is the time of the heat treatment,  $C$  is the weight per cent of chromium ion in the paper,  $T$  is the temperature in degrees absolute used in the heat treatment,  $A$  is a constant having a value in the range from about  $10^{-10}$  to  $10^{-12}$ , and  $B$  is a constant having a value of from about 8000 to 9000.

6. In a process for imparting hydrophobic character to paper, the steps comprising exposing paper in a substantially dry condition to

contact with chromyl chloride in a treating zone, then removing the paper from the treating zone and thereafter heating the paper, the time and temperature of heating being related by the expression  $t = A/C \cdot 2.7183^{B/T}$ , where  $t$  is the time of the heat treatment,  $C$  is the weight per cent of chromium ion in the paper,  $T$  is the temperature in degrees absolute used in the heat treatment,  $A$  is a constant having a value in the range from about  $10^{-10}$  to  $10^{-12}$ , and  $B$  is a constant having a value of from about 8000 to 9000.

7. In a process for imparting hydrophobic character to hydrophilic, water-insoluble polysaccharides, the steps comprising exposing a water-insoluble substantially dry polysaccharide to contact with a vapor comprising chromyl chloride in a treating zone, then removing the polysaccharide from the treating zone and thereafter heating the polysaccharide whereby a water-repellent orientated layer of interaction products of the polysaccharide and the chloride is produced on the surface of the polysaccharide.

8. In a process for imparting hydrophobic character to hydrophilic, water-insoluble polysaccharides, the steps comprising exposing a water-insoluble substantially dry polysaccharide to contact with chromyl chloride in a treating zone, then removing the polysaccharide from the treating zone and thereafter heating the polysaccharide to a temperature of from about 38 to about 200° C., whereby a water-repellent orientated layer of interaction products of the polysaccharide and the chloride is produced on the surface of the polysaccharide.

9. A water-insoluble polysaccharide having a hydrophobic surface characterized by the presence thereupon of an orientated layer of thermal interaction products of the polysaccharide and chromyl chloride, the chromium ion present in the chromyl chloride comprising from about five hundredths to twenty-five hundredths per cent by weight of the polysaccharide.

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