Patented June 24, 1930 1,767,662

UNITED STATES PATENT OFFICE

ROBERT R. FULTON, OF WILKINSBURG, PENNSYLVANIA, ASSIGNOR TO THE KOPPERS COMPANY, A CORPORATION OF DELAWARE

PROCESS OF TREATING CELLULOSE TO PRODUCE VULCANIZED FIBER AND THE LIKE

No Drawing. Application filed March 16, 1927. Serial No. 175,932.

This invention relates to the treatment of cellulose to gelatinize or dissolve the same. The invention has particular application to the production of vulcanized fiber, imitation parchment and the like.

An object of my invention is to provide an improved process of gelatinizing cellulose and of manufacturing vulcanized fiber therefrom.

A second object of my invention is to provide a process of treating cellulose for the manufacture of vulcanized fiber and the like whereby high temperatures, the use of highly corrosive solutions and other undesirable features of the prior art may be avoided.

My invention has for further objects such other operative advantages or results as may hereinafter be found to obtain.

At the present time, the manufacture of vulcanized fiber is generally conducted according to the well-known zinc chloride method. According to this process, a certain grade of cotton rag paper is subjected for a few seconds to the action of a 70° Baumé solution of zinc chloride at a temperature of about 50° C. After this treatment and while the paper retains some of the solutions, the paper is rolled upon a large heated drum and is subjected to a slight pressure from an adjacent roll. When the desired thickness is obtained, the spongy mass is cut from the roll and placed flat on a table or the like for a short time to assume the proper form. It is then placed on edge in a dilute solution of zinc chloride. Subsequently, the treated fiber is washed, dried and pressed in the usual manner to form the hard sheet known as vulcanized fiber.

In the above-recited process, the concentration of the zinc chloride solution, the temperature of the bath and the time of the treatment must be carefully controlled to prevent the formation of a dark, brittle fiber.

The use of concentrated calcium thiocyanate solutions has been proposed in U. S. Patents Nos. 1,301,652 and 1,333,465, to Clayton et al., who discovered that the solvent properties of such solutions with respect to cellulose could be utilized to gelatinize cellulose. According to the patented process, cellulosic material, such as cotton rag paper, is treated with calcium thiocyanate solutions of such concentration as to boil at 157° C., and preferably having an acid reaction. The paper is treated with such solution at a temperature of 130° C. for about 30 seconds and is thereafter washed and dried in the usual manner.

The solutions proposed in the above recited patents are very concentrated, being, in fact, so concentrated that they are very viscous, even at 130° C., and solidify at atmospheric temperatures, especially in acid condition.

According to my invention, I treat cotton rag pulp paper, paper made from chemical wood pulp, or the like, with a neutral or alkaline solution of calcium thiocyanate or other thiocyanates of such concentration as to have a boiling point of from about 130° to about 140° C., and preferably containing comparatively large amounts, for example, from about 15% to about 30% of formaldehyde. The treatment is carried out at substantially atmospheric temperatures, for example, from about 20° to 40° C. Preferably I do not allow the fiber to remain in the treating bath until gelatinization is complete, but I remove the fiber from the bath after a short time and allow the treated fiber to lie flat for a sufficient interval to insure that gelatinization is carried to a satisfactory degree.

By "formaldehyde" is meant the usual aqueous solution thereof containing approximately 40% by volume of CH_2O and some times known as "formalin."

It will be obvious to those skilled in the art that the actual treatment of the fiber will be subject to many modifications, such as time of treatment, concentration of solution, nature and state of cellulosic materials used, pressure and the like, according to the nature of the materials treated or the character of the results desired. However, in order that my invention may be clearly set

forth and understood, a preferred example of its performance is given.

Cotton rag or wood pulp paper is run through a bath containing 3 parts of an 80% solution of $Ca(CNS).3H_2O$ and one part of formaldehyde. The reaction of the solution is preferably neutral or slightly alkaline and the temperature of the solution is maintained at any convenient point within the approximate range of from 20° to 40° C. Higher temperatures are to be avoided. The paper is run through the bath at any speed that permits thorough wetting without retaining the paper in the bath for extended intervals. It is then wound, as in prior practice, upon a large drum, except that the drum is not heated. After a sufficient number of layers of the paper have been wound upon the drum to produce a sheet of desired thickness, it is removed, cut to desired size and allowed to lie flat for from 30 minutes to several hours in order to permit gelatinization to take place. It is then pressed, either with or without heat, washed, preferably by the counter-current system, dried and again pressed to form a flat sheet of hard fiber which may be drilled, machined and polished, as desired.

Although a certain amount of adhesion of the built-up layers or laminations of fiber may take place prior to the initial pressing operation, such pressing is desirable to insure that the layers adhere thoroughly to each other.

The length of time required for the gelatinization period will vary considerably with the nature of the raw material treated and the quality of the result desired and is best determined by previous experiment for every condition.

There are many advantages to be gained by treating cellulose according to my invention. It requires no high temperatures, the use of which is always attended with considerable cost. Hot solutions of calcium thiocyanate are much more corrosive, especially in acid condition, than the cold, less concentrated and neutral or alkaline solutions which I prefer. Cold solutions of calcium thiocyanate give rise to less occupational hazards than hot solutions. Moreover, the presence of formaldehyde in my preferred solution reduces its corrosive action.

A solution of calcium thiocyanate having a boiling point of 157° C., is very viscous, and, although applied to the paper at 130° C., cools quickly on the surface of the paper, becoming more viscous, or even crystalline, and rendering its removal from the forming rolls difficult. Much excess material is thus carried to the washing vats.

In my work, I have found that neutral or alkaline solutions of calcium thiocyanate crystallize much less readily than acid solutions. Furthermore, the solutions of calcium thiocyanate which I prefer to use, with a boiling point of about 134° C., although viscous, show no tendency to crystallize at ordinary temperatures, and the addition of formaldehyde reduces the viscosity of such solution and actually increases the gelatinizing action.

In the process of the aforesaid patents and the present zinc chloride process, gelatinization of the cellulose takes place in the treating bath. Consequently, the fiber leaving the bath is very tender and requires extreme care in handling to avoid damage.

In my process, gelatinization does not take place to any substantial extent in the treating bath and the issuing fiber contains much of its original mechanical strength. The sheets can be removed from the forming roll without difficulty. Furthermore, hard fiber produced by my process is not subject to that tendency to blister which at present is the cause of a great deal of annoyance and loss to the manufacturers of vulcanized fiber. Blistering is caused by the presence in the paper of spots which have not been gelatinized to the same degree as surrounding areas and, therefore, do not adhere to the adjacent laminations in the fiber sheet. Especially in the zinc chloride process, the extremely brief period of time which is allowed for subjecting the paper to the action of the bath makes uniformity of degree of gelatinization very uncertain. A dense area in the paper being treated, being relatively less absorbent than the surrounding paper, will be insufficiently gelatinized.

My process has a further advantage with respect to the present zinc chloride method in that the fungus growth which occurs in fiber treated according to the prior method, especially during warm months, and resulting in the formation of white and friable spots, is not incident to the treatment of fiber according to my invention. Obviously, fiber made from solutions containing approximately 25% formaldehyde would not be subject to the growth of fungi.

My invention is not limited to the specific examples given hereinabove by way of example for many modifications of such procedure will be apparent to those skilled in the art, but my invention may be embodied and practiced within the scope of the following claims.

I claim as my invention:

1. The process of gelatinizing cellulosic material which comprises treating it with a solution of calcium thiocyanate and formaldehyde at substantially atmospheric temperatures.

2. The process of gelatinizing cellulosic material which comprises treating it with a solution of formaldehyde and calcium thiocyanate, the latter not being present in suf-

ficient amount to cause crystallization at atmospheric temperatures.

3. The process of gelatinizing cellulosic material which comprises treating it with a solution of calcium thiocyanate and formaldehyde at substantially atmospheric temperatures, and allowing the treated material to gelatinize.

4. The process of producing vulcanized fiber which comprises treating paper with a solution of calcium thiocyanate and formaldehyde, allowing the treated paper to stand until gelatinized, and converting the thereby gelatinized paper into vulcanized fiber.

5. The process of producing vulcanized fiber which comprises treating paper with a solution of calcium thiocyanate of such concentration as to have a boiling point of from 130° to 140° C., and containing formaldehyde, allowing the treated paper to gelatinize, and subjecting it to finishing operations to convert it to vulcanized fiber.

6. The process of producing vulcanized fiber which comprises treating paper with a solution composed of substantially 3 parts of an 80% solution of calcium thiocyanate and one part of formaldehyde and converting the thereby treated paper into vulcanized fiber.

7. The process of producing vulcanized fiber which comprises treating paper with a solution composed of substantially 3 parts of an 80% solution of calcium thiocyanate and one part of formaldehyde, and of neutral or slightly alkaline reaction, and converting the thereby treated paper into vulcanized fiber.

In testimony whereof, I have hereunto subscribed my name this fifteenth (15) day of March 1927.

ROBERT R. FULTON.