Patented Sept. 14, 1937 2,092,749

UNITED STATES PATENT OFFICE

2,092,749

PROCESS AND COMPOSITION OF MATTER

George B. Bradshaw, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application October 12, 1932, Serial No. 637,559

10 Claims. (Cl. 210—204)

This invention relates to acid resistant material, particularly fibers and fabrics which are capable of withstanding the chemical action of mineral acids, and a process for the manufacture thereof. It especially contemplates the production of filter-cloths which are not only highly acid resistant but possess excellent mechanical strength.

As is well known, it is impossible to filter solid materials from an acid medium with ordinary filter cloth, for the reason that the cloth is destroyed by the action of the acid. It is known also that when cloth of cellulosic origin is subjected to the action of nitric acid there results a change in the cloth which makes it less susceptible to the action of mineral acids such as, for example, hydrochloric, sulfuric, phosphoric and nitric acids. Heretofore, this increase in resistance to acids has always been accompanied by a lowering of the tensile strength of the cloth to the extent that it was of little commercial value. Furthermore, the treatment of the cloth with nitric acid caused it to become harder, more or less brittle, and somewhat gelatinized.

It is an object of the present invention to produce fibers and fabrics, and especially filter cloths, which are highly acid resistant, are pliable, and possess good tensile strength. A further object is the provision of a new and improved process for producing materials of the character above described. Other objects of the invention will be apparent by reference to the following description thereof.

These objects are accomplished according to the invention whereby highly acid-resistant materials are obtained by treating certain cellulosic fibers and/or fabrics with a nitrating acid to produce a product containing in excess of 13.0%, and preferably about 13.4% nitrogen by weight, while regulating the concentration of the acid, the temperature and the time of treatment to avoid substantial gelatinization of the cellulose and substantial loss of tensile strength. The process of nitration is preferably effected by subjecting the cellulosic materials to the action of nitric acid in stages.

While the invention is susceptible of considerable variation and modification in the manner of its practical application, particularly as regards the nature and proportions of the materials and the exact procedure employed, the following examples will illustrate how the invention may be practiced. The proportions and concentrations are given by weight.

Example I

Unbleached loosely woven cotton cloth formed of loosely spun threads and containing about 3% to 9% of moisture was produced without subjecting the cotton to artificial heat or otherwise treating it in any manner so as to cause deterioration of the cellulose. More specifically, the fabric referred to was a carded Chafer Peeler, 9¼ ounce per square yard weight, 30 pick warp, 30 pick filler, threads 20–4 ply and square weave. A piece of this material was immersed in eighty times its own weight of a mixed acid solution containing about 83% nitric acid, 11% sulfuric acid, and 6% water, the temperature being maintained at about 20° C. to 25° C. The treatment was continued for about 30 minutes (or until the maximum nitrogen content possible without loss of tensile strength had been obtained). The cloth was then removed from the first acid bath and quickly submerged in a body of practically anhydrous mixed acid containing about 50% nitric acid and 50% sulfuric acid. The volume of acid and temperature employed were substantially the same as for the first acid. This second treatment was continued for about one hour. The cloth was then removed from the second acid bath and washed. It contained by analysis about 13.4% nitrogen on the dry basis. Samples of the original cloth and the nitrated cloth were tested for tensile strength, and it was found that for the same linear width of sample, the tensile strength of the nitrated cloth was substantially the same as that of the un-nitrated cloth.

Example II

A piece of 21 ounce per square yard weight loosely woven twill, the fibers of which had never been deteriorated by boiling or otherwise, was treated by the procedure set out in Example I. It was found desirable to continue the treatment in the first acid for about one and one-half hours and the treatment in the second acid for about three hours. The tensile strength of the nitrated cloth was about 85% of that of the unnitrated cloth for the same linear length. It was noted, however, that the shrinkage of this heavier cloth was not as much as that of the lighter weight cloth described in Example I.

Example III

A piece of 5 ounce per square yard weight Chafer fabric woven from combed Egyptian cotton yarn which had not been boiled, sized or subjected to any chemical treatment whatsoever, other than the usual process of fumigating Egyp-

tian cotton upon its arrival in the United States, was treated as described in Example I. The most desirable results were obtained with a 20 minute treatment in the first acid and a 40 minute treatment in the second acid. The tensile strength of the nitrated cloth was substantially the same as that of the unnitrated cloth.

All of the cloths described in the examples were tested by immersion in 40% sulfuric acid for thirty minutes at 90° C., and it was found that all of the cloths retained at least 50% of their tensile strength. It will be recognized that these testing conditions are rather severe and are not such as are likely to be encountered in ordinary filtering operations. Nitrated cloths of the type described may be used in filtering 55% phosphoric acid solutions at 80° C. for over 100 hours without difficulty. Again, it will be recognized that these are rather severe filtering conditions.

The general procedure described in the examples is applicable to the treatment of fabrics of any weight. In general, the relatively heavy fabrics such as described in Example II have been found to be most desirable for filter press operations. While the most highly advantageous results have been obtained in the treatment of cotton fabrics, in its broader aspects the invention contemplates the treatment of certain other cellulosic materials. It has been found that linen, for example, may also be treated with very satisfactory results. In general, the process of the invention is preferably applied to materials of the class known as pecto celluloses (cotton, ramie, flax, hemp and the like) as distinguished from the ligno celluloses (wood and the like).

When cloth is nitrated as herein described, the nitration may cause it to shrink from 15% to 30% in area and, for this reason, it is desirable to use a loosely woven material. Furthermore, a tightly woven fabric does not allow the acid to penetrate satisfactorily. The best results are generally obtained when the warp and woof of the fabric are equi-distant and have substantially the same tensile strength.

In the practice of the invention, it has been found that the results obtained in nitrating natural cellulosic materials of the class described are far superior to those obtained in the nitration of materials which have been chemically treated. Thus, it was found that when a cotton twill comparable to that used in Example II was boiled in a weak alkaline solution (about 2% soda ash based on the weight of the cloth) for six to eight hours, washed until neutral and dried at 105° C. to constant weight, then nitrated as in Example II, the nitrated cloth obtained had a much lower tensile strength than the cloth of Example II and was of little value for commercial filter-press operations. Since it is customary in the manufacture of cellulosic fabrics to heat, bleach, or otherwise chemically treat them, the discovery that natural fibers and fabrics yield better results is considered to be a feature of the present invention.

If it is desired to condition or purify the cellulosic fiber or fabric to be nitrated, it is preferable that such conditioning be effected without ever removing therefrom substantial amounts of the natural moisture, that is, the moisture which remains in the cellulose fiber when it is allowed to air-dry under normal atmospheric conditions. The removal of this "water of condition", or "water of hygroscopicity", as it is sometimes called, apparently has some deteriorating effect on cellulosic materials which renders them unsatisfactory for the purposes of the invention. Generally speaking, the water content may vary from about 3% to 12% by weight of the various cellulose materials and, for any particular kind of cellulose, may vary on either side of the average water content by about 1% to 2% by weight within the extreme range of ordinary atmospheric conditions.

The composition of the nitrating acid may vary widely. It should preferably be so regulated as to effect nitration of the fiber or fabric without substantial gelatinization. At the same time, the concentration of nitric acid present should preferably be sufficiently high to insure penetration of the fiber or fabric. If nitrating acid of relatively high HNO_3 content is not used initially, the reaction with the cellulose, which forms water, may dilute the acid to such an extent that the cellulosic fibers are not uniformly nitrated. Also, in the initial treatment of the cellulosic material, if sulfuric acid is used in the nitrating acid, it is desirable that it be present in relatively small amounts, since the formation of cellulose sulfate esters which would occur to a considerable extent if large proportions of sulfuric acid were present has the effect of weakening the fibers undesirably. On the other hand, a relatively small amount of sulfuric acid may increase the penetrating power of the nitric acid without weakening the fiber substantially. After the cellulosic material has been nitrated to some extent, larger proportions of sulfuric acid appear to aid the nitration without unduly weakening the material. Instead of sulfuric acid, the nitrating acid may contain other reagents adapted to increase the penetrating power of the nitric acid, as for example, acetic acid or phosphoric acid.

For the practical application of the nitrating process, it has been found desirable to carry out the nitration in two stages, that is, by two acid treatments. Considerable variation is permissible in the acid composition used for the first treatment. As illustrations of nitrating acids which may be used in this stage may be mentioned anhydrous nitric acid, nitric acid containing water, or a nitric acid-sulfuric acid solution which may contain water. If a nitric acid-water solution is employed, the amount of water present should preferably be less than about 4% by weight. In general, it is preferable to employ a mixed nitric-sulfuric acid solution having an HNO_3 content of at least about 76% by weight, the remainder being sulfuric acid and/or water (preferably not exceeding 12%).

The composition of the acid solution employed for the second treatment may also vary within relatively wide limits. It is preferable, however, that the water content of this second acid should vary from about 4% to slightly fuming. The acid content of this second solution should preferably be more than about 40% and less than about 60% HNO_3, the remainder being H_2SO_4. Especially desirable results are obtained when the first acid solution contains about 82% to 83% HNO_3, 7% to 8% H_2O and about 10% H_2SO_4, and the second acid solution contains about 50% to 55% HNO_3 and 45% to 50% H_2SO_4. Small amounts of N_2O_3 may also be present in the acid solutions employed.

The volume of each acid bath should preferably be such that the heat of reaction is quickly dissipated and that the strength of the acid is maintained nearly uniform in spite of the water formed from the reaction with the cellulose.

Generally speaking, an acid volume corresponding to 60–100 times the weight of the material treated gives satisfactory results.

During the nitration, the temperatures of the acid baths should preferably be not lower than about 12° C. or higher than about 30° C. The reaction slows up to an undesirable extent when temperatures much lower than 20° C. are utilized and a slowing up of the reaction is particularly disadvantageous for the reason that time is allowed for side reactions. When the temperature utilized exceeds about 30° C., reactions may occur which weaken the fiber or fabric.

While the time of nitration may vary within relatively wide limits depending largely upon the temperatures and concentrations of the acids employed, practical application of the process has demonstrated that the length of time of the immersion in both the first and second acids should be properly controlled. Too short a time of immersion of the material in the first acid results in a partial nitration or chemical change which gives undesirable results, while too long an acid treatment may cause gelatinization of the cellulose. A method of procedure which may be used in actual practice involves immersing the material in the first acid until the maximum nitrogen content is obtained without substantial loss of tensile strength.

Close control of the second nitrating step is also important since in this step the fibers are subjected to a most intensive nitrating or chemical action. It has been found that the second treatment is desirable if material having commercial possibilities is to be produced. It is not intended to indicate that cloth which has not been subjected to the second acid treatment has no use. The cellulosic fiber may have its nitrogen content raised to about 13% in the first treatment, but such material does not withstand filtration media containing sulfuric or phosphoric acids as well as the after-treated materials.

The method of nitration may be varied widely. It may conveniently be a so-called pot process in which the nitrating acids are contained in open vessels. The cloth is then immersed in the first acid by suspending it from rods and weighting it at the bottom. After the desired nitration is effected, it is removed from the first acid and transferred to the second acid. In the transfer some of the first acid is carried along. After immersion in the second acid, it may be withdrawn and washed with a stream of water. The finished cloth is preferably preserved in a damp or wet state.

Insofar as is known, nitrated fabrics produced in accordance with the preferred process of this invention are more resistant to acids than any of the types of filter-cloths previously known. They are particularly advantageous for use in filter press filtrations because in such operations it is desirable that the filter cloth used should possess not only good mechanical strength and resistance to acids but also pliability to the extent that the cloth will return to its original shape when the filter cake has been removed. In a given filter press filtration involving an acidic solution, the improved filter cloths prepared according to the present invention will last at least seventy times longer than the same cloth unnitrated.

As many apparent and widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that I do not limit myself to the foregoing examples or description except as indicated in the following claims.

I claim:

1. In a process of producing nitrated cellulosic materials highly resistant to acids, the steps which comprise treating cellulose materials with a nitrating acid sufficiently high in nitric acid and deficient in water and auxiliary penetrating acid, and at a temperature and for a time such that partial nitration is effected without substantially changing the appearance of the material treated and without substantially altering its tensile strength, and continuing the nitration with a more strongly nitrating acid which contains less nitric acid, about 0–4% water and materially more auxiliary penetrating acid than the first acid, until the nitrogen content of the material treated is in excess of 13%.

2. In a process of producing nitrated cellulosic materials highly resistant to acids, the step which comprises nitrating a cellulose material to a nitrogen content in excess of 13% with a nitrating acid containing about 40% to about 60% HNO_3, 0–4% water, the remainder being an auxiliary penetrating acid.

3. In a process of producing materials highly resistant to acids, the steps which comprise subjecting a natural cellulosic material of the pecto cellulose class to the action of a nitrating acid selected from the group consisting of anhydrous nitric acid, nitric acid containing less than about 4% water, nitric-sulfuric acid mixtures containing more than about 76% HNO_3, and nitric-sulfuric acid-water mixtures containing more than about 76% HNO_3, less than about 12% water, the remainder being sulfuric acid; and then treating the resultant product with a nitrating acid containing less than about 4% water, about 40% to 60% HNO_3, the remainder being sulfuric acid.

4. In a process of producing acid resistant materials, the steps which comprise subjecting natural cotton fabrics to the action of a nitric-sulfuric acid solution containing more than about 76% by weight HNO_3, less than about 12% water, the remainder being sulfuric acid, thereafter treating the resultant product with a nitric-sulfuric acid solution containing less than 4% of water and about 40% to about 60% HNO_3.

5. In a process of producing acid resistant materials, the steps which comprise subjecting natural cotton fabrics to the action of an acid solution containing about 82% to 83% HNO_3, 7% to 8% H_2O, and about 10% H_2SO_4 and thereafter treating the resultant product with an acid solution containing about 50% to 55% HNO_3 and 45% to 50% H_2SO_4.

6. The process of producing acid resistant materials which comprises subjecting an undeteriorated cotton fabric to the action of an acid solution containing at least 76% HNO_3, not more than 12% water, the remainder being H_2SO_4, until the maximum nitrogen content of the product is obtained without substantial loss of tensile strength and thereafter treating the resultant product with a nitric-sulfuric acid solution containing less than about 4% water, and more than about 40% HNO_3 but less than about 60% HNO_3, until the nitrogen content of said product is about 13.4% by weight, while maintaining a temperature of 20° C. to 30° C. in both acid solutions.

7. The process of producing an acid resistant filter cloth of high tensile strength which comprises immersing unbleached loosely woven cotton cloth containing about 3% to 9% of mois-

ture and which has never been boiled in aqueous solutions, subjected to relatively high temperatures, or in any manner had substantial amounts of the natural moisture removed therefrom, in an 80 fold volume of a mixed acid solution containing about 83% nitric acid, 11% sulfuric acid and 6% water at a temperature of about 20° C. to 30° C. until the maximum nitrogen content of the product without substantial loss of tensile strength has been obtained, and then removing the resultant cloth from the acid bath and immediately thereafter submerging it in a substantially anhydrous acid mixture containing about 50% nitric acid and 50% sulfuric acid until the nitrogen content of the product is about 13.4% by weight.

8. A nitrated natural cellulosic fabric characterized by the properties that it contains in excess of 13% nitrogen, has practically the same general appearance as the original unnitrated fabric, possesses at least 85% of the tensile strength of the original unnitrated fabric for the same linear width and retains at least 50% of its tensile strength after being immersed in 40% sulfuric acid for thirty minutes at 90° C.

9. A nitrated natural cellulosic fabric containing about 13.4% nitrogen, characterized by the properties that it possesses at least 85% of the tensile strength of the original unnitrated fabric for the same linear width and retains at least 50% of its tensile strength after being immersed in 40% sulfuric acid for thirty minutes at 90° C.

10. A nitrated natural cotton fabric containing about 13.4% nitrogen, characterized by the properties that it possesses at least 85% of the tensile strength of the original unnitrated fabric for the same linear width and retains at least 50% of its tensile strength after being immersed in 40% sulfuric acid for thirty minutes at 90° C.

GEORGE B. BRADSHAW.