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MANUFACTURE OF CARBON CLOTH

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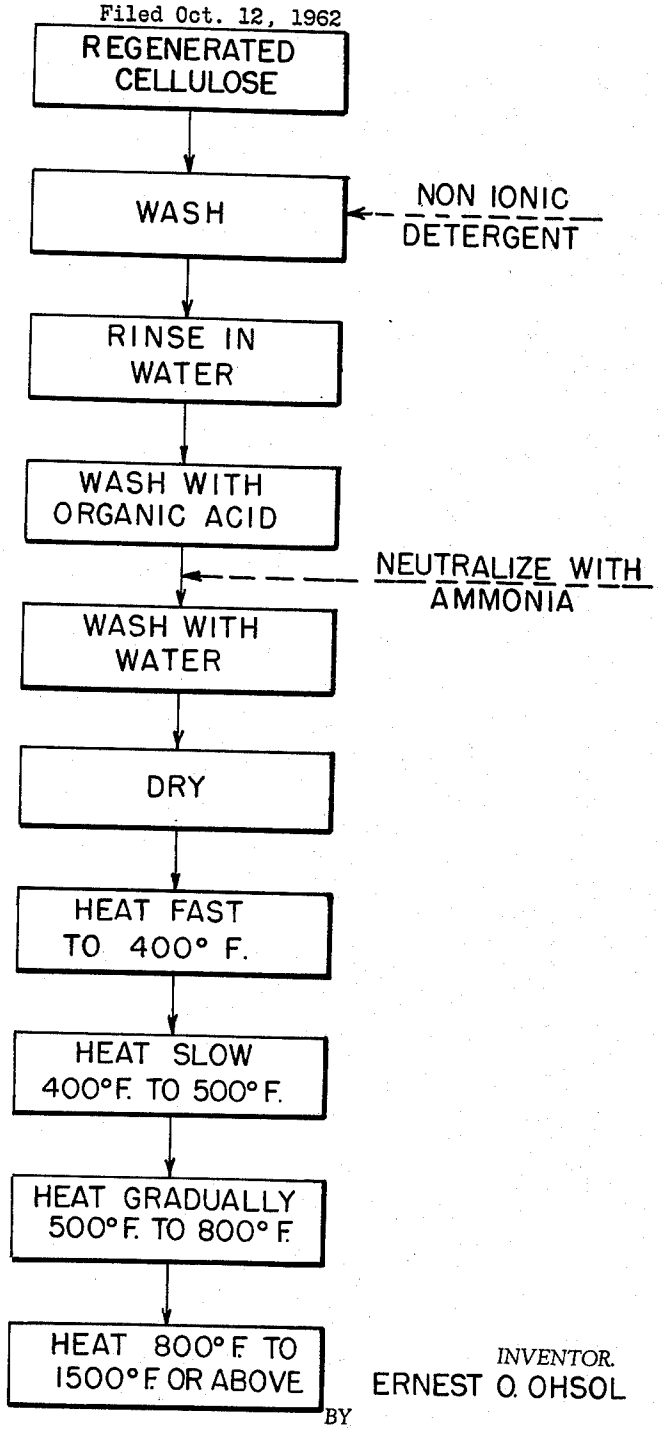

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MANUFACTURE OF CARBON CLOTH

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This invention relates to the preparation of carbon fibers.

It has been proposed in the past to prepare carbon fibers from cellulosic materials, e.g., Edison Patent 470,925, or more especially from regenerated cellulose, e.g., Soltes Patent 3,011,981 and Abbott Patent 3,053,775. However, it has been found difficult to obtain reproducible, good quality, high strength carbon fibers, e.g., in the form of yarn or cloth, by present procedures. While good quality products are obtained in some runs, in other runs employing exactly the same conditions the quality is poor.

Accordingly, it is an object of the present invention to prepare good quality carbon fibers from regenerated cellulose, e.g., in the form of yarn, cloth and the like, with reproducible results.

Another object is to prepare carbon fibers from regenerated cellulose in the form of yarn and cloth having increased tensile strength.

A further object is to device an improved procedure for forming carbon fibers from regenerated cellulose.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained if regenerated cellulose fibers, preferably in the form of cloth, are washed to a sodium content below 25 parts per million (p.p.m.) and preferably below 10 p.p.m.

Sodium, generally in the form of salts, is introduced into the regenerated cellulose cloth or yarn during the processing and it has been found essential to limit the sodium content in the manner indicated. Certain special regenerated celluloses have a sodium content below 25 p.p.m. and it is not necessary to employ the instant washing procedure thereon.

As used in the present specification and claims the term "regenerated cellulose" is intended to embrace fibers of viscose rayon, cuprammonium rayon and saponified cellulose ester rayon, e.g., saponified cellulose acetate rayon.

The invention will be best understood with reference to the accompanying drawing which is a diagrammatic illustration of the invention.

There is provided regenerated cellulose, preferably high tenacity rayons, in the form of cord, yarn, cloth or the like having a sodium content above 25 p.p.m. While the sodium content can be reduced to below 25 p.p.m. simply by copious washing with water, it has been found preferable to hasten the process utilizing the procedure in the flow sheet. Furthermore, while the most important factor is to reduce the sodium content below 25 p.p.m., most preferably below 10 p.p.m., it is also desirable to reduce the total ash below 200 p.p.m. and preferably below 50 p.p.m.

The regenerated cellulose is first washed in water. The water most preferably contains a detergent. While potassium and ammonium containing anion detergents can

be used, e.g., potassium lauryl sulfate, potassium dodecyl benzene sulfonate, ammonium decyl benzene sulfonate, potassium sulfosuccinate, ammonium di (2-ethylhexyl) sulfosuccinate, it is preferable to employ nonionic detergents such as Triton X–45, Triton X–114, Triton X–100, Triton X–102, Triton N–101 and Triton N–128. The Tritons of the X series are the reaction products of t-octylphenol with ethylene oxide and the Tritons of the N series are reaction products of t-nonylphenol with ethylene oxide, i.e., the Tritons are alkylphenoxy polyalkoxyalkanols. In Triton X–45 there are five ethylene oxide groups, in Triton X–114 there are 7 to 8 ethylene oxide groups, in Triton X–100 and Triton N–101 there are 9 to 10 ethylene oxide groups, and in Triton X–102 and Triton N–128 there are 12 to 13 ethylene oxide groups.

There can be used corresponding surface active agents where the ethylene oxide groups are replaced by propylene oxide groups, e.g., t-octylphenol oxypropylated with 10 propylene oxide groups. Other nonionic surface active agents include sorbitan sesquioleate, sorbitan-polyethylene oxide monolaurate, Ethofat 3 (the reaction product of ethylene oxide with a mixture of palmitic, stearic, oleic and linoleic acid), Ethofat 15 (the reaction product of ethylene oxide with a mixture of caprylic acid, capric acid and lauric acid), Ethomid 8 (the reaction product of the amides of caproic, caprylic and capric acids with ethylene oxide), Ethomid 18 (the reaction product of the amides of palmitic, stearic and oleic acid with ethylene oxide), polyethylene glycol stearate (Myrj 45), tertiary dodecyl polyethylene glycol thioether (Nonionic 218), Pluronics (condensation products of ethylene oxide with polypropylene glycol), sorbitan monopalmitate, polyethylene glycol lauryl ether (Brij). The preferred nonionic detergents are the higher alkyl phenol-alkylene oxide addition products.

The detergent is used in an amount of 0.01 to 0.5% of the wash water, usually 0.1%.

If a detergent is employed in the wash water, then the regenerated cellulose is preferably rinsed in water to remove the detergent.

This is followed by an acid wash, generally at a pH of between 1 and 5. The acid wash contains a 1 to 10% solution of a water soluble organic or inorganic acid such as acetic acid, propionic acid, formic acid, oxalic acid, hydrochloric acid, phosphoric acid or sulfuric acid. Preferably acetic acid or hydrochloric acid is employed.

After the acid wash the regenerated cellulose is thoroughly washed with water. As indicated in the drawing, the acid is preferably neutralized first with ammonia prior to the water wash. The neutralization can be omitted but in such case considerably more water is required in the water wash. The regenerated cellulose is then dried either at room temperature or more preferably in an oven at a temperature up to 212° F.

The dried regenerated cellulose, e.g., in the form of cloth or yarn, is then converted to carbonized fibers, e.g., as cloth or yarn, either in known manner such as shown in the Soltes Patent 3,011,981, December 5, 1961, or Abbott Patent 3,053,775, September 11, 1962, or by an improved procedure as set forth below.

The dried regenerated cellulose which has been purified by removal of the sodium compounds and other non-cellulosic materials is heated in a nonoxidizing atmosphere in order to carbonize the fibers. As the nonoxidizing atposphere there can be used inert gases such as nitrogen, helium, argon or even a vacuum, e.g., 0.001 mm. Also, there can be employed reducing gases such as hydrogen. Such procedures are known in the art, such as Soltes and Abbott, for example. Preferably, however, there is employed ammonia since superior results can be attained therewith. The use of ammonia as the gas is an improve-

ment over the procedures which have been employed in the past.

While ammonia gas is preferably employed in the present process for forming carbon fibers in which regenerated cellulose having a sodium content above 25 p.p.m. is reduced to a sodium content below 25 p.p.m., it is also possible to use the ammonia gas to improve prior art processes such as those of Soltes or Abbott.

The purified and dried regenerated cellulose in the nonoxodizing atmosphere is heated fairly rapidly, e.g., in less than 2 minutes, to a temperature of 250 to 400° F., preferably between 300 and 400° F. It is then heated slowly at a temperature of 250° F. to 500° F., most preferably between 300 and 500° F. While the time can be as short as 2 hours, it is preferably at least 12 hours and can be as long as a week. The product is then gradually heated at a temperature of from 500 to 800° F. for 2 to 24 hours or longer, usually for 4 to 12 hours. Next, the temperature is raised from 800 to 1500° F. or above over a period of 2 to 1800 hours. At a top temperature of 1500° F. the product has 94% carbon, at a top temperature of 1800° F. the product has 96.5 to 97.5% carbon, and at a top temperature of 2000° F. the product contains 98 to 99% carbon. If the final temperature is elevated to 3500° F. or above, e.g., 5000° F., the product is converted into graphite fibers or cloth.

It has been found desirable to use a final temperature of 1800° F. because the resulting fiber product, whether in the form of cord, yarn or cloth, is very strong and, in fact, has ¼ the strength of the original regenerated cellulose prior to carbonization. Such carbonized products have a much higher strength than carbon fibers or cloths made from rayons having higher sodium contents than 25 p.p.m.

Unless otherwise indicated, all parts and percentages are by weight.

Example 1

Viscose rayon yarn having a sodium content of 100 p.p.m. was washed thoroughly with water until the sodium content was 10 p.p.m. and the total ash content was below 50 p.p.m. The rayon was then dried at 212° F. The dry product was placed in an oven at 350° F. in a nitrogen atmosphere and heated at 350 to 500° F. for 24 hours. It was then heated in a nitrogen atmosphere at a temperature of 500 to 800° F. for 6 hours and finally heated in a nitrogen atmosphere at a temperature increasing from 800 to 1800° F. over a period of 4 hours to obtain a carbon fiber product having 96.5% carbon.

Example 2

Wellington-Sears Fortisan-36 cloth, i.e., instantaneously saponified cellulose acetate rayon (regenerated cellulose), having 3400 filaments in the yarn and having 20 x 20 threads per square inch and having a sodium content above 50 p.p.m. was washed with water containing 0.1% Triton X-100, rinsed with water, washed with 2% aqueous acetic acid, neutralized with 6% aqueous ammonia and rinsed with water to give a cloth product having 22 p.p.m. of sodium. This product was dried at 212° F. and then converted to carbonized cloth by heating in a nitrogen atmosphere in the manner indicated below. The dry purified saponified cellulose acetate rayon was placed in an oven at 400° F. and heated at 400 to 500° F. for 12 hours. It was then heated at a temperature of 500 to 800° F. for 6 hours and finally heated at a temperature increasing from 800 to 1800° F. over 12 hours to obtain a strong carbon cloth having a carbon content of 97%, and a Mullen burst strength of 47 p.s.i.

Example 3

The process of Example 2 was repeated but ammonia was employed in place of nitrogen for the inert atmosphere to obtain a product which was even better than that of Example 2.

Example 4

The process of Example 2 was repeated utilizing 2% hydrochloric acid in place of the 2% acetic acid with similar results.

Example 5

The procedure of Example 2 was repeated but the regenerated cellulose was only washed to a sodium content of 52 p.p.m. The carbon cloth had a Mullen burst strength of only 12 p.s.i. This illustrates the importance of thorough washing to a sodium content below 25 p.p.m.

Example 6

The procedure of Example 2 was repeated but the acid was with a mixture of oxalic acid and acetic acid. The sodium content was only reduced to 26.6 p.p.m. The Mullen burst strength of the carbonized cloth was less than 19.

In another run wherein the sodium content was only reduced to 28.4 p.p.m. the Mullen burst strength was only 11.

Example 7

North American viscose rayon identified as Viscose CX658 was employed as the regenerated cellulose cloth. There were about 3400 filaments in the yarn and there were about 20 x 20 threads per square inch. The acid employed in the scouring was 5% acetic acid. The sodium content of the cloth after purification and prior to carbonization was 25 p.p.m. The final carbon cloth product had a Mullen burst strength of 15 p.s.i.

In another experiment when washing was carried out to a sodium content of 6.4 p.p.m. and the viscose cloth carbonized, the Mullen burst strength of the carbonized cloth was 62 p.s.i. This further illustrates the importance of sodium removal.

I claim:

1. A process of preparing carbon fibers of increased strength comprising washing regenerated cellulose fibers selected from the group consisting of viscose rayon, cuprammonium rayon and saponified cellulose acetate rayon having a sodium content above 25 p.p.m. with water until the sodium content is below 25 p.p.m., and then heating the regenerated cellulose in a nonoxidizing atmosphere, said heating being carried out at a temperature of 250° F. to 500° F. for from 2 hours to a week, and then at a temperature of 500 to 800° F. for 2 to 24 hours, and then at a temperature of 800 to 1500° F. for from 2 to 1800 hours to convert the fibers to carbon fibers.

2. A process according to claim 1 wherein the regenerated cellulose fibers are in the form of cloth.

3. A process according to claim 1 wherein at least a portion of the water wash is an aqueous acid wash.

4. A process according to claim 3 wherein at least a portion of the water wash is with water containing a nonionic detergent.

5. A process according to claim 1 wherein the regenerated cellulose fibers are washed to a sodium content below 10 p.p.m.

6. A process according to claim 5 wherein the regenerated cellulose fibers are in the form of cloth.

7. A process according to claim 1 wherein the nonoxidizing atmosphere is an inert gas.

8. A process according to claim 1 wherein at least a portion of the water wash is with a member of the group consisting of acetic acid and hydrochloric acid.

9. A process according to claim 8 wherein after the acid wash the regenerated cellulose is washed with aqueous ammonia.

10. A process according to claim 1 wherein the heating at the temperature of 500° F. and above is carried out in an ammonia atmosphere.

11. A process of preparing carbon fibers of increased strength comprising washing regenerated cellulose fibers selected from the group consisting of viscose rayon, cu-

prammonium rayon and saponified cellulose acetate rayon having a sodium content above 25 p.p.m. with water until the sodium content is below 25 p.p.m., and then heating the regenerated cellulose in a nonoxidizing atmosphere selected from the group consisting of nitrogen, helium, argon, ammonia, and a vacuum, said heating being carried out at a temperature of 250° F. to 500° F. for from 2 hours to a week, and then at a temperature of 500 to 800° F. for 2 to 24 hours, and then at a temperature of 800 to 1500° F. for from 2 to 1800 hours to convert the fibers to carbon fibers.

12. A process according to claim 11 wherein the nonoxidizing atmosphere is ammonia vapor.

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