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PREPARATION OF CARBON CLOTH

Edward R. Degginger, Convent Station, N.J., assignor to Allied Chemical Corporation, New York, N.Y., a corporation of New York

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ABSTRACT OF THE DISCLOSURE

A process for preparing fibrous carbonaceous mats or cloth comprising the steps of impregnating a fibrous cellulosic substrate with an aqueous solution containing borate and polyvinyl alcohol, allowing the aqueous component of said solution to evaporate from said impregnated cellulosic substrate, and then igniting said substrate.

BACKGROUND OF THE INVENTION

The invention relates to a process for the transformation of an interwined, fibrous cellulosic material into a carbon fiber having substantially the same structural form as the cellulosic precursor.

More particularly, the invention relates to a process for the preparation of carbon cloth or matting useful as a catalyst support or filtration medium or in other applications which utilize carbon.

Still more particularly, this invention relates to the preparation of interlaced or interwined fibrous carbon mats, cloths, or the like, from a mat or cloth or other fibrous form of cellulose using an aqueous solution containing borate and polyvinyl alcohol.

Carbon is well known to be substantially inert to most organic and inorganic chemical reagents such as organic solvents, inorganic and organic acids, aqueous caustic, and the like. Because of this chemical inertness, carbon is widely used as a catalyst support or as a filtration medium. In the latter field of application, the fact that carbon will preferentially adsorb certain polar organic compounds makes it particularly useful. Unfortunately, the fact that carbon is currently readily available only in the form of solid chunks or powder, e.g., charcoal briquettes or carbon black, limits its utility in some instances. In many cases, it is desirable to have carbon in fibrous form, e.g., a mat or cloth that is an integral and self-supporting, but nonetheless porous, foraminous, unit.

Although carbon filaments are known, to date, I have been unable to discover any teaching of a practical, inexpensive way to make an intertwined fibrous carbon, e.g., a cloth or mat.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an efficient and inexpensive process for the production of carbon cloths, mats, and the like.

Further objects and advantages will become apparent from the description of the invention which follows in greater detail.

The invention comprises impregnating a fibrous cellulosic material, hereinafter referred to as "substrate," with borate-polyvinyl alcohol aqueous solution, as hereinafter more specifically defined, removing the water component of such solution from the impregnated cellulosic substrate, preferably by evaporation, and then igniting or roasting the thus-treated cellulosic substrate which is thereby transformed into its carbon counterpart.

The cellulosic substrates which are amenable to transformation into their structurally analogous carbon counterpart include any fibrous, intertwined cellulosic material such as cotton-wool, woven or knitted cotton or

linen cloth, felted cotton or linen, cotton or linen twine or rope, and hemp, jute fiber, kapok, and similar processed, unprocessed, or partially processed, fibrous cellulosic matter.

When such fibrous cellulosic substrate is exposed, without treatment in accordance with the instant invention, to flame or to a temperature above its ignition point, it will decompose giving off flammable gases which, if sufficient air is present, also ignite and tend to further increase the temperature of the cellulosic material, thereby increasing its rate of decomposition. If the cellulosic substrate is exposed to a flame in the presence of excess air, it will ignite and burn. This burning continues until only carbonaceous material remains, whereupon the flame generally subsides, but the oxidation of the carbonaceous residue, i.e., afterglow, continues, until the initially formed carbonaceous residue is substantially totally consumed. For example, cotton cloth will burn and then glow until only a small amount of fragile, crumbly ash remains. If the cellulosic substrate is heated above its combustion temperature in the absence of an open flame, it will either ignite and carbonize or carbonize without ignition depending upon whether an excess, or merely a stoichiometric, quantity of air is present. In either event, crumbly ash will be formed.

However, if the fibrous cellulosic substrate, e.g., cheesecloth, which has been impregnated in accordance with the teaching of my invention, is exposed to a flame, it will ignite and burn, it will burn only to the point of forming a structurally analogous carbon counterpart, i.e., a carbon cheesecloth. It will not burn to a crumbly ash having little or no structural integrity. Likewise, if the cellulosic substrate, impregnated in accordance with the teaching of the instant invention, is heated, i.e., roasted, above about 200° C. in the absence of an open flame, it will again form a structurally analogous carbon counterpart and will not go to a crumbly ash.

The impregnation of the fibrous cellulosic substrate with the borate-polyvinyl alcohol mixture in accordance with my invention may be carried out by any of the known conventional procedures utilized for the impregnation of cellulosic fiber materials which are water soluble. For example, the cellulosic substrate may be immersed in the borate-polyvinyl alcohol aqueous solution, or the solution may be brushed or sprayed on the fibrous cellulosic substrate. After impregnation, the aqueous component of the solution is allowed to evaporate from the impregnated cellulosic fiber substrate leaving the borate and polyvinyl alcohol constituents of the solution both within and on the surface of the substrate. Such evaporation of the water may be effectuated either at ambient or above ambient temperature.

It is desirable that the amount of the combined borate and polyvinyl alcohol constituents of the aqueous impregnating solution which remains within or on the surface of the cellulosic substrate after evaporation of the water shall be from about 5 to about 40 percent by weight of the weight of the cellulosic substrate, preferably from about 10 to about 30 weight percent.

The solutions used in the practice of the instant invention are aqueous solutions containing (a) from about 0.5 to about 5.0 percent by weight of an alkali metal borate; and (b) from about 0.5 to about 5.0 percent by weight of a water-soluble polymer of vinyl alcohol. Such solutions are disclosed and claimed in copending commonly assigned U.S. application Ser. No. 602,760 filed Dec. 19, 1966.

The term "alkali metal borate" embraces not only the alkali metal salts of the common boric acids, i.e., tetraboric acid, $H_2B_4O_7$, meta-boric acid, HBO_2, and ortho-boric acid, H_3BO_3, but also the alkali metal salts of the other

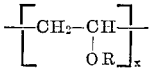
boric acids such as $H_2B_2O_4$, $H_2B_6O_{10}$, $H_2B_8O_{13}$, $H_2B_{12}O_{19}$, $H_6B_4O_9$, and $H_6B_8O_{15}$. With the exception of meta- and ortho-borate salts, such alkali borates have the general formula:

$$M_2O.mB_2O_3$$

wherein M denotes an alkali metal and m can range from 1 to 4. Hydrates of any of the foregoing borate salts are also suitable. The preferred borate is borax, i.e., sodium tetraborate decahydrate.

The term "water-soluble vinyl alcohol polymer" embraces vinyl alcohol polymers having up to 50% of the hydroxyl groups thereof replaced by methoxy, ethoxy, acetyl, propionyl or butyryl radicals, i.e., partially etherified or esterified polyvinyl alcohol. Said methoxy and ether radicals can be unsubstituted or substituted with hydroxyl or carboxyl groups. Said acetyl, propionyl and butyryl radicals can likewise be unsubstituted or can be halogen- or hydroxyl-substituted. Preferably, no more than about 20% of the polyvinyl alcohol hydroxyl groups will be replaced by any of the aforementioned ether or ester radicals.

The vinyl alcohol polymers utilized in the practice of the instant invention can, therefore, be represented by the structure:



wherein x can range from about 1200 to about 5000, preferably 1600 to 3000, and wherein R represents hydrogen-, methyl-, ethyl-, acetyl-, propionyl-, butyryl-, hydroxyl-, or carboxyl-substituted methyl or ethyl, or halogen- or hydroxyl-substituted acetyl, -propionyl or -butyryl, and wherein at least about 50% of said R groups are hydrogen. As heretofore indicated, preferably at least about 80% of said R groups will be hydrogen.

The water-soluble vinyl alcohol polymers of the instant invention have molecular weights ranging from about 50,000 to about 450,000, preferably 70,000 to 200,000.

Polyvinyl alcohol is conventionally obtained by polymerizing esters of vinyl alcohol followed by removal of the ester groups by saponification. To prepare the vinyl alcohol polymers of the instant invention, wherein up to about 50% of the hydroxyl groups are ester substituted, it is merely necessary to polymerize the corresponding vinyl ester and then partially saponify the resulting polyvinyl ester and thereby remove 50% or more of the ester groups. For example, to prepare polyvinyl alcohol containing 20% acetyl groups, a polyvinyl acetate polymer would be 80% saponified and the remaining 20% acetyl groups left unsaponified. A 99+% polyvinyl alcohol is substantially fully saponified. To prepare the methoxy- and ethoxy-ether derivatives of polyvinyl alcohol, a polyvinyl alcohol having substantially 100% hydroxyl groups is etherified up to the desired degree, i.e., up to about a maximum of 50% using conventional etherification agents such as diazomethane, dimethyl sulfate, or diethyl sulfate.

The preferred concentration of alkali metal borates and of vinyl alcohol polymers in the solution of the instant invention ranges from about 1.0 to about 3.5% by weight of each.

The aqueous borate-vinyl alcohol polymer of the instant invention can be prepared by adding the appropriate quantity of borate and vinyl alcohol polymer either simultaneously or consecutively to the water, preferably with agitation to insure rapid dissolution of the borate and vinyl alcohol polymer. Most preferably such water is heated up to about 95° C. to further enhance the rate of dissolution. Alternatively, aqueous solutions of borate and of vinyl alcohol polymer can be prepared separately and then combined.

The following specific examples further illustrate my invention.

Example 1

Ten grams of 87–89% hydrolyzed polyvinyl alcohol (PVA) (Vinol 523, Airco Chemicals and Plastics) is added to 750 grams of water heated at 70°–90° C. The PVA dissolves virtually instantaneously. A second solution is prepared by dissolving 10 grams of borax in 230 grams of water at 85° C. The two solutions are then combined. A one-square-foot piece of ordinary cheesecloth is immersed in 100 cc. of the combined solution for a few seconds, removed, excess fluid squeezed out, and the cloth air-dried. Weighing after drying indicates a 25% weight gain. The dried impregnated cheesecloth is ignited over its entire surface with a Bunsen burner. It burns to the carbon cloth counterpart of the cheesecloth.

Example 2

A one-foot-square swatch of shirting grade, 100% cotton broadcloth is immersed for about 30 seconds in 150 cc. of aqueous solution containing 1.5 weight percent borax and 1.5 percent (99+% hydrolyzed) PVA. The swatch is removed, squeezed to remove excess liquid, air dried, and roasted in a closed oven at 350° C. for 30 minutes. The resultant product is a fine-weave carbon fabric.

Example 3

Strips of shirting grade 100% cotton broadcloth 3" x 6" are immersed for one minute in one of the solutions tabulated below, removed, and air-dried for 24 hours at room temperature. The impregnated strips are then mounted horizontally and ignited with a match at one corner. Samples No. 1–3 burn up completely leaving only a small amount of crumbly unstructured ash. Samples No. 4–13 burn to a carbon cloth having the same woven structure as the original cotton cloth.

COMPOSITIONS OF AQUEOUS TREATING SOLUTIONS

	(1) Polyvinyl alcohol		(2) Borate	
	Compound	Weight percent	Compound	Weight percent
Solution No.:				
1 (untreated)				
2			A	3.0
3	A	3.0		
4	A	1.0	B	1.0
5	B	1.0	A	1.0
6	A	3.0	B	3.0
7	B	3.0	B	3.0
8	C	3.0	B	3.0
9	D	3.0	B	3.0
10	A	3.0	A	3.0
11	B	3.0	A	3.0
12	C	3.0	A	3.0
13	D	3.0	A	3.0

(1) Polyvinyl Alcohol:
A=99+% polyvinyl alcohol, i.e., at least 99% saponified polyvinyl acetate. M.W.=70,000.
B=80% polyvinyl alcohol. M.W.=200,000.
C=50% polyvinyl alcohol. M.W.=100,000.
D=Polyvinyl alcohol 30% ethoxylated. M.W.=75,000.
(2) Borate:
A=Borax, i.e., sodium tetraborate decahydrate.
B=Potassium tetraborate pentahydrate.

Example 4

In a 2000-cc. beaker is placed 1600 cc. of aqueous solution containing 3.0 weight percent borax and 3.0 weight percent 99+% hydrolyzed PVA. A variety of fibrous cellulosic substrates are consecutively immersed in this solution, removed, pressed to remove excess liquid, air-dried, and roasted for ½ hour at 300° C. in a closed oven. In all cases, the treated material forms its carbon structural analog and does not degrade to a fragile ash. The thus-treated substrates are listed below, along with the weight gain by impregnation.

Substrate:	Weight gain (percent)
Cotton-wool	39
Linen suiting	31
Cotton rope, ¼" dia.	26
Jute fiber	17
Kapok	10

Example 5

Part A. Preparation of palladium-carbon hydrogenation catalyst.—180 grams of ¼" diameter cotton rope cut in 3" lengths is immersed for 30 sec. in a one-liter solution containing 3 weight percent borax and 3 weight percent 99+% hydrolyzed PVA. The samples of rope are then drained, dried in the atmosphere, placed on a glass tray, and roasted in a closed oven at 400° C. for one hour. On removal from the oven, the carbon structural analog of the rope is obtained. The carbon rope is heated on a steam bath with 10% nitric acid for 3 hours, washed free of acid with distilled water, and dried at 100° C.

Nine grams of this acid-washed carbon rope is added to a mixture of 10 ml. of an aqueous palladium chloride solution containing 0.1 gram of palladium and approximately 0.05 gram of hydrogen chloride per milliliter and a solution of 27 grams of sodium acetate trihydrate in 100 ml. of water. The carbon rope-containing mixture is then placed in a Parr bomb and hydrogenated at 50 p.s.i. H_2 pressure until hydrogen absorption ceases. The carbon rope is then separated from the solution, washed with water, and dried with an airstream for 30 minutes.

Part B. Reduction of dihydro-α-naphthol using the palladium-on-carbon-rope catalyst prepared in Part A.—106 grams of industrial grade 5,8-dihydro-1-naphthol, M.P. 69°–72° C., dissolved in 250 ml. of ethyl acetate, is placed in a one-liter Parr bomb. Five grams of the palladium-on-carbon-rope catalyst (prepared in Part A) is added to the bomb, the bomb then staled and shaken for 45 minutes with 3 atm. hydrogen pressure maintained in the bomb during the shaking period. The palladium-on-carbon-rope catalyst is removed by filtration, the filtrate evaporated, leaving 105 grams of an oil which quickly solidifies on standing (M.P. 67°–69.5° C.).

Recrystallization from 250 ml. petroleum ether (B.P. 98° C.) affords 93 grams of colorless crystals of tetrahydro-α-naphthol (M.P. 68°–68.5° C.).

Example 6

Use of carbon cloth as a filtration medium.—One hundred cc. of a methanol solution of impure ethylene glycol is filtered through a mat of 100 grams of the carbon cloth prepared as in Example 3, and placed in a Buchner funnel. Prior to filtration the methanol solution is an amber color. Following filtration through the carbon cloth mat, the solution is a straw color.

Various modifications will be apparent to one skilled in the art, and it is not intended that this invention be limited to the details in the specific examples presented by way of illustration. Accordingly, the scope of the invention is limited only by the appended claims.

I claim:

1. A process for the preparation of carbon in fibrous form comprising the steps of:

(a) impregnating a fibrous cellulosic substrate with an aqueous solution containing from about 0.5 to about 5.0 weight percent alkali metal borate and from about 0.5 to about 5.0 weight percent water-soluble vinyl alcohol polymer;

(b) removing the aqueous component of said solution from said impregnated substrate;

(c) carbonizing said substrate by igniting or by roasting at a temperature of at least about 200° C.

2. A process in accordance with claim **1**, wherein said alkali metal borate is borax.

3. A process in accordance with claim **1**, wherein said vinyl alcohol polymer is substantially fully saponified.

4. A process in accordance with claim **1**, wherein said borate and said vinyl alcohol polymer are each present in said aqueous solution at a concentration ranging from about 1.0 to about 3.0 weight percent.

5. A process in accordance with claim **1**, wherein said fibrous cellulosic substrate is cotton.

6. A process in accordance with claim **5**, wherein said cotton is in the form of a woven cloth.

7. A process in accordance with claim **1**, wherein said carbonizing is effectuated by roasting said substrate at a temperature of at least about 200° C.

References Cited

UNITED STATES PATENTS

3,050,907	8/1962	Hicks et al.	117—46 XR
3,427,120	2/1969	Shindo et al.	117—46 XR

ALFRED L. LEAVITT, Primary Examiner

E. G. WHITBY, Assistant Examiner

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